

Functional Molecular Spacers for Plasmonic Nanojunctions: Design, Synthesis and Self-Assembly



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Declaration of Originality

This thesis is the result of my own work and includes nothing which is the outcome of work done in collaboration except as declared in the preface and specified in the text. It is not substantially the same as any work that has already been submitted before for any degree or other qualification except as declared in the preface and specified in the text. It does not exceed the prescribed word limit for the Department of Chemistry Degree Committee.

Charles Arthur (Charlie) Readman, 03/04/2022.

Abstract

This thesis is centred around the interaction of few-molecule arrays with gold surfaces and the enhanced optical fields that occur in nanoscale junctions between gold nanoparticles (AuNPs). This behaviour is enabled by optically resonant collective electron density oscillations (and electrostatic coupling thereof) at the nanoparticle and nanojunction surfaces, which confine incident light to nanoscale volumes and boost the local electromagnetic field strength - a phenomenon known as plasmonic enhancement. This facilitates enhanced light-matter interactions with broad potential for advanced nanophotonic applications, including few-molecule sensing, reaction monitoring, quantum information systems, molecular electronic devices, nanometrology, light harvesting and catalysis.

The utility of these plasmonic nanostructures is strongly influenced by the chemical structure of the molecular spacers used for nano self-assembly. In this work, I develop bespoke spacer molecules based on a set of functional design criteria for optimisation of the nanophotonic applications described above. Three different classes of molecular spacer are investigated in this thesis; their ability to self-assemble plasmonic nanostructures is characterised, and the functionality of the resulting nanostructures is assessed. The knowledge gained from each chapter is used for iterative re-design and optimisation of the molecular spacer system, as well as inspiration for future nanophotonic devices.

The first class of molecular spacer is the bis-phthalocyanine (BPc) family: rare-earth sandwich complexes with a well-studied plethora of complex physicochemical properties and applications in sensing, optics and spin-resolved molecular electronics. BPcs were used here for their potential to create nanostructures with atypically large plasmonic enhancement; BPc@AuNP nanostructures were investigated from a plasmonic sensing and nanometrology perspective. No sensing behaviour was observed under the conditions tested, but an anomalously large shift in plasmon resonance wavelength was observed upon variation of the BPc metal centre. Several candidate hypotheses for this are discussed, and the results highlight the limitations of the approximations and assumptions often used to model tightly coupled plasmonic systems.

The second spacer class uses supramolecular chemistry to provide control over orientation, intermolecular coupling and Au affinity of aryl viologen (ArV) molecules within plasmonic nanocavities, using a macrocyclic cucurbit[*n*]uril (CB[*n*]) host. Successful self-assembly of AuNPs using various ArV⊂CB[*n*] inclusion complexes was confirmed using a variety of spectroscopic and theoretical techniques. This demonstrates the possibility of multi-component molecular spacers, the modular nature of which represents a supramolecular toolbox for incorporating an expanded range of optoelectronic & chemical functionality into plasmonic hotspots.

The third and final class of spacer incorporates additional optical and chemical functionality into the ArV structure via a porphyrin moiety. The design, synthesis and characterisation of the new porphyrin species and its metal complexes are reported, together with a brief investigation of the compounds' solvchromic properties and aqueous stability. The electronic structure, excitonic coupling and internal dynamics within the discrete inclusion complexes formed between the novel porphyrins and CB[n] are then probed with various spectroscopies. Finally, the porphyrins and supramolecular CB[n] complexes thereof are used to assemble plasmonic nanostructures, and the electronic interactions between the spacer and plasmonically enhanced near field are probed.

This work uses established techniques to investigate the suitability of novel molecular junctions for advanced nanophotonic applications. In combination with cutting-edge plasmonic analysis techniques developed by others in parallel to this work, the functional spacer molecules developed here can now be used for enhanced exploration of light harvesting, electrocatalysis, charge transfer, charge transport, molecular switching and quantum cavity electrodynamics within self-assembled plasmonic nanojunctions.

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List of Publications

1. Readman, C.; de Nijs, B.; Szabó, I.; Demetriadou, A.; Greenhalgh, R.; Durkan, C.; Rosta, E.; Scherman, O. A.; Baumberg, J. J. Anomalous Large Spectral Shifts near the Quantum Tunnelling Limit in Plasmonic Rulers with Subatomic Resolution. *Nano Lett.* **2019**, *19* (3), 2051–2058.
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Abbreviations

4-MTA	4-methylthioaniline
5-HT	5-hydroxytryptophan; serotonin
5FBVI	(pentafluorobenzyl)vinylimidazole
AC	alternating current
AFM	atomic force microscopy
AgNPs	silver nanoparticles
ALD	atomic layer deposition
Ant910Me	4,4'-(anthracene-1,4-diyl) <i>bis</i> (1-(<i>p</i> -tolyl)pyridin-1-ium) dichloride
APP	5,10,15,20- <i>tetrakis</i> (4-(<i>N</i> -arylpyridinium))porphyrin
Ar	aryl
ArV	aryl viologen; 1,1'- <i>bis</i> (aryl)-[4,4'-bipyridine]-1,1'-dium
ArVH	1,1'- <i>bis</i> (phenyl)-[4,4'-bipyridine]-1,1'-dium dichloride
ArVNH₂	1,1'- <i>bis</i> (4-aminophenyl)-[4,4'-bipyridine]-1,1'-dium dichloride
ArVSMe	1,1'- <i>bis</i> (4-thioanisyl)-[4,4'-bipyridine]-1,1'-dium dichloride
ATR	attenuated total reflection
a.u.	arbitrary units
au	atomic units
AuNPs	gold nanoparticles
BEM	boundary element method
BPc	bis-phthalocyanine
Bu₄NCI	tetrabutylammonium chloride
BVI	benzylvinylimidazolium
CB[<i>n</i>]	cucurbit[<i>n</i>]uril; <i>n</i> = 5, 6, 7, 8
CCD	charge-coupled device
CI	configuration interaction
CM	coupled mode
COSY	correlation spectroscopy (NMR)
CP	colloidal particle
CT	charge transfer
CW	continuous wave
DA	dopamine
DAS	diaminostilbene
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DC	direct current
DCM	dichloromethane

Abbreviations

DF	darkfield
DFT	density functional theory
DLCA	diffusion-limited colloidal aggregation
DLVO	Derjaguin-Landau-Verwey-Overbeek (theory)
DMAc	<i>N,N</i> -dimethylacetamide
DMF	<i>N,N</i> -dimethylformamide
DMSO	dimethyl sulfoxide
DNAo	DNA origami
DNCB	2,4-dinitrochlorobenzene
DNPP	5,10,15,20- <i>tetrakis</i> (<i>N</i> -(2,4-dinitrophenyl)pyridinium-4-yl)porphyrin
DNTB	2,4-dinitrotoxybenzene; 2,4-dinitrophenyl tosylate
DLS	dynamic light scattering
DOSY	diffusion-oriented spectroscopy (NMR)
EA	elemental analysis
EELS	electron energy loss spectroscopy
EPI	epinephrine
ESI-MS	electrospray ionisation mass spectrometry
Et₂O	diethyl ether
EtOAc	ethyl acetate
EtOH	ethanol
EV	extended viologen
FDTD	finite-difference time domain
FRET	Förster resonance energy transfer
fsTA	femtosecond transient absorption (spectroscopy)
FTIR	Fourier transform infrared (spectroscopy)
FWHM	full width at half maximum
GGA	generalised gradient approximation
HAADF-STEM	high-angle annular dark field scanning TEM
HOMO	highest occupied MO
HOPG	highly oriented pyrolytic graphite
HPLC	high performance liquid chromatography
ITC	isothermal titration calorimetry
LB	Langmuir-Blodgett
LBL	layer-by-layer (deposition)
LC	liquid chromatography
LCMS	liquid chromatography-mass spectrometry
LCR	inductor/capacitor/resonator (circuit)
LCRECP	large core RECP

Abbreviations

Ln	lanthanide; lanthanoid
LSPP	localised surface plasmon polariton
LSPR	localised surface plasmon resonance
LUMO	lowest unoccupied MO
MALDI-TOF	matrix-assisted laser-induced desorption/ionisation - time of flight (MS)
MeCN	acetonitrile
MeOH	methanol
MO	molecular orbital
MPc	metallophthalocyanine
MS	mass spectrometry
MSTM	multiple-sphere T-matrix
MV	methyl viologen
NMR	nucleo-magnetic resonance (spectroscopy)
NOESY	nuclear Overhauser effect spectroscopy (NMR)
NP	nanoparticle
NPoM	nanoparticle-on-mirror
NPR	normalising plasmon resonance (spectroscopy)
NRR	nonradiative relaxation
OAc	acetate
OEP	octaethyl porphyrin
OTs/TsO	tosylate; <i>p</i> -toluenesulfonate
PAO	pseudo-atomic orbital
Pc	phthalocyanine
PDT	photodynamic therapy
Ph13Me	4,4'-(1,4-phenylene) <i>bis</i> (1-(<i>p</i> -tolyl)pyridin-1-ium) dichloride
PL	photoluminescence
QY	quantum yield
RC	recrystallised
RECP	relativistic effective core potential
RF	retention factor
RLCA	reaction-limited colloidal aggregation
SAM	self-assembled monolayer
SCRECP	small-core RECP
SEC	size exclusion chromatography
SEM	scanning electron microscope/microscopy
SERS	surface enhanced Raman spectroscopy/scattering
SERRS	surface enhanced resonance Raman spectroscopy/scattering
SMe	methylthio

Abbreviations

SMM	single molecule magnet
S_N^{Ar}	nucleophilic aromatic substitution
SNOM	scanning near-field optical microscopy
SOMO	singly occupied MO
SPM	scanning probe microscopy
SPP	surface plasmon polariton
SPR	surface plasmon resonance
STM	scanning tunnelling microscopy
SUMO	singly unoccupied MO
TAPP	5,10,15,20- <i>tetrakis</i> (4-(<i>N</i> -(4-thioanisyl)pyridinium))porphyrin
TBAF	tetrabutylammonium fluoride
TCB	tetrakis(4-aminophenyl)cyclobutene
TCSPC	time-correlated single photon counting
TD-DFT	time-dependent DFT
TEM	transmission electron microscopy
THF	tetrahydrofuran
TLC	thin layer chromatography
TM	transverse mode
TMPPyP	5,10,15,20- <i>tetrakis</i> -(4-(<i>N</i> -methylpyridin-1-ium))porphyrin
TPPS	5,10,15,20- <i>tetrakis</i> (4-sulfonatophenyl)porphyrin
TPyP	5,10,15,20- <i>tetrakis</i> -(4-pyridyl)porphyrin
TSG	template-stripped gold
UHV	ultrahigh vacuum
UV-Vis	ultraviolet-visible (spectroscopy)
vdW	van der Waals
VOC	volatile organic compound
VT-NMR	variable-temperature NMR
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

Introduction

The upcoming introductory chapters outline the themes of the work presented in this thesis, an overview of the fundamentals required to understand the concepts involved and a literature review on each of the topics. **Chapter 1** first introduces the main linking theme of this thesis: self-assembled plasmonic nanocavities based on coupled gold nanoparticles (AuNPs; **Figure 1a**), and the history, applications, characterisation techniques and current perspectives thereof.

These nanostructures can be assembled and characterised using a range of molecules and spectroscopic techniques. This thesis reports the development of novel chemical compounds for this role, with design principles based on utilisation of enhanced light-matter interactions for sensing, catalysis and nanophotonic applications. The objective is to explore and characterise the interaction of these molecules with both the AuNP surface and the enhanced, tightly confined electromagnetic fields created by the nanocavity. The purpose is to build on existing options for enhanced chemistry and sensing within plasmonic nanocavities and better understand the role of molecular electronic structure in nanophotonic devices.

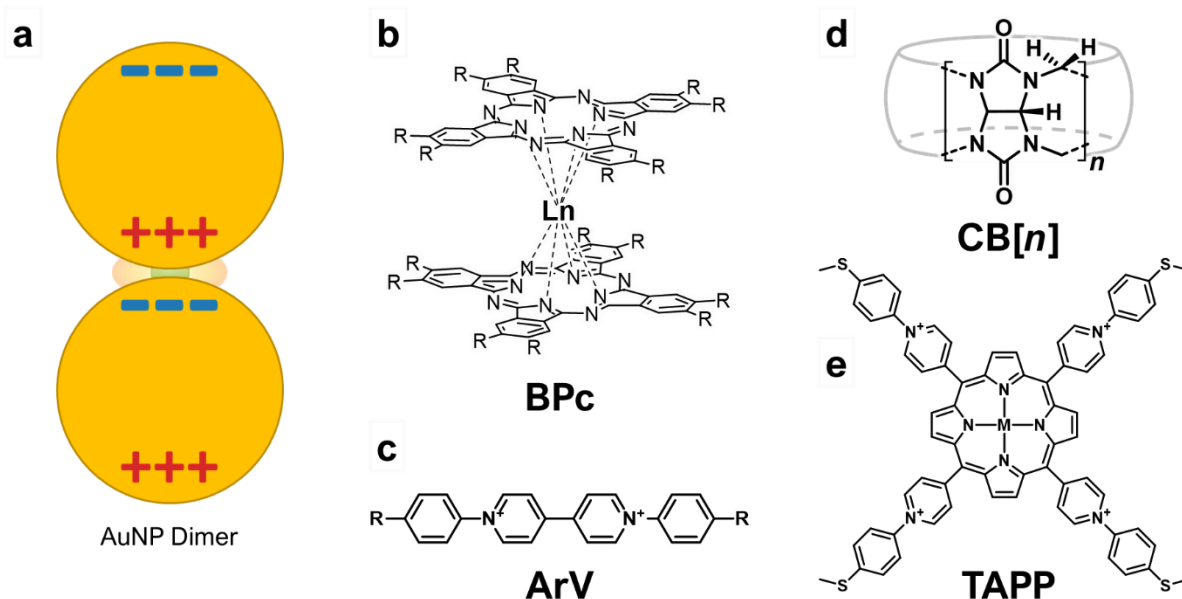


Figure 1. (a) Schematic of coupled AuNP dimer separated by a layer (green area) of spacer molecules, illustrating transient surface charge distribution and enhanced electromagnetic field within the interparticle gap (not to scale). (b-e) Chemical structures of molecular spacers used in this work: (b) LnPc_2 aka BPC; (c) ArV; (d) CB[n]; (e) *tetrakis*-(*N*-thioanisylpyridinium) porphyrin, aka TAPP.

The bulk of the thesis explores the synthesis, characterisation and nano-assembly properties of different molecular spacers using established bottom-up assembly and characterisation techniques. **Chapter 2** introduces the three molecular spacer types explored in this work, their current presence in plasmonics, applicability to systems studied in this thesis and possible future applications.

Section 2.1 discusses rare earth bis-phthalocyanines (BPcs; **Figure 1b**) - lanthanide-based macrocyclic sandwich complexes - and their applications in sensing, catalysis and molecular devices, plus their potential for nanometrology. **Section 2.2** introduces the host-guest chemistry, molecular recognition and nano-assembly properties of cucurbit[*n*]uril (CB[*n*]; **Figure 1d**), the redox activity and electrochromism of aryl viologens (ArVs; **Figure 1c**) and the emergent chemical and optoelectronic properties of supramolecular ArV⊂CB[*n*] inclusion complexes. **Section 2.3** discusses porphyrins, with a brief overview of their properties, applications and academic interest, followed by a review of their utility in supramolecular and plasmonic systems and design of a new porphyrin structure compatible with AuNP self-assembly (**Figure 1e**).

Each experimental chapter then begins with key objectives, hypotheses and work outlines for the molecular spacer system used. The main bulk of each chapter reports the chemical synthesis, supramolecular assembly and/or nano self-assembly behaviour of the molecular spacer in question, followed by characterisation of the systems at each assembly level, where appropriate.

Chapter 3 begins with the design and synthesis of BPc derivatives with improved solubility and Au surface affinity. AuNP self-assembly methods are developed and the resulting nanostructures characterised and tested for gas sensing activity. An unexpected, anomalous spectral shift in plasmonic response with BPc metal centre is reported,¹ the reasons for which are explored in depth.

Chapter 4 uses previously synthesised² ArV and CB[*n*] species that are known to form supramolecular complexes and have potential for customization and extension with a wide range of functional groups. The chapter focuses on the AuNP self-assembly properties of the ArV⊂CB[*n*] supramolecular complexes and investigates the conditions required for control over alignment and structural retention of the complexes during the process.

Chapter 5 uses the findings of **Chapters 3-4** to design a molecular spacer combining the water solubility, Au binding and supramolecular assembly properties of ArVs with the metal ligation capability of phthalocyanines. A novel water-soluble porphyrin with interchangeable ArV-like terminal moieties (**Figure 1e**) is designed and a synthetic route is developed. The solvchromism, aqueous stability, metal ligation and supramolecular CB[*n*]-binding behaviour are explored with liquid chromatography-mass spectrometry (LCMS), UV-Visible (UV-Vis) absorption spectroscopy, photoluminescence (PL) spectroscopy and proton nuclear magnetic resonance (¹H-NMR) spectroscopy. The AuNP self-assembly properties of the novel porphyrins and their supramolecular CB[*n*] complexes are then tested, followed by preliminary investigation of the PL properties of the resulting plasmonic nanostructures.

1. Self-Assembled Plasmonic Nanojunctions

The central theme of this thesis is the unique interaction of molecules with the confined, enhanced optical fields that occur at nanostructured metal-dielectric interfaces. Excitation of a metal's conduction electrons leads to collective charge density oscillations known as surface plasmon polaritons (SPPs) or, more simply, plasmons. For metallic nanostructures smaller than the optical diffraction limit, plasmons exhibit characteristic resonance frequencies that can be excited by incident photons. These emergent optical-frequency electromagnetic modes can confine light to the metal-dielectric interface at dimensions far smaller than optical wavelengths.³

This confinement can lead to extreme enhancement of the electromagnetic near field, with localisation, intensity and resonances that are exceptionally sensitive to the nanostructure morphology and surrounding environment. Through careful nanostructure design, this ability to capture, direct and manipulate light far below the diffraction limit facilitates a wealth of optical and chemical functionality based on efficient light-matter interactions, which can be extremely challenging to achieve via other methods.

This thesis focuses on development of molecular building blocks for the self-assembly of plasmonic nanocavities with novel chemical functionality. This chapter delivers an application-based perspective of nanophotonics towards nanostructural and molecular design. **Sections 1.1-1.2** begin with a brief history of plasmonic field enhancement, nanostructure design principles and an introduction to the nanostructure types used in this work. Plasmonic modelling and optical nano-characterisation techniques are then discussed in **Section 1.3**. Finally, **Section 1.4** explores recent developments and applications of self-assembled plasmonic nanocavities and outlines molecular design criteria to improve the chemical functionality of plasmonic devices.

1.1 Background & Context

1.1.1 Raman Spectroscopy

The popularity and utility of nanophotonics arguably began with surface enhanced Raman spectroscopy (SERS),⁴ a phenomenon whereby nanostructured metal surfaces perturb and enhance the Raman scattering process. First reported by Raman & Krishnan in 1928,⁵ Raman scattering is the inelastic scattering of light by matter, where a portion of the incident optical energy is exchanged with vibrational modes in the scattering medium. Spectroscopic analysis of Raman-scattered monochromatic light was discovered to reveal insights into the structure of the scattering substance, earning Raman a Nobel Prize two years later.

Briefly, an incident photon (of energy $h\nu_0$) typically undergoes elastic (Rayleigh) scattering, but may also experience inelastic (Brillouin or Raman) scattering upon interaction with, for example, a molecule. In each case, the molecule is excited to a virtual state, followed by immediate relaxation to the ground state (of energy E_0) or an excited state ($E_0 + h\nu_m$) emitting a photon of energy $h\nu_0$ or $h\nu_0 - h\nu_m$, respectively (**Figure 1.1a**). The observed energy difference (aka Stokes shift) between incident and Raman scattered photons reveals the energy, $h\nu_m$ of the vibrational transition. Through the inverse process, anti-stokes scattering events generate blueshifted photons ($h\nu_0 + h\nu_m$) via interaction with molecules that are already vibrationally excited; this provides insights into molecular temperature, but signals are usually very weak. Therefore, only Stokes shifts are considered in this work.

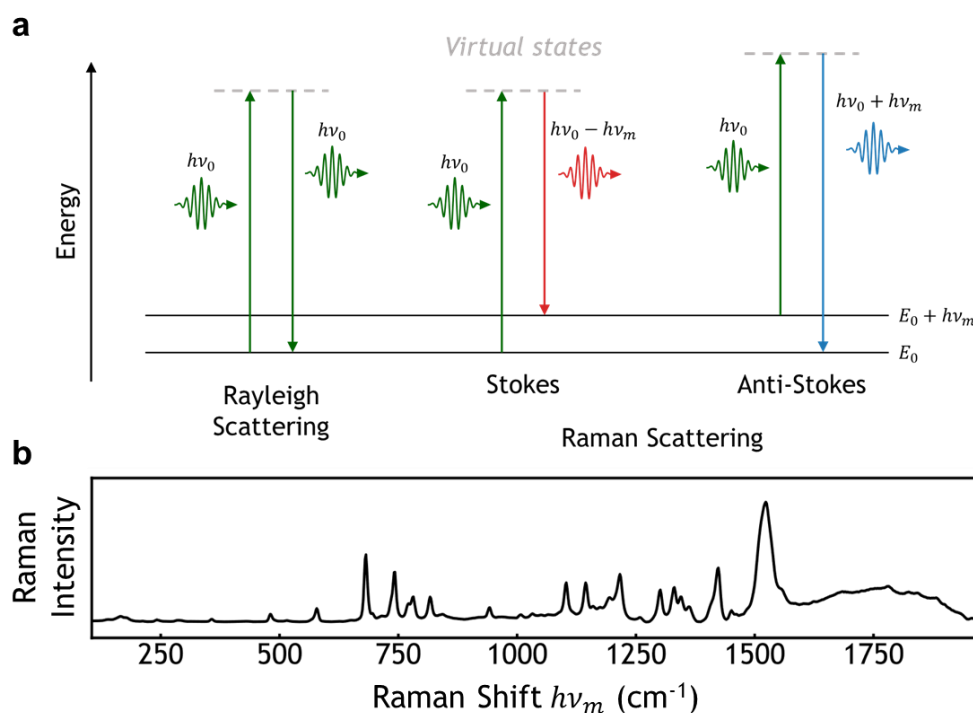


Figure 1.1. Raman scattering process. **(a)** Energy diagram of elastic (Rayleigh) and inelastic (Raman) scattering processes. **(b)** A typical Raman spectrum (here of lutetium BPc a.k.a. LuPc₂), in which each peak corresponds to one or more vibrational energies, with intensity corresponding to the scattering cross-section of the transition.

Raman spectroscopy is frequently used to visualise the energy and probability of vibrational transitions. The resulting Raman spectrum (**Figure 1.1b**) has multiple sharp peaks representing the scatterer's unique vibrational fingerprint; Raman spectroscopy is therefore widely used for chemical sensing.⁶⁻⁸ The Raman scattering event probability is incredibly low and spectroscopic analysis therefore requires high concentrations and/or intense optical irradiation. Consequently, the technique was rarely utilised until a suitably intense, monochromatic light source (i.e. the laser) was invented in the 1960s.⁹

1.1.2 Plasmonic Confinement

Meanwhile, the field of plasmonics was emerging, driven by the discovery of quantised electromagnetic modes occurring at metal-dielectric interfaces under certain conditions.^{10,11} Metallic electrons can be approximated as a gas within a fixed, positively-charged background lattice. This gas can be modelled as a harmonic oscillator that is perturbed by an external electromagnetic field, e.g., a photon. Under these assumptions, the frequency-dependent dielectric function for a metal can be approximated (for $\lambda > 500$ nm) using the Drude model:

$$\epsilon_m(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\Gamma\omega} \quad (1)$$

Here, ω is angular frequency and the metal-dependent constants Γ and ω_p are the scattering rate (accounting for electron energy loss to phonons) and plasma frequency, respectively.

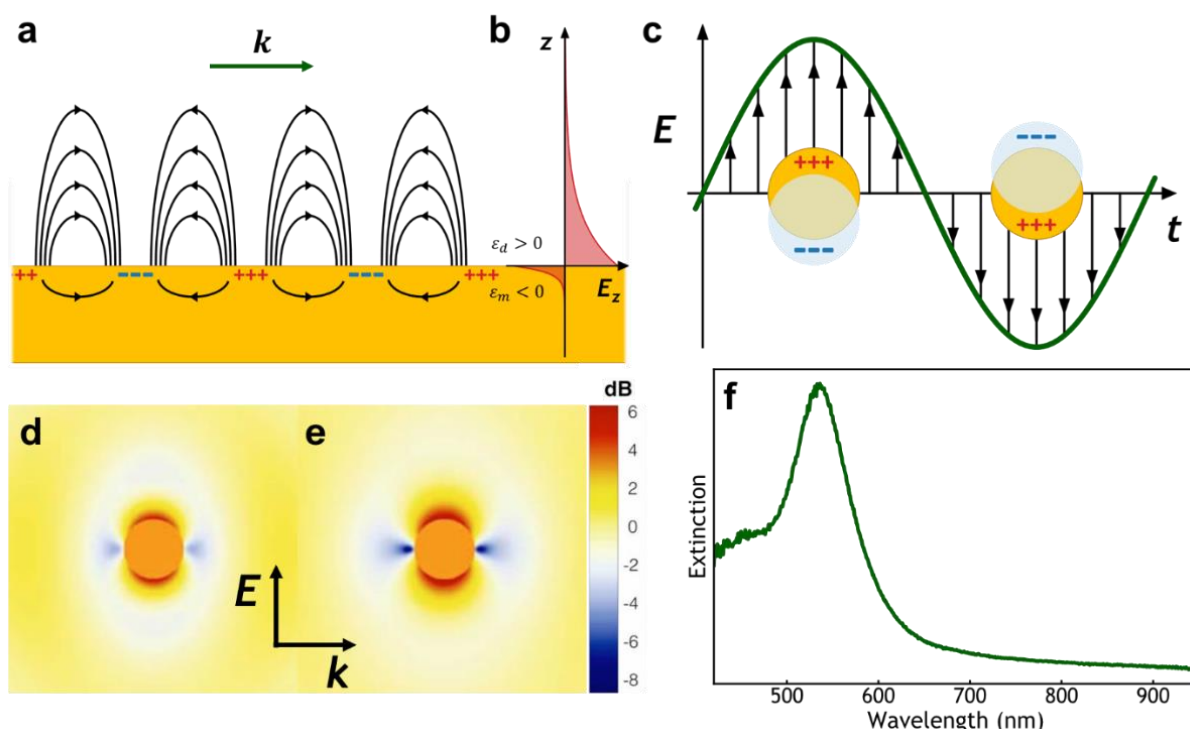


Figure 1.2. Schematics illustrating (a) electric field lines/surface charge distribution and (b) electric field strength (z-component) of an SPP, and (c) temporal evolution of electric field and charge distribution associated with the LSP of a spherical AuNP. (d, e) Calculated field enhancement at AuNP surface (diameter $D = 50$ nm) at (d) 600 nm and (e) 700 nm excitation, adapted from [12]. (f) Measured extinction spectrum of the colloidal aqueous AuNPs ($D = 60$ nm)¹³ used in this work.

At interfaces across which $\text{Re}\{\epsilon_m(\omega)\}$ changes sign (e.g. a metal with $\text{Re}\{\epsilon_m(\omega)\} < 0$ placed in a dielectric medium such as water or air), a consequence of this behaviour is the SPP, an optical-frequency electromagnetic mode confined to the metal-dielectric interface.¹⁴ SPPs can propagate over macroscopic distances (**Figure 1.2a**) with greater momentum than the incident light, accompanied by an exponential decay in electric field strength away from the surface (**Figure 1.2b**). This difference in momentum (wavevector k in **Figure 1.2a**) is such that the SPP is nonradiative and cannot couple to free-space photons.

For subwavelength-sized nanostructures, the SPP is confined and no longer propagates, instead manifesting as an oscillating dipole accompanied by transient charge buildup either side of the nanostructure (**Figure 1.2c**) and electromagnetic near-field enhancement¹⁵ (**Figure 1.2d,e**). These localised SPPs (LSPPs) couple to photons more efficiently and are accessible to standard optical techniques. Consequently, intense scattering and absorption are observed (**Figure 1.2f**), with intensity and resonant wavelength sensitive to the shape, size, material and surface chemistry of the nanostructure, as well as the refractive index of the surrounding environment.^{16,17}

1.2 Nanostructure Design

First introduced mathematically at the turn of the 20th century^{18,19} and experimentally demonstrated at visible frequencies many decades later,^{10,11} the plasmonics field truly gained traction in the 1970s with the observation of anomalously large Raman signals of pyridine on a roughened silver electrode.^{20–22} This discovery of SERS boosted the utility and accessibility of the Raman technique, transforming the plasmon from a physical curiosity into a major tool for chemical sensing and other nanophotonic applications.

1.2.1 Plasmonic Substrates & SERS

Initially, the reproducibility of SERS enhancement was limited by the available nanofabrication and optical characterisation techniques. A drive to overcome this has led to many studies devoted to understanding and optimising light-matter interactions using metallic nanostructures, accelerating the development of nanophotonics and unearthing a wealth of plasmonic applications (**Section 1.3**). Matters were complicated by an infamous debate over the enhancement mechanism (chemical versus electromagnetic) which, according to Moskovits,⁸ hindered general understanding for several decades. SERS is now understood to be electromagnetic in nature, arising from the intense local fields created by the LSPP charge oscillations.⁴

Near the nanostructure surface, a molecule is excited by an enhanced electromagnetic field of strength $E_s = gE_0$ (for incident intensity $I_0 \propto |E_0|^2$), where E_0 is the incident field strength and g is the plasmonic enhancement factor. The Raman-scattered light therefore has field strength $E_R \propto \alpha_R E_s \propto \alpha_R g E_0$, where α_R is the molecular Raman tensor - related to

molecular polarisability. Outgoing Raman light is similarly enhanced, with final field strength $E_{\text{SERS}} \propto g' E_R \propto \alpha_R g g' E_0$ and intensity $I_{\text{SERS}} \propto |E_{\text{SERS}}|^2 \propto |\alpha_R|^2 |g g'|^2 |E_0|^2$, where g' is the plasmonic enhancement at the Raman-shifted wavelength. The values of g and g' depend on the overlap between nanostructure resonance and the wavelengths of the incident and Raman scattered light. Assuming $g \approx g'$ for small Stokes shifts, SERS intensity can be approximated as $I_{\text{SERS}} \propto |\alpha_R|^2 |g|^4 I_0$. A key consequence is $I_{\text{SERS}} \propto \left| \frac{E_s}{E_0} \right|^4$, transforming modest field enhancements into enormous SERS signals.

In addition to plasmonic enhancement, Raman and SERS signals can also be boosted by electronic resonance between incident photons and the analyte. In certain cases, direct excitation of an electronic molecular transition by the incident laser yields a large polarisability change across the molecule.²³ As Raman-active vibrational transitions depend on polarisability changes, such electronic excitation can increase Raman cross-sections by several orders of magnitude. This mechanism is known as resonance Raman scattering (RRS); simultaneous occurrence of RRS and SERS is possible, the effect of which is known as SERRS.²⁴

Moskovits highlights that “*Molecular resonances, charge-transfer transitions and [...] ballistic electrons transiently probing the region where the molecule resides and modulating electronic processes [...] contribute to the rich information that SERS reports*”.⁸ Therefore, while this now-infamous debate may have slowed some aspects of understanding, such intense scrutiny of electronic interactions at the metal-molecule interface has yielded chemical insights crucial for the development of molecular junction devices^{3,25–27} and plasmonic catalysts.^{28–31}

The first requirement for a useful plasmonic substrate is a material with $\text{Re}\{\varepsilon(\omega)\} < 0$ (usually a metal with high free-electron mobility)¹⁴ and an optical LSPR. The former is necessary for near-field enhancement, while the latter ensures compatibility with standard optics and the visible spectrum. Gold, silver, copper and aluminium all satisfy these conditions, with silver and gold most commonly used.⁴ While silver generally delivers higher field enhancements,³² gold is less chemically reactive and will be used throughout this work.

The second requirement is nanostructure. The effect of plasmonic confinement was directly measured in 1999 with scanning near-field optical microscopy (SNOM), revealing wavelength-dependent field enhancements around nanoscale features of roughened gold films.³³ Nanoscale confinement of charge density oscillations yields quantised resonant plasmon modes that act as optical frequency nano-antennae. This allows efficient communication between the near- and far-field for manipulation of light at scales inaccessible to conventional optics. Unlike semiconductors, whose optical properties are determined mostly by band gap, the plasmon resonance wavelength is extraordinarily sensitive to geometry and environment and can be tuned to interact with any part of the solar spectrum.⁴

Precise geometric control is therefore crucial for the realisation of functional nanophotonic devices.

The electrochemically roughened surfaces originally used for SERS achieved significantly higher sensitivity and lower detection limits than non-enhanced methods. However, because $I_{\text{SERS}} \propto \left| \frac{E}{E_0} \right|^4$, small variations in local field strength are hugely magnified. Poor control over film morphology led to irreproducibility in quantitative sensing performance and hindered theoretical understanding.

Fortunately, nanofabrication techniques have progressed significantly, allowing greater control over nanostructure design and therefore optical response. The common methods are “top-down” fabrication via lithography^{34,35} (**Figure 1.3a,d**) “bottom-up” synthesis, via colloidal nanoparticle growth^{36,37} (**Figure 1.3b,e**), or a combination of both, via material growth onto a self-assembled template^{38–40} (**Figure 1.3c,f**).

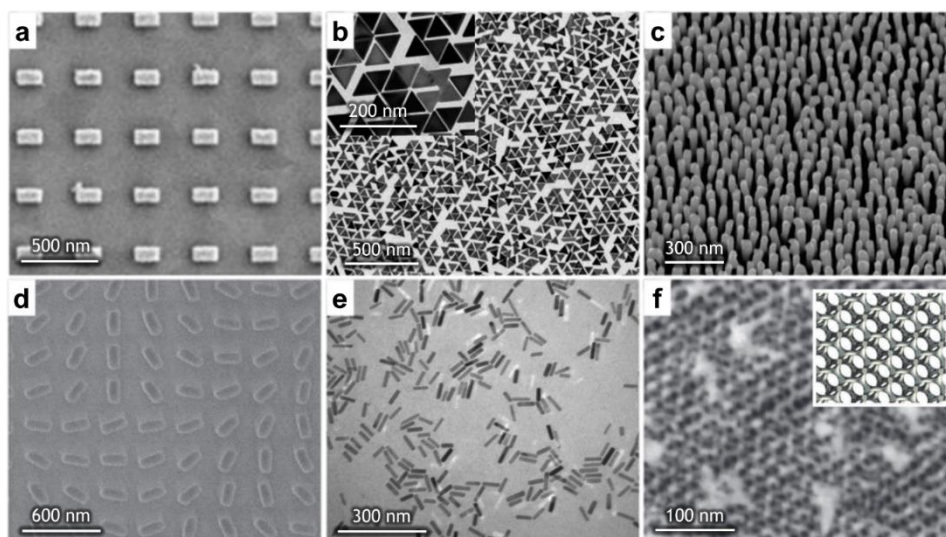


Figure 1.3. Electron micrograph images of nanostructures fabricated using top-down (**a, d**), bottom-up (**b, e**) and combined (**c, f**) methods. (**a**) Regular array of surface-bound AuNPs fabricated with electron-beam lithography.³⁴ (**b**) Colloidal Au nanotriangles.³⁶ (**c**) Surface-bound AuNRs grown using Al_2O_3 nanotube template.⁴⁰ (**d**) Custom Au metasurface fabricated with electron beam lithography and lift-off methods.³⁵ (**e**) Colloidal Au nanorods.³⁷ (**f**) Au gyroid metamaterial grown around a self-assembled polymer gyroid template.³⁹

While top-down methods offer custom control over shape and arrangement of nanostructured surfaces, it often requires time-consuming multi-step processes, complex/expensive instrumentation and harsh fabrication conditions.^{34,35} Colloidal nanoparticles, by contrast, can be easily synthesised with fine shape and size control using wet chemistry techniques^{36,37} and standard formulations are commercially available.¹³ Depending on size and shape, individual AuNPs exhibit approximately tenfold⁴¹ near-field enhancements (far higher around sharp vertices) collectively acting as a one-pot SERS substrate.^{42,43}

Field enhancements of this magnitude are suitable for basic sensing applications.⁸ However, even the smallest monomeric structures fall short of achieving the efficient sub-nanometre optical confinement required to understand and influence light-matter interactions

at the few to single molecule level, which is necessary for advanced plasmonic chemistry and molecular nanophotonic devices.

1.2.2 Coupled Plasmons

An alternative approach exists via plasmon coupling, with the “SERS hotspot” concept first developed in the early 1980s.^{4,8,44,45} Single-molecule SERS was first achieved in 1997⁴⁶ via “NaCl activation” of colloidal plasmonic nanoparticles, in which salt-induced aggregation (**Section 1.2.3**) led to dramatic increase in SERS performance. In such systems, small (< 10 nm) interparticle separation leads to coupling of the plasmonic modes accompanied by a distinct change in spectral response (**Section 1.3**). Capacitive coupling and interaction of neighbouring enhanced fields creates a plasmonic “hotspot” (**Figure 1.4**) with a new set of tightly-confined optical modes and near-field enhancements of 10^2 – 10^3 ,⁴⁷ boosting SERS intensity by more than 11 orders of magnitude as the gap size is decreased.

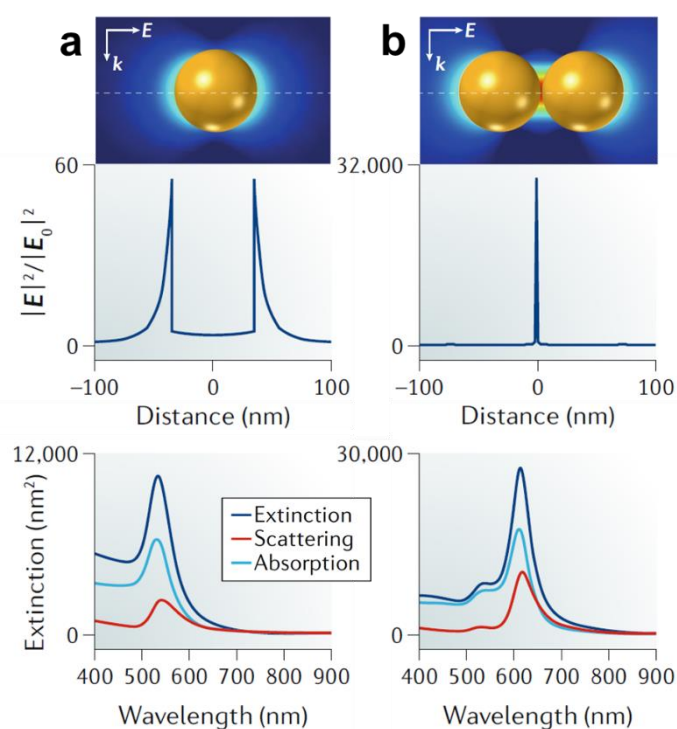


Figure 1.4. Schematic (top), field enhancement profile (middle) and extinction cross-section (bottom) of (a) isolated AuNP and (b) AuNP dimer ($D = 60$ nm; $d = 1$ nm), calculated by and adapted from Zhan *et al.*⁴¹ Note the difference in y-axis scales for (a) and (b).

This huge increase in field strength facilitates single-cavity nano-optics previously only achievable at cryogenic temperatures.^{48,49} The hybridised plasmonic modes in such a small cavity offer new and unusual functionalities (**Section 1.3**) with enormous geometric and environmental sensitivity, responsive even to atomic-scale crystal defects and protrusions.^{50–53} This enables extremely localised spectroscopy, single atom tracking and unprecedented nanostructure characterisation capability, although greater nanomorphology control is now required if these systems are to be understood and utilised.

Coupled plasmonic nanostructures, like monomeric systems, can be controlled through top-down and/or bottom-up techniques. Lithographic and nanotemplating techniques achieve custom shapes and control over interparticle distance and orientation, either as arrays for ensemble measurements and photonic devices,^{34,54} or as isolated structures for single-cavity experiments.^{43,55} Unfortunately, lithographic techniques require expensive, sophisticated instrumentation and achieving the smallest available resolutions can be very slow when using electron-beam or focused-ion-beam methods. More importantly, despite many advances, top-down methods are unable to achieve the < 1 nm resolutions required for the highest field enhancements, which restricts utility for many advanced nanophotonic applications.

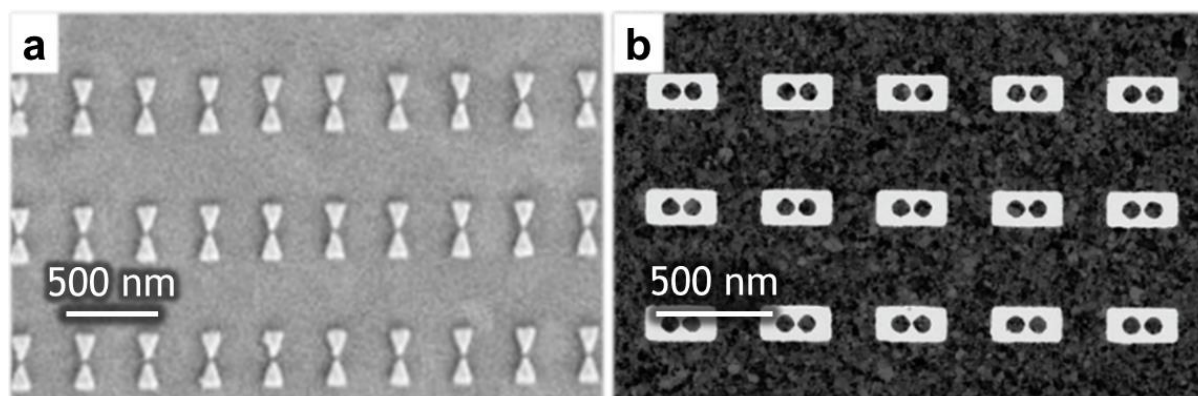


Figure 1.5. Scanning electron microscopy (SEM) images of lithographically fabricated arrays of coupled (a) nanotriangles/bowtie antennae³⁴ and (b) nanodisks.⁵⁴

Bottom-up self-assembly generally involves aggregation of colloidal nanoparticles,⁵⁶ offering a high-throughput alternative with precise geometry control under the right conditions. Self-assembled nanostructure reproducibility is dependent on the quality and uniformity of the nanoparticles, and the method of aggregation. Thankfully, nanoparticle synthesis has progressed dramatically over the past few decades (**Figure 1.3**) and monodisperse, well-defined plasmonic nanoparticles are now commercially available and affordable.¹³ The following section discusses two bottom-up assembly methods of preparing well-defined plasmonic nanocavities via aggregation and surface binding of colloidal AuNPs.

1.2.3 AuNP Aggregates

Colloidal AuNPs are thermodynamically unstable, preferring to exist as bulk Au, but are kinetically stabilised via electrostatic or physical methods. Aggregation behaviour is highly sensitive to surface structure and ligand chemistry⁵⁷ and reproducibility requires consistency in both. The pseudo-spherical AuNPs used in this work¹³ are charge-stabilised by anionic citrate ligands and can be aggregated via several methods. Charge stabilisation relies on sufficient long-range electrostatic repulsion to offset the short-range, attractive van der Waals (vdW) forces between particles⁵⁸ (see **Sections 4.2, 8.3.3** for theoretical treatment). Destabilisation can therefore be achieved by decreasing the AuNP surface charge, or decreasing the charge screening length via an increase in ionic strength of solution.

Ionic strength can be increased by addition of salt, while AuNP surface charge can be decreased by lowering the pH to protonate and neutralise the citrate ligands. The resulting aggregates exhibit significantly higher field enhancements and SERS signals than roughened surfaces, but offer poor control over nanocavity morphology. Without directional bonding, inclusion of functional or analyte species within the hotspots is purely statistical, with little control over geometry, position or intermolecular interactions. Such systems are therefore difficult to characterise and have limited utility towards quantitative sensing, molecular devices or anything else requiring precise light-matter interactions.

AuNPs can also be destabilised via displacement of citrate by higher-affinity ligands and uniform and well-defined interparticle spacing can be achieved if ligands are bidentate and rigid⁵⁹ (**Figure 1.6**). While the extended aggregate structure is statistical and governed by aggregation kinetics, molecular control over nanocavity size and permittivity allows precise control over the strength and resonance of the confined field, as well as intermolecular interactions and orientation within the cavity.^{6,49,60}

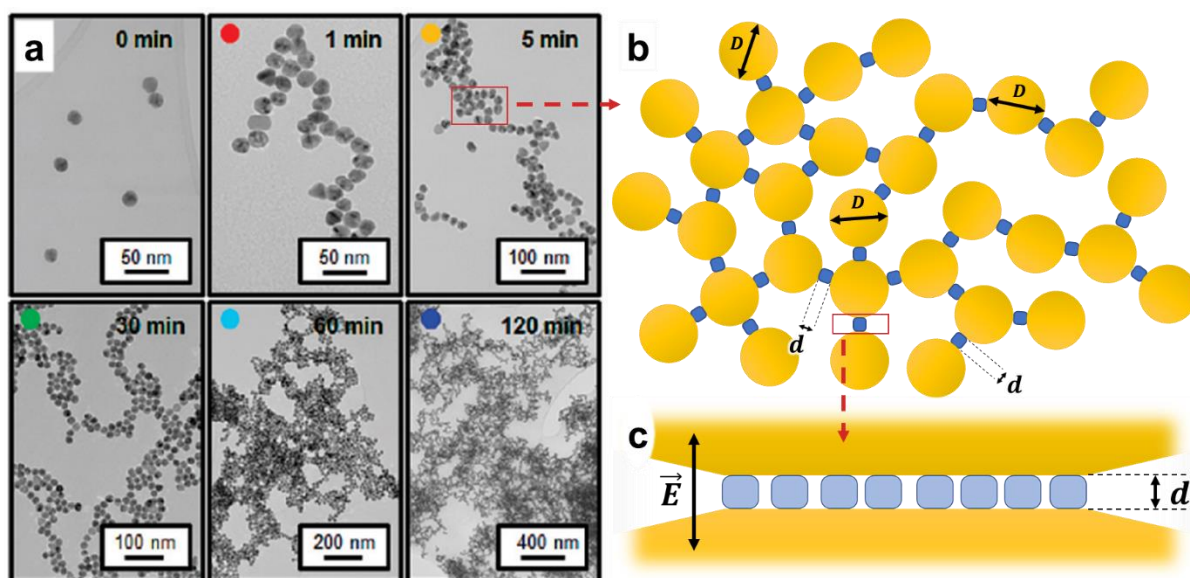


Figure 1.6. Aggregation of AuNPs using a rigid, bidentate molecular spacer; adapted from [59]. (a) Transmission electron microscopy (TEM) images showing time evolution of nanostructure after addition of aggregant. (b) Schematic illustrating AuNP aggregates with random extended structure but uniform interparticle gaps. (c) Schematic of close-up view of nanocavity with controlled gap size, d , and local enhanced field ($\vec{E}$).

Cavity uniformity is crucial for reproducible, quantitative sensing.^{6,60} SERS signals are dominated by the few spacer molecules in the hotspot, all of which are similarly aligned with the enhanced near-field (**Figure 1.6c**). Therefore, even ensemble measurements of randomly oriented hotspots enable analysis of relative molecular orientation, intermolecular interactions and surface binding.^{57,61} The understanding of the micro,⁵⁹ nano⁴⁷ and atomic⁵⁷ scale behaviour of such aggregates has rapidly increased over the past decade and the reproducibility of SERS performance is improving.^{6,60}

However, while the far-field response facilitates SERS sensing and some structural characterisation, the observed plasmon modes are significantly broadened due to many-cavity coupling and geometric polydispersity of the hotspots.^{59,62,63} This precludes the single-cavity analysis necessary for understanding the underlying mechanisms of various nanophotonic applications (**Section 1.3**). Such analysis requires a more robust, high-throughput method of isolating individual, optically resolvable nanocavities.

Several methods exist for further controlling nanoparticle self-assembly (**Figure 1.7**). Microfluidics can be used to lower the solution volume and, at low concentrations, achieve two particles per droplet - with Poissonian statistics - which can then be joined⁶⁴ (**Figure 1.7c**). Kinetic trapping of dimers is also possible (**Figure 1.7a**), but yields are, again, statistical.⁶⁵

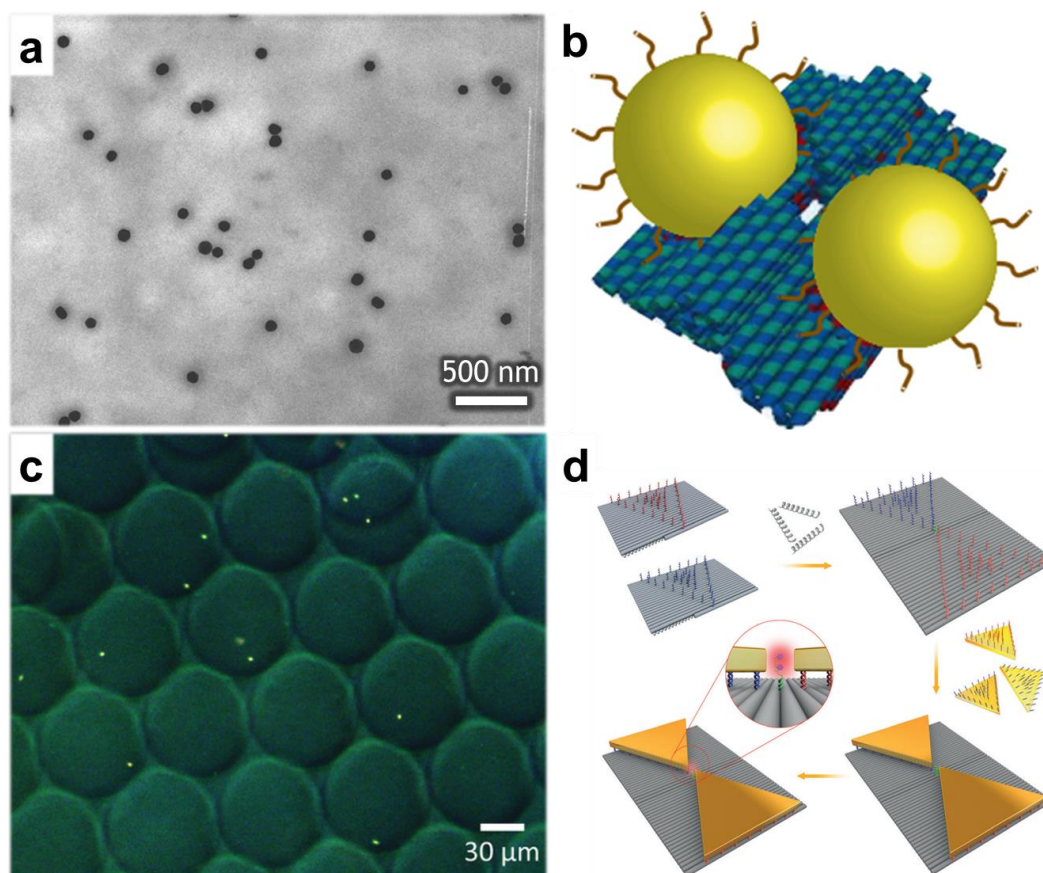


Figure 1.7. Methods of controlling AuNP dimerisation. **(a)** TEM image of AuNP dimers kinetically arrested in agarose gel.⁶⁵ **(c)** Optical image of microdroplets containing optically resolvable AuNPs (bright spots).⁶⁴ **(b, d)** Schematics illustrating programmed AuNP dimerisation using DNAo.^{66,67}

DNA origami (DNAo) offers programmable, directional interactions, including nanoparticle self-assembly with programmable gap size and contents^{66,68} (**Figure 1.7b,d**). However, the geometric resolution is limited to ~1.5 nm by size and shape of the double helix⁴⁸ and the complexity of the system currently limits its general use, much like top-down lithographic methods.

These techniques are not ideal for the high-throughput experiments required to study and characterise the self-assembly properties and single-cavity light-matter interactions of new

molecular spacers. Fortunately, the past few decades have seen the development of a simple, robust model dimer system involving a nanoparticle near a metallic surface,⁶⁹ referred to hereafter as the Nanoparticle-on-Mirror (NPoM) geometry.

1.2.4 Nanoparticle-On-Mirror (NPoM)

Scanning probe microscopy (SPM) tips can produce well-defined nanocavities above a metallic surface. While this affords extremely high spatial resolution and control over SERS response,^{70–72} plasmonic performance is vulnerable to tip morphology, the systematic effect of which is difficult to probe due to low fabrication throughput.⁷² The accessibility of the technique is also restricted by complex equipment and/or ultrahigh-vacuum (UHV) requirements.

Fortunately, this effect is also achievable with an AuNP near an Au surface.^{1,3,17,73–75} Large vdW forces between AuNP and substrate facilitate reproducible self-assembly of NPoMs with a downward-facing flat facet,⁷⁶ offering a more robust geometry. Unlike SPM-based methods, NPoM assembly allows fast fabrication of millions of nanocavities under ambient conditions. In this system, the AuNP charge oscillations couple to their induced charge image in the nearby Au surface, creating a perfectly aligned virtual AuNP dimer with similar optical confinement and response (**Figure 1.8a**).^{77,78}

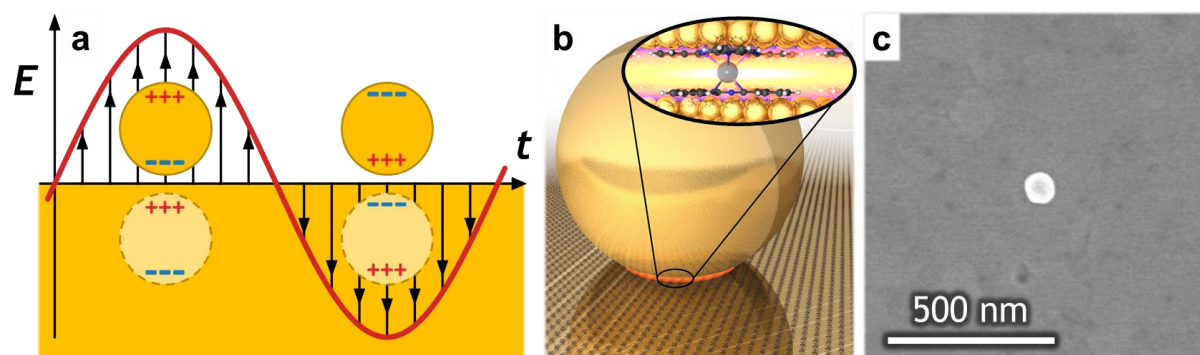


Figure 1.8. (a) Schematic illustrating simplified interaction of AuNP LSPP with its charge image in a nearby Au surface (*cf.* **Figure 1.2c**). (b) Schematic of NPoM atop a molecular monolayer; inset shows side profile of monolayer in plasmonic cavity. (c) SEM image of typical, isolated NPoM. (b, c) Adapted from [1].

Fabrication is achieved by depositing AuNPs on an Au surface separated by a thin (< 10 nm) dielectric layer. This gap can be realised using a wider range of spacer materials than aggregate systems, including thin films of insulators or semiconductors,⁷⁹ mono or multilayers of 2D materials,^{77,80–82} self-assembled molecular monolayers,^{17,26} polyelectrolytes^{73,83} and DNAo.^{48,84} This yields isolated nanocavities of predetermined size (down to 0.3 nm^{17,77,79}) containing specific molecules and/or materials using simple solution deposition methods, with associated control over field enhancements and light-matter coupling.

The assembly of self-assembled monolayers (SAMs)^{85,86} - including Au-bound alkanethiols^{87,88} and arylthiols^{89,90} - has been studied for several decades⁹¹ and ordered molecular films can readily be assembled. Combining established techniques for fabrication

of flat Au substrates^{92,93} and functionalisation thereof^{91,94,95} with commercially available monodisperse, pseudo-spherical AuNPs¹³ allows fast, reproducible fabrication of well-defined individual nanodevices.

A typical SAM-based NPoM sample is prepared by functionalisation of a flat, clean Au surface via solution deposition (**Methods 7.3**), followed by brief (5-30 s) exposure of the treated surface to colloidal AuNP solution. Short AuNP deposition time leads to sparse, randomly-distributed coverage of isolated, optically resolvable NPoMs (**Figure 1.8c**, **Section 1.3.2**). Assuming successful SAM formation, each AuNP is separated from the Au substrate by the same molecular layer, creating an array of plasmonic nanocavities with identical thickness, orientation, and chemical contents (**Figure 1.8b**).

NPoMs facilitate optical communication between the near and far field; efficient mixing of confined nanogap modes with radiative nanoparticle plasmons efficiently couples free-space light into and out of the cavity.^{3,76} The far-field optical response of the individual NPoMs is therefore dominated by the geometric and physicochemical properties of the nanoparticle, cavity and cavity contents^{17,26} (**Sections 1.3.1, 1.3.2**). The NPoM optical response is still perturbed by the AuNP size and shape, but, unlike AuNP aggregates, the dimer response is not averaged over the ensemble and the spectral effects of polydispersity and hotspot contents are decoupled. The absence of many-particle modes reveals well-defined, dimer-like resonances (**Figure 1.8d**) that allow efficient characterisation of the physicochemical properties of the spacer layer and the light-matter interactions in the hotspot.^{17,49} With a uniform spacer layer, the effect of nanoparticle and cavity shape on plasmonic response can now be characterised.¹⁶

Such fine control over light-matter interactions of individual nanostructures leads to a range of advanced nanophotonic behaviour based on the manipulation of light at sub-wavelength scales, mediated by carefully chosen molecular spacers. Over the past few decades, a growing body of work has manifested around the assembly, characterisation and analysis of these structures, with applications in sensing,^{6,61,96} reaction monitoring,^{97,98} strong coupling,⁴⁹ and trapping of high-energy electrons,²⁷ all at the few-to-single-molecule level, as well as tracking the movement of single Au atoms^{50,51,99} and transient crystal defects.^{52,53} **Section 1.4.1** introduces a select few of these applications, demonstrating the importance of well-defined molecular spacers.

1.3 Interpreting the Plasmonic Response

Both the near- and far-field optical response of a plasmonic nanostructure depend intimately on nanostructure geometry and physicochemical properties of the hotspot and surrounding environment. In a plasmonic hotspot, the resonant nanocavity modes are perturbed by the molecular spacers; these modes simultaneously couple to the antenna-like LSPP modes of the

nanoparticle, allowing efficient communication between the near- and far-field. In this way, the nanostructure and cavity can be characterised via the far-field optical response, with geometric^{65,76,100} and physicochemical¹⁷ information contained in scattering and absorption spectra.

This section introduces a simple analytical treatment for the optical response of the NPoM model dimer system, providing context for understanding the characterisation methods and far-field spectra of NPoM samples and many-particle AuNP aggregates. The utility of both systems as SERS substrates will be briefly discussed. In this thesis, the introduced plasmonic analysis techniques are primarily used to characterise incorporation, orientation and surface binding of the novel spacer molecules within the hotspot.

1.3.1 Dimer Coupling/Scattering Theory

Although dimers are difficult to isolate, the optical response of an NPoM is equivalent to an AuNP dimerised with its charge image inside the metal surface.^{69,74,77} Provided a well-defined AuNP size and shape, darkfield (DF) scattering spectroscopy enables characterisation of the molecular spacer layer via position and intensity of the coupled plasmonic modes.¹⁷

To a first approximation, the nanocavity acts like a metal-insulator-metal waveguide (**Figure 1.9b**), the lowest plasmonic modes of which can be solved analytically.³ Decreasing the gap size increases the in-plane wavevectors (shortening the effective wavelength), accompanied by a decrease in field penetration into the metal. The continuum of available modes is broken by the finite size of the cavity, with the nature and symmetry of available discrete gap modes defined by the size and shape of the downward-facing AuNP facet (**Figure 1.9c,d**).^{3,76,80,101}

Due to their effective wavelength mismatch, these nanocavity modes couple poorly to incident light. Fortunately, the AuNP LSP modes (**Section 1.1.2**) span the whole NP-substrate system and couple efficiently to both free-space photons (with coupling strength $\propto D^3$ for AuNP diameter D)¹⁶ and the confined cavity modes, acting as a light-harvesting antenna for the cavity and allowing far-field visualisation of the hotspot contents.^{3,17,26,76}

These antenna modes can be estimated analytically by modelling the system as a lumped inductor-capacitor-resistor (LCR) electrical resonator¹⁰² (**Figure 1.9a**), whereby two identical LC circuits are capacitively coupled across the gap to give the lowest-energy antenna mode (λ_1^l), with wavelength

$$\lambda_1^l = \lambda_p \sqrt{\varepsilon_\infty + 2\varepsilon_d + 4\varepsilon_d C_g / C_{NP}} \quad (2)$$

where ε_d is the permittivity of the surrounding dielectric (with refractive index $n_m = \sqrt{\varepsilon_d}$), $C_{NP} = \pi D \varepsilon_0$ is the AuNP capacitance and $C_g = C_{NP} \varepsilon_g^\chi \ln[1 + \zeta D / 2d]$ is the gap capacitance for gap size d , gap permittivity ε_g and NPoM constants $\chi \approx 0.5$ and $\zeta \approx 0.15$.

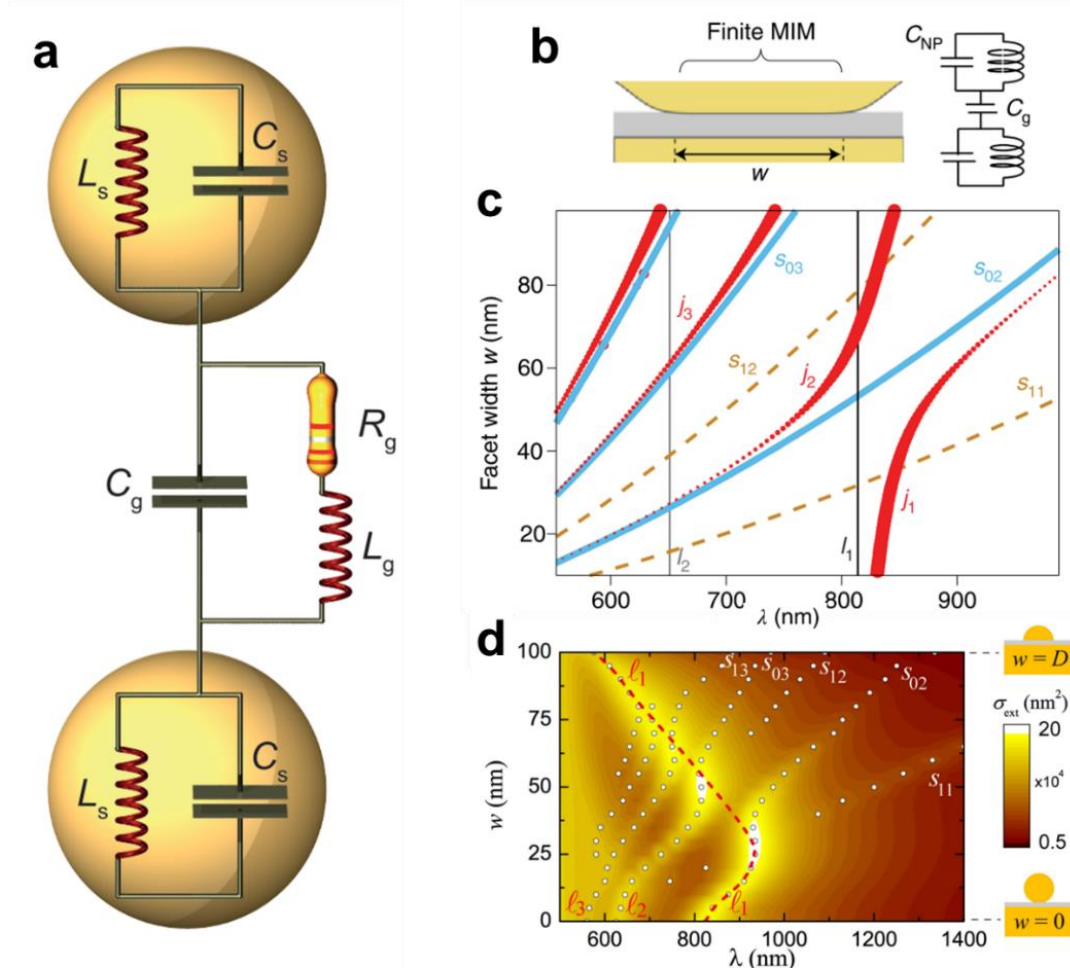


Figure 1.9. (a) Schematic of AuNP dimer modelled as an LCR circuit with particle/gap inductance L_s , L_g and capacitance C_s , C_g , and gap resistance R_g .¹⁰² (b) Schematic illustrating profile of faceted nanoparticle atop a thin insulating layer (c) Calculated wavelength of antenna (l_i ; grey lines) and cavity (s_{mn} ; blue/gold lines) resonances for NPoM ($D = 100$ nm) with a range of bottom facet widths (w). Radiative mixed modes (j_i) are shown in red.⁷⁶ (d) Mapped extinction spectra calculated for the same NPoM, with maxima occurring at the symmetry-matched antenna/cavity mode anticrossings. Adapted from [3,76,102]

For a perfectly insulating layer, C_g depends primarily on gap size (d) and gap permittivity (ϵ_g). The ϵ_g depends on the refractive index of the spacer (n_g); $\epsilon_g = n_g^2/\mu_g = n_g^2$ for diamagnetic materials. For a conductive layer, the antenna modes are blueshifted due to charge screening of the plasmon mode by nonzero gap current; the extent and limit of the blueshift depends on the resistance (R_g) and inductance (L_g) of the gap.^{26,102}

Antenna modes couple to specific cavity modes, with greatest extinction occurring at symmetry-matched anticrossings (**Figure 1.9c,d**). Cavity modes of appropriate symmetry mix with antenna modes and emit to the far-field, while the rest are dark. For circular facets, the cavity resonance wavelengths (λ_i) can be modelled analytically as:^{76,80}

$$\lambda_i \approx \lambda_p \sqrt{\frac{w\epsilon_g}{d\alpha_i} + \epsilon_\infty} \quad (3)$$

where w is the facet diameter, α_i are phase-shifted antinodes of the J_0 Bessel function⁸⁰ and ϵ_∞ is the high-frequency background permittivity. The wavelength (λ_C) of the dominant radiative mode can then be approximated via:

$$\frac{hc}{\lambda_C} \approx \frac{\omega_1^l + \omega_i}{2} - \sqrt{\left(\frac{\omega_i - \omega_1^l}{2}\right)^2 + V^2} \quad (4)$$

where $\omega_1^l = \frac{hc}{\lambda_1^l}$, $\omega_i = \frac{hc}{\lambda_i}$ and V is an energy describing the mixing rate of antenna and cavity modes. This relatively simple analytic treatment allows rapid, user-friendly simulation of the main physical parameters governing plasmonic dimers for validation of experimental results, in quantitative agreement with numerical simulations.^{76,102}

1.3.2 NPoM: Darkfield (DF) Spectroscopy

The NPoM optical response can be interrogated using DF spectroscopy (**Methods 7.4.1**). Samples are illuminated with incoherent white light at high annular angles (63-75°); scattered light is collected at lower angles (< 63°) and spectroscopically analysed (**Figure 1.10**).

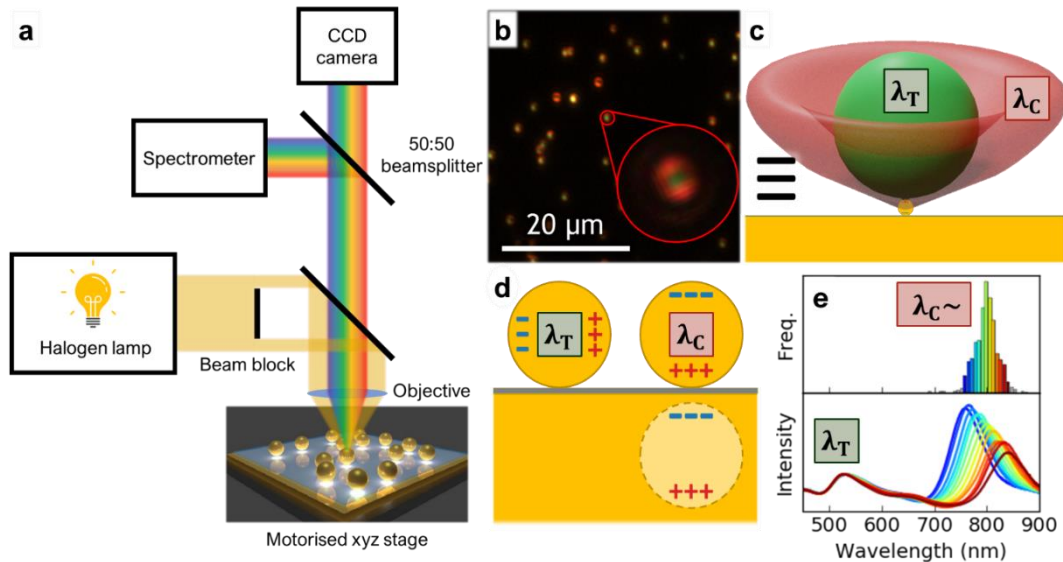


Figure 1.10. (a) Basic DF scattering spectroscopy setup. Bottom schematic adapted from [80]. (b) DF image of NPoM sample with randomly distributed, optically resolvable NPoMs. Inset shows close-up of single NPoM with distinct emission pattern. (c) Illustration of 3D emission pattern, made by Demelza Wright.¹⁰³ (d) Schematic of surface charge distributions for the two bright NPoM modes considered in this work. (e) Top: histogram of measured λ_C positions for ~1000 NPoMs across sample collection area, showing approximately normal distribution. Bottom: averaged DF spectra from each λ_C histogram bin of corresponding colour.

The primary bright modes analysed in this work are the non-coupled “transverse mode” (TM), with wavelength λ_T and scattering intensity I_T , and the coupled $s_{02} + l_1 = j_1$ mode (hereafter called the “coupled mode” (CM) for simplicity) with wavelength λ_C and scattering intensity I_C . The TM field oscillates in the xy plane and emits normal to the substrate, visible as a green spot (**Figure 1.10b-d**). The CM is emitted at high angles due to z-polarisation of the gap field, with maximum intensity at ~60° and FWHM of 10° (**Figure 1.10c,d**),^{17,75} visible under darkfield illumination as a characteristic ring-shaped emission profile^{73,104} (**Figure 1.10b**). Higher-order

($j_{i>1}$) modes can reveal geometric, positional and directional information info e.g. single emitter location¹⁰⁵ and NP shape anisotropy.¹⁰⁶ Nevertheless, λ_C is suitable for monolayer/nanocavity characterisation in most cases^{1,17} and higher-order modes are not considered further here.

Efficient mixing of antenna and cavity modes leads to strong perturbation of λ_C and I_C by the spacer layer, of which the important properties are gap size (spacer thickness) d , refractive index n_g , and conductance G . Qualitatively, λ_C , I_C and field enhancement factor $g \propto |E/E_0|$ all increase with n_g and decrease with d and G (**Figure 1.11**).

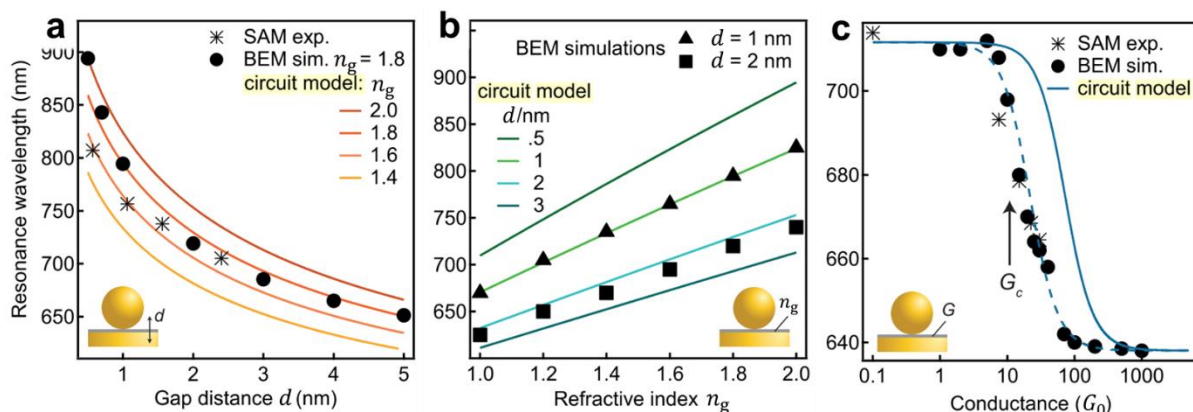


Figure 1.11. Effect of gap properties on analytically calculated CM resonance wavelength λ_C . **(a)** Gap size d , **(b)** refractive index n_g and **(c)** conductance G , showing agreement with experimental and/or numerical boundary element method (BEM) simulation data. Adapted from [102].

In contrast, λ_T and I_T are relatively unaffected by the cavity contents and the TM serves as an internal standard for the CM. For certain insulating gaps, combined measurement of λ_C and I_C/I_T allows indirect measurement of d and n_g ,¹⁷ although this is complicated by the inherent size/shape polydispersity of most colloidal nanoparticle solutions,^{16,77} as well as differences in emission angle, focal height and collection efficiency of the two NPoM modes.^{3,17}

To correct for polydispersity, spectra are collected from 100-1000 NPoMs per sample. While this can be done quickly as an ensemble measurement,⁸³ spectroscopy of individual NPoMs allows deeper statistical interrogation and single-cavity analysis.^{17,26,49} λ_C scales with $\ln D$ which, for average AuNP diameter $\bar{D}$ of 80 nm and size polydispersity of 8%,¹³ yields an approximately normal distribution in λ_C with FWHM ≈ 30 nm for a near-perfect spacer layer¹⁷ (**Figure 1.10e**). This reveals the average CM wavelength ($\bar{\lambda}_C$) associated with $\bar{D}$, while the distribution width reflects monolayer and substrate variability (**Figure A3**). Inspection of the spectral average of each λ_C histogram bin (**Figure 1.10e, bottom**) yields similar information, with single-mode CM peaks indicative of a uniform monolayer.

Chromatic aberration and emission angle differences are corrected for by collecting spectra at a range of focal heights (z) for each NPoM (**Figure 1.12a**). The focal position and optimum intensity is then extracted for each wavelength (via the centroid of the height-dependent scattering intensity) and scaled according to optical collection efficiency.¹⁷ The

resulting spectra (**Figure 1.12b**) contain aberration-corrected λ_C and I_C/I_T information, a scatter plot of which allows estimation of d and n_g via comparison with numerical simulation data (**Figure 1.12c**). This treatment is known as normalising plasmon resonance (NPR) spectroscopy.¹⁷ I_C/I_T is extremely sensitive to small changes in optical collection path alignment/efficiency, as well as perturbation of plasmonic outcoupling efficiency by, (e.g.) variation in AuNP and facet geometry.^{16,76,100} Consequently, I_C/I_T distributions are often broad and d , n_g values obtained from this method are approximate. Nevertheless, NPR spectroscopy is a useful additional tool for semi-quantitative characterisation/conformation of molecular assembly and orientation within the NPoM cavity.

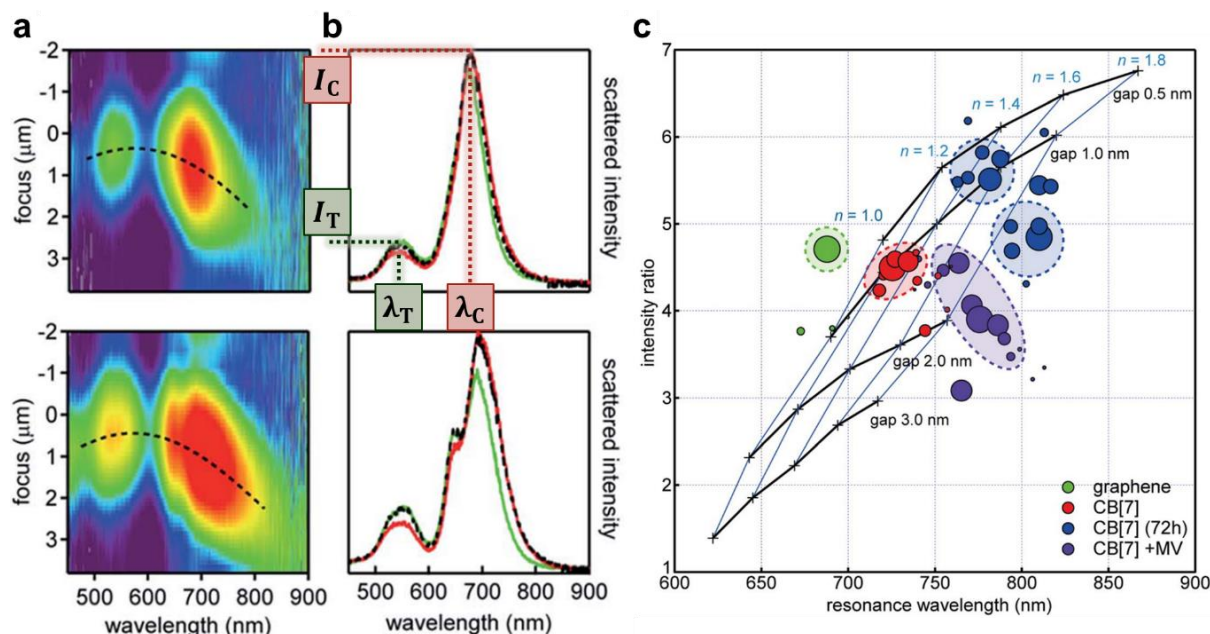


Figure 1.12. (a) z-stack of DF scattering spectra for two typical NPoMs showing variation in focal height with wavelength. (b) Scattering spectra at focal height of the two dominant modes - TM (green) @ 0.35 μm and CM (red) @ 0.65 μm (top) and 1.05 μm (bottom) - and aberration-corrected spectra shown in black. (c) Intensity ratio (I_C/I_T) vs resonance wavelength (λ_C) scatter plot for four different spacer systems, overlaid on grid of calculated (λ_C , I_C/I_T) positions for a range of (n_g , d) combinations (black, blue lines). Comparison of experimental and simulated data allows indirect approximation of n_g and d from experimental (λ_C , I_C/I_T). Adapted from [17].

1.3.3 AuNP Aggregates: Extinction Spectroscopy

Aqueous AuNP aggregation can be monitored in-situ⁵⁹ via extinction spectroscopy (**Methods 7.4.3**), which allows reporting of local aggregate growth in the far field. Unlike dynamic light scattering (DLS) - which generally reports ensemble parameters like average size, zeta potential and anisotropy with long acquisition times - far-field extinction spectra are highly sensitive to real-time aggregate growth and nanoscale topology.^{59,62,63} The following AuNP aggregate examples use cucurbit[5]uril (CB[5]), a rigid, bidentate (with respect to Au surface affinity) molecular spacer (see **Section 2.2.1**).

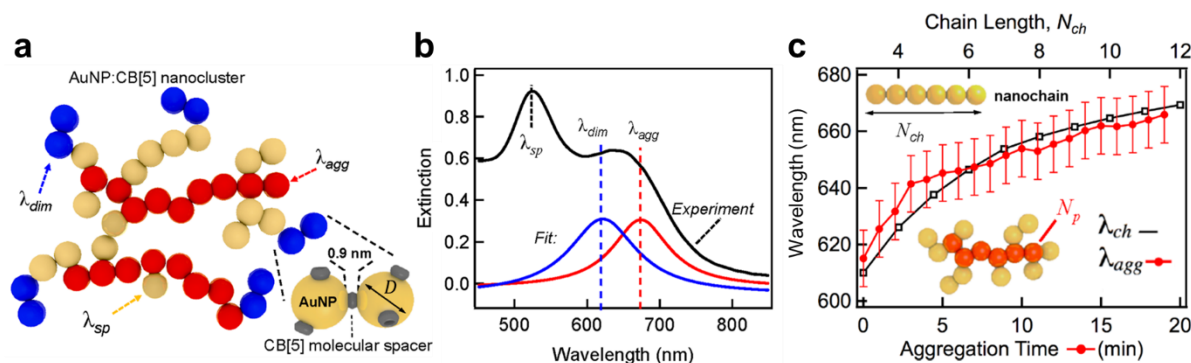


Figure 1.13. (a) Schematic of typical AuNP nanocluster structure, with dimers (blue) and chains (red) highlighted. Inset: pair of AuNPs within the aggregate, illustrating uniform 0.9 nm gap spacing facilitated by cucurbit[5]uril molecular spacer. (b) Typical experimental extinction spectrum (black) for AuNP aggregate ($d = 0.9$ nm, $D = 30$ nm) with single particle resonance (λ_{sp}) highlighted, deconvoluted to show dimer (λ_{dim} , blue) and chain (λ_{agg} , red) resonances. (c) Comparison of experimental λ_{agg} evolution with calculated resonance wavelength (λ_{ch}) of linear AuNP chains ($d = 0.9$ nm, $D = 20$ nm). Adapted from [62].

A monomeric aqueous AuNP extinction spectrum has a single peak ($\lambda = \lambda_{sp}$, $I = I_{sp}$) around 510-550 nm,^{59,62,63} analogous to λ_T of NPoMs, and broadband absorption at shorter wavelengths (**Figure 1.13b**). Upon aggregation with uniform spacing, two new resonances appear over time: the dimer mode (λ_{dim}), analogous to λ_C , and the aggregate mode, λ_{agg} .^{59,64}

λ_{dim} usually appears before λ_{agg} and, like λ_C , depends on d , n_g , G , D and w and can be used for cavity and spacer characterisation. The λ_{dim} spectral peak remains visible and stationary throughout (even for larger aggregates) due to its orthogonal polarisation relative to adjacent chain modes; the stability in λ_{dim} position indicates presence of many equivalent nanogaps⁵⁹ (**Figure 1.13a**). λ_{agg} is a complex set of many-body coupled modes whose evolution reflects growth kinetics and extended plasmonic structure. Coupling of adjacent gap plasmons leads to a series of chain modes which, due to gap size uniformity, have discrete resonance wavelengths that are robust to disorder and redshift predictably with increasing particle number, up to a saturation limit⁶² (**Figure 1.13c**). The chain modes are visible in the far field as λ_{agg} , a single, broad mode that redshifts, broadens and increases in area as the aggregate evolves (**Figure 1.14**).

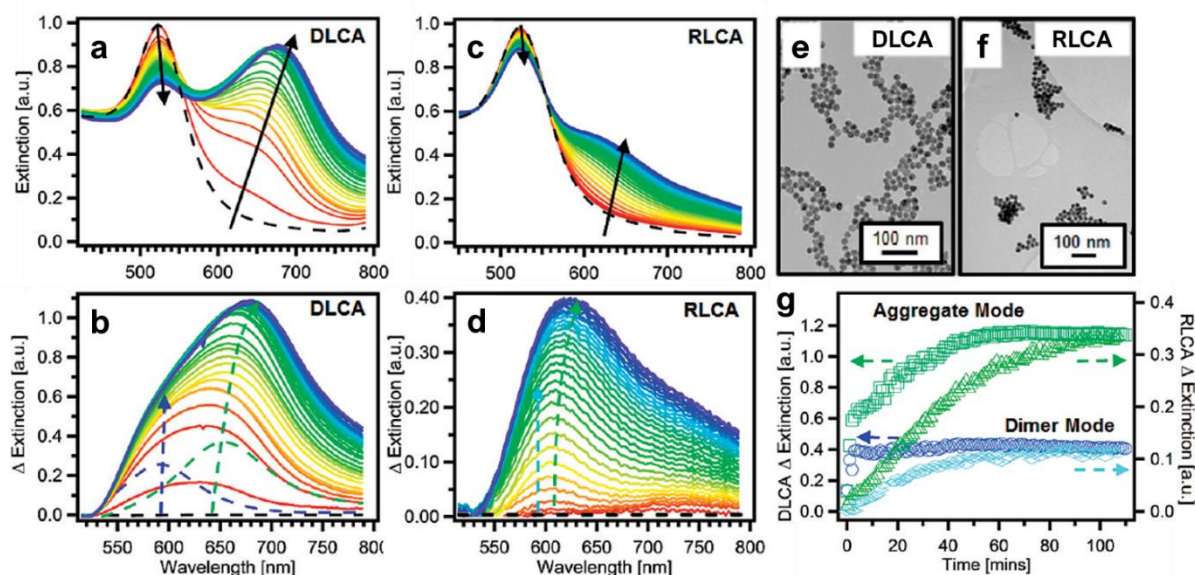


Figure 1.14. Typical characterisation of AuNP aggregation structure and kinetics using CB[5]. $D = 20$ nm, $d = 0.9$ nm. Temporal evolution (in direction of arrows) of AuNP extinction spectra after addition of (a, b) 80 or (c, d) 60 molar equivalents of CB[5], exhibiting DLCA or RLCA growth kinetics, respectively. Difference spectra (b, d) are equivalent to (a, c) with monomeric AuNP spectrum (dashed black line) subtracted and show growth of λ_{dim} and λ_{agg} modes over time (arrows guide the eye). (e, f) TEM images showing structural differences between DLCA and RLCA aggregates after 30 min. (g) Evolution of λ_{dim} and λ_{agg} intensities over time, showing rapid initial increase of both peaks in DLCA regime (left axis; λ_{dim} blue circles; λ_{agg} green squares) and more gradual increase for RLCA (right axis; λ_{dim} blue diamonds; λ_{agg} green triangles). Adapted from [59].

Growth kinetics and spectral evolution of these systems are governed by the aggregant concentration via coverage at the AuNP surfaces. The surface coverage determines the sticking probability upon collision of two AuNPs, leading to growth kinetics consistent with reaction-limited and diffusion-limited colloidal aggregation (RLCA, DLCA) models.^{107–109}

High aggregant concentration and surface coverage results in DLCA growth. Short-range interparticle attraction is large and most particles stick upon collision (i.e. diffusion is the rate-determining step), leading to kinetic, open, quasi-fractal structures (**Figure 1.14e**). Lower aggregant concentrations yield RLCA growth, where sticking probability is low for single AuNPs and increases with aggregate size, leading to denser clusters with a thermodynamic, “annealed” appearance (**Figure 1.14f**).

This topology difference directly influences the spectral evolution of all three plasmonic modes.⁶² DLCA growth exhibits a rapid intensity decrease and broadening of the λ_{sp} mode, accompanied by appearance of a strong secondary band (comprised of λ_{dim} and λ_{agg}) that quickly grows and redshifts (**Figure 1.14a,b**). RLCA growth shows a similar but much slower spectral evolution (**Figure 1.14c,d**). Subtraction of the monomeric AuNP spectrum and deconvolution of the resultant difference spectra (**Figure 1.14b,d**) yields a pair of Lorentzian peaks for λ_{dim} and λ_{agg} . In both growth regimes, λ_{dim} grows in intensity over time but does not change position, while λ_{agg} increases in intensity and redshifts.

DLCA is characterised by a rapid increase in intensity of both coupled modes, after which the λ_{dim} intensity saturates and λ_{agg} intensity continues to increase, but more slowly (**Figure 1.14g**). This is caused by rapid initial formation of dimers and short chains, followed by gradual longer chain growth.⁵⁹ RLCA instead exhibits a gradual increase in the intensity of both modes over a few hours, with slow agglomeration of single AuNPs leading to dense clumps containing shorter chains and a slower λ_{agg} redshift.

Using this information, analysis of far-field extinction spectra provides information on the hotspot properties and shape and size of the aggregates without the need for TEM or other nanoscale measurements. The ability to control aggregation kinetics and topology via molecular spacer concentration is important for optimisation of geometry-dependent plasmonic behaviour, e.g. SERS,^{6,60,63} plexcitonic coupling^{49,110,111} and photocatalysis³¹ (**Section 1.4.1**).

1.3.4 Nanocavity SERS

The plasmonic response of AuNP aggregates is controlled via AuNP diameter, molecular spacer properties and aggregation conditions. Extinction spectra give a fair representation of the wavelength-dependent field enhancement experienced by hotspot-bound molecules; **Figure 1.15** shows typical AuNP aggregate extinction spectra ($D = 60$ nm) using two different spacer molecules, overlaid with common excitation laser wavelengths and their corresponding Raman Stokes shift regions (≤ 2500 cm⁻¹).

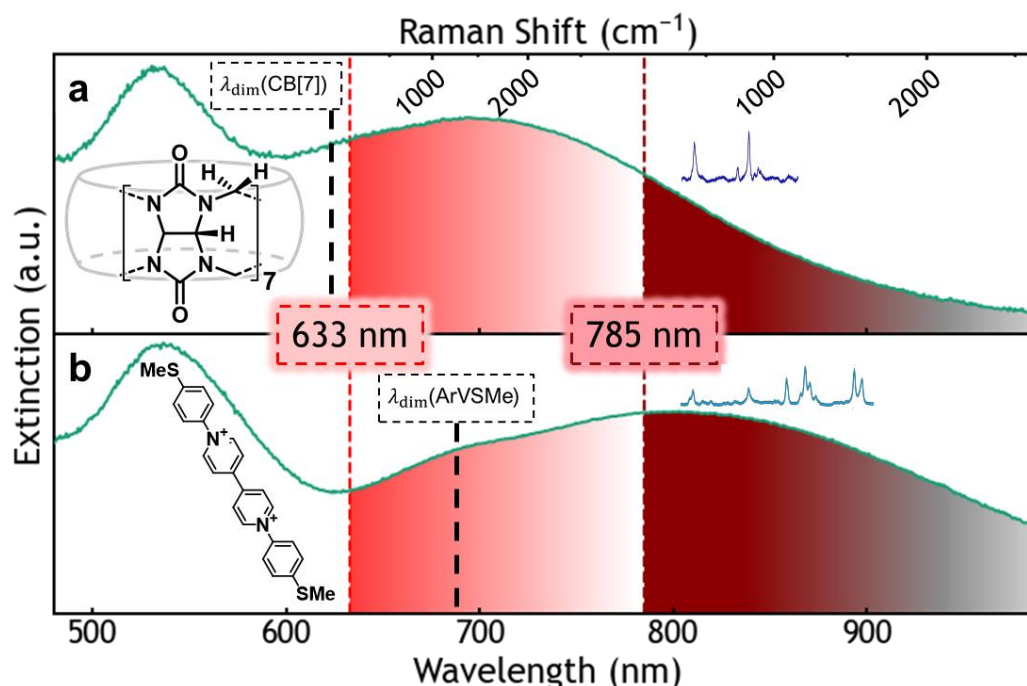


Figure 1.15. Extinction spectra of AuNPs ($D = 60$ nm) aggregated using (a) CB[7] and (b) ArV with terminal methylthio groups (ArVSMc). Aggregant/AuNP molar ratio = 100,000:1; aggregation time = 25 s. Difference in extinction spectra illustrates control over plasmonic response via size and refractive index of molecular spacer. Excitation laser wavelengths (633 and 785 nm) are highlighted; shaded areas indicate spectral windows of interest for Raman-scattered light. Insets (blue, teal traces) shows SERS spectra of CB[7]@AuNP (top) and ArVSMc@AuNP (bottom) aggregates excited at 785 nm.

The broad aggregate resonance yields strong Raman enhancements for excitation with 633 or 785 nm laser light.⁴⁷ The difference in extinction (and therefore field enhancement) between and within the two Raman regions for each system **Figure 1.15** illustrates the importance of molecular spacer, aggregation conditions and excitation wavelength for reproducibility in quantitative SERS and other plasmonic applications.⁶⁰

Notwithstanding, the accessibility of Raman measurement techniques makes SERS a useful tool for qualitative characterisation of molecular orientation, intermolecular interactions and/or surface binding within the nanocavity.⁵⁷ Extended nanoscale architecture of aggregates can also be probed via quantitative SERS, although this is beyond the scope of this work. Using a standard Raman spectroscopy setup (**Methods 7.4.4**), AuNP aggregates can be directly analysed in solution,⁶ or dried onto a substrate and analysed as a solid.⁴⁷ Solution-phase measurements allow monitoring of plasmonic evolution, while solid-state measurements provide larger signals due to increased local density of hotspots and well-defined focal planes allowing for wider optical collection angle.

NPoM SERS measurements can be performed by augmenting the DF spectroscopy setup from **Section 1.3.2** with a laser and Raman spectrometer (**Methods 7.4.2**), allowing single-cavity analysis. The spatial intensity of the confined optical field (at λ_c) decays laterally away from the hotspot centre, with FWHM $\Delta x \approx \sqrt{Dd}/n_g$.¹¹² $\Delta x \approx 6$ nm for a typical SAM-based NPoM with ($D = 80$ nm, $d = 1$ nm and $n_g = 1.4$), which means (assuming $w = 20$ nm) SERS emission is dominated by <10% of the spacer molecules. This facilitates observation of few-molecule processes for much finer analysis of the cavity contents than with AuNP aggregates, but also gives far more complex spectra.

1.4 Molecular Spacer Design

The emerging applications of coupled plasmonic nanostructures now comprise a significant body of research, and many aspects of nanostructure assembly and characterisation are well studied. Extensive experimental and theoretical study has gone into the geometry-dependent optical response of isolated and coupled nanostructures, and distribution and orientation of the enhanced near-field. This understanding has driven development of various nanophotonic applications, accompanied by the design of novel nanostructure geometries.

These applications emerge from precise control over nanocavity size, as well as position, orientation and surface binding of molecules within the hotspot. This control is primarily achieved via careful chemical design of the molecular spacers used for plasmonic self-assembly. The geometry, functionality and intermolecular interactions of these spacers have enormous influence over the field enhancement, light-matter coupling, charge transport properties and spectral response of the hotspot. A select few examples of these molecular-

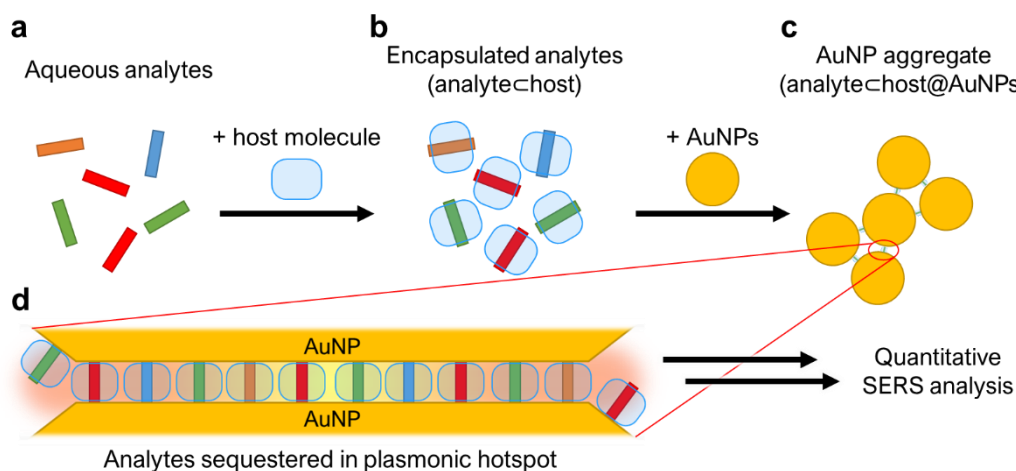
nanophotonic hybrid systems are outlined in **Section 1.4.1**, highlighting applications in sensing, cavity quantum electrodynamics, catalysis, molecular electronics and nanometrology.

New nanostructure designs necessitate advances in self-assembly and fabrication methodologies, which further advance understanding of the synergistic interplay between plasmonic nanostructures and their chemical environment. Development of molecular self-assembly techniques, in particular, has advanced understanding of interactions between molecules and enhanced optical fields and highlights the importance of control over molecular orientation and intermolecular interactions. Crucial to these developments is the rational design of molecular building blocks; key criteria for this are outlined in **Sections 1.4.2-1.4.3**.

1.4.1 Recent Developments & Coming Attractions

The extreme, controllable SERS enhancement achieved within plasmonic nanocavities facilitates solution-phase chemical sensing with ultralow (nM) detection limits,^{6,96} and real-time detection of single molecule events.^{27,50,53,99} Meanwhile, the spectral sensitivity of the nanostructures to their environment enables structural characterisation based on small changes in far-field plasmonic response.^{17,26,59,62,63,113} The enhanced field in and around the hotspot bypasses the need for electronically resonant or fluorescent molecules, which significantly decreases bleaching and allows sensing of anything with a Raman cross-section above 10^{-29} cm².⁶⁸

One recent development is a SERS substrate based on AuNP aggregates for quantitative multiplexed sensing of small molecules in complex media.^{6,60,114,115} The technique utilises specific molecular spacers (**Section 2.2.1**) that simultaneously control gap size, act as internal standards and shepherd analytes from solution into the hotspot^{6,59,115} (**Scheme 1.1**). The technique is non-invasive and offers >99% quantitative reproducibility⁶⁰ within minutes, with potential economic viability for rapid, personalised medical assays and continuous health screening⁶ environmental monitoring,⁷ drug detection⁹⁶ and food safety⁶¹ applications.



Scheme 1.1. Multiplexed sensing with AuNP-based SERS substrate. **(a-b)** Aqueous small molecule analytes form 1:1 inclusion complexes with CB[7] in solution. **(c)** Colloidal AuNPs added to this solution aggregate rapidly, leading to **(d)** reproducible sequestration of analytes in the interparticle plasmonic hotspots and allowing simultaneous quantitative SERS detection.^{6,60,96,115}

Electromagnetic and chemical perturbation of the local electromagnetic environment also has important consequences for fluorescent emitters in the cavity. The enhanced field mediates coupling between spectrally overlapped excitons and plasmons, perturbing the optical response of both nanostructure and emitter. Normally, PL of an emitter near a plasmonic nanostructure is quenched via increased non-radiative relaxation (NRR) into dissipative plasmonic modes.¹¹⁶ For coupled systems, however, enhanced in- and out-coupling (**Section 1.3.1**), together with steric confinement, can increase both the rate¹¹⁷ and efficiency¹¹⁸ of the emitter's excitation and PL.^{49,111} These effects are geometry-dependent, and allow inference of emitter orientation and position in NPoM cavities (**Figure 1.16a**).

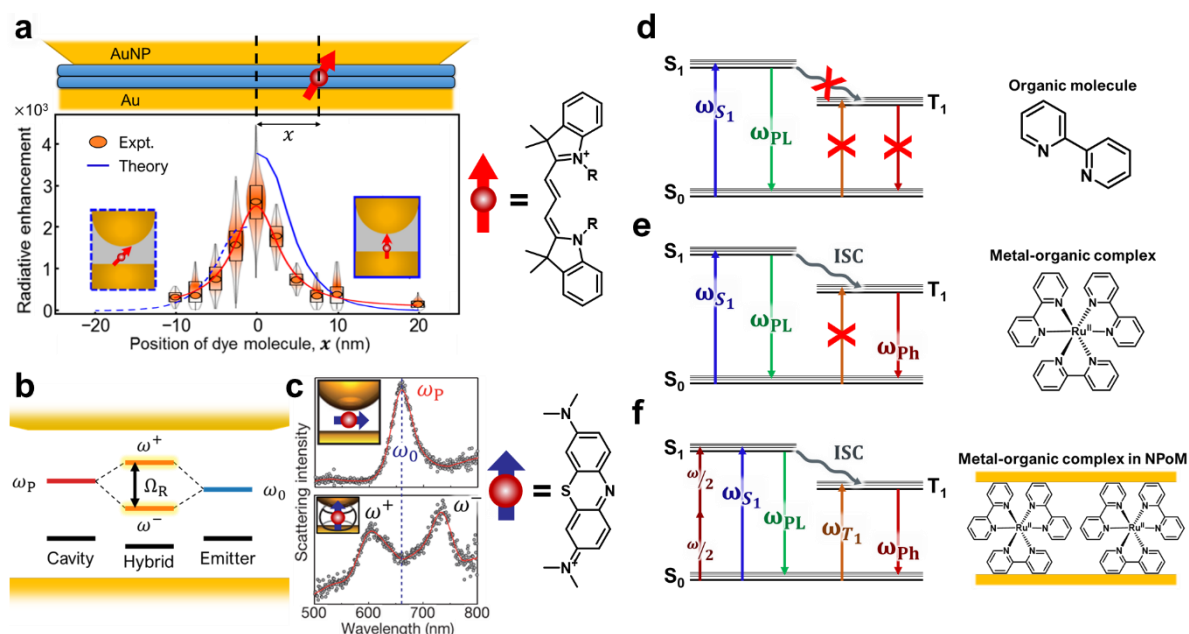


Figure 1.16. Modified energy landscapes and excitation pathways of molecular emitters in plasmonic nanocavities. **(a)** Top: Schematic of Cy5 molecular emitter positioned in an NPoM hotspot using DNAo. Bottom: experimental (violin plot) and theoretical (blue lines) radiative enhancement for different lateral displacements of Cy5 molecule in hotspot, illustrating strong position and orientation dependence. **(b)** Jablonski diagram illustrating strong coupling between nanocavity (with plasmon resonance ω_p) and emitter (exciton resonance ω_0) to form hybrid light-matter modes ω^+ and ω^- with splitting energy Ω_R . **(c)** Experimental NPoM scattering spectra with transition dipole of single methylene blue emitter oriented parallel (top) or perpendicular (bottom) to the substrate; strong coupling only occurs for the latter, evidenced by splitting of ω_p about the emitter absorption ω_0 (blue dashed line). **(d, e)** Jablonski diagrams illustrating allowed and forbidden electronic transitions of molecular emitters in solution **(d)** without and **(e)** with an internal heavy atom. **(f)** Jablonski diagram for emitter with internal heavy atom in NPoM cavity; spin-orbit coupling effect of external Au atoms facilitates two-photon absorption and direct singlet-triplet excitation.

Ultrasmall cavity mode volumes, dark plasmon resonances and external heavy-atom spin-orbit coupling all modify the excitonic energy landscape, bypassing selection rules to unlock previously forbidden electronic and vibrational transitions. Notable effects include enhanced two-photon absorption,¹¹⁹ direct singlet-triplet excitation¹²⁰ (**Figure 1.16d-f**) and selective emission from specific excited states.¹²¹

So far, these effects all exist within the weak coupling regime. Through careful nanostructure and emitter design, energy exchange rates between the cavity and emitter can

be made to exceed all decay processes, leading to strong coupling. This coherent plasmon/exciton interaction creates hybrid light/matter “plexcitonic” states,¹²² characterised by a splitting of the observed plasmon resonance into two distinct peaks^{49,110,123,124} (**Figure 1.16b,c**). Originally requiring high-quality microcavities and cryogenic temperatures,^{125,126} single-molecule strong coupling is now accessible under ambient conditions.^{49,110} This is possible thanks to the ultrasmall mode volume of the plasmonic cavity, which offsets the nonradiative losses prevalent at room temperature.

Historically, the vision of strong coupling was directed towards optoelectronic applications, e.g. lasing, low-power switching and quantum information devices.^{49,127,128} However, coupling of electronic molecular transitions to cavity modes can also generate new eigenstates and energies, perturbing the thermodynamic landscape and yielding distinct chemistry.^{122,129–131} Current studies in this area mostly explore modification of direct photochemical processes involving high-QY fluorophores.^{129,132,133} Expanding on this, an alternative possibility involves strong coupling of metal-ligating dye molecules, which could allow plexcitonic modification of reaction pathways in transition metal catalysis.¹³⁴

Illumination of plasmonic nanostructures can also catalyse and initiate chemical reactions of non-resonant species.^{135–137} Here, high near-field strengths,^{138,139} localised heating^{31,140} and nonthermal charge carriers (“hot electrons”)^{27,43,141,142} all yield fundamentally different chemistry from semiconductor photocatalysts. Key features include synergistic coupling of thermal and photonic stimuli,¹³⁵ geometry-dependent chemical selectivity¹⁴³ and utilisation of broadband radiation.¹⁴⁴

For example, self-assembled AuNP nanostructures have been shown to photocatalyse (and monitor *in-situ* via SERS) thermal reactions³¹ (**Figure 1.17a,b**), while NPoM systems can directly initiate free-radical polymerisation via direct hot carrier injection into nearby monomers, in the absence of chemical initiators.^{145,146} Both processes require significantly lower energy inputs than the bulk thermal or photolytic activation normally required for such reactions.

Effective utilisation of hot charge carriers is currently restricted by short lifetimes (<1 ps)¹⁴⁷ and poor mechanistic understanding,^{29,136} requiring more in-depth analysis of electron transfer across the metal-molecule interface.^{27,31,144} Conveniently, the highest hot electron yields occur in the regions of largest field enhancement, making single-cavity NPoM SERS ideal for exploring this behaviour.^{27,29,143} Molecular spacer structure and surface connectivity can be modified to induce and stabilise discrete redox events, via tuning of the through-gap electron transport mechanism (**Figure 1.17c,d**). Real-time monitoring of these processes provides detailed insights into the mechanism and chemical dependence of plasmonic hot electron transfer²⁷ and electroreduction⁹⁷ at the nanoscale.

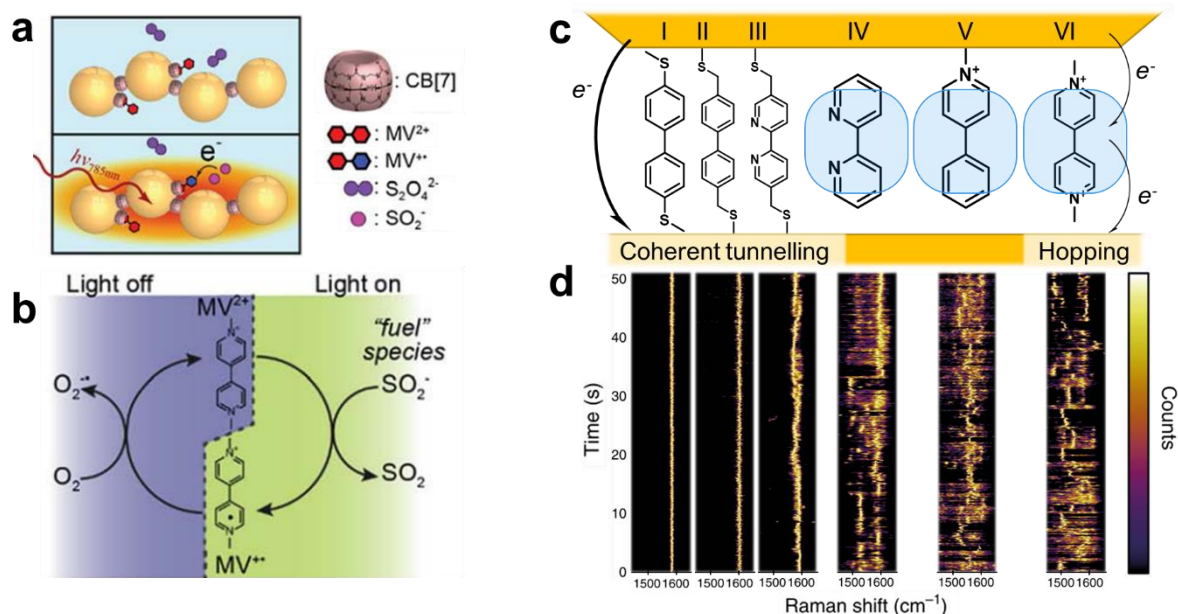


Figure 1.17. (a) Schematic illustrating thermal dissociation and activation of $S_2O_4^{2-}$ reducing agent with CB[7]@AuNP aggregates upon illumination. (b) Reaction scheme illustrating reduction/oxidation cycle of methyl viologen (MV^{2+}) with SO_2 and O_2 . Adapted from [31]. (c) Chemical structure of various molecular junctions with decreasing Au connectivity and structural homogeneity from left to right. (d) SERS timescans of single NPOMs using molecular junctions in (c). Raman line movement corresponds to chemical reduction; decreasing connectivity/conjugation and introducing heteroatoms lowers ballistic tunnelling probability and increases redox event lifetime. Adapted from [27].

This behaviour raises the possibility of systems involving molecular spacers with catalytic centres for plasmon-driven electron transfer, whose structural effects on reactivity can be studied via SERS.^{27,97} Further systematic study with carefully-designed junction molecules may provide new optical control over catalysis, particularly if paired with electrochemistry.^{97,148,149} An important next step is design of appropriate spacer molecules to mediate energy and charge transfer between plasmonic structures and reactants.²⁹

This in-depth molecular junction analysis should also prove useful in the growing field of molecular electronics. The use of small molecules as electronic components may allow bottom-up fabrication of devices with vastly increased information density, reduced energy requirements and chemically tuneable performance.^{25,150,151} This field is still in its infancy, however, with most studies focusing, again, on understanding the non-equilibrium charge transport properties of the metal molecule interface.^{151–153} In addition to the stochastic molecular redox monitoring described above²⁷ (Figure 1.17c,d), nanogap-assisted optical characterisation has also been used to characterise current-dependent molecular torsion,²⁵ adatom formation,^{50,51,99,154} contact geometry,^{65,76} surface reconstruction⁵⁷ and crystal defect evolution.^{52,53}

Finally, the intimate relationship between plasmonic nanostructure geometry and optical response has powerful implications for nanometrology. A widely studied example of this is the “plasmon ruler”, which monitors the optical response of a coupled plasmonic system (e.g.

AuNP dimer or NPoM) as a function of gap size^{83,155,156} (**Figure 1.18**). The optical sensitivity of plasmonic dimers allows nanoscale geometry measurements of soft matter systems over greater length scales than Förster resonance energy transfer (FRET) methods, with high photostability and brightness.^{157–160} At smaller lengthscales, plasmon rulers can also be used for materials characterisation,^{17,26,79,83} gas sensing^{113,146,161} and probing the ultimate limits of plasmonic enhancement.^{74,93}

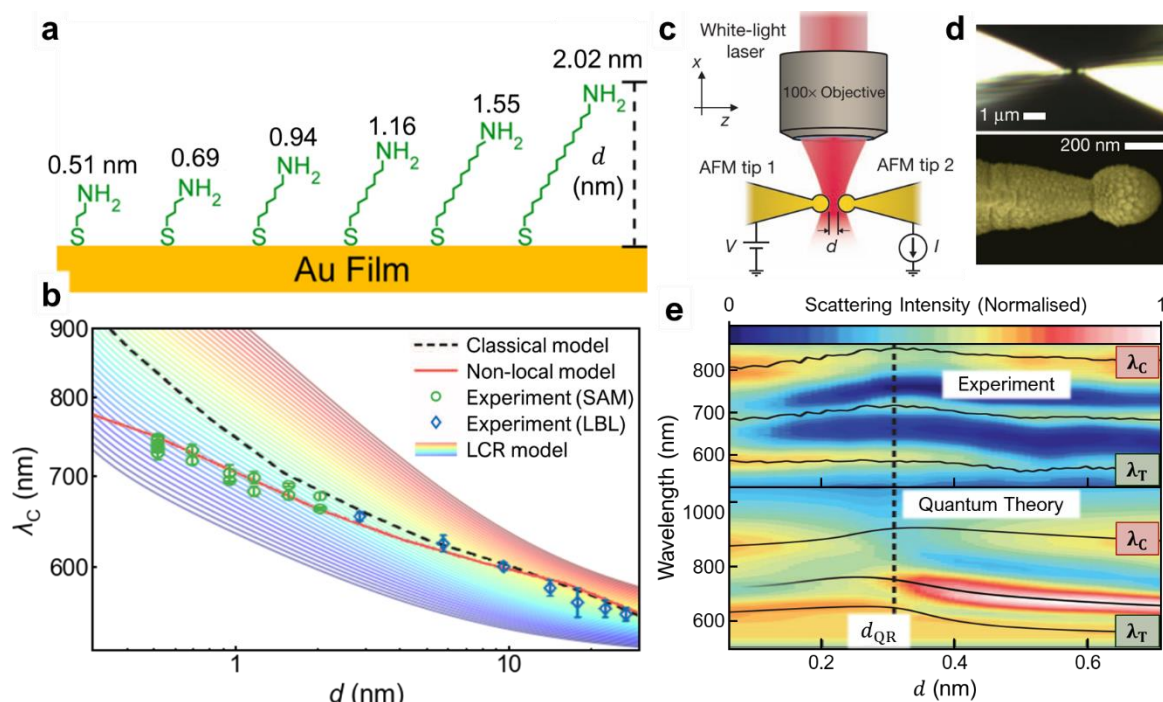


Figure 1.18. Complementary plasmon ruler calibration techniques. **(a, b)** Amine-terminated alkanethiol SAMs of various known lengths are used to experimentally calibrate the optical response of NPoM systems with gap size $d > 0.5$ nm. **(b)** Comparison of experimental λ_c data from **(a)** with classical and non-local analytical models reported by Ciraci *et al.*,⁷⁴ overlaid with results of the LCR model of Benz *et al.*¹⁰² for a range of n_g . **(c)** Schematic and **(d)** darkfield optical (top) & SEM (bottom) images of Piezoelectrically-controlled AuNP dimer. **(e)** Comparison of experimental distance-dependent optical response (top) of the system in **(c,d)** with a quantum-corrected plasmonic model (bottom) for $d < 0.7$ nm, illustrating reversal of $\partial\lambda_c/\partial d$ (due to quantum tunnelling) at small d .¹¹²

Experimental calibration requires in-depth understanding of the distance-dependent optical response and many analytical,^{74,102,162} numerical^{74,83,163} and empirical^{155–157,164,165} models have been developed. While numerical and analytical models based on Maxwell's equations allow modelling of the plasmonic response for $d > 1$ nm,⁷⁴ such treatment generates singularities in field enhancement and λ_c shift as $d \rightarrow 0$.¹⁶⁶ In reality, gap capacitance is limited by electron degeneracy pressure, which decreases the gradient of $-\partial\lambda_c/\partial d$ when $d < 1$ nm^{74,167} (**Figure 1.18b**). Non-local hydrodynamic corrections^{74,167,168} and/or empirical parametrisation^{102,165} are required to model these systems accurately.

For $d < 0.5$ nm, electron spillover becomes significant, leading to quantum tunnelling across the gap and increased effective gap conductance.^{1,112,169–171} The resulting charge transfer plasmonic modes decrease the field enhancement and effectively reverse the sign of

$\partial\lambda_c/\partial d$ ^{77,112} (**Figure 1.18e**). To model this, existing theory must be augmented with quantum corrections,^{112,168,170–172} derived from time-dependent density functional theory (TD-DFT) simulations of dimers with smaller particle size ($D < 10$ nm) and metals with fewer electrons (e.g. Na).^{168,172}

Despite the increasing number of theoretical studies, achieving fine structural resolution remains a major experimental challenge. The gap size resolution of alkanethiol SAMs (**Figure 1.18a**) is sufficient to test hydrodynamic/non-local models,^{74,83,173} but insufficient for probing quantum tunnelling behaviour around $d = 0.4$ – 0.5 nm.^{74,83,173} Atomic layer deposition,⁷⁹ thermal expansion techniques¹⁶¹ and 2D materials^{77,80} provide data points for $d < 0.5$ nm, but reports are relatively sparse and cross comparison is complicated by large geometric and physicochemical variability. While piezoelectric control¹¹² (**Figure 1.18c,d**) in principle offers very fine geometric resolution, the actual gap size is non-trivial to calibrate and experimental complexity limits the amount of data available. Distinctly lacking are high-throughput experiments with multiple well-defined data points in the quantum gap size regime.¹

1.4.2 Current Bespoke Spacers

The developments in **Section 1.4.1** depend intimately on the nature of the materials and molecules used to assemble and modify the nanocavity. The nanophotonics field combines materials science and physics; subsequently, many new materials-based fabrication methods and optics-based analysis techniques have been developed in recent years. Despite this, molecular self-assembly of existing AuNP aggregates and NPoMs still broadly makes use of commercially available spacer molecules^{27,50,52,174} which, while useful and accessible, provide inherently limited opportunity for development.¹⁷⁵

Bespoke molecular spacers offer far greater potential for advancement of nanostructure functionality. A popular, semi-bespoke spacer system involves the host-guest interactions of cucurbit[n]uril (**Section 2.2.1**) with various guest molecules, allowing placement and orientation of non-Au-binding guests in plasmonic nanocavities.^{6,27,49,105} This works for both AuNP aggregates and NPoMs, offers increased spacer versatility and bypasses the need for Au binding groups. Unfortunately, the secondary analyte is normally fully encapsulated^{27,49} and/or located away from the hotspot.⁹⁶ This is useful for sensing,^{6,59,96} optical devices⁴⁹ and investigation of model systems,²⁷ but restricts chemical interactions between hotspot molecules and the outside environment, which would preclude macro-scale chemical turnover in hotspot-based catalysis. Controlled AuNP aggregation is restricted by solubility, charge and Au affinity of molecular spacer and, beyond CB[n], few novel molecular spacers delivering controllable gap size and aggregation kinetics have been developed.

DNAo offers a highly customisable option for NPoM systems, yielding precise nanostructures with predetermined number and position of functional molecules.^{48,110} These systems have proved useful for measuring spatial dependence of fluorophore-cavity

interactions,⁴⁸ single-emitter photon statistics¹¹⁰ and single-bond dynamics.⁸⁴ DNAo-based plasmonic cavities also often have large, convoluted SERS signals and a high local ion concentration, which complicates understanding of optical and chemical behaviour. DNAo-mediated gaps are often larger (>10 nm) than molecular monolayers (typically <5 nm), which limits the field enhancement and limits applicability of certain plasmonic phenomena, e.g. strong coupling.^{49,110}

1.4.3 Design Criteria

This work describes the development of novel compounds with the potential to advance the applications described in **Section 1.4.1** using the nanostructures introduced in **Section 1.1**. As such, the compounds should self-assemble plasmonic nanostructures while incorporating properties conducive to one or more applications in **Section 1.4.1**.

One way of turning a functional molecule into a molecular spacer is to add a thiol group at one or more points. However, thiols have specific properties that perturb molecular structure in specific and sometimes unexpected ways.⁹⁷ While a useful tool, it is important to develop other Au-binding options. Fortunately, a wealth of understanding exists around formation of molecular layers on metallic substrates, thanks to the surface science community, with extensive study into the surface interactions and self-assembly properties of all kinds of functional molecules. Consequently, while not yet widely applied to plasmonic nanocavities, NPoMs can already be made with a wide range of molecules and materials.

A successful molecular spacer should ideally form well-defined junctions between Au surfaces. Aqueous AuNP aggregation requires a spacer that can destabilise the negatively charged colloid, with desirable properties including water solubility, bidentate Lewis basicity or other Au affinity, rigidity, and/or positive charge. For NPoM fabrication, the main criterion is ability to form a self-limiting (sub)monolayer on Au. This requires solubility in a substrate-compatible solvent and stronger affinity to surface than solvent.⁹¹ Thiols are ideal for this, but other Au-binding groups such as carbonyls,^{6,27,49,105} isothiocyanate⁹⁷ and extended π -systems¹⁷⁶ are also effective; species with non-specific binding can also form uniform spacer layers under the right deposition conditions.^{119–121}

For plasmonic sensing, spacers must sequester analytes within the hotspot via host-guest interactions^{6,98,177} or modification of local environment.⁹⁶ For indirect sensing of species with negligible Raman cross sections, the spacer must have an intense vibrational fingerprint easily perturbed by analytes,⁷ or be able to stabilise adatoms that boost the SERS effect.^{50,99}

Applications involving enhanced emission or strong coupling require molecules with strong visible-wavelength absorption and/or emission that can overlap with the nanostructure resonance,^{49,110,111} while ensuring control over orientation, position, packing density and intermolecular interactions.

Plasmonic catalysis may be facilitated by redox-active spacer molecules that behave as electron donors or acceptors,³¹ with appropriate skeletal and terminal functionality to mediate charge transport²⁷ and moieties (e.g. a metal centre) that facilitate coordination to and charge transfer with the chemical substrate.⁹⁷ Restricted diffusion in nanocavities - particularly those containing dense molecular layers - is likely to limit catalytic utility.¹⁰⁵ To overcome this, steric bulk should be included such that molecular packing density is decreased to provide diffusion channels through the hotspot.

Plasmon ruler studies require a rigid spacer molecule that yields a known, well-defined and tuneable d . Ideally, the molecule height should be fine-tuneable to give multiple data points in the $d < 1$ nm regime without significant modification of the gap conductance or permittivity.

Precise and dynamic characterisation of molecular junctions requires molecular spacers with well-defined Au binding and charge transport properties that can be probed via the far-field optical response of the nanostructure. Development of molecular switching technologies requires spacers that respond reversibly to external stimuli via changes in oxidation state, conductance, polarisability, size, conjugation and/or surface binding.

This thesis explores the synthesis, characterisation and self-assembly properties of three novel molecular spacer types, introduced in **Chapter 2**. Each spacer family has been designed/chosen based on the above criteria and all combine plasmonic nanostructure self-assembly capability with a potential range of sensing, catalytic, and optoelectronic functionality.

2. Molecular Spacers

This chapter introduces the three molecular spacer systems used in this work, chosen for their ability to bind to Au while fulfilling several of the functional design criteria outlined in **Section 1.4.3**.

Bis-phthalocyanines (BPcs; **Section 2.1**) have a rich electronic structure and redox chemistry, the combination of which manifests as versatile sensing and actuation behaviour. They behave as electrocatalysts, organic semiconductors, and single-molecule magnets, with implications for molecular switching, green chemistry and quantum information technologies. The ability to fine-tune molecular height and electronic structure via the central ion size hints at advanced plasmon ruler utility.

Aryl viologens (ArVs; **Section 2.2**), well-known for their redox activity and electrochromic behaviour, are often used as model electron transfer reporters. Non-covalent complexation with cucurbit[*n*]uril (CB[*n*]) imparts bidentate Au affinity to these compounds, with control over orientation and intermolecular coupling. ArV structural tuneability presents a supramolecular toolbox for assembly and orientation of novel chemical functionality within plasmonic nanocavities.

Porphyrins functionalised with arylpyridinium moieties (**Section 2.3**) combine concepts from the first two systems, introducing a new modular molecular spacer class that can be readily modified for a range of sensing, switching, catalytic and optoelectronic behaviour, all with supramolecular control over plasmonic self-assembly.

2.1 Bis-Phthalocyanines

First synthesised in 1965,¹⁷⁸ BPCs are sandwich complexes with two phthalocyanine (Pc, **Figure 2.1a**) ligands encapsulating a large metal ion, usually a lanthanide (Ln), via their isoindole nitrogens in a square antiprismatic arrangement (**Figure 2.1c-e**). Smaller ions (e.g. transition metals) rarely ligate two phthalocyanines, instead forming singly-bound metallophthalocyanines (MPcs; **Figure 2.1b**).¹⁷⁹

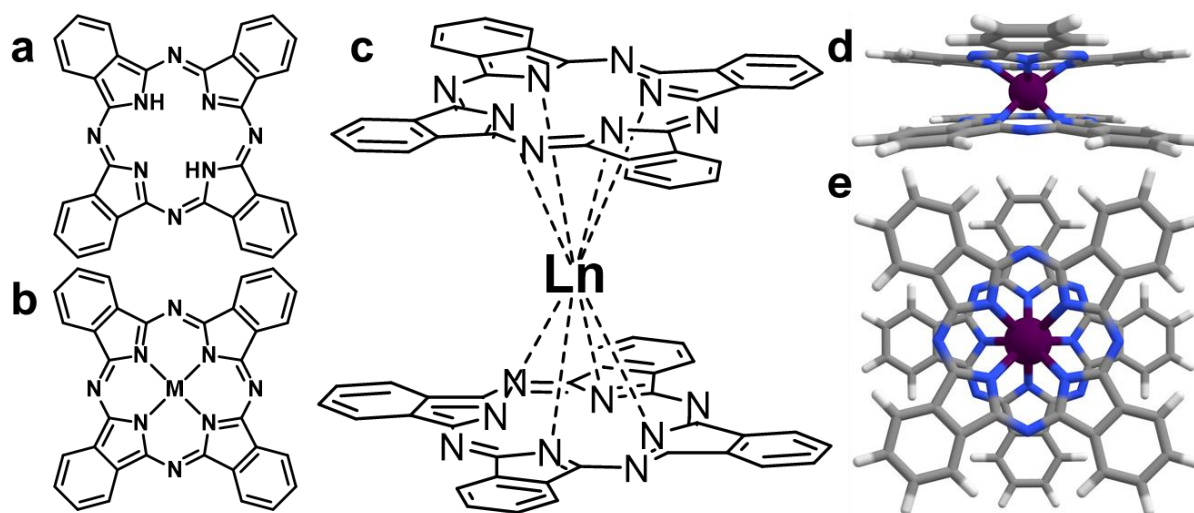


Figure 2.1. Phthalocyanine and complexes thereof. **(a-c)** Chemical structures of **(a)** freebase phthalocyanine (H_2Pc), **(b)** metallophthalocyanine (MPc) and **(c)** lanthanide bis-phthalocyanine (LnPc_2 or BPC). **(d, e)** Side and top view of TbPc_2 DFT-optimised structure, (see **Methods 3.7.3** for computational details). Atom colours in **(d, e)**: C (grey), H (white), N (blue), Tb (purple).

(Bis-)phthalocyanines have received consistent attention in nanotechnology for decades.^{180,181} Their stability, broad chemical tailorability, rich electronic structure and redox activity have led to advances in electrochromic displays,^{182,183} telecommunications,^{184–186} photovoltaics^{187–189} and chemical sensing.^{181,190} BPCs can act as both organic semiconductors¹⁹¹ and single-molecule magnets (SMMs)¹⁹² and have been used as spin valves,^{193–198} molecular switches^{196,197,199} and field-effect transistors.^{200,201} Certain variants exhibit liquid crystal behaviour and self-assemble into molecular wires with dramatically higher charge carrier mobilities than MPcs.^{189,202,203}

Phthalocyanines can form monolayers on metallic surfaces, with many recent STM studies investigating assembly and electronic structure for various phthalocyanine/substrate combinations.^{193,194} Importantly for this work, BPC can self-assemble on Au surfaces^{194,201,204} and aggregate AuNPs with well-defined interparticle junctions (**Figure 2.2**). Noda *et al.*¹⁷⁶ investigated the magnetic and charge transport properties of these structures, but no plasmonic or optical experiments were performed.

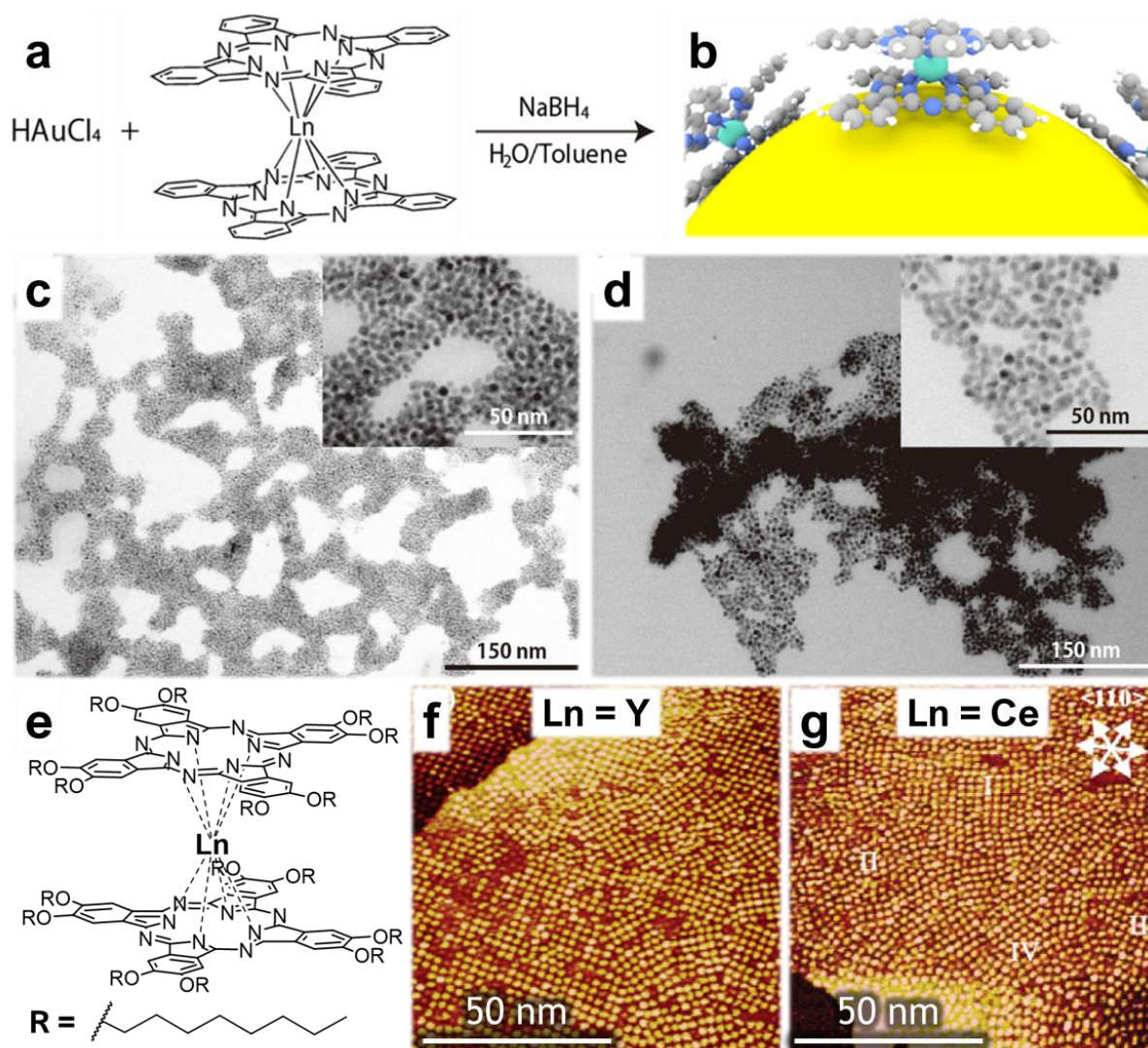


Figure 2.2. (a - d) Growth and aggregation of AuNPs with BPc surface ligands, adapted from [176]. (a) Reaction scheme for nanoparticle synthesis via NaBH_4 reduction of HAuCl_4 in the presence of LnPc_2 ($\text{Ln} = \text{Tb}, \text{Lu}$). (b) Schematic illustrating AuNPs ($D = 4 \text{ nm}$) stabilised with BPc molecules. (c, d) TEM images of (c) $\text{LuPc}_2\text{@AuNPs}$ and (d) $\text{TbPc}_2\text{@AuNPs}$. (e - g) Assembly of alkoxy-substituted LnPc_2 (e) ($\text{Ln} = \text{Y}, \text{Ce}$) on $\text{Au}(111)$ surface, forming (f, g) pseudo-ordered monolayers, measured with STM. Adapted from [205]. Atom colours in (b): C (grey), H (white), N (blue), Ln/Tb (cyan).

To date, no studies (beyond this thesis and related publication¹) explore light-matter interactions of BPcs within plasmonic nanojunctions. **Chapter 3** primarily explores the utility of BPc as a plasmonic spacer for vapour sensing and fine-tuning of d and n_g near the quantum tunnelling limit.¹ BPcs offer a wealth of exciting optoelectronic, magnetic and chemical properties, most of which are beyond the scope of this work. Building on the foundation laid in **Chapter 3**, future experiments should explore current-dependent chiral switching,^{196,197,199} electrochemical tuning of plasmon resonance via redox-dependent n_g modification^{206–209} and optical manipulation of magnetic moments via spin-resolved plasmonic incoupling^{210–213} (Section 2.1.1).

2.1.1 Electronic & Magnetic Structure

The optoelectronic properties of BPc are subject to extensive theoretical scrutiny^{214–218} and mostly result from electronic coupling between the two 18-electron aromatic π -systems of the closely-bound (~ 0.3 nm) Pc rings.^{217,218} The optical spectra are dominated by excitonic and charge-transfer states within the Pc dimer,²¹⁶ with negligible spectral contribution from the Ln orbitals.¹⁸² Ln fluorescence is quenched by low-lying Pc_2 states and fast intersystem crossing,²¹⁹ and remaining Pc_2 fluorescence is weak.¹⁸⁹ The main contribution of Ln is its coordination radius, which controls the Pc-Pc distance and cofacial π - π overlap.^{214,220} The well-defined geometry and minimal chemical influence of Ln make BPcs useful systems for modelling structurally similar photosynthetic reaction centres.^{217,221}

BPc's atypical redox behaviour comes from a mismatch between the ligand and Ln oxidation states. Lanthanides primarily exist as Ln(III), while each Pc is an L_2X_2 ligand with a formal charge of -2; the neutral LnPc_2 complex therefore has an odd number of valence electrons (ignoring the Ln 4f orbitals). While a source of disagreement for many years,^{202,222–225} the resulting neutral radical is now understood to be a “ π -hole” delocalised over both ligands (**Figure 2.3a**).^{223,226,227} Unlike MPcs, where any paramagnetism generally comes from the metal ion,²²⁷ the Ln orbitals do not interact chemically with the Pc dimer due to mismatched energy, symmetry and spatial localisation; the radical exists purely in the ligand pair.^{214,225,228,229}

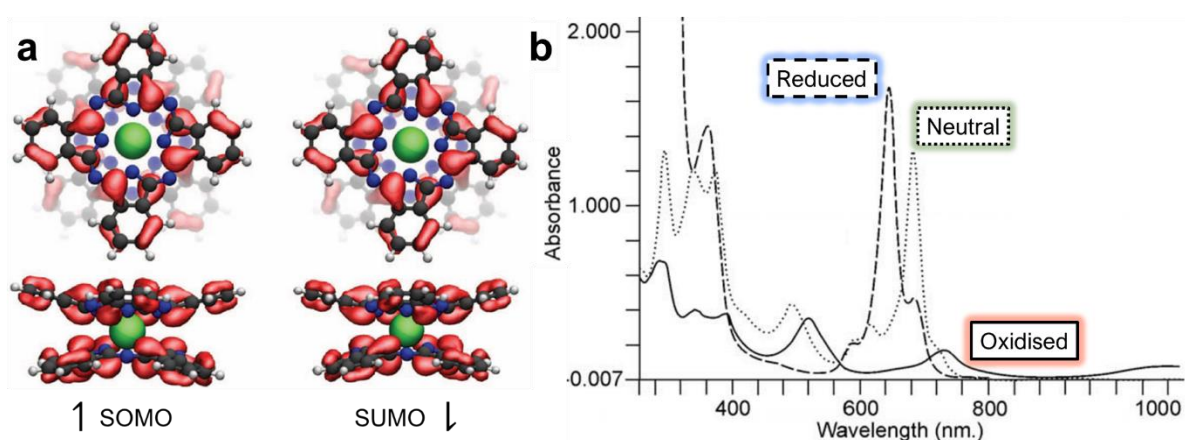


Figure 2.3. (a) Calculated spin populations of singly-occupied (SOMO) and singly unoccupied (SUMO) frontier molecular spin orbitals of LuPc_2 , adapted from [230]. (b) UV-Vis spectra of reduced, neutral and oxidised LnPc_2 thin films, adapted from [181]. Atom colours in (a): C (black), H (white), N (blue), Lu (green).

The singly occupied molecular orbital (SOMO) of BPc is easily reduced, while the SOMO's antibonding character also facilitates oxidation.^{220,231} This easy, reversible redox leads to high intrinsic charge carrier densities and low resistivity in BPc films, which act as open-shell, narrow-band semiconductors with six orders of magnitude higher conductance than MPcs.^{191,223} The band structure is dominated by inter and intramolecular π - π coupling and charge transport is readily tuned by metal centre and chemical functionalisation.^{231–234} BPc can form charge-transfer complexes with electron donors²³⁵ or acceptors,²³⁶ allowing p/n -

doping.^{181,216} The oxidised, neutral and reduced states of BPc are red/orange, green and blue, respectively (**Figure 2.3b**), and all strongly absorbing,^{206–209,237} spurring interest in BPc-based optical displays since the 1980s.²⁰⁶

BPcs also behave as SMMs at low temperatures.^{192,219} The magnetically anisotropic Pc_2 ligand field splits the low-lying Ln^{3+} 4f states,^{192,219} creating a large magnetic reversal barrier that is sensitive to oxidation state²³⁸ and Pc-Pc distance.²³⁹ While chemical interaction between the 4f states and ligand spin is negligible,^{214,225,240} recent studies demonstrate exchange coupling between the Ln magnetic moment (J) and the orbital (L) and spin (S) angular momenta of the Pc_2 π -system, allowing manipulation of the 4f J states via photostimulation with circularly polarised light.^{210–212}

This SMM behaviour is retained upon surface self-assembly, allowing incorporation into future spin-based molecular information storage.^{193,241,242} Plasmonic enhancement of the magneto-optical interaction has been observed, together with calls for optimisation of optical nanoantennae and self-assembly methods.²¹³ Therefore, while SMM behaviour is not investigated in this thesis, successful integration of BPcs into plasmonic cavities is one step closer to readout-enabled molecular magnetic devices.^{193,194,243}

2.1.2 Sensing

The solid-state optoelectronic properties of BPc films are extremely sensitive to molecular ordering and physicochemical environment, responding dynamically to many different analytes at room temperature, with far greater sensitivity than MPcs.^{181,244} BPc has enjoyed particular attention in gas sensing for its chemoresistive^{24,190,191,233} and vapochromic^{184,185} behaviour, explored via optical and electrical measurements of Langmuir-Blodgett (LB) films exposed to different atmospheres.^{222,244}

Gas sensing is important from an environmental and public health perspective. Atmospheric pollutants like NO_x , SO_x and CO_x all threaten human health and require strict monitoring.²⁴⁵ In indoor environments, outgassing of building materials, upholstery and various everyday products and household items generates very low, yet harmful, levels of volatile organic compounds (VOCs) like formaldehyde and benzene. While various mature gas sensing technologies exist, some gases still have safe exposure levels well below detection limits for fast sensing.²⁴⁵

BPcs have been widely explored for optical detection of strong redox agents (**Figure 2.4a**) like NO_x ,^{236,246} NH_3 ,^{231,232,234} Cl_2 ,^{224,233} Br_2 ,^{24,231} and hydrazine,²³⁵ but also exhibit sensitivity towards VOCs, with chemical fingerprinting studies for VOC ensembles present in tobacco smoke^{232,246} (**Figure 2.4d**) and the headspaces of wine^{184,190} and olive oil.²⁴⁷ BPc responds differently to analytes depending on metal centre, ring substitution (**Figure 2.4e,f**) and film morphology,^{231–234} with multiple derivatives often required as a multi-sensor array.^{190,247}

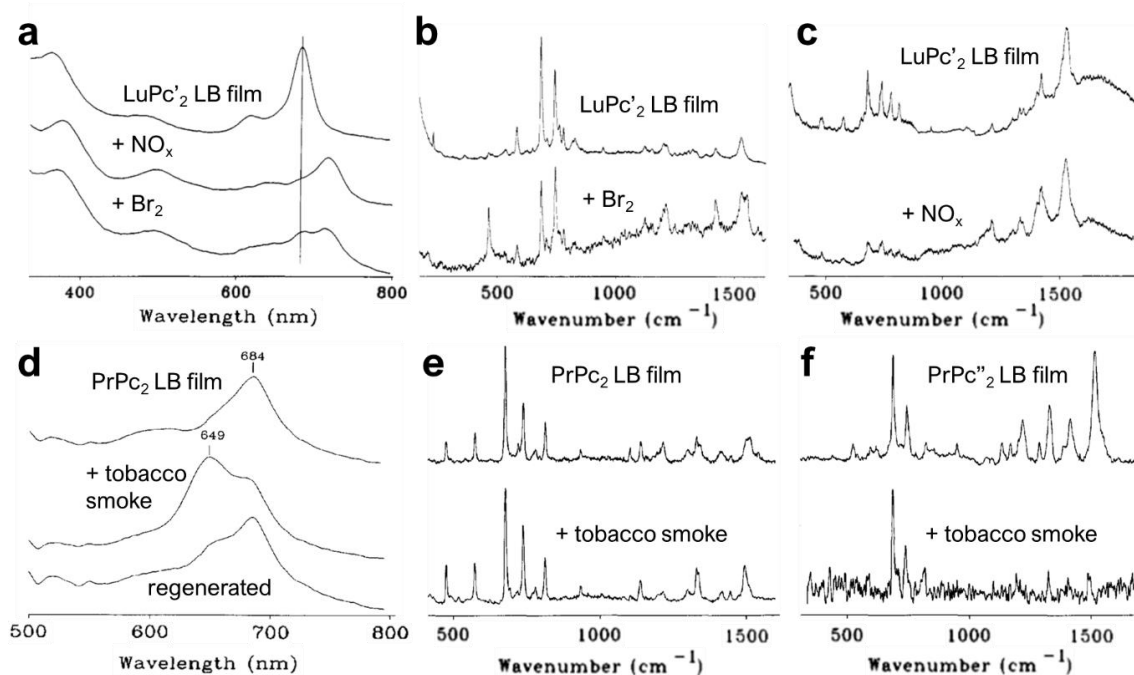


Figure 2.4. Optical (**a, d**) and vibrational (**b, c, e, f**) sensitivity of BPC derivatives to (**a-c**) oxidising gases and (**d-f**) tobacco smoke. (**a**) UV-Vis spectra and (**b, c**) SERRS spectra of LuPc'₂ LB films before and after exposure to Br₂ and NO_x, adapted from [24,208]. (**d**) UV-Vis spectra and (**e**) SERRS spectra of PrPc₂ LB film before and after exposure to tobacco smoke. (**f**) same as (**e**) but with PrPc''₂. Adapted from [246]. Pc' and Pc'' indicate Pc ligands functionalised with different organic side-groups.

Meanwhile, AuNP aggregates are non-specific sensing substrates, capable of multiplexed small molecule detection under the right conditions, with small gap sizes yielding large field enhancements and extremely low detection limits.^{6,96} Unfortunately, direct SERS is of limited use for species with small Raman cross-sections;⁷ gases can be sequestered using host-guest chemistry to increase their concentration within hotspots,²⁴⁸ but even with the large field enhancements of a ~1 nm plasmonic gap, their SERS signals are still negligible.²⁴⁹

An alternative method utilises Raman probes whose vibrational signatures change upon interaction with analytes,^{7,208,236,246} an effect magnified by SERS enhancement.^{98,115,250,251} BPCs behave in this way, possessing large Raman cross sections^{235,246} and vibrational fingerprints that change upon exposure to both redox agents²³⁵ (**Figure 2.4b,c**) and VOCs²⁴⁶ (**Figure 2.4e,f**) when bound to Au-based SERS substrates. BPC is optically resonant at common Raman excitation wavelengths, allowing surface-enhanced resonance Raman (SERRS) analysis.^{24,208,246}

The perturbative effects of VOCs on BPC's vibrational signature are weaker than strong redox gases, making them harder to detect in this way.^{184,185,246} Notwithstanding, the apparent height of BPC on Au (0.4 nm^{194,196}) suggests an ability to form ultrasmall nanocavities approaching the tunnelling limit of plasmonic enhancement^{1,55,74} (**Sections 1.4.1 & 2.1.4**). This combination of resonance Raman and perturbative vibrational effects with unprecedented single-cavity field enhancements at few-molecule scales may allow gas-phase SERS detection of VOCs at lowered detection limits.

2.1.3 Catalysis

BPCs are stable over many redox cycles and multiple reductions are possible, buffered by the extensive π -delocalisation.^{220,252–254} The subsequent possibility of low overpotentials and high turnover numbers has gained sporadic attention from electrochemists.^{254,255} Despite the sterically hindered Ln centre,^{254,256} BPC complexes have some electrocatalytic activity and selectivity towards CO₂ reduction^{255–257} and carbamate formation²⁵⁴ and can facilitate charge transfer from Au substrates.²⁰⁵

While the prospect of a metal centre in the plasmonic hotspot was the initial attraction of this project, literature review revealed that catalysis occurs at the azomethine nitrogen atoms, rather than Ln²⁵⁶ (**Figure 2.5**). While possible in solution, the proposed CO₂ binding shown in **Figure 2.5b** is likely to be unfavourable in the confined hotspot environment. The interaction of neutral BPCs with redox agents (e.g. NO₂^{236,246}) is also now understood to occur through the external faces of the Pc₂ dimer.²¹⁵ Because of this, **Chapter 3** does not explore electrocatalytic or sensing activity of BPC@AuNP nanostructures towards CO₂ or redox gases and instead investigates SERS-based VOC detection and plasmon ruler behaviour. The understanding gained from BPC@AuNP systems is then used as a foundation for rational design of the porphyrins in **Chapter 5**.

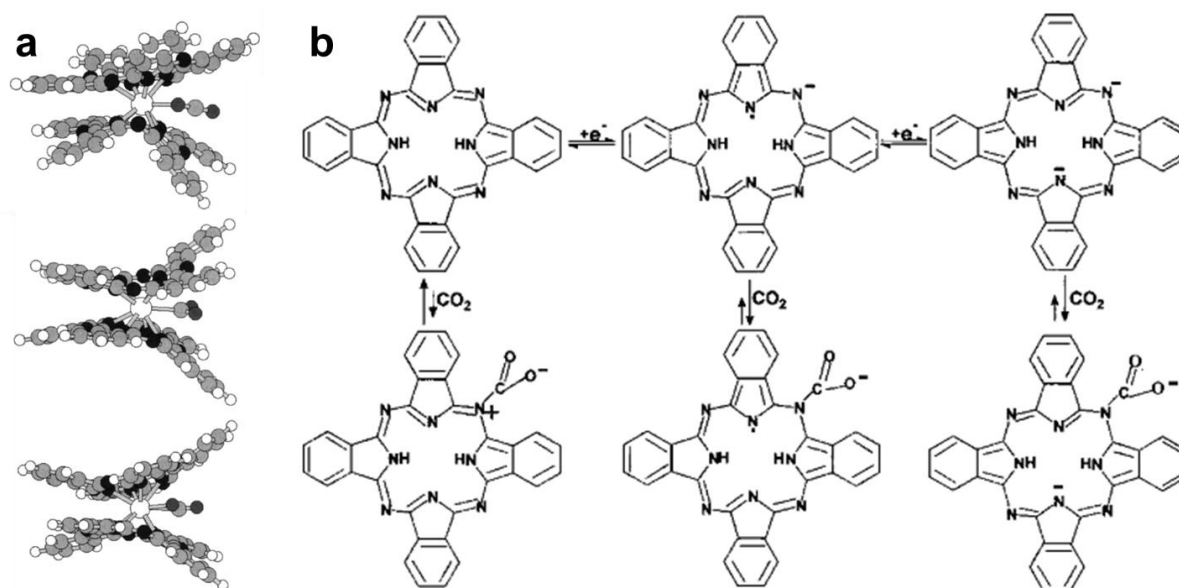


Figure 2.5. Hypothesised binding geometries of CO₂ with BPC. **(a)** Molecular mechanics simulation of various Ln-CO₂ binding geometries; steric clash causes the Pc dimer to splay unfavourably. **(b)** Predicted electrocatalytic binding mechanism of CO₂ with a single Pc ligand via an azomethine nitrogen atom. Atom colours in **(a)**: C (grey), H (white, small), Ln (white, large), N (black).

2.1.4 Plasmon Rulers

The small apparent height of BPc on Au surfaces (0.3-0.5 nm)¹⁹⁴ puts it near the quantum limit for plasmonic enhancement as an NPoM spacer.^{1,74} At sub-nanometre lengthscales, λ_c and I_c are extremely sensitive to small changes in gap properties. Unfortunately, the understanding, characterisation - and therefore utility - of such systems is hampered by the sparse experimental data for $d < 1$ nm. While piezoelectric¹¹² and electron-beam^{55,172} methods offer extremely precise gap size control, transfer of understanding to other plasmonic dimer systems is hindered by low throughput and structural heterogeneity.^{72,258} 2D materials and ALD-based methods provide the smallest NPoM gaps and highest sub-nm precision, but monolayer thickness limits the data resolution for each system.^{77,79} Analysing separate sub-nm systems (e.g. Al₂O₃,⁷⁹ graphene,⁷⁷ 2D chalcogenides^{80,81} etc) yields several data points for $d < 1$ nm, but differences in electronic structure complicate direct comparison.

As an NPoM spacer, BPcs present a complementary method with the simplicity of a SAM-based system. BPc derivatives can be synthesised with most or all of the lanthanide series, which, due to the lanthanide contraction,²⁵⁹ tune the Pc-Pc distance - and therefore SAM thickness - with picometre precision (**Figure 2.6**).¹

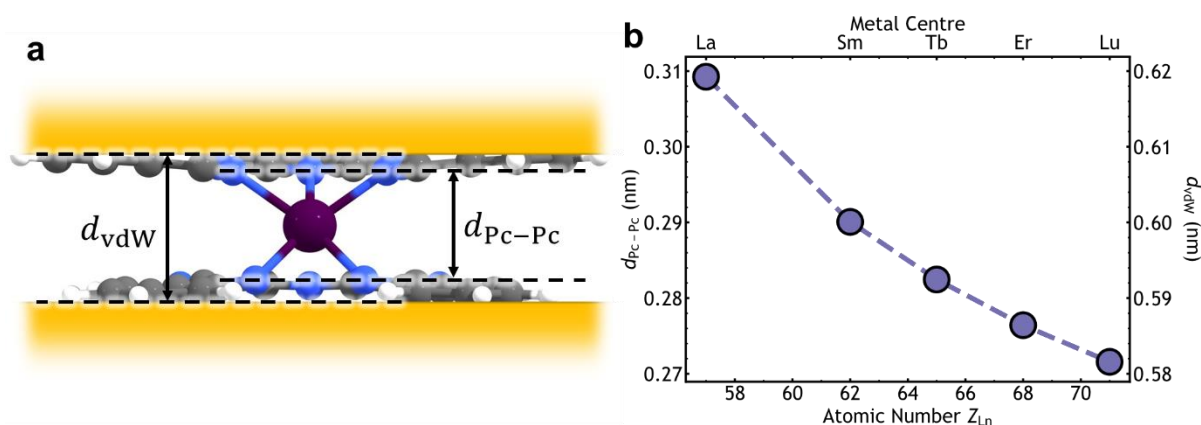


Figure 2.6. (a) Schematic illustrating centre-centre distance of the Pc central pyrrole N atoms (d_{Pc-Pc}) and subsequent control over BPc vdW height (d_{vdW}). (b) Calculated d_{Pc-Pc} and d_{vdW} (see **Methods 3.7.3**) for Ln = (La, Sm, Tb, Er, Lu), illustrating smooth contraction across the Ln series. Atom colours in (a): C (dark grey), H (white), N (blue), Ln (purple).

The lanthanide 4f valence orbitals have no radial nodes and are simultaneously poorly shielding and poorly shielded from the nuclear charge, leading to immediate contraction of the 4f orbitals upon one-electron oxidation, rendering them chemically inaccessible.²⁵⁹ Removal of the remaining valence electrons from the 6s and/or 5d orbital leads to a stable +3 oxidation state in most cases, regardless of 4f population. Chemically, Ln³⁺ ions are almost identical, with negligible 4f bonding contribution and very similar electronegativities. The primary difference is a contraction of atomic radius from La to Lu, providing a series of hard ionic spheres with sub-angstrom diameter variation.

The Pc-Pc distance ($d_{\text{Pc-Pc}}$) ranges from 2.71 to 3.09 Å (based on calculated centre-centre distance between the central pyrrole N planes; **Figure 2.6a**, **Section 3.5.2**, **Methods 3.7.3**), providing control over a very small change in SAM thickness at precisely the region of interest where field enhancement peaks and classical theory breaks down.^{74,173} While the NPoM gap size will be slightly larger, depending on atomic vdW radii and degree of covalency between Au and the outer Pc faces, this yields 15 possible data points across a ~0.04 nm range within the 0.3 - 0.6 nm gap size region (**Figure 2.6b**).

As the difference in LnPc_2 physicochemical properties across the Ln series is almost entirely governed by Pc-Pc coupling, the Ln size (r_{Ln}) variation allows fine-tuning of other gap properties (e.g. n_g) via choice of metal centre and oxidation state, allowing systematic study of complex light-matter interactions in molecular junctions near the quantum plasmonic limit.

2.2 Aryl Viologens and Cucurbit[n]uril

The realisation of viable molecular nanophotonic devices requires precise control over surface binding and intermolecular interactions. Long-range exciton coupling and intermolecular charge transfer can complicate understanding of nanoscale light-matter interactions in close-packed molecular arrays,^{260,261} highlighting the need for well-defined, discrete molecular spacers.

Covalent modification offers a wide range of control over molecular properties, but is often complex and synthetically challenging. A complementary toolbox is available via non-covalent assembly, which exploits molecular recognition between chemical building blocks to form discrete²⁶¹ or extended²⁶² supramolecular assemblies - analogous to nano self-assembly²⁶³ but with more well-defined geometries and interactions. This allows rapid formation of complex structures with emergent synergistic properties that would otherwise require advanced synthetic techniques to achieve.

Many types of supramolecular complex exist, including enzyme-substrate complexes,²⁶⁴ extended fluorophore aggregates,^{265,266} and DNAo.^{48,67} Aqueous-phase noncovalent interactions are commonly driven by π - π vdW attraction, ion-dipole interactions and hydrophobic effects,²⁴⁸ all of which are tuneable via molecular design, offering control over various emergent optical and chemical properties of the parent complex.^{260,261} Some common tools for aqueous supramolecular complex formation are water-soluble macrocyclic molecules with hydrophobic cavities. These compounds encapsulate hydrophobic guest molecules with selectivity controlled by local functionality. One such family of macrocyclic hosts are cucurbit[n]urils (CB[n]), which are used throughout **Chapters 4-5**.

2.2.1 Cucurbit[n]uril

The CB[n] family are barrel-shaped, cyclic, methylene-bridged glycoluril oligomers formed by the condensation of glycoluril and formaldehyde (**Figure 2.7**), named cucurbituril for their pumpkin-like appearance (Latin: *Cucurbitaceae*).²⁶⁷ They represent an important class of molecular receptor and exhibit high non-covalent guest binding strengths in aqueous solution. For a comprehensive review of CB[n] molecular recognition properties, see Barrow *et al.*²⁴⁸

CB[n] comes in different sizes, where n denotes the number of glycoluril units; most commonly $n = 5, 6, 7$, or 8 . Each homologue has an internal hydrophobic cavity and carbonyl-terminated portals with a constant height of 9.1 Å (**Figure 2.7**). The portal diameter, cavity volume and electrostatic profile all vary with n , greatly affecting interactions with different guest molecule types. This tuneability allows size-selective, reversible encapsulation of various molecules, while the combination of polar portals and a non-polar cavity leads to strong, selective and directional binding, determined by hydrophobic interactions, size/shape complementarity and ion-dipole attraction.^{248,267,268}

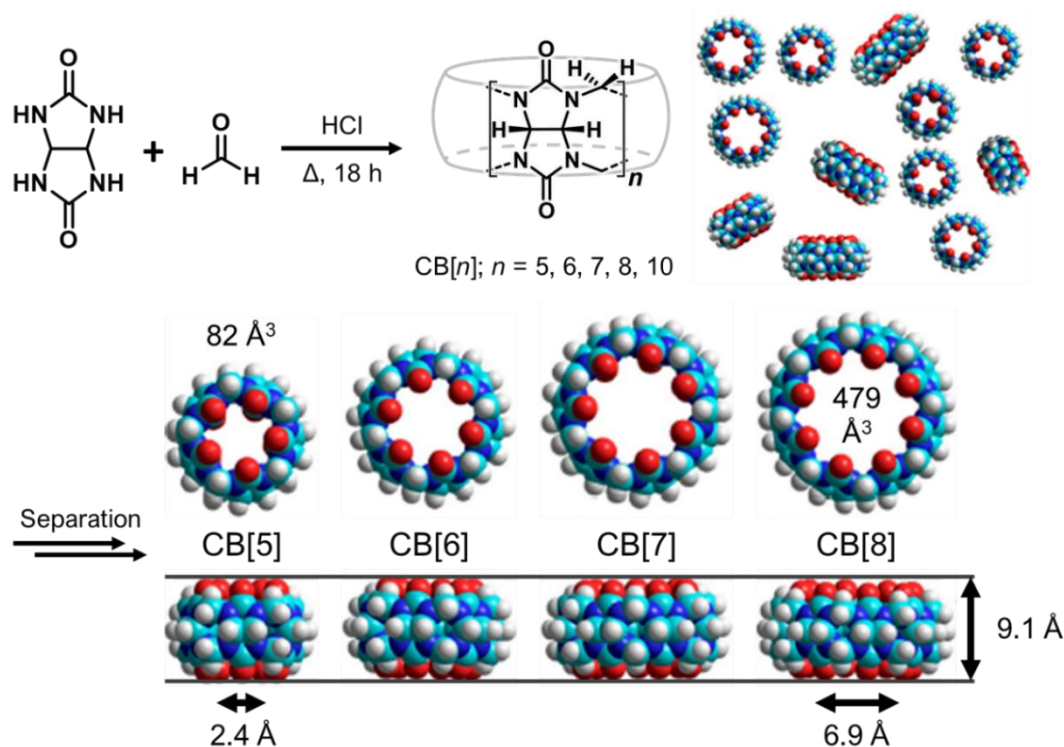
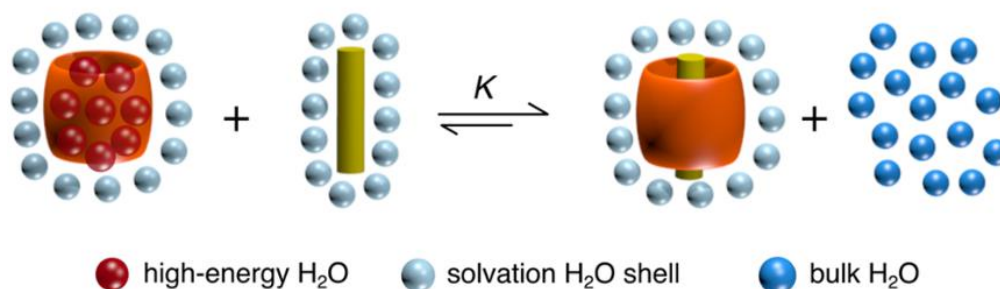


Figure 2.7. Synthesis, chemical structure and X-Ray structures of various CB[n]. Cavity volume and inner portal diameters shown for CB[5] and CB[8]. Adapted from [248]. Atom colours: C (cyan), H (white), N (blue), O (red).

These properties have increased the academic and industrial popularity of CB[n] over the past few decades, with emerging applications in drug delivery,²⁶⁹ sensing,^{6,98,115,177} catalysis,^{249,270–272} switchable materials,^{268,273} supramolecular hydrogels²⁷⁴ and, crucially, nano self-assembly.^{59,261,275} The cavity offers a solvent-free environment to protect and stabilise reactive species and excited states^{98,268,276} and facilitates reaction rate moderation,²⁷⁷ while its optical

transparency allows photochemistry⁹⁸ and optical characterisation of encapsulated species.²⁷⁶ The nano self-assembly properties stem from the Au affinity of the Lewis-basic carbonyl portals. This combines the utility described above with plasmonic light confinement, and is responsible for many of the powerful applications outlined in **Section 1.4.1**.

CB[n] boasts higher aqueous guest binding constants than other macrocyclic hosts.^{248,278} The major driving force is the non-classical hydrophobic effect, caused by release of frustrated “high-energy” water (with fewer hydrogen bonds per molecule) from the hydrophobic cavity upon guest encapsulation^{276,278–280} (**Scheme 2.1**). Even if host-guest interactions are weak, the significant free energy advantage of removing this encapsulated water yields remarkably strong binding,^{278,280} capable of inducing reactive conformation of otherwise unreactive substrates for enzyme-like catalysis.^{272,281} The binding effect is maximised when all frustrated water is displaced, and binding strength and selectivity are often governed by guest/cavity size complementarity. The tapered portal geometry also sterically raises the complexation-decomplexation energy barrier, leading to extended complex lifetimes in solution.



Scheme 2.1. Schematic illustration of reversible host-guest complex formation between CB[n] (orange barrel) and hydrophobic guest (yellow cylinder), with equilibrium greatly favouring complexation due to release of high-energy water. Adapted from [276].

Quantification of these factors allows rational design of guests for specific applications.^{248,278} CB[n] favours molecules with a mixture of cationic and hydrophobic moieties, particularly dications with non-polar cores and charged periphery. A popular guest is methyl viologen (MV²⁺), a widely-used model electron acceptor that forms 1:1 complexes with CB[7]²⁸² (**Section 2.2.2**). The aromatic framework is encapsulated within the central cavity, while binding is strengthened by ion-dipole interactions between the pyridinium cations and carbonyl portals.

CB[5] encapsulates small gases and solvents and the carbonyl groups allow external cation binding^{283,284} (**Figure 2.8a,b**). CB[6] has a bigger cavity that binds aliphatic amines and amino acids.^{73,277} CB[7] is larger still and forms 1:1 complexes with biologically relevant small molecules including neurotransmitters, peptides and drugs.^{6,248,269,285} The cavity size of CB[7] leads to the highest overall energy gain upon release of encapsulated water and some of the highest guest:CB[n] binding constants when size complementarity is achieved.^{248,279} Combined with its high water-solubility (up to 30 mM), this makes CB[7] particularly useful for sensing^{6,115} and drug delivery.²⁶⁹

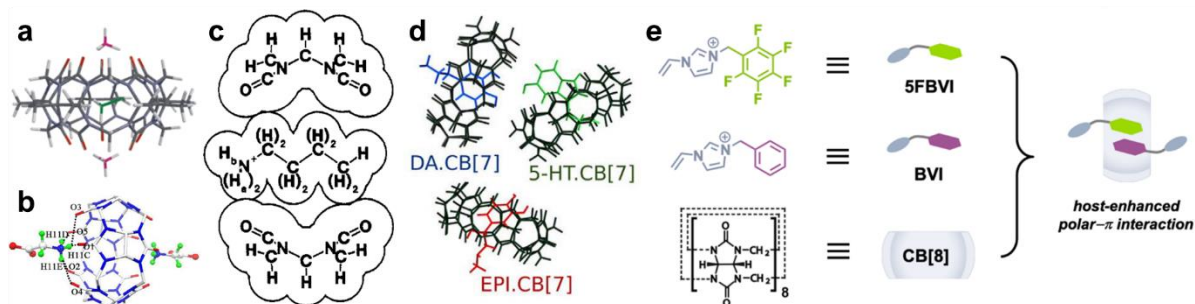


Figure 2.8. CB[*n*] (*n* = 5, 6, 7, 8) and examples of their guests. **(a, b)** Calculated structure of CB[5] with **(a)** MeOH guest & externally bound NH_4^+ ions²⁸³ and **(b)** externally bound glycine.²⁸⁴ **(c)** Schematic side profile of CB[6] with butylamine guest; vdW loci are shown to illustrate size complementarity.²⁶⁷ **(d)** CB[7] with dopamine (DA), serotonin (5-HT) and epinephrine (EPI) neurotransmitter guests.⁶ **(e)** CB[8]-templated heteroternary charge-transfer complex between *N,N*-benzylvinylimidazolium (BVI) and its pentafluorinated analogue 5FBVI.²⁸⁶

CB[8] is large enough to accommodate two aromatic guests^{268,276,287} in homoternary (1:2) or heteroternary (1:1:1) fashion²⁸⁶ (**Figure 2.8e**). As with 1:1 CB[7] complexes, ternary CB[8] binding is strong due to size complementarity, and affinity of the second guest can be tailored by choice of the first.^{248,287} This versatile ternary binding facilitates fluorophore coupling,^{49,275,286} photoswitchable materials,^{98,288–290} inter- and intramolecular linkages^{274,275,291–294} and polymeric self-assembly.²⁹⁵ Particularly interesting from an optoelectronic perspective is the formation of strongly coupled π -dimers^{260,261,275,296} and stabilisation of intermolecular charge transfer complexes.^{276,287,295} Both significantly perturb guests' optical response, offering supramolecular control over quantum yield, excited state lifetime and electron transfer dynamics.^{260,261}

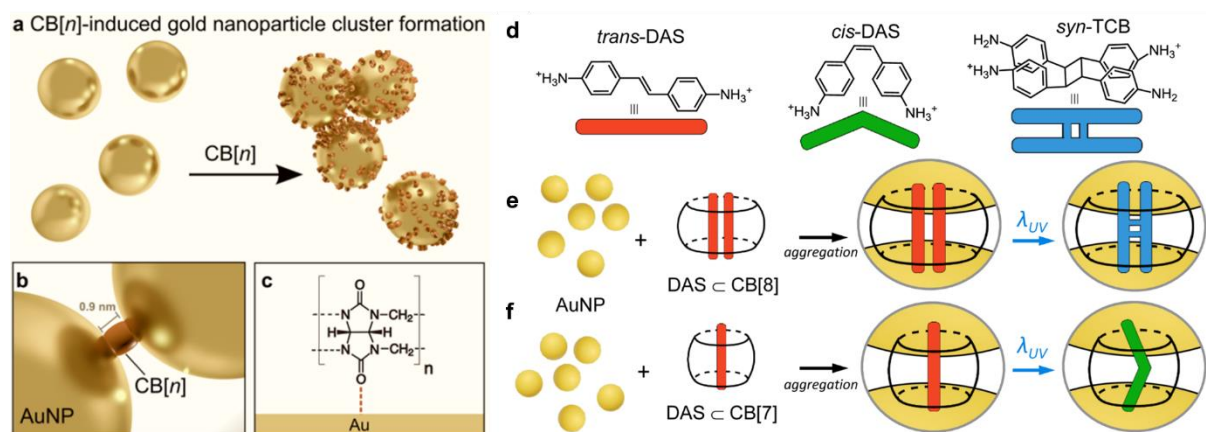


Figure 2.9. **(a - c)** Schematic of CB[*n*]-AuNP binding and aggregation, adapted from [248]. **(a)** CB[*n*] acts as a “glue” in the aggregation of AuNPs. **(b)** The rigidity and uniform height of CB[*n*] reproducibly yields interparticle distances of 0.9 nm. **(c)** CB[*n*] binds to Au surface via C=O--Au coordination. **(d - f)** CB[*n*]-templated photoreactions, adapted from [98]. **(d)** *cis* and *trans* isomers of diaminostilbene (DAS) and *syn*-tetrakis(4-aminophenyl)cyclobutene (*syn*-TCB) adduct. **(e)** CB[8]-templated selective photodimerisation of *trans*-DAS, forming only the *syn* isomer of TCB. **(f)** CB[7]-templated photoisomerism of *trans*-DAS to *cis*-DAS. Both transformations occur in or near the inter-AuNP plasmonic hotspot and can be monitored in real time via SERS.

The Lewis basic carbonyl portals impart bidentate Au affinity^{59,250,297,298} which, combined with their rigidity, symmetry, water solubility and constant (independent of *n*) height, facilitates

aqueous AuNP self-assembly with consistent $d = 0.9$ nm (**Figure 2.9a-c; Figure 1.6**).^{59,297} This uniformity, combined with small molecule sequestration capability, unlocks the multiplexed detection capabilities of AuNP aggregates as self-calibrating SERS substrates with CB[n] as an internal standard (**Section 1.4.1**).^{6,59,60,115}

CB[n] retains its molecular recognition properties when bound to Au, enabling a synergistic combination of supramolecular chemistry and nanophotonics.^{299,300} The molecular alignment responsible for single-molecule strong coupling⁴⁹ in **Figure 1.16c** is also facilitated by CB[7], as is the positioning of molecular tunnel junctions²⁷ in **Figure 1.17c,d**. By protecting guest molecules from the environment, CB[7] prevents extended intermolecular coupling and allows study of single-molecule events.^{49,98} Similarly, CB[8] can enforce dimerisation for investigation of discrete pairwise interactions within the hotspot. One example is supramolecular catalysis with real-time reaction monitoring, whereby CB[8] acts as both a SERS transducer and nanoreactor^{27,98,249,301} (**Figure 2.9d-f**). Non-covalent binding brings previously “inert” molecules close to the Au surface, increasing hotspot accessibility without requiring inherent Au affinity or covalent modification.^{6,250,298} Molecular structure is relatively unchanged, but steric confinement, modified electrostatic potential and alignment within the hotspot can all affect reaction selectivity and kinetics.^{31,98,249}

Two drawbacks of CB[n] as a molecular spacer are: limited size in the z-direction, and complete chemical isolation upon encapsulation. Both factors severely inhibit the chemical accessibility and structural possibility of guest molecules, precluding hotspot-based catalysis applications with any appreciable turnover. Alternatively, using CB[n] as an anchoring group,^{293,298,302} rather than encapsulating agent, should allow scaffold-like binding of Au surfaces, bridged by functional molecules with CB[n]-binding end groups; this has been demonstrated for various surfaces with CB[n] and other macrocycles.^{302–305} In this way, CB[7] and CB[8] can be used to incorporate a wider range of molecules in the hotspot, preventing extended intermolecular coupling and/or enforcing dimerisation whilst leaving certain parts of the molecule exposed and chemically accessible.^{260,261,275,306} To test this hypothesis with AuNP nanostructures, **Chapter 4** explores the AuNP self-assembly capability of simple scaffold-like systems, involving 1:2 and 2:2 complexes of aryl viologens² (**Section 2.2.2**) with CB[7] and CB[8], respectively.

2.2.2 Viologens

Viologens are a well-studied class of molecules, with electrochemical behaviour first reported in the 1930s³⁰⁷ and repeated waves of scientific interest throughout the past century.³⁰⁸ Originally a name for 4,4'-dipyridinium compounds, the simplest being methyl viologen (MV), a.k.a. paraquat, the name “viologen” loosely applies to compounds with multiple quaternary pyridinium moieties^{260,261,309} (**Figure 2.10**). Aryl viologens (ArVs) have aromatic substituents attached to the quaternary nitrogens, peripheral functionalisation of which can strongly modify

the optical and electrochemical behaviour.^{310,311} Expansion of the viologen core (to yield extended viologen; EV) allows incorporation of virtually any compatible functional group. Recent supramolecular studies mostly incorporate fluorophores and explore emergent optical properties of EV-CB[n] structures.^{260,261,275,306} Additionally, possibilities also exist for, but are not limited to, photodynamic therapy and transition metal ligation^{312–316} (**Section 2.3**).

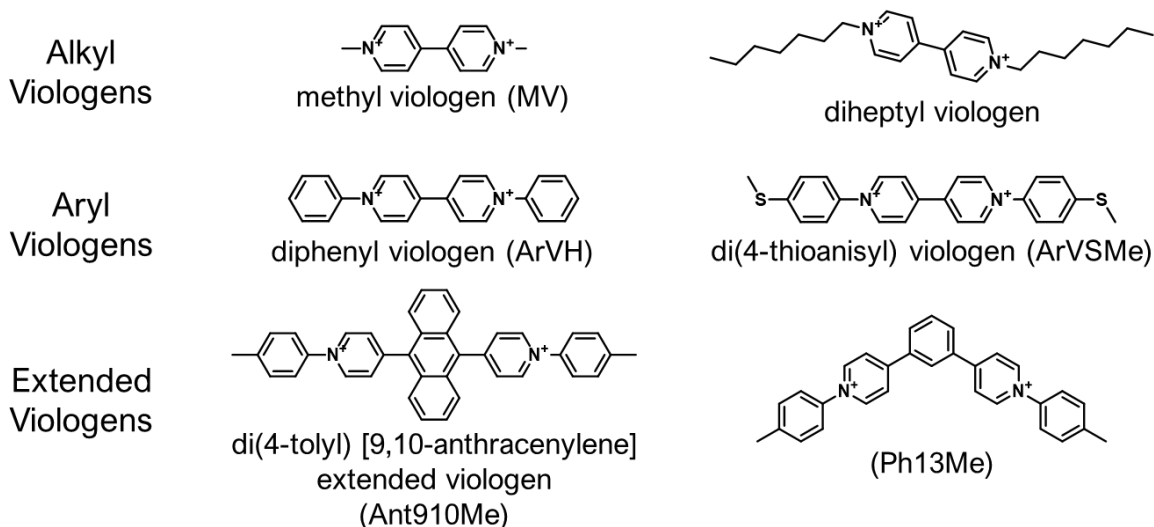
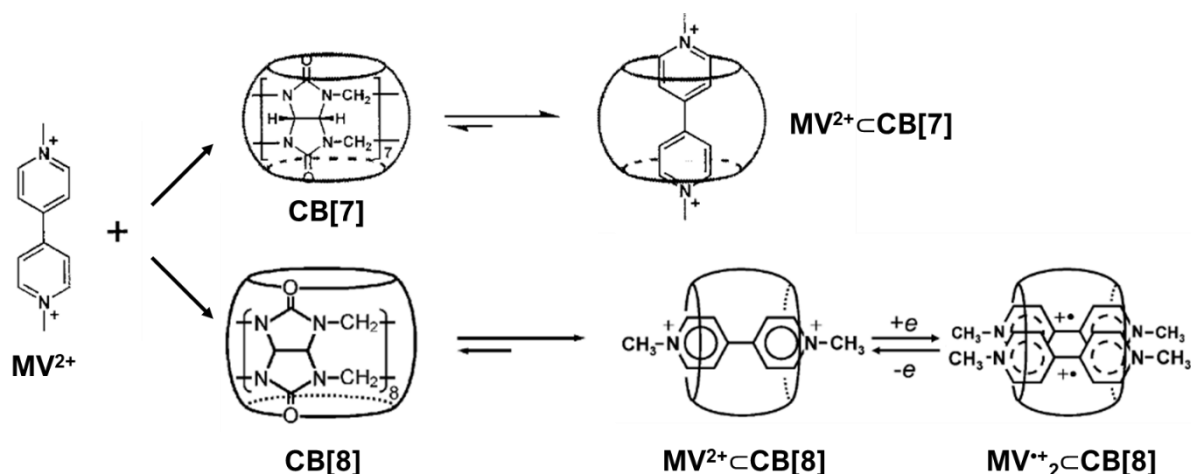


Figure 2.10. Examples of alkyl, aryl and extended aryl viologen chemical structures, including the two ArV structures (ArVH, ArVSMe) used in **Chapter 4**. Extended viologen nomenclature here follows that used by Wu *et al.*^{261,275}

Like BPCs, viologens are easily reduced; dicationic MV²⁺ is colourless, whereas the air-sensitive, singly reduced radical cationic MV^{•+} has a deep blue-violet colour.^{307,308} This distinct electrochromism^{183,317} and photochromism³¹⁸ has led to wide use of viologens as organic redox indicators and model electron transfer agents.^{27,31,308,319} Because of their water solubility and redox activity, many viologens are effective herbicides^{308,320} (and unpleasantly toxic³²¹). Other applications include aqueous redox flow batteries,³²² electrochromic displays³¹⁰ and photovoltaics.³²³

MV and other alkyl viologens are widely used as model guests for CB[7] and CB[8], with near ideal size complementarity for MV-CB[7] and MV₂-CB[8] complexes^{268,282,287} (**Scheme 2.2**). Ternary CB[8] complexation is precluded by charge repulsion within the MV²⁺ dimer, and only occurs upon reduction. Viologen electrochromism can be quenched by dimerisation-induced disproportionation, which may be prevented³¹⁷ or stabilised²⁶⁸ by CB[7] or CB[8], respectively. Recent years have seen some incorporation of MV into plasmonic nanocavities,^{17,27,31} often in combination with CB[n], where it is used as Raman-active reporter molecules for real-time SERS observation of redox processes,^{27,31} and electron acceptors for funneling hot electrons from excited nanostructures.²⁹



Scheme 2.2. Host-guest interactions between MV^{2+} and CB[7, 8], adapted from [268,282]. Top: $MV^{2+} \subset CB[7]$ exhibits strong 1:1 binding due to size complementarity and ion-dipole interactions. Bottom: $MV^{2+} \subset CB[8]$ exhibits 1:1 binding with poor size complementarity. 2:1 complexation is precluded by charge repulsion within MV^{2+} dimer, but favoured for $2xMV^{+}$.

2.2.3 ArV $\subset$ CB[n] Complexes

ArVs and EVs tend to bind CB[n] in a multidentate fashion, forming $V \subset CB[7]_x$ and $V_2 \subset CB[8]_x$ complexes, where V = viologen and x = number of pyridinium groups. $V \subset CB[7]_x$ binding offers similar de-aggregation and PL enhancement effects as 1:1 complexation.³²⁴ Unlike MV, however, which only dimerises in CB[8] when reduced,²⁶⁸ the extra π -conjugation of ArV/EV stabilises the excess positive charge, allowing formation of stable, discrete $V_2 \subset CB[8]_x$ dimer complexes (**Figure 2.11**), with slower exchange kinetics and longer lifetimes in solution.^{260,261,275} This is facilitated by structural rigidity of the ArVs/EVs, but precluded by electron withdrawing groups, if present, which destabilise the positive charges.²

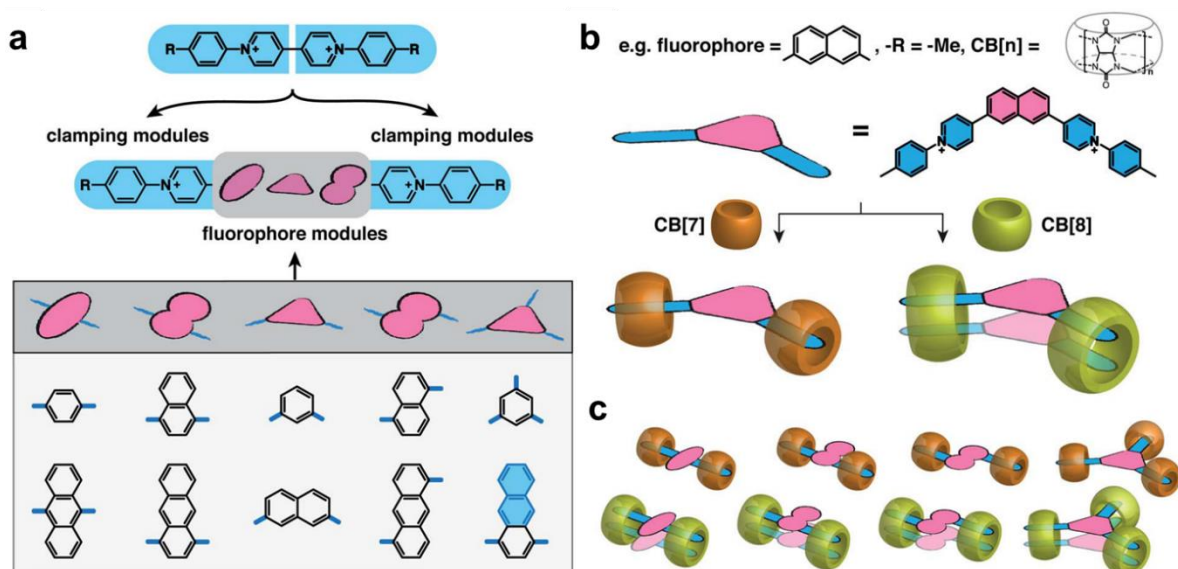


Figure 2.11. Molecular design for isolation or dimerisation of fluorophores by CB[n]-mediated modular assembly, adapted from [261]. **(a)** ArVs can be extended with a range of core moieties and geometries **(b)** Example of fluorophore binding with EV[2,7-Naphthyl]Me and **(c)** EVs with a range of other fluorescent cores, demonstrating the geometric versatility of the technique.

For EVs, the core extension moiety is not inside a CB[n] cavity and its size and shape are unrestricted, allowing a larger range of possible functionality²⁶¹ (**Figure 2.11**). Directional CB[8] binding facilitates long-lived dimerisation with significant π -overlap and small intermolecular distance, leading to an electronically coupled ground state exhibiting excimer-like and/or charge transfer behaviour, with redshifted absorption and emission.^{260,261,275,325} This provides supramolecular control over PL relaxation pathways and allows study of short-range, non-instantaneous interactions within closely-bound non-covalent fluorophore dimers. The excited state lifetime, PL QY, molecular conductance and charge transfer behaviour are all affected by functionality, overlap geometry and binding dynamics.^{2,326} The wide range of possible core and peripheral functionality offers a toolbox for supramolecular chemical and optoelectronic devices.^{260,261,327,328}

Importantly, $\text{ArV} \subset \text{CB}[n]$ complexes retain their structure when used for NP functionalisation, bridging and self-assembly^{302–305} (**Figure 2.12**) and tip-surface junctions.³²⁶ With CB[n] as a stabilising group, peripheral functionality can be gradually tuned for probing metal-molecule interactions and charge transport behaviour.^{25–27} The optical response, and therefore plexcitonic coupling, can be further controlled by molecular stacking.^{132,329} The PL intensity is affected by molecular torsion³³⁰ and can be controlled by current across the molecule, hinting at tuneable molecular junctions with current-switchable PL.²⁵ Precise overlap geometry in $\text{ArV}_2 \subset \text{CB}[8]_2$ complexes affects the selection rules of absorption and emission³³¹ and opportunities exist for tweaking this using cavity-stimulated emission and external heavy atom effects for advanced optical applications.^{119,120}

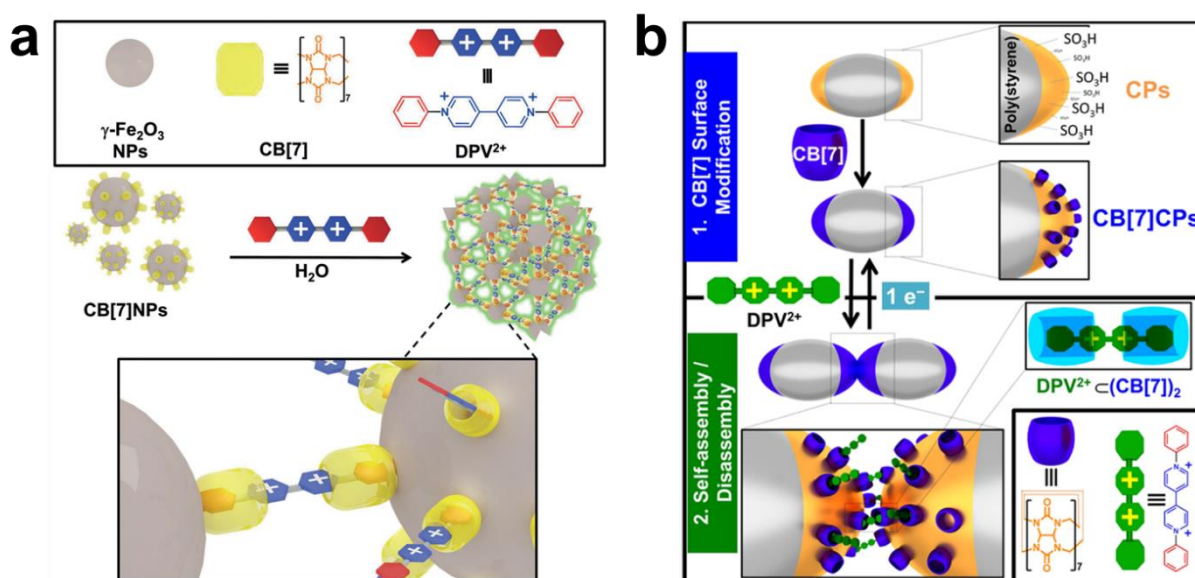


Figure 2.12. Aqueous self-assembly of (a) Iron oxide nanoparticles ($\gamma\text{-Fe}_2\text{O}_3$ NPs)³⁰⁵ and (b) patchy polystyrene colloidal particles (CPs)³⁰² with $\text{ArVH} \subset \text{CB}[7]_2$ scaffolds that retain their supramolecular structure upon surface binding and bridging. Here, $\text{DPV}^{2+} \equiv \text{ArVH}$.

2.2.4 General Comments

The aim of **Chapter 4** is to test the suitability of $\text{ArV}\subset\text{CB}[n]$ complexes as plasmonic molecular spacers. Specifically, to investigate whether supramolecular structure is retained upon self-assembly of NPoMs and AuNP aggregates. The effects of concentration, deposition time and peripheral ArV functionality are characterised using DF spectroscopy, extinction spectroscopy, and SERS. The available functionality and host-guest behaviour should allow improved control over, and thus future study of, orientation, intermolecular coupling and molecule-surface interactions in plasmonic molecular junctions. As the ArV scaffold can be arbitrarily extended with various bridging groups, these junctions will open the door to incorporation of molecular switches or accessible catalytic centres within plasmonic hotspots.

Having demonstrated successful assembly of plasmonic nanostructures with supramolecular control over geometry and binding, future experiments should explore the effects of surface binding and intermolecular coupling upon the plexcitonic,^{49,120} charge transfer,²⁷ charge transport^{25,26} and spectroelectrochemical⁹⁷ properties of the devices. Parallel to ongoing development of the optical techniques enabling these studies,³ the next chemical step of this work was to incorporate more useful functionality into the $\text{ArV}\subset\text{CB}[n]$ system by expansion with metal-ligating core moieties. **Chapter 5** introduces such a system - porphyrins augmented with arylpyridinium groups, and transition metal complexes thereof.

2.3 Porphyrin/Viologen Hybrids

The third and final molecular spacer used here is based on porphyrins. The knowledge gained from BPc and ArV $\subset$ CB[n] (**Chapters 3-4**) inspired design of a more functional spacer system. BPc is interesting - physically - for its strongly coupled π -system, $4f$ J states and electrochromism, but less so catalytically due to chemical and steric inaccessibility of the metal centre, further restricted by the ultrasmall NPoM cavity (**Figure 2.13a,d**). Any vapochromic or catalytic behaviour largely occurs via the outer Pc faces and is therefore less relevant when sandwiched in a molecular junction.^{181,255}

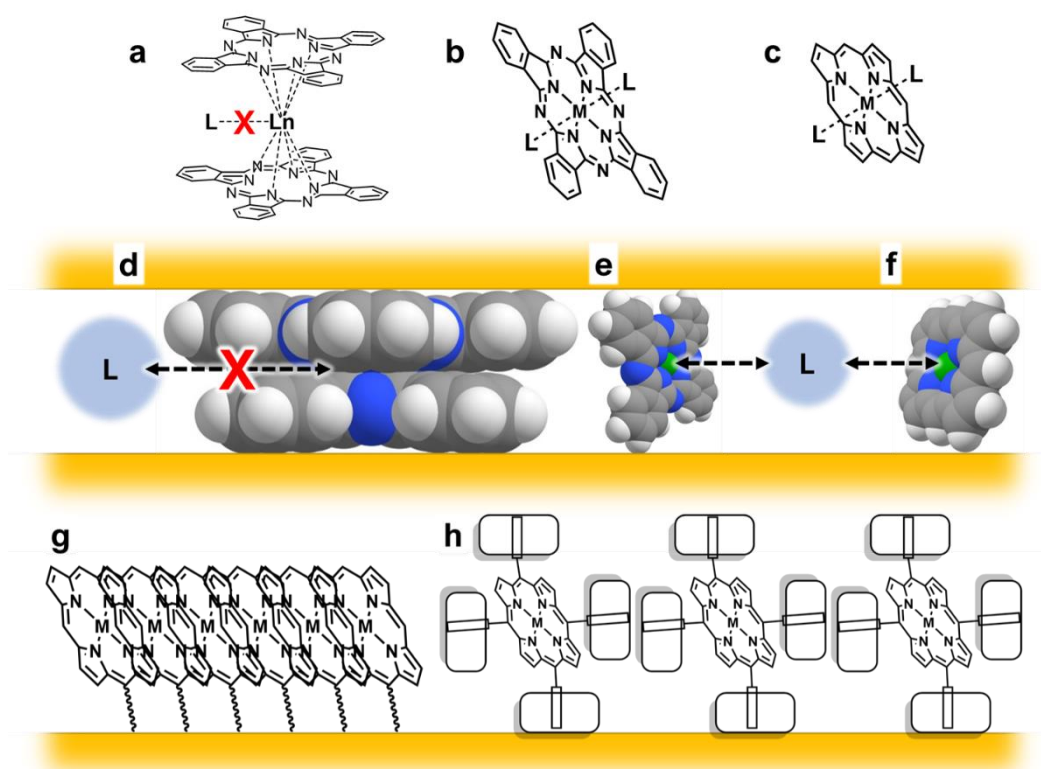


Figure 2.13. (a - c) and (d - f) Schematic illustrating relative chemical accessibility of BPc (a, d), MPc (b, e) and metalloporphyrin (c, f) metal centres (not to scale). Space filling models (d - f) (all atoms displayed as vdW radius spheres) illustrate (d) inherent steric inaccessibility of BPc metal centre for arbitrary ligand L, while (e) MPc and (f) metalloporphyrin are open to axial ligation, with greater potential for chemical accessibility within the nanocavity. (g) Close-packed porphyrin-based SAM. (h) Sparser SAM using supramolecular chemistry to spatially separate molecules; rectangles and rounded rectangles represent arbitrary guest moieties and supramolecular hosts, respectively. Atom colours in (d-f): C (grey), H (white), N (blue), M (green).

Monomeric phthalocyanines and porphyrins, however, can ligate catalytically active transition metals, the axial coordination sites of which are chemically accessible thanks to the square planar geometry (**Figure 2.13b,c,e,f**). Vertical incorporation of such metalloporphyrinoids into plasmonic hotspots should yield more interesting chemical behaviour than BPc, while retaining many of its optical and electrochromic properties, and with potential for combining plexcitonic coupling and electrocatalysis (**Section 1.4.1**). The close packing present in most SAMs may

hinder the chemical accessibility of MPc or porphyrin directly bound to Au (**Figure 2.13g**), but strategic introduction of steric bulk - such as non-covalently bound CB[n] - could disrupt packing and provide diffusion channels within the spacer layer (**Figure 2.13h**).

Chapter 4 demonstrates that $\text{ArV}\subset\text{CB}[n]$ complexes can indeed be used as plasmonic nanojunction spacers. **Chapter 5** therefore investigates the design, synthesis and supramolecular and nano self-assembly properties of a water soluble, CB[n]-binding, porphyrin/viologen hybrid structure, serving as a foundation for future plasmonic sensing and catalysis applications. This section introduces the properties and applications of porphyrins and a summary of their current presence in plasmonic and supramolecular systems, followed by rationalisation of the new molecular spacer design.

2.3.1 Overview

Porphyrins (**Figure 2.14**) are structurally similar to phthalocyanines but, as key active biological components in both respiration and photosynthesis, naturally receive more attention. The electronic structure and distinct visible absorption spectrum of porphyrinoids (see **Chapter 5**) are tuned by their metal centre and aromatic substituents, leading to the red colour of our blood and the green colour of our environment. Heme³³² (**Figure 2.14b**) uses a central Fe atom to capture gaseous O_2 and transport it for respiratory use in the human body. Chlorophyll (**Figure 2.14a**), as part of a multi-component reaction centre, photocatalyses charge separation in plants and other photosynthetic organisms for biological water splitting and CO_2 utilisation.

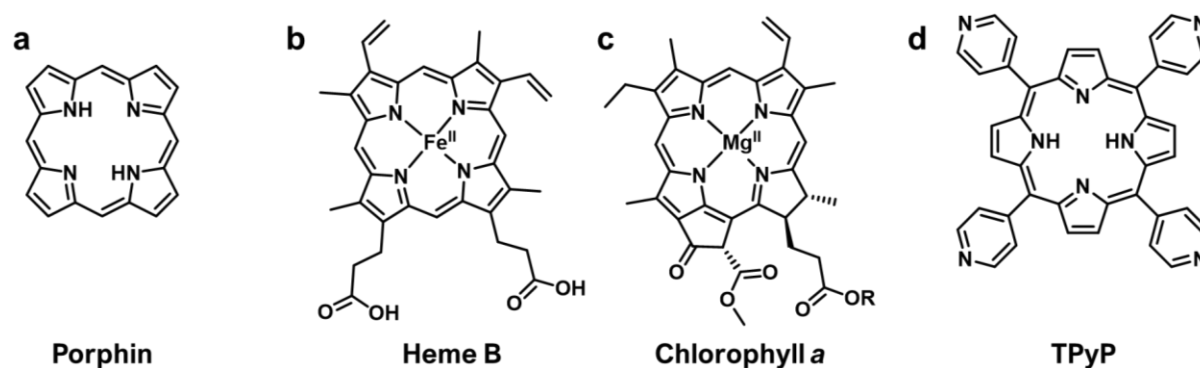
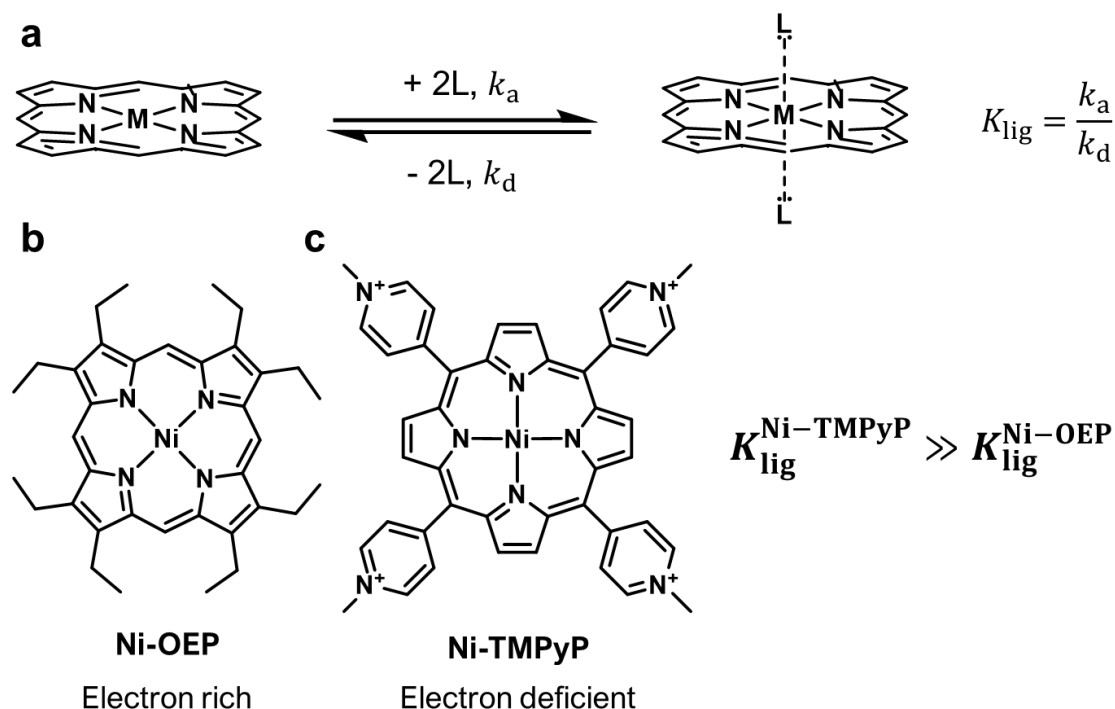


Figure 2.14. Chemical structures of (a) porphin, the simplest porphyrin; (b) heme B, a major O_2 -transporting component of haemoglobin; (c) chlorophyll a, closely related to porphyrin and one of several chlorophyll structures involved in photosynthesis; (d) 5,10,15,20-*tetrakis*-(4-pyridyl)porphyrin (TPyP), a synthetic porphyrin derivative.

Already, these examples demonstrate porphyrins' potential for sensing,³³³ gas separation,³³⁴ light harvesting^{319,335–339} and catalysis.^{340–344} Porphyrins are also widely used in photodynamic therapy (PDT) as cancer treatments^{325,345,346} and antimicrobial agents.³⁴⁷ The affinity of certain porphyrins for DNA nucleotides, combined with facile photogeneration of singlet oxygen via long-lived triplet excited states, yields efficient photoactivated cell death.^{345,348,349} This photosensitization also aids photocatalytic water splitting on semiconductor³³⁷ and

metallic^{319,338,339} catalysts, as well as charge separation in dye-sensitised photovoltaics, offering a cheaper, sustainable alternative to ruthenium-based dyes.^{335,336}



Scheme 2.3. (a) Square planar metalloporphyrin in equilibrium with hexacoordinate species bearing two Lewis basic ligands in solution. (b) Electron-rich nickel octaethyl porphyrin (Ni-OEP). Electron-donating groups destabilise axial ligand binding and shift equilibrium to the left. (c) Electron-deficient nickel 5,10,15,20-*tetrakis*-(4-(*N*-methylpyridin-1-ium))porphyrin (Ni-TMPyP). Electron withdrawing groups increase Lewis acidity of metal centre and shift equilibrium to the right.^{350,351}

As with MPcs/BPcs, the porphyrin ligand acts as an electron density buffer for its metal centre, with profound effects on the thermodynamics of axial ligation^{350,351} (**Scheme 2.3**). The stability of certain binding configurations can be controlled via inductive/mesomeric effects, or intramolecular interactions.³⁵² Porphyrins are therefore widely explored as tailorable, low-cost electrocatalysts for various reactions including water splitting³⁴¹ and selective CO₂ conversion.^{342–344} This conjugation and physicochemical tuneability also shows promise in molecular junction research^{353,354} and, like BPc, their complex electronic structure, redox activity and paramagnetic metal centre stabilisation indicate potential for molecular information storage devices.^{355,356}

2.3.2 Porphyrins & Plasmonics

Far-reaching academic attention has led to a well-established theoretical background surrounding the optical properties of porphyrins^{357,358} (more details in **Section 5.3.3**), which provides a starting point for understanding plasmonically enhanced light-matter interactions. Despite this, few studies investigate porphyrins as molecular spacers for plasmonic nanojunctions.

Some literature exists regarding surface binding of porphyrins,³⁵⁹ often involving STM analysis.^{353,359,360} Simple porphyrins tend to lie flat on Au surfaces^{360,361} (**Figure 2.15a**), but can be encouraged to stand vertically if functionalised with thiols³⁵³ (**Figure 2.15b**) or tethered with alkanethiol chains.^{362,363} Such studies often probe information storage, charge transport and molecule-surface binding properties^{353,359,360} and contain useful insights for future plasmonic nanojunction experiments.^{25,27}

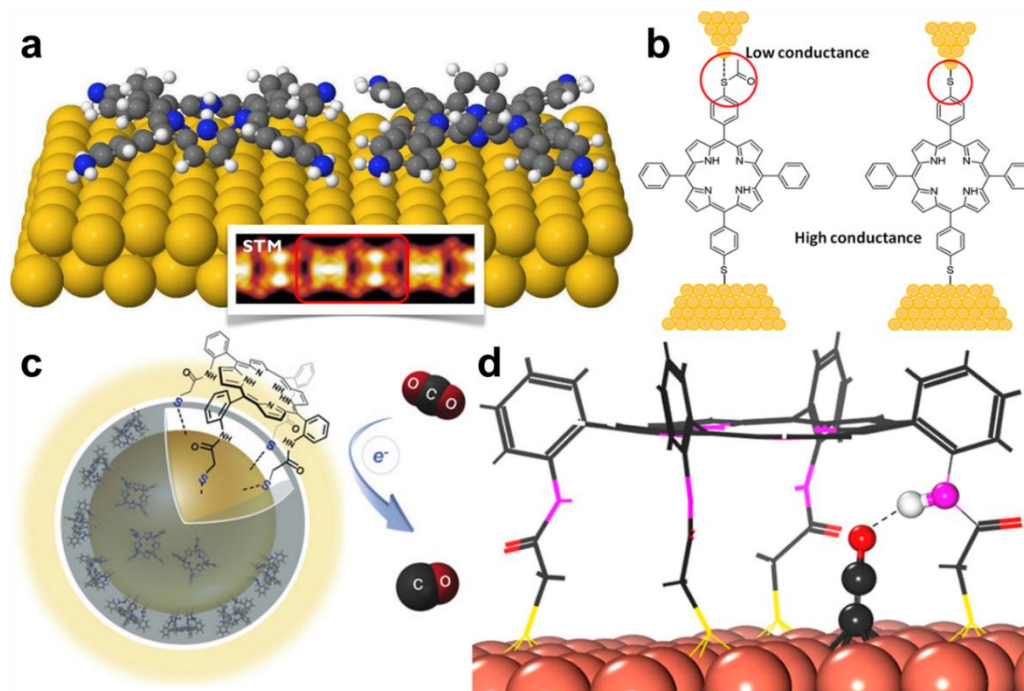


Figure 2.15. Schematics illustrating non-plasmonic examples of porphyrins at Au surfaces and nanojunctions. **(a)** Self-assembled, hydrogen-bonded porphyrin chains with π -systems parallel to Au surface. **(b)** Modification of molecular conductance of thiol-based tetraphenyl porphyrin by STM-induced deprotection of vertically bound molecules. **(c)** AuNP modified with porphyrin cages for electrocatalytic CO₂ reduction. **(d)** Calculated structure of porphyrin from **(c)** interacting with a CO₂ reduction intermediate on a Cu surface, illustrating chemical accessibility of surface and supramolecular modification of reaction environment by porphyrin cage. Atom colours in **(a)**: C (black), H (white), N (blue), Au (gold). Atom colours in **(d)**: C (black), H (white), N (magenta), O (red), S (yellow), Cu (copper).

Electrocatalytic properties of immobilised porphyrins have also been investigated on Au,³⁶⁴ and chemically accessible, cage-like structures have been investigated as immobilised surface electrocatalysts³⁶⁵ and AuNP protecting groups for control over CO₂ reduction selectivity^{365,366} (**Figure 2.15c, d**). Other porphyrin@AuNP studies exist, again focusing on charge transport³⁶⁷ and electron transfer³⁶⁸ behaviour or PDT applications.³⁶⁹ While plasmonic properties were not deeply explored, these studies provide inspiration for incorporating plasmonic enhancement into similar systems.

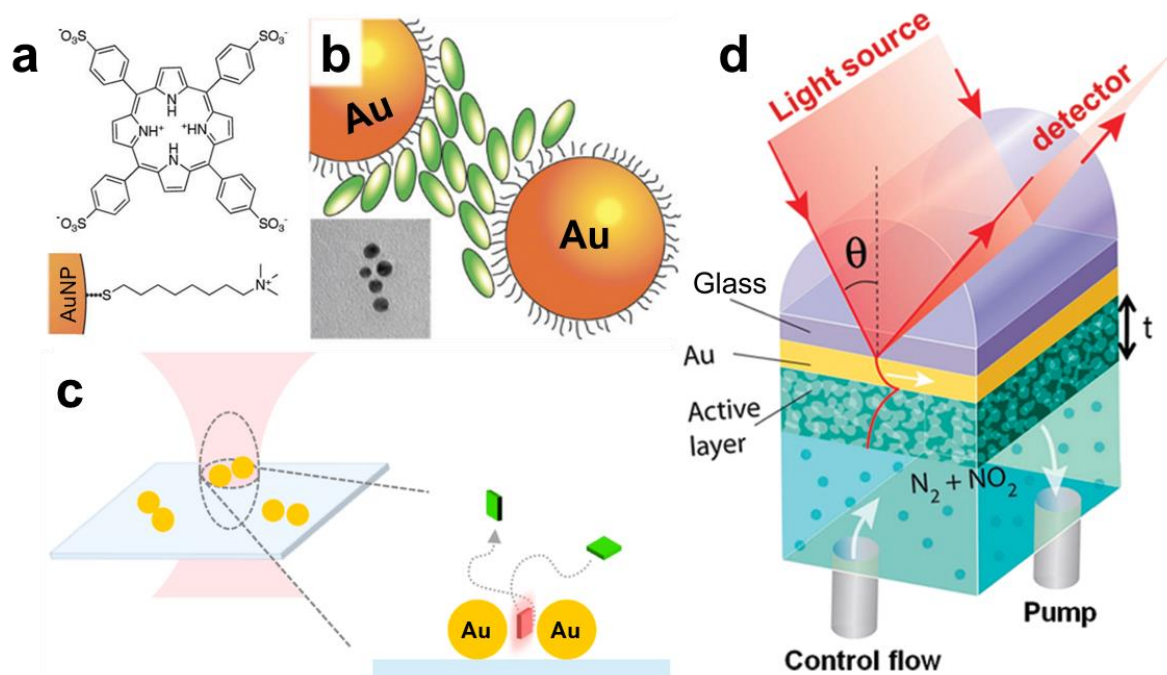


Figure 2.16. Schematics illustrating interaction of porphyrins with different plasmonic systems. **(a, b)** Aggregation of cationic AuNPs with excitonically coupled anionic porphyrin molecules. **(a)** Chemical structure of anionic porphyrin and AuNP surface ligand; **(b)** required aggregation geometry of AuNPs and ordered porphyrin aggregates (green ovals) for strong coupling conditions. Inset: TEM image of porphyrin/AuNP cluster. **(c)** Stochastic diffusion of metalloporphyrins (green squares) in and out of DNAo-mediated AuNP dimer hotspots in aqueous solution, exhibiting PL enhancement when weakly coupled to the hotspot (red square). **(d)** SPR excitation of Au surface with attached silica/porphyrin nanocomposite, exhibiting sensitivity to NO_2 gas, measured via changes in plexcitonic coupling strength.

Other studies combining porphyrins and plasmonic enhancement mostly explore plexcitonic coupling. Originally performed with a Zn porphyrin-filled microcavity,³⁷⁰ more recent studies include aqueous co-aggregation of anionic porphyrins with cationic AuNPs³⁷¹ (**Figure 2.16a,b**), stochastic diffusion of porphyrins through DNAo-mediated plasmonic dimers³⁷² (**Figure 2.16c**) and SPR excitation (via attenuated total reflection; ATR) of Au surfaces functionalised with porphyrin-terminated alkanethiols.^{363,373} In the latter case, the anisotropically enhanced field allowed study of SAM nanostructure, dynamics and electrochemical behaviour via enhanced fluorescence. Plexcitonic coupling was observed in a similar ATR system using a porphyrin/silica nanocomposite (**Figure 2.16d**), facilitated by intermolecular exciton coupling and exhibiting sensitivity to NO_2 gas.³⁷⁴

The subject of porphyrins & plasmonics is sparse, but growing in popularity. However, while STM studies of porphyrin-Au surface binding are generally precise and well-defined,³⁵³ studies investigating porphyrins in coupled nanostructures are less so, often involving transient, stochastic and/or non-specific interactions, often with little directional control.^{371–375} No studies yet exist employing porphyrins as discrete molecular spacers for controlled plasmonic nanojunction self-assembly.

2.3.3 Supramolecular Porphyrin Assembly

Conversely, supramolecular porphyrin chemistry is already an enormous field, with many emergent, tuneable properties arising from encapsulation or multi-porphyrin coupling^{376,377} (**Figure 2.17**). Like BPc, cofacial porphyrin dimers and other suprastructures have been historically used as synthetic models for biological photosynthetic reaction centres,^{377–380} with catalytic, electrochromic and charge transfer properties that depend intimately on functionality and π - π overlap.^{381,382}

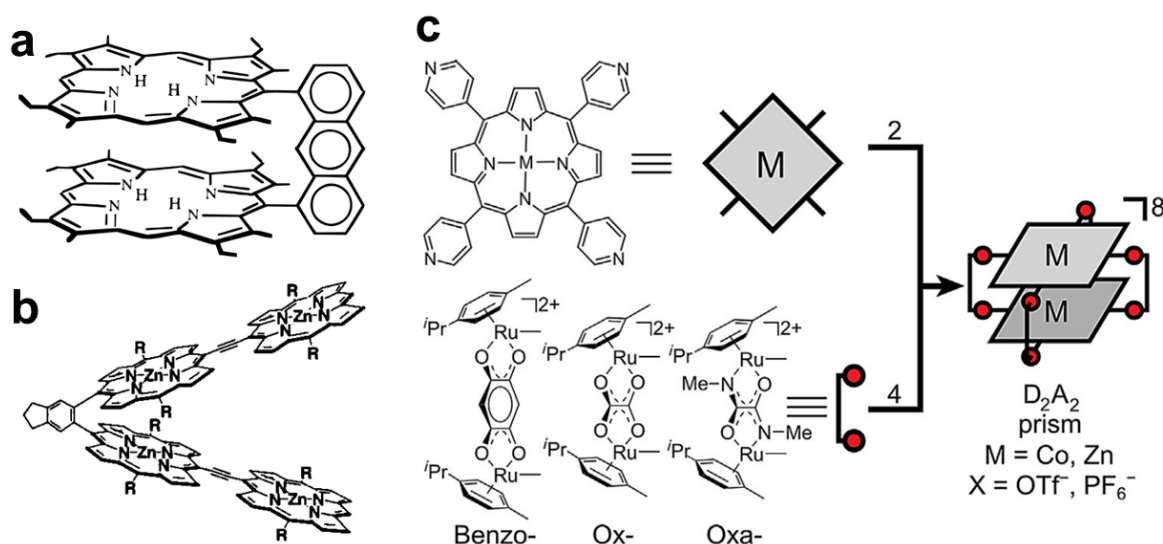
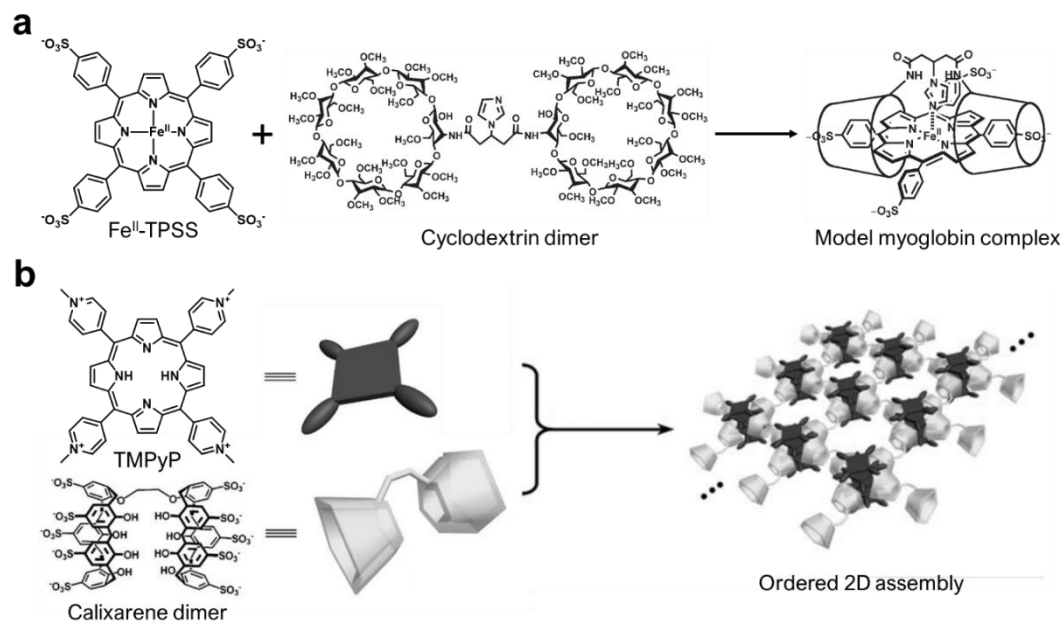


Figure 2.17. Examples of covalent and coordination-based porphyrin assembly. **(a)** Covalently-linked cofacial porphyrin dimer.³⁷⁹ **(b)** Multi-porphyrin pincer structure exhibiting both cofacial and linear inter-porphyrin π - π coupling.³⁸³ **(c)** Cofacial porphyrin dimer held together with organometallic molecular clips.³⁸²

Electronic coupling within metalloporphyrin oligomers can improve catalytic reaction rate and selectivity via electronic structure perturbation and bimetallic host-guest interactions.^{382,383} Covalent modification can introduce pendant functional groups for enzyme-like modification of substrate ligation environment,^{344,352,384} photoswitchable groups for reversible intramolecular charge-transfer isomerisation³⁸⁵ and modular porphyrin arrays for multi-bit information storage.³⁵⁵ However, all these applications require many complex synthetic steps, limiting potential for future scale-up.³⁷⁸

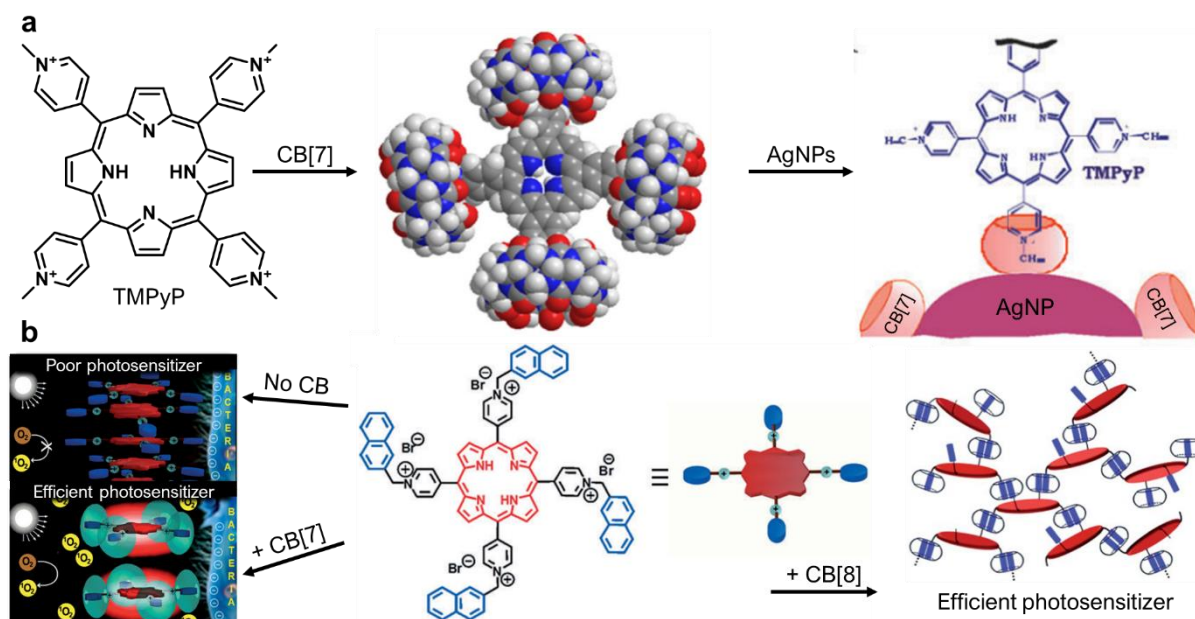
As previously mentioned, supramolecular assembly offers a number of benefits, one of which is reduced synthetic complexity.³⁸² Aqueous aggregation can be used to modify porphyrin's optical response, with dimerisation and extended assembly tuneable via porphyrin concentration, solvent composition and ionic strength.^{386–389} Common water-soluble porphyrin derivatives are 5,10,15,20-*tetrakis*-(*N*-methyl)-4-pyridinium)porphyrin (TMPyP) and 5,10,15,20-*tetrakis*(4-sulfonatophenyl)porphyrin (TPPS), also popular for their PDT utility and interaction with macrocyclic receptor molecules (**Scheme 2.4**). Photoexcited M-TMPyP has been shown to reduce MV²⁺ with high QY,^{339,390} hinting at the favourable charge transfer capabilities of these compounds.



Scheme 2.4. Two common water-soluble porphyrins and existing examples of their self-assembly behaviour with calixarene and cyclodextrin derivatives. **(a)** Anionic Fe^{II}-TPSS interacts with an imidazole-functionalised cyclodextrin dimer to form a discrete supramolecular 1:2 complex with intramolecular Fe-imidazole coordination, acting as a myoglobin functional model.³⁹¹ **(b)** Cationic freebase TMPyP interacts with an anionic calixarene dimer via hydrophobic and charge-transfer interactions to form a supramolecular 2D network.³⁹²

As with ArV, macrocyclic hosts facilitate assembly of well-defined supramolecular porphyrin structures.³⁹³ Cyclodextrin has been widely studied for this, forming stable complexes with anionic porphyrins like TPPS.³⁹⁴ It can be used as a protective barrier to de-aggregate water soluble porphyrin³⁹⁵ or impart solubility to hydrophobic porphyrins.^{396,397} Covalent attachment of cyclodextrin and porphyrin leads to structures with pH-sensitive aggregation properties,³⁹⁸ and functionalised cyclodextrin can turn simple porphyrins into artificial heme protein analogues^{391,399,400} (**Scheme 2.4a**). Cyclodextrin can also be used to form supramolecular porphyrin SAMs on Au; Damos *et al.*⁴⁰¹ even made an NPoM-like structure from this, although AuNPs were used for electrochemical stability and optical properties were not investigated. Calixarenes have also been explored, with reports of pH-controlled electrostatic assembly,^{392,393} facial capping⁴⁰² and charge transfer complexation⁴⁰³ (**Scheme 2.4b**).

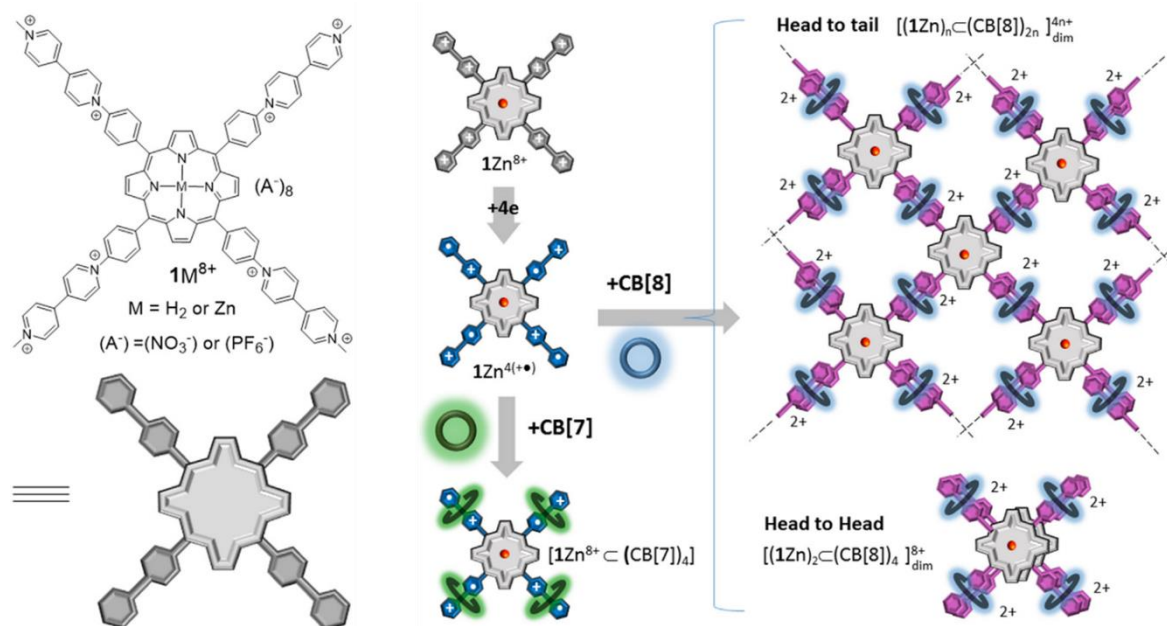
CB[*n*] has also been used for porphyrin encapsulation over the past decade, offering higher stability and non-covalent binding strength than cyclodextrins or calixarenes. Mohanty *et al.*³¹³ reported a TMPyP⊂CB[7] complex with a 1:4 stoichiometry (**Scheme 2.5a**), evidenced by NMR and PL measurements, with increased PL QY caused by hindered rotation of the pyridinium moieties. Unlike MV, TMPyP cannot fit inside CB[7] and, unlike ArV or EV, the pyridinium groups are only partially encapsulated, yielding a low kinetic complexation barrier and highly dynamic binding.⁴⁰⁴ Barooah *et al.*⁴⁰⁵ characterised the CB[7]-mediated attachment of TMPyP to AgNPs with PL spectroscopy for drug delivery and PDT purposes. Despite this, nanoscale surface binding was not explored and neither, again, was plasmonic behaviour.



Scheme 2.5. Supramolecular assembly of viologen-like porphyrins with CB[*n*]. **(a)** TMPyP dynamically binds with 4x CB[7] in aqueous solution.⁴⁰⁴ TMPyP-CB[7]₄ can bind to Ag surfaces and forms conjugates with AgNPs.⁴⁰⁵ **(b)** *N*-methylene-linked naphthyl groups allow stronger CB[*n*] binding for longer complex lifetime and increased photosensitizing activity, either as discrete, isolated complexes (with CB[7], left)³¹⁴ or as a hyperbranched supramolecular polymer (with CB[8], right).⁴⁰⁶ Adapted from corresponding references. Atom colours in **(a)**: C (grey), H (white), N (blue), O (red).

For stable, uniform surface binding (and successful nanocavity assembly), higher supramolecular binding constants and slower dynamics are desirable; this is achievable by including size-complementary moieties to displace water from the CB[*n*] cavity. Various studies explore TMPyP derivatives augmented with methylene-bridged naphthyl,^{314,315} phenyl³¹⁶ or azobenzene⁴⁰⁷ groups. These compounds bind more strongly to CB[7]³¹⁴ and cyclodextrin⁴⁰⁷ in aqueous solution and form extended polymeric structures with CB[8].⁴⁰⁶ Such stable complexation also improves PDT efficiency⁴⁰⁷ and photocatalytic activity³¹⁵ of these systems (**Scheme 2.5b**).

To achieve discrete supramolecular dimerisation (*cf.* **Figure 2.11**) and associated control of electronic structure and bimetallic interactions, more rigid binding moieties are required.^{260,261,275,328} This was previously attempted via augmentation of tetraphenyl porphyrin with MV moieties, yielding a four-armed, octacationic structure^{408,409} (**Scheme 2.6**). This forms a discrete 1:4 complex with CB[7] or CB[8], with similar binding dynamics to free MV. However, like MV, dimerisation was only possible upon reduction of all dicationic binding groups. Even then, electrochemical and DFT analyses indicated preference of extended networks, suggesting a maximum charge requirement of 1+ per binding group for discrete dimerisation.



Scheme 2.6. Reduction and self-assembly of tetrakis(methyl-phenyl-viologen)porphyrin (MPVP) with CB[7] and CB[8]. MPVP forms a 1:4 complex with CB[7] (green, bottom) or, in its 4-electron reduced state, discrete or extended complexes with CB[8] in a 1:2 (2:4) stoichiometry (pink/blue, right). Extended head-to-tail assembly (top right) is favoured over discrete head-to-head geometry (bottom right).⁴⁰⁹

Based on the existing porphyrin, viologen and CB[n] literature, together with the results of **Chapter 4**, the next section discusses design of a new water-soluble porphyrin species capable of discrete CB[8]-mediated dimerisation. These new compounds afford improved supramolecular control over electronic structure and fulfil many of the plasmonic self-assembly criteria outlined in **Section 1.4.3**.

2.3.4 New Molecule Design

The novel structure, 5,10,15,20-*tetrakis*(4-(*N*-arylpyridinium))porphyrin (APP) (**Figure 2.18a**), was designed for water solubility and the ability to form 1:4 and 2:4 inclusion complexes with CB[7] and CB[8] (**Figure 2.18c,d**) for supramolecular control over electronic structure, chemical accessibility and bimetallic interactions. The low conformational entropy of APP encourages discrete, rather than extended, assembly with CB[8]. The synthetic pathway (**Chapter 5**) is similar to that of ArVs/EVs and allows arbitrary peripheral functionalisation while retaining CB[n] affinity, providing a supramolecular toolbox for further fine-tuning the system's electronic structure, optical response and interaction with Au surfaces.

The strong optical absorption and emission, coupled with the ability to bind transition metals, provides a starting point for combining plexcitonic coupling with molecular catalysis. Meanwhile, the arylpyridinium groups are likely to exhibit electrochromic behaviour, creating further opportunity for chemical and electrochemical tuning of the optical response and plexcitonic coupling.

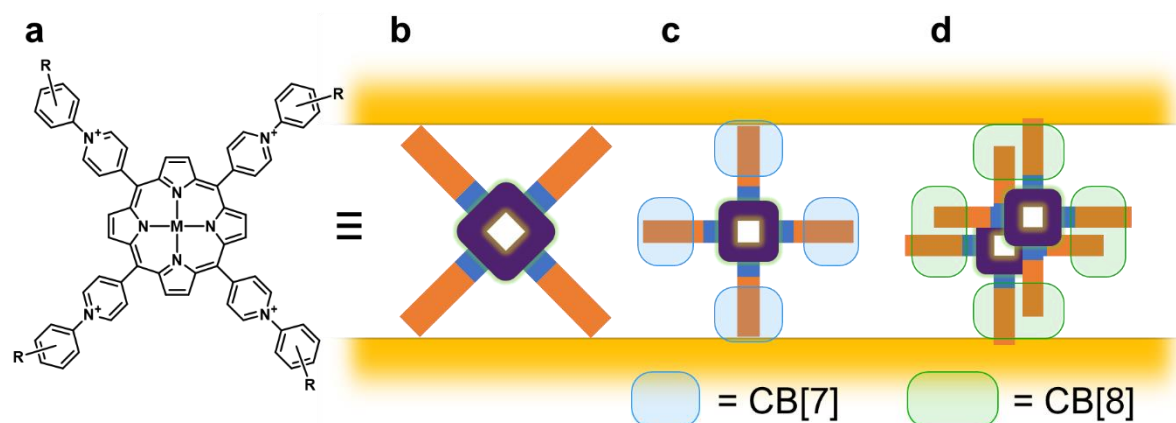


Figure 2.18. (a) General structure of APP, with various possible metal centres and peripheral functionality. (b-d) Schematics of (b) predicted APP binding geometry in a plasmonic nanocavity if Au-binding peripheral functionality is present, and (c, d) supramolecular structure and nanocavity orientation of $\text{APP} \subset \text{CB}[7]_4$ and $(\text{APP})_2 \subset \text{CB}[8]_4$ complexes.

First, peripheral functionality and metal centre(s) must be chosen, and a synthetic procedure must be established. Supramolecular complexation with CB[7] and CB[8] must then be confirmed, followed by characterisation of the system's AuNP self-assembly properties. Synthesis, characterisation and self-assembly properties are presented and discussed in **Chapter 5**, together with the perturbative effects of solvent, CB[*n*] binding and plasmonic enhancement upon the PL spectra.

Following this, future work should focus on the spectroelectrochemical behaviour of these compounds and the effects of metal centre, functionality and CB[*n*] complexation. Strong coupling behaviour should then be explored by tuning plexcitonic interactions via metal centre, peripheral functionalisation, CB[8] dimerisation, AuNP size and/or applied potential. In parallel, the catalytic activity of these systems - towards CO₂ reduction, water splitting or other industrially relevant reactions - should be tested both in solution, and in the NPoM cavity using recently developed SERS-electrochemistry techniques.⁹⁷ The effects of plexcitonic coupling on reaction selectivity should then be investigated. Other routes may investigate the effects of peripheral functionality²⁷ and electrical current²⁵ on the charge transport and optical response of the system.

3. BPcs

3.1 BPc Introduction

This chapter describes the development of BPc derivatives and self-assembled plasmonic nanostructures thereof. While the BPc@AuNP systems explored here showed poor suitability for sensing and catalysis applications, they proved useful for exploring the d - and n_g -dependent plasmonic response near the quantum plasmonic limit.¹ An anomalous NPoM $\overline{\lambda}_C$ shift was observed with variation of BPc SAM thickness; an in-depth investigation into the nature of this shift is the main focus of this chapter.

3.1.1 Objectives & Hypotheses

The first step in developing BPc@AuNP plasmonic nanostructures was to design a suitable BPc derivative via the criteria outlined in **Section 1.4.3**. Preliminary experiments with non-functionalised LuPc₂ and TbPc₂ demonstrated possible SAM/NPoM formation, but poor BPc solubility led to large scattering impurities at the Au surface (**Section 3.3.1**), which indicated poor SAM and data quality and hindered optical analysis. The hydrophobicity of BPc also complicated aqueous AuNP self-assembly. The first synthetic objective was therefore to add functionality for improvement of solubility and self-assembly at the Au surface.

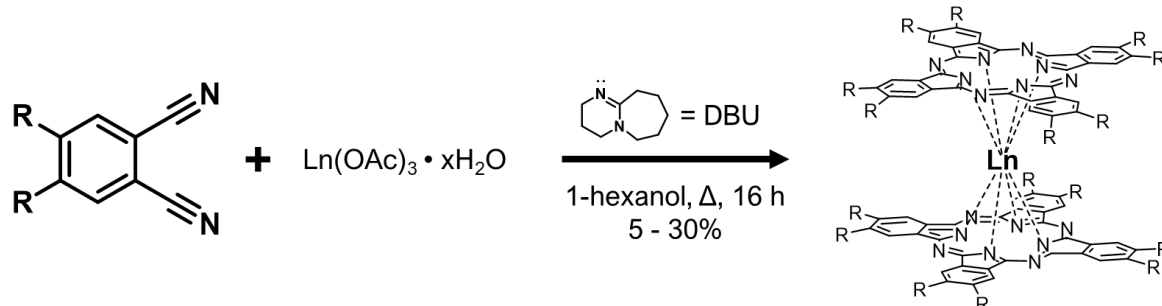
The next objective was to optimise BPc NPoM and/or AuNP aggregate self-assembly procedures, and characterise the resulting nanostructures. The main goal of this chapter was to expose the BPc@AuNP nanostructures to VOCs and identify any resultant changes in SERS spectra. These experiments also build a foundation for iterative re-design of new plasmonic spacers with improved optical, sensory and chemical functionality.

Based on existing literature and preliminary experiments, the project began with several hypotheses. Extensive STM studies demonstrate BPc assembly on Au surfaces;¹⁹⁴ SAM formation of BPc on a template-stripped gold (TSG) substrate⁹² (**Sections 3.3, 7.2**) should therefore be possible. BPc is predicted to adsorb with Pc planes oriented parallel to the substrate for maximised π -Au and N-Au interactions, and self-assembly may be encouraged via functionalisation of Pc with organic side chains.^{241,410} This should allow bottom-up NPoM assembly, and the presence and orientation of BPc can be characterised with SERS and DF spectroscopy. AuNP aggregation often requires water-soluble molecular spacers, calling for hydrophilic BPc functionalisation. Successful AuNP aggregation and BPc gap orientation may be confirmed using extinction spectroscopy and, again, SERS.

The extremely small interparticle gaps, together with the strong visible absorption of BPc, are expected to generate large SERRS signals, possibly allowing observation of single-molecule interactions. This could allow detection of certain gases interacting with BPc within the nanocavity, potentially enabling multiplexed sensing at the few-molecule scale.

3.1.2 Synthetic Plans

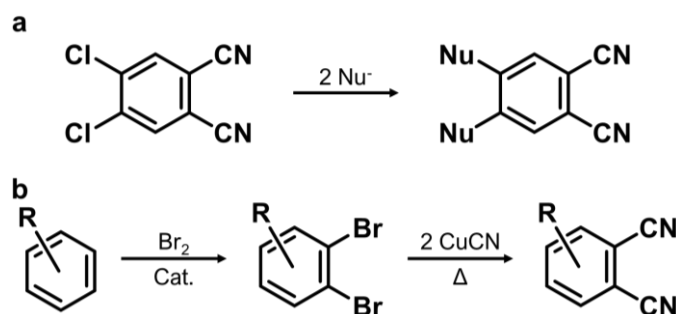
Several routes exist for BPC synthesis.^{253,411,412} The method used here, chosen for its simplicity and versatility,²⁵³ is a base-catalysed phthalonitrile (aka 1,2-dicyanobenzene) tetramerization in the presence of a metal salt and a high boiling point solvent^{4202,413,414} (**Scheme 3.1**). Briefly, a phthalonitrile derivative is refluxed overnight in 1-hexanol with an excess of both 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; a strong, non-nucleophilic base) and a lanthanide acetate (**Methods 3.7.1**). The crude product is purified via column chromatography to yield the LnPc₂ or LnPc*₂ complex (where * denotes peripheral functionalisation).



Scheme 3.1. General base-catalysed BPC synthesis from arbitrary phthalonitrile derivative and lanthanide acetate hydrate. Here, Ln = Sm, Tb, Er, Lu and R = H or *n*-dodecylthio.

Preliminary NPoM experiments (**Section 3.3.1**) were performed with unsubstituted LuPc₂ and TbPc₂ (R = H in **Scheme 3.1**), synthesised using literature methods.⁴¹³ Unsubstituted BPCs are soluble in chloroform (CHCl₃) and sparingly soluble in benzene, toluene and dichloromethane (DCM); solubility in most other solvents is negligible due to strong intermolecular π - π interactions.^{253,413} These harsh solvents interfere unpredictably with the epoxy adhesive used for substrate preparation (**Methods 7.2**) and BPC aggregation and multilayer formation (due to low solubility) can disrupt uniform SAM assembly.⁴¹⁵

Fortunately, BPC solubility is tuneable via choice of Pc substituent, determined by functionality of the phthalonitrile precursor in the peripheral (4,5; **Scheme 3.1**) and/or non-peripheral (3,6; not pictured) positions. A versatile method begins with functionalisation of 4,5-dichlorophthalonitrile^{202,416} via nucleophilic aromatic substitution at the 4,5 positions, facilitated by the strong electron withdrawing effect of the CN groups (**Scheme 3.2a**).



Scheme 3.2. Two routes to phthalonitrile functionalisation. **(a)** Nucleophilic aromatic substitution of 4,5-dichlorophthalonitrile to yield a range of peripheral functionality; limited versatility, but safe and straightforward **(b)** Bromination of functionalised benzene, followed by conversion of bromide to nitrile via the Rosenmund-von-Braun reaction; more versatile, but very hazardous and not used in this work.

A symmetrical precursor ensures a single, symmetric BPc product with octasubstituted Pc ligands (**Scheme 3.1**). An alternative route involves bromination and bis-cyanylation of a pre-functionalised benzene ring via the Rosenmund-von-Braun reaction^{253,417} (**Scheme 3.2b**). However, despite offering greater functional versatility, the use of CuCN carries risk of death if handled improperly and this method was not pursued.

Common solubility-improving BPc substituents include branched^{207,236} or linear^{202,418,419} alkyl,^{207,415,420} alkoxy^{241,421} and/or alkylthio^{202,209,422,423} moieties, and water solubility can be introduced via charged^{412,417,424} or polar groups.^{232,425–427} Hydrophilic oligo(ethyleneoxy) chains, for example, may be introduced via **Scheme 3.2a**.^{425,426} However, the repeated chromatographic purifications typically required in BPc synthesis^{202,413} are likely to be complicated by polar products, requiring expensive reverse-phase techniques. Lipophilic BPc derivatives are easier to purify and offer a simpler synthetic starting point for BPc NPoM spacers. Additionally, oligo(ethyleneoxy)-substituted Pc synthesis has only been demonstrated for MPcs,^{425,426} whereas synthetic routes to alkoxy-^{241,410} and alkylthio-substituted^{202,209,422} BPcs (also via **Scheme 3.2a**) are already known.

The BPc derivative chosen here is peripherally functionalised with *n*-dodecylthio moieties (**Figure 3.1a**).²⁰² The alkyl chains improve organic solubility and encourage ordered SAM formation with Pc planes parallel to the substrate,^{194,199,205,241,410} while minimising angled cofacial stacking^{428,429} and multilayer formation.^{198,430} Large steric separations also minimise intermolecular magnetic/electronic coupling, which limits perturbation of the already complex optoelectronic behaviour.^{196,204,229}

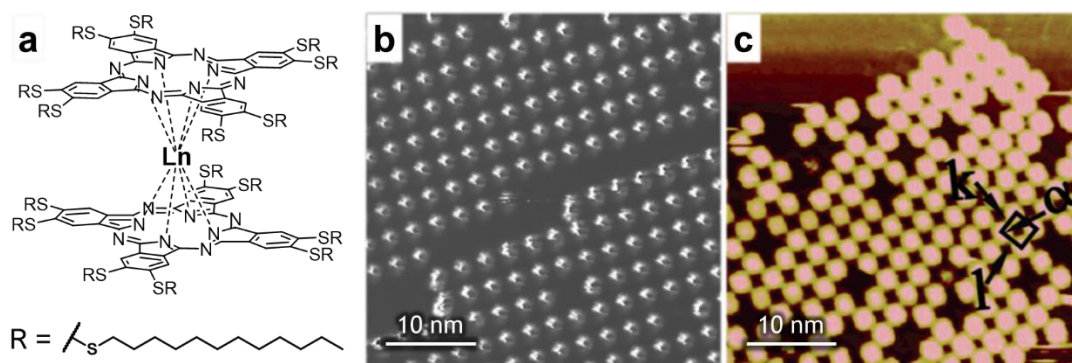


Figure 3.1. (a) General structure of BPc* complexes used in this work. Ln = Sm, Tb, Er, Lu. (b, c) STM images of analogous *n*-alkoxy BPc compounds on HOPG. (b) Er(Pc[O^{*n*}C₁₂H₂₅]₈)₂ adapted from [241]; (c) Pr(Pc[O^{*n*}C₈H₁₇]₈)₂, adapted from [410]. 2D lattice parameter is proportional to alkoxy chain length.

The BPc* structure (**Figure 3.1a**) was inspired by STM measurements of ordered *n*-alkoxy BPcs SAMs on highly-oriented pyrolytic graphite (HOPG)^{241,410} (**Figure 3.1b,c**); literature evidence suggests that *n*-alkylthio BPcs behave similarly on Au.^{209,422} Alkylthio groups were favoured over alkoxy due to easier nucleophilic substitution in **Scheme 3.2b** and thioether-Au affinity.^{209,422}

3.2 Synthesis & Characterisation

3.2.1 Unsubstituted BPc

LuPc₂ and TbPc₂ were synthesised using literature methods⁴¹³ (R = H in **Scheme 3.1**). The low yield (2-3%) was improved (to 5-10%) by CHCl₃ Soxhlet extraction of the crude product before chromatographic separation (**Methods 3.7.1**). SmPc₂ was synthesised but exhibited poor chemical stability, evidenced by multiple TLC spots after prolonged exposure to ambient conditions. BPc synthesis is known to be lower-yielding for larger Ln,⁴¹⁴ and exposure to air, light and heat should be avoided during workup of future SmPc₂ syntheses. Characterisation utilised UV-Vis, FTIR, elemental analysis (EA) and mass spectrometry (MS); NMR characterisation was precluded by Ln and/or ligand paramagnetism. All products were deep green powders.

BPc UV-Vis spectra (**Figure 3.2**) consist of 3 main bands: the UV/Soret band below 400 nm, the B/radical band between 400-500 nm and the Q band around 600-700 nm. Of these, the Q band is most relevant here for its spectral proximity to λ_c (**Section 3.5**). The Q band position (λ_Q) is determined by excitonic coupling between the cofacial Pc ligands, which creates a Q band splitting.^{214,216–218} Only the higher-energy transition is allowed, manifesting as a blueshift that increases as Ln radius and Pc-Pc distance shrinks (and π - π coupling strength increases) from Sm to Lu. Comprehensive theoretical discussions have been published by Rousseau,²¹⁴ Ishikawa²¹⁶ and Prall,^{217,218} but are beyond the scope of this work.

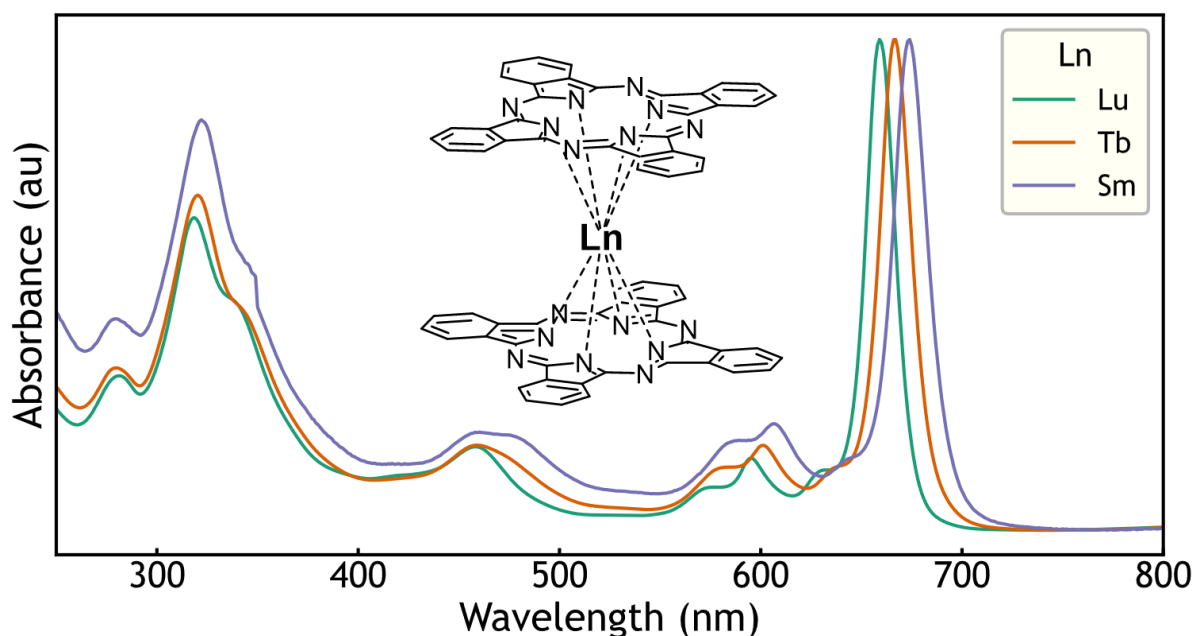
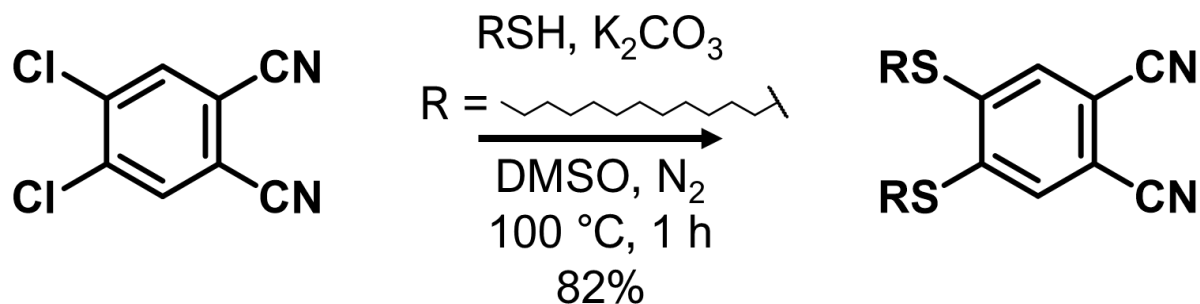


Figure 3.2. Unsubstituted LnPc₂ UV-Vis spectra (normalised), measured at approx. 1 μ M in CHCl₃. Red shift in Q-band (~660-680 nm) from Lu to Sm is caused by distance-dependent π - π coupling between the Pc ligands, mediated by r_{Ln} .

3.2.2 Substituted BPc*

LnPc^*_2 complexes were synthesised using a method adapted from Ban *et al.*²⁰² 4,5-bis-(dodecylthio)phthalonitrile was synthesised via **Scheme 3.3**. 4,5-dichlorophthalonitrile, excess *n*-dodecanethiol and potassium carbonate were stirred in dry dimethyl sulfoxide (DMSO) at 100 °C for 1 h under N_2 . A deep pink colour remained after the recommended workup procedure and was removed with flash column chromatography to yield a white, crystalline product, characterised via NMR, FTIR, EA and X-Ray crystallography (**Methods 3.7.1**).



Scheme 3.3. Synthesis of BPc* precursor, 4,5-bis(dodecylthio)phthalonitrile.

The subsequent step was performed via **Scheme 3.1** ($\text{R} = n$ -dodecylthio; $\text{Ln} = \text{Sm, Tb, Er, Lu}$), with similar procedure and results for each Ln. 4,5-bis-(dodecylthio)phthalonitrile was refluxed overnight in 1-hexanol with excess $\text{Ln}(\text{OAc})_3$ and DBU, then precipitated with MeOH and isolated by column chromatography. The literature procedure reports chromatic separation over silica (CHCl_3 eluent), followed by size exclusion chromatography (SEC) with Bio-Rad beads (tetrahydrofuran (THF) eluent), to yield a dark green product.²⁰² This method generated low yields ($< 5\%$) of green waxy solid and, due to poor/streaky separation, several repetitions were required to separate the deep green first fraction from the second, rusty red/black fraction (**Figure A4**). Purification was repeated using a DCM/petroleum ether mixture over silica, with similar results in a shorter time. Repeating the synthesis under anhydrous and anaerobic conditions further decreased the green product yield, and increased the yield of the red/black side product.

Gurek *et al.*²⁰⁹ reported a brown/purple colour for alkylthio-substituted BPc, rather than the deep green observed for other BPc derivatives. UV-Vis analysis of both products revealed that the second, red/black fraction was the desired LnPc^*_2 . The deep green first fraction was possibly the triple-decker Ln_2Pc_3 complex, as its large retention factor (RF) on both SEC and silica columns indicates higher molecular weight and greater lipophilicity. A third, dark orange/brown fraction was also obtained, whose organic solubility and smaller RF suggests a single-decker $\text{LnPc}(\text{OAc})$ complex or similar. As these side products were not the primary synthetic goals, they were not investigated further.

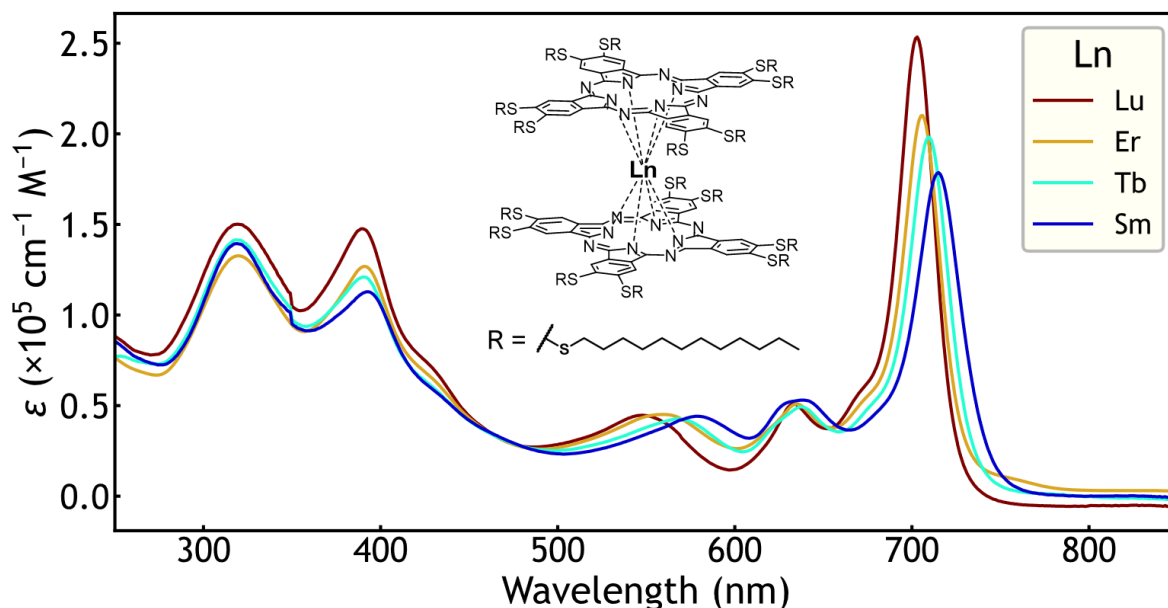
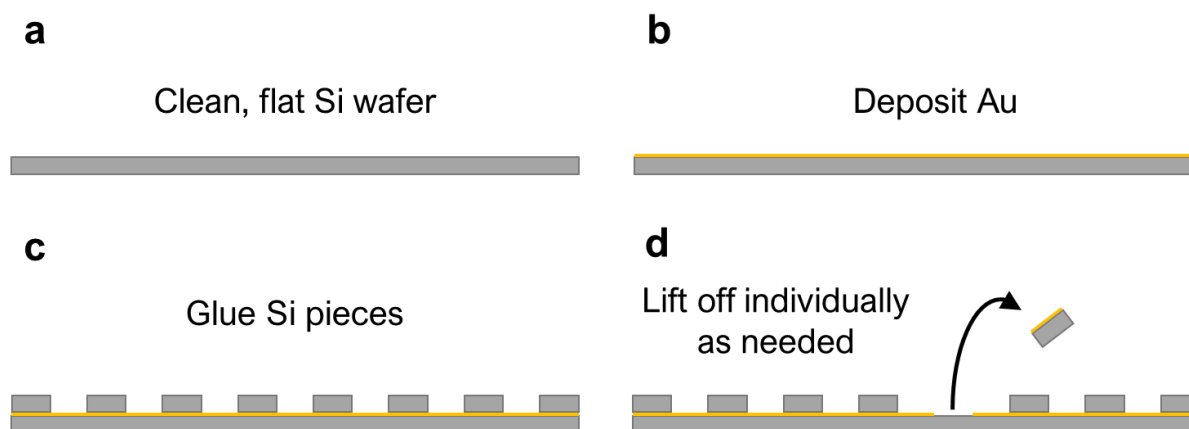


Figure 3.3. UV-Vis spectra of LnPc*₂ (Ln = Sm, Tb, Er, Lu), measured at 1 μ M in CHCl₃.

The BPC* complexes were all isolated with low to moderate yield (15 – 30%), but high purity, and characterised with UV-Vis, FTIR, EA and MS (**Methods 3.7.1**). The BPC* UV-Vis spectra (**Figure 3.3**) are redshifted with respect to unsubstituted BPC (**Figure 3.2**), characteristic of similar *n*-alkylthio BPC derivatives.¹⁷⁹ The Q-band peak absorption wavelength (λ_Q) redshifts and decreases in intensity with increasing $r_{1,n}$, as observed earlier (**Section 3.2.1**).

3.3 NPoM Assembly & Characterisation

NPoM samples were fabricated as in **Methods 7.3**. To make the TSG substrate, Au is thermally evaporated onto a clean, flat Si wafer under vacuum. Next 1 cm² pieces of Si are glued to the exposed Au with epoxy resin and lifted off as needed to expose a clean, flat Au surface, templated by the Si wafer underneath (**Scheme 3.4**).



Scheme 3.4. Schematics (not to scale) illustrating TSG preparation procedure. For full details, see **Methods 7.2**. TSG substrates were prepared by either myself or Bart de Nijs*

* NanoPhotonics Centre, Dept. of Physics, University of Cambridge

A freshly stripped TSG substrate is immersed in molecular spacer solution for some time (minutes to days) to allow SAM formation. The Au surface is quickly rinsed and dried, exposed to colloidal AuNP solution ($D = 80$ nm), typically for up to 60 seconds, then rinsed/dried again. AuNP coverage and SAM quality are determined by optical inspection and DF spectroscopy (Section 1.3.2); the results are then used to iteratively optimise SAM and AuNP deposition conditions.

3.3.1 Unsubstituted BPc

Preliminary experiments were performed using 0.5 mM LnPc₂ in toluene. 10- to 60-minute BPc deposition was sufficient to form NPoMs (with 30-60 sec AuNP deposition) but yielded large, brightly scattering impurities - likely aggregates of BPc due to poor solubility - on the substrate surface (Figure 3.4a), which interfered with automatic particle detection and precluded data collection (Methods 7.4.1, Appendix 8.1). Longer deposition times (6 - 24 h) led to dissolution of the epoxy adhesive and lifting-off of the Au substrate. Deposition was repeated using 1 mM LnPc₂ in CHCl₃. 10- to 60-minute deposition led to sparse NPoM samples (Figure 3.4b) and inconclusive DF spectra (Figure A5); 24 h deposition yielded some measurable NPoM samples (Figure 3.4b,c), but also often led to destruction of the epoxy adhesive and broad spectra with poor reproducibility.

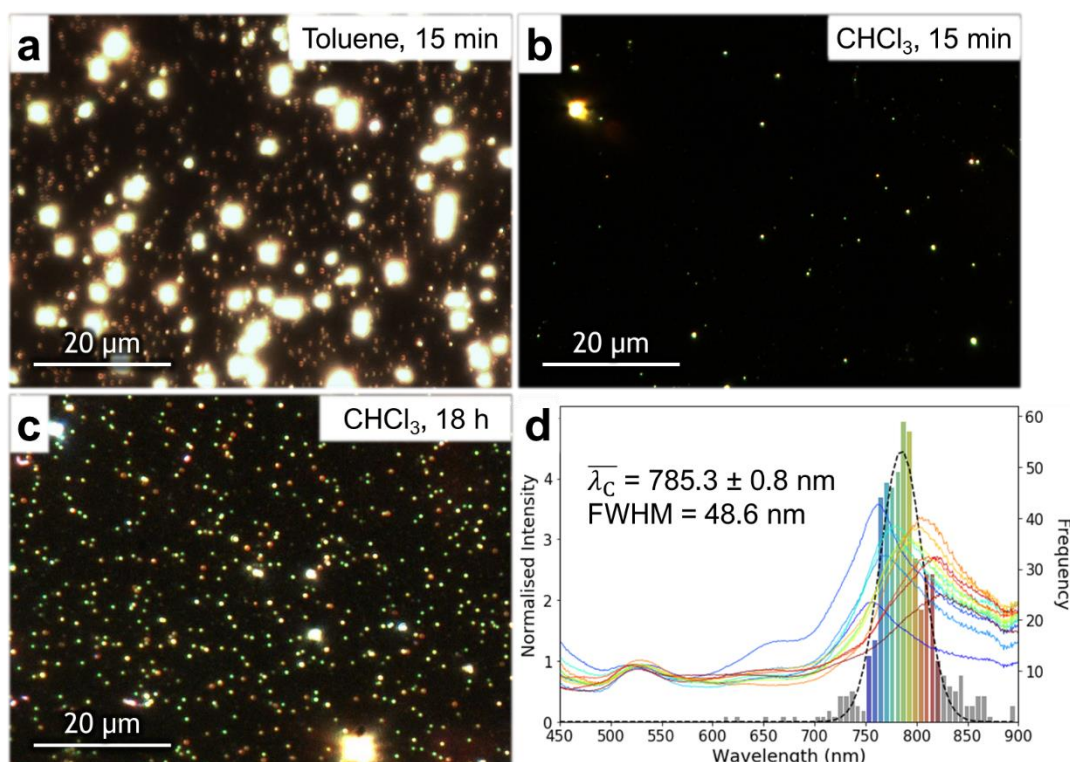


Figure 3.4. Initial NPoM sample fabrication attempts using unsubstituted LuPc₂. **(a-c)** Optical DF images of NPoM samples. **(a)** Short deposition from toluene caused large, scattering aggregates that preclude automated data collection; longer deposition times led to destruction of the sample (not shown). **(b)** Short deposition times from CHCl₃ gave low NPoM density. **(c)** Overnight deposition from CHCl₃ yielded some acceptable samples, evidenced by **(d)**, showing histogram of measured λ_C positions for several hundred NPoMs across the sample (bar chart; right axis) and averaged DF spectra (coloured traces; left axis) from each λ_C histogram bin of corresponding colour.

3.3.2 Substituted BPc*

BPc* is far more soluble in non-polar solvents, of which aliphatic hydrocarbons were least disruptive to the epoxy adhesive; most BPc* SAM deposition was therefore performed with *n*-hexane or *n*-heptane. Optimum BPc* SAM formation was achieved with 10-90 min deposition from 1 mM solution; negligible variation in microscopic appearance or λ_C position was observed between samples with these deposition times; longer deposition (6 - 24 h) led to impurities at the sample surface. The BPc* hydrophobicity necessitated longer AuNP deposition (60-120 sec) for sufficient NPoM density.

Overall, BPc* NPoM samples were visually and spectrally more uniform than their unsubstituted BPc counterparts, with distinct individual NPoMs and clean λ_C distributions (**Figure 3.5**). $\overline{\lambda_C}$ values varied between 775-810 nm, exhibiting a smooth redshift as BPc* height decreases from Sm to Lu. Using the LCR model (**Equations (2)-(4); Section 1.3.1**), the experimental $\overline{\lambda_C}$ values imply $d \leq 0.6$ nm for $n_g \approx 1.1 - 1.3^{74,83,173}$ (n_g likely underestimated due to classical nature of LCR model; **Section 3.5**).

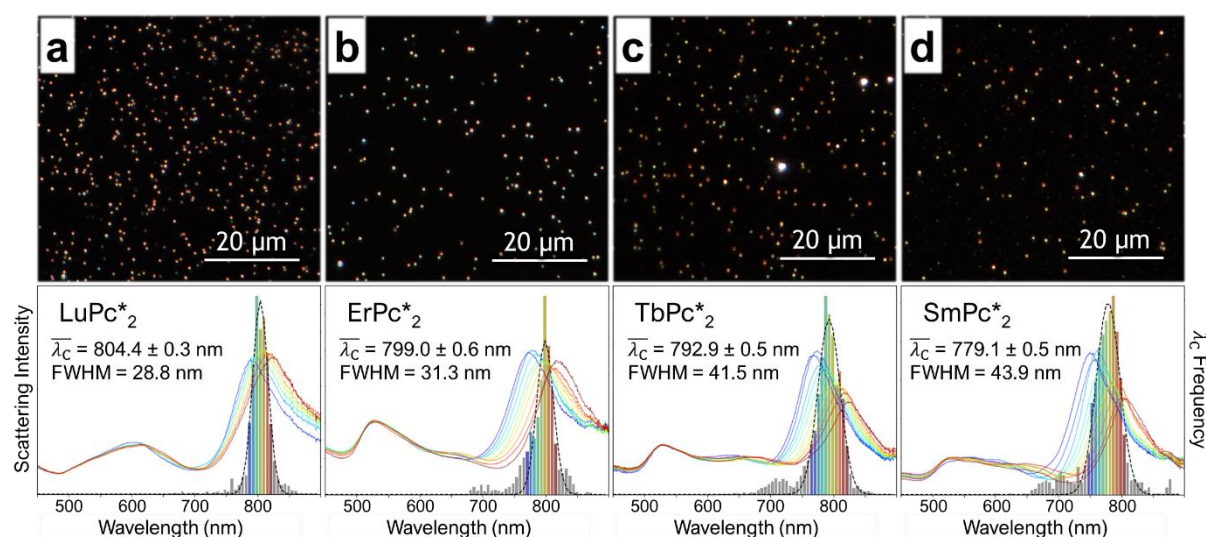


Figure 3.5. Top: DF optical images and bottom: averaged DF spectra (coloured traces; left axis) & λ_C distributions (coloured bars; right axis) for (a) LuPc*₂, (b) ErPc*₂, (c) TbPc*₂ and (d) SmPc*₂.

I_C/I_T distributions were broad and variable (**Figure A6**), and not used for estimation of n_g and d . This method is unreliable for strongly non-classical systems (i.e. with $d \lesssim 0.5$ nm), predicting $n_g < 1$ for graphene ($d = 0.34$ nm).^{17,77} I_C and I_T may be susceptible to very small changes in AuNP facet geometry, gap conductance and surface reconstruction at such gap sizes, as well as chemical and/or magnetic impurities within the spacer layer and substrate. The high I_C/I_T variability - despite stable λ_C - may suggest untapped potential for sensing, nanometrology and materials characterisation, currently limited by sparse experimental calibration data. In future, I_C/I_T behaviour should therefore be studied for other $d < 0.5$ nm systems under a wider range of physicochemical conditions.

Nevertheless, the indication of $d \lesssim 0.5$ nm, together with relatively sharp λ_c distributions and reproducible DF spectra, suggests a BPc* (sub)monolayer with $0.3 < d < 0.6$ nm, consistent with DFT calculations (**Section 3.5.2**) and literature STM measurements.¹⁹⁴ The magnitude of the smooth $\overline{\lambda_c}$ redshift from Sm to Lu ($\Delta\overline{\lambda_c} = 25\text{-}30$ nm) is not predicted by the LCR - nor any other - plasmonic dimer model¹ for the expected $\Delta d \approx 0.04$ nm. This anomalous result is discussed in **Section 3.5**.

NPoM SERS spectra were collected for each LnPc*₂ spacer. Significant spectral wandering was observed (**Figure A7**), implying strong BPc*-Au interactions and Au surface reconstruction, even at modest (10-100 μW) laser powers. This behaviour has been investigated for simpler SAMs,^{50,52} but is beyond the scope of this work. Combining low incident laser powers (< 50 μW) with long collection times yielded stable SERS spectra, confirming presence of BPc* in the nanocavity (**Figure 3.6**).

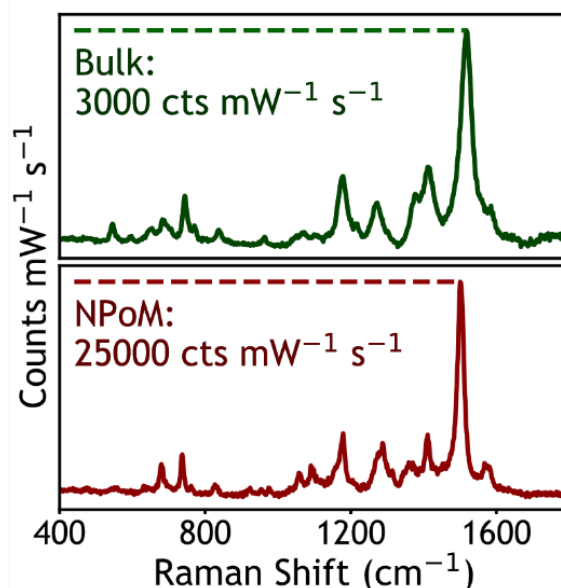


Figure 3.6. ErPc*₂ NPoM SERS (bottom) vs Bulk Raman (top). NPoM SERS intensity is an order of magnitude higher than the bulk Raman intensity, despite the significantly lower number of molecules in the NPoM system. This is consistent with BPc* in an enhanced hotspot field.

The NPoM SERS spectra exhibit sharper resonances and different relative peak intensities than bulk BPc*. This implies ordered SAMs in the NPoM cavity - with consistent molecular environment - and a highly directional enhanced field, in contrast with the isotropic excitation and varied intermolecular interactions for the randomly oriented molecular solid. Despite λ_c resonances near the common 785 nm NPoM SERS excitation wavelength^{50,52,97} (**Figure 3.5**), 633 nm excitation yielded higher SERS signals, indicating electronic resonance with the BPc* Q side-band around 630 nm (**Figure 3.3**).

This extra enhancement gives surface-enhanced resonance Raman scattering (SERRS) signals⁵⁷ of ~ 25000 cts $\text{mW}^{-1} \text{s}^{-1}$ per NPoM, allowing acquisition times as low as 30 ms. Assuming ordered monolayers with ~ 3.0 nm intermolecular spacing²⁴¹ and $w = 20$ nm, ≤ 95 BPc* molecules exist in the cavity. A hotspot field FWHM of $\sqrt{Dd/n_g} \approx 6$ nm (for $D = 80$ nm,

$d = 0.6$ nm and $n_g = 1.4$; see **Section 1.3.4**) implies the signal is dominated by ~ 10 BPc* molecules, with SERRS of ~ 2500 cts $\text{mW}^{-1} \text{s}^{-1}$ per molecule (*cf.* ~ 10 cts $\text{mW}^{-1} \text{s}^{-1}$ molecule $^{-1}$ for CB[7] NPoMs⁴⁷). Such signals should allow real-time observation of chemical changes at the single molecule level, even without the assistance of picocavities^{50,51} or other physical signal enhancements.^{53,99}

This signal strength may be useful for probing potential BPc*-VOC interactions. NPoM samples were placed in a gas flow cell equipped with gas in/outlets and a glass coverslip for optical analysis (**Figure 3.7a**). Unfortunately, no SERS signals were detected, possibly due to high emission angles (**Section 1.3**) and consequent reflection from the underside of the coverslip (**Figure 3.7b**). This issue has since been solved by decreasing sample-coverslip distance to < 1 mm and using a higher numerical aperture (i.e. larger collection angle) objective.⁹⁷ At the time, VOC sensing experiments were instead performed using isotropically-emitting dried BPc@AuNP aggregates immobilised directly on the underside of the coverslip (**Figure 3.7c**).

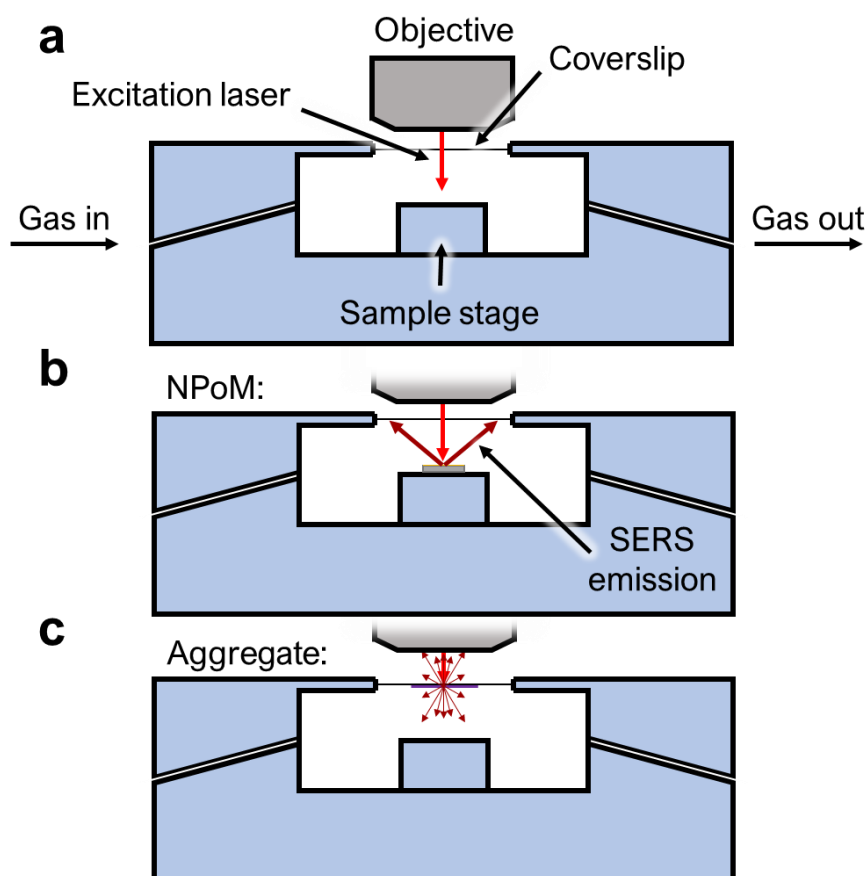


Figure 3.7. Schematics of optical gas sensing apparatus with NPoM and AuNP aggregate samples. **(a)** Gas flow cell with gas inlet and outlet, cover slip and raised platform to allow focusing on sample with a microscope objective for laser excitation and SERS collection. **(b)** NPoM sample on raised stage, with dark red arrows indicating high-angle SERS emission. **(c)** Dry BPc@AuNP aggregate attached to underside of coverslip and emitting in all directions, yielding improved optical collection efficiency.

3.4 BPc@AuNP Aggregation

Aqueous AuNP aggregation usually requires a water soluble aggregant (**Section 1.3.3**). Although water-soluble functionalisation of BPc is possible (**Section 3.1.2**), AuNP aggregation was first attempted with the current BPc and BPc*. All AuNPs were citrate-stabilised in colloidal solution.¹³ Successful aggregation was confirmed and characterised using extinction spectroscopy, TEM and SERS. BPc@AuNP aggregates were exposed to solvent vapours using the device in **Figure 3.7c** and simultaneously monitored with SERS.

3.4.1 Aggregation Method Optimisation

The first attempt combined 0.1 mM LnPc₂ (Ln = Lu, Tb, Sm) in toluene with a 90:10 EtOH/AuNP (*D* = 60 nm) mixture. No immediate colour or spectral changes were observed, but after 4 days at room temperature, a pale blue colour developed. Extinction spectra (**Figure 3.8a**) resembled those of reduced [LnPc₂]⁻,^{181,209} likely due to reduction of BPc by citrate in the AuNP buffer solution. No aggregation was observed, precluded by electrostatic repulsion between AuNPs and [LnPc₂]⁻.

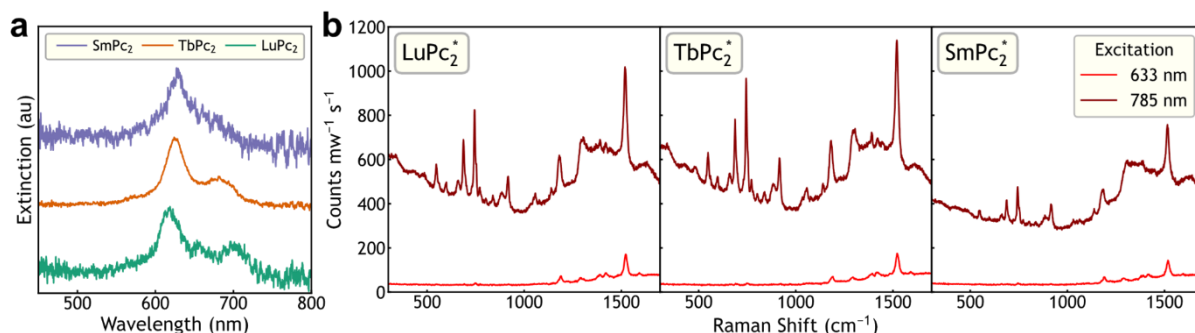


Figure 3.8. (a) Extinction spectra of homogeneous unsubstituted BPc/toluene + AuNPs/EtOH mixture after four days. (b) Raman/SERS spectra of AuNP (60 nm) colloidal solutions after dropwise addition of BPc*/THF solution. Greater SERS signals with 785 nm excitation implies enhancement by chain modes of AuNP aggregates.

Under certain conditions, BPc*/THF solution was found to be dispersible in water. A second aggregation attempt therefore involved dropwise addition of 1 mM BPc* in THF to AuNP solution (*D* = 60 nm) in a 340 μ L well plate, followed by direct Raman analysis. Excitation wavelength λ_{ex} = 785 nm yielded larger Raman signals than λ_{ex} = 633 nm (**Figure 3.8b**), implying greater resonance at 785 nm (despite the BPc* electronic resonance near 633 nm) and therefore some co-aggregation of AuNPs and BPc*. However, precipitation of BPc* at the water/air interface precluded extinction measurements, and experiments were discontinued.

The most successful method used a two-phase approach. Aqueous AuNPs (*D* = 16, 40, 50, 60, 80 nm) were exposed to 1 mM CHCl₃ solutions of LuPc₂ and LuPc*₂. With LuPc₂, AuNP aggregation was evidenced by an aqueous colour change from red to purple after 15 min, accompanied by a gradual optical density decrease (**Figure 3.9a**).

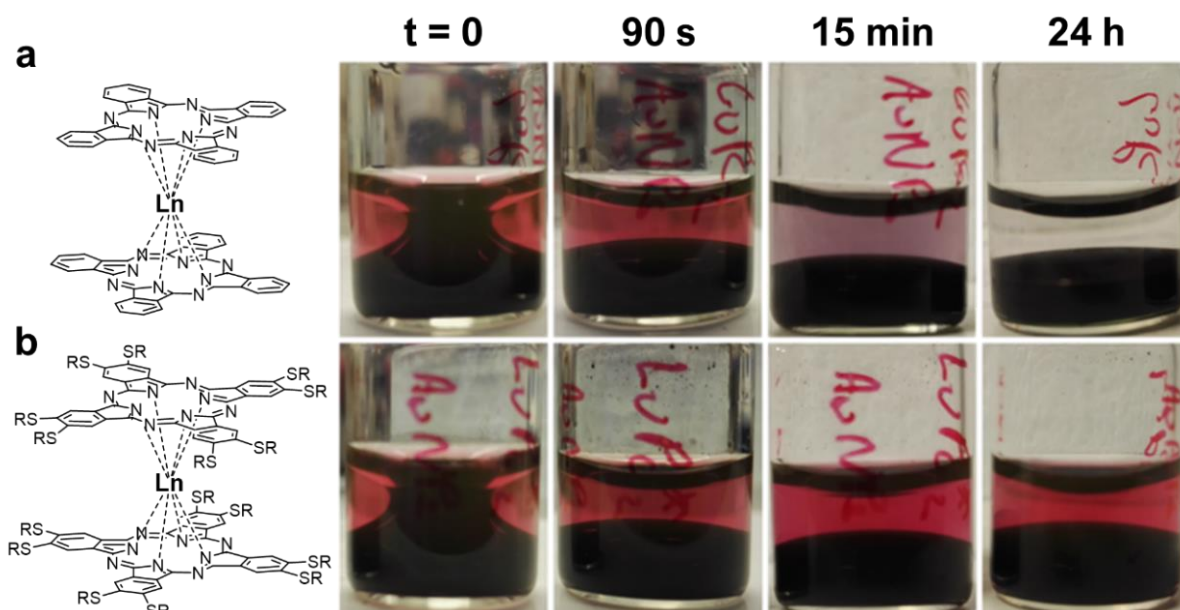


Figure 3.9. Colloidal aqueous AuNPs ($D = 60$ nm; upper liquid phase of each sample) exposed to 1 mM CHCl_3 solutions (dark bottom phase) of (a) LuPc_2 and (b) LuPc^*_2 . LuPc_2 exposure led to AuNP aggregation after 15 min (evidenced by purple colour of AuNP solution) - and sedimentation after 24 h. Exposure to LuPc^*_2 solution had no effect.

Complete aqueous colour loss was observed after 24 h, accompanied by formation of a gold mirror at the liquid-liquid interface. For $D = 80$ nm, no colour change was observed but sedimentation occurred similarly after 24 h, indicating interfacial aggregation with size-limited diffusion into aqueous solution. This is distinct from $\text{CB}[\eta]$ -based AuNP aggregation, in which the AuNP solution rapidly turns a deep blue/violet colour upon mixing, followed by gradual sedimentation. BPC@AuNP aggregation was possible only with fresh nanoparticle solutions, demonstrating the sensitivity of the technique to AuNP surface aging.⁵⁷

LuPc^*_2 did not aggregate AuNPs under these conditions (**Figure 3.9b**), nor did neat CHCl_3 . BPC* likely occupies a larger AuNP surface area than unsubstituted BPC,¹⁹⁴ requiring displacement of more citrate ligands per binding event. Evidently, the BPC-Au adsorption density is sufficient to offset the energy penalty of citrate removal with LnPc_2 , but not for bulkier LnPc^*_2 . This is likely augmented by the greater CHCl_3 solubility of BPC* than BPC, lowering the drive for BPC* to leave the organic phase.

3.4.2 Aggregate Characterisation

Extinction spectra of the aqueous layer were collected over time (**Figure 3.10**) for LnPc_2 @AuNP aggregates ($\text{Ln} = \text{Lu}, \text{Tb}$; $D = 60$ nm). The spectral evolution differed from the DLCA/RLCA behaviour (**Section 1.3.3**) observed with homogeneous $\text{CB}[\eta]$ -mediated aggregation,^{59,62,63} instead exhibiting a gradual increase of both I_{dimer} and I_{chain} , with $I_{\text{chain}} \geq I_{\text{dimer}}$ at all times. λ_{dim} appears around 695 nm (**Figure 3.10a**) which, for $D = 60$ nm, $w = 15$ nm, $n_g = 1.4$ and $n_{\text{water}} = 1.333$, implies $d \approx 1.2$ nm and therefore a BPC multilayer in the gap.

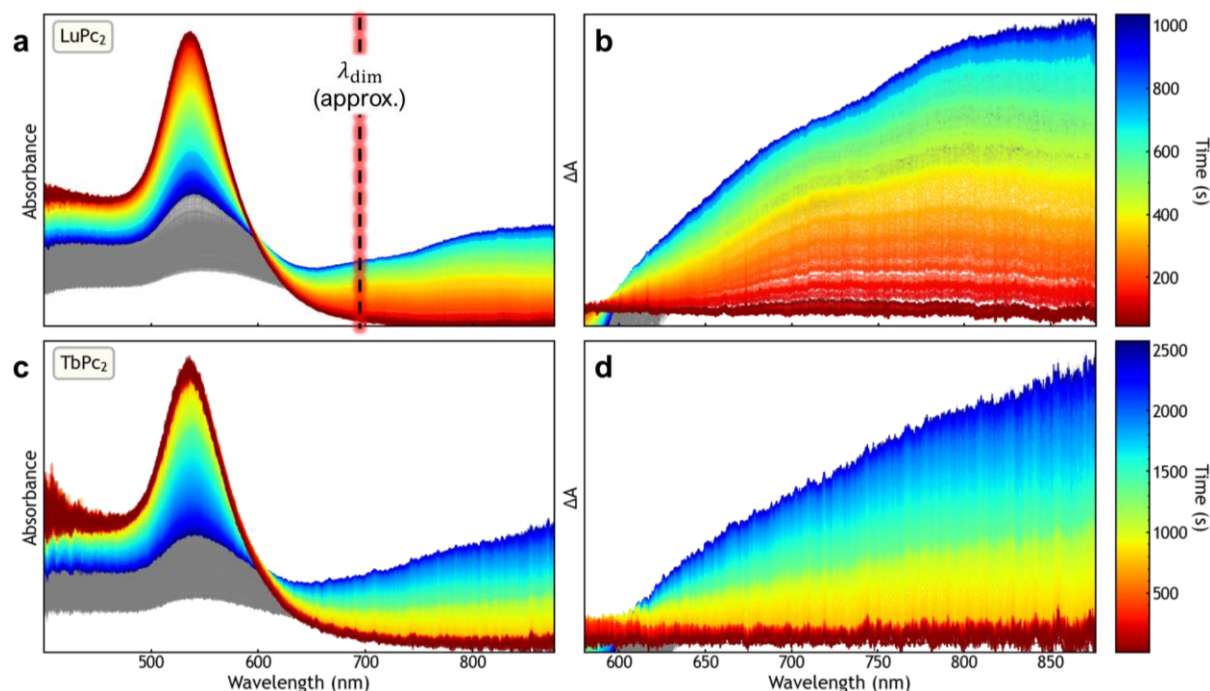


Figure 3.10. Extinction spectra time series for aggregation of AuNPs ($D = 60$ nm) exposed to 1 mM CHCl_3 solutions of (a, b) LuPC₂ and (c, d) TbPC₂. (b, d) are equivalent to (a, c) with the single-particle ($t = 0$) spectrum subtracted.

The multilayer gap and distinct kinetics can be explained by the interfacial nature of the system. The majority of BPC-AuNP binding likely occurs at the organic/aqueous interface, with reversible diffusion of AuNPs and/or aggregates between the interface and aqueous layer, with negligible aqueous BPC concentration. Two possible aggregation mechanisms are proposed: (a) AuNPs diffuse to and from the interface, accompanied by an increase in average BPC@AuNP surface coverage, or (b) AuNP aggregates only grow at the interface, akin to reversible deactivation polymerisation,⁴³¹ with most AuNPs and aggregates “dormant” in aqueous solution.

Mechanism (a) is equivalent to gradual addition of aqueous aggreant, which would yield negligible aggregation until a threshold concentration is passed, after which RLCA kinetics should be observed, with spectral response similar to **Figure 1.14c,d (Section 1.3.3)**. Mechanism (b) should yield plasmonic evolution that reflects the AuNP sticking probability at the interface and interface/solution equilibrium of the aggregates, both of which likely vary as a function of aggregate size. Deviation from RLCA/DLCA behaviour suggests that aggregation occurs more via mechanism (b), although more information is required to confirm this.

Aqueous aliquots were extracted at $t = 30$ min and dried for further analysis. High-angle annular dark field scanning TEM (HAADF-STEM) images of the dried aggregates revealed small, dense clumps and short chains (**Figure 3.11a,b**), similar to the RLCA structures in **Figure 1.14f**.⁵⁹ Pixel grey values were measured across interparticle gaps (**Figure 3.11c**) for several aggregates, revealing smooth, gaussian-shaped profiles (**Figure 3.11d**). The average gap size FWHM is $d = 2.25$ nm ($\therefore n_g \approx 1.6$ for $\lambda_{\text{dim}} = 695$ nm, $D = 60$ nm), and variance is

large. While this variability can be attributed to variable (mis)alignment between the interparticle gaps and the electron beam direction, the average gap size observed clearly indicates multilayers of BPc in the gap. This is in direct contrast with similar TEM measurements of CB[5]@AuNP aggregates,⁵⁹

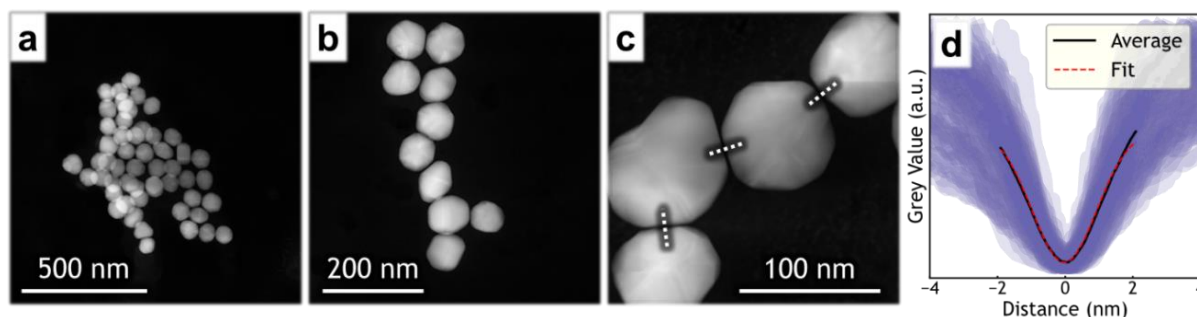


Figure 3.11. (a-c) HAADF-STEM images of LuPc₂@AuNP aggregates ($D = 60$ nm), exhibiting (a) dense clumps or (b) short chains. (c, d) Pixel grey value profiles (white dashed lines in (c)) were measured across interparticle gaps (using ImageJ) over all images to estimate gap spacing, although large variability was observed (purple traces in (d)). Average profile and gaussian fit are shown as black, red traces in (d).

SERS characterisation (**Figure 3.12**) was performed for LuPc₂@AuNP aggregates with $D = 16, 40, 50, 60$ nm, $\lambda_{\text{ex}} = 633, 785$ nm and laser power 10 - 2200 μW . SERS spectra agree well with bulk LuPc₂ Raman (**Figure A8**) and remained stable over time. $\lambda_{\text{ex}} = 633$ nm, $D = 16$ nm gave the highest signal-to-noise ratio (SNR) overall (due to resonance of λ_{dimer} , λ_{agg} and LuPc₂ absorption at 633 nm) and were used for subsequent VOC exposure experiments.

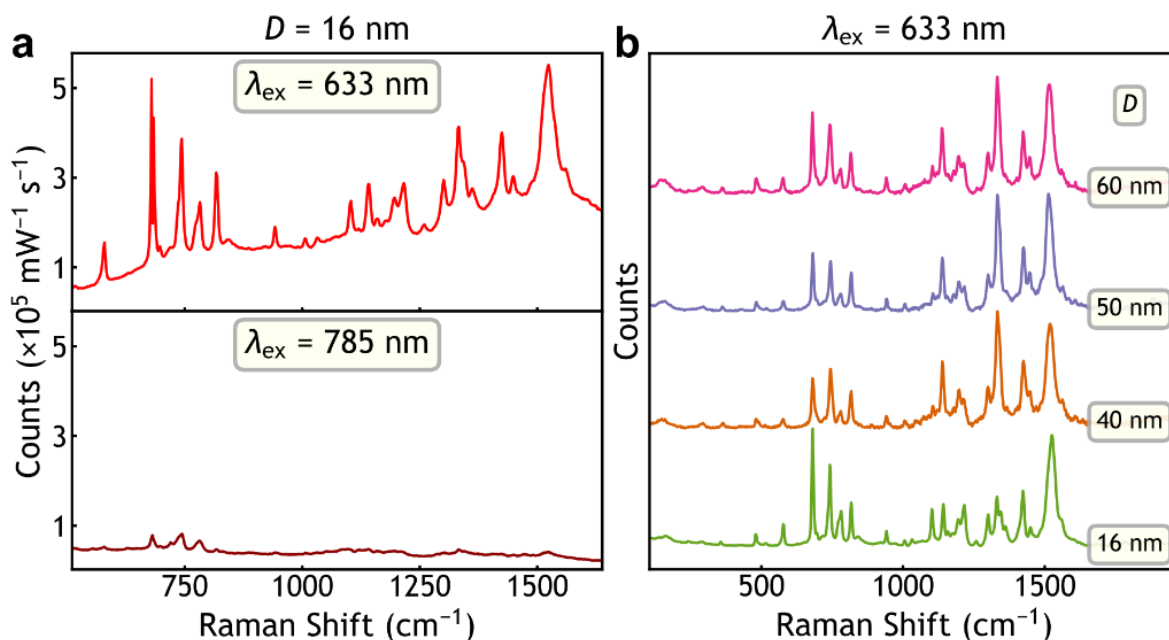


Figure 3.12. SERS spectra of dried LuPc₂@AuNP aggregates. (a) Comparison of $\lambda_{\text{ex}} = 633, 785$ nm for $D = 16$ nm. (b) Comparison of $D = 16, 40, 50, 60$ nm for $\lambda_{\text{ex}} = 633$ nm. The combination of $D = 16$ nm and $\lambda_{\text{ex}} = 633$ nm exhibited the highest SNR and was used for VOC exposure experiments.

3.4.3 SERS + VOC Exposure

The many randomly oriented hotspots in AuNP aggregates delivers isotropic SERS with higher photon yields than NPoM, at the expense of single-molecule sensitivity. Direct deposition onto the glass coverslip also allows shorter working distance and higher collection angles, yielding further signal enhancement. The SERS intensity decreases slightly when imaged through the coverslip (**Figure 3.13a**), but the spectra remain clear and sharp.

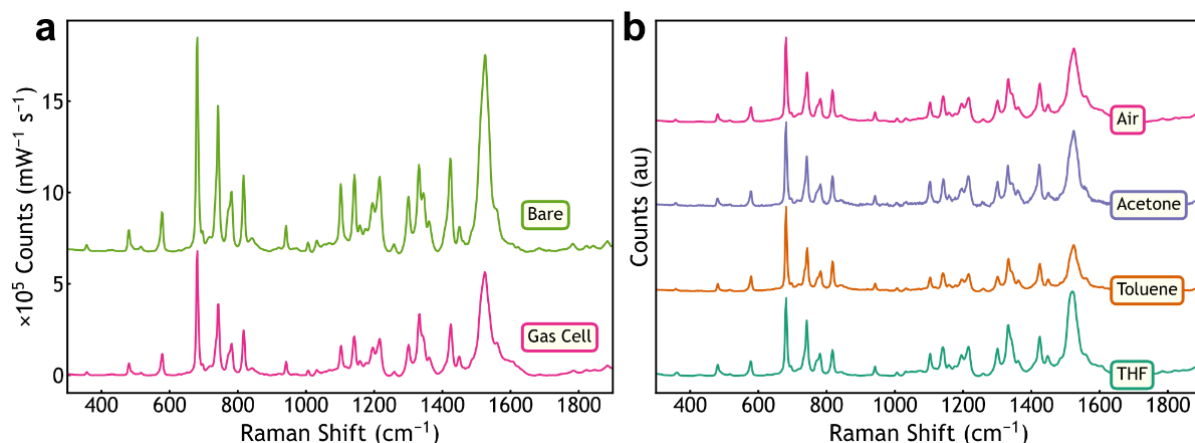


Figure 3.13. SERS spectra of dried LuPc₂@AuNP ($D = 16$ nm) aggregates in various atmospheres. **(a)** Comparison of data collected directly (Bare) and through coverslip (Gas Cell). **(b)** Comparison of LuPc₂@AuNP SERS spectra when exposed to various VOC vapours in the gas cell. Little spectral variation was observed.

LuPc₂@AuNP aggregates were exposed to solvent vapours by allowing 30 μ L of solvent to evaporate inside the sealed gas cell. No SERS change was observed during or after complete evaporation and 15 min equilibration (**Figures 3.13b, A9**) for any of the solvents tested. The combination of properties required for BPc to act as an indirect SERS probe for non-redox VOCs are evidently not present in these BPc@AuNP aggregates.

Solid-state intermolecular interactions play a large role in BPc-based sensors that detect changes in film structure via swelling and redox upon bulk gas absorption.¹⁸¹ The confined BPc@AuNP nanojunction removes this factor and any BPc-analyte interactions are limited to few-molecule adsorption. The dense BPc packing and small nanocavity size are also likely to sterically prevent VOC diffusion into the hotspot, and smaller, redox active gases (NO_x, NH₃, Cl₂, hydrazine etc) may yield better results. However, BPc-analyte interactions often occur via the external Pc π -system faces,²¹⁵ and not Ln as previously thought.²³⁵ Therefore, even with favourable diffusion, SERS gas sensing seems unlikely with BPc@AuNP aggregates.

The system may be improved via optimisation of BPc structure to improve interactions with and diffusion of analytes within the hotspot. Recent improvements to device geometry⁹⁷ and/or applied potential^{256,257} may also allow real-time observation of BPc-analyte interactions. Overall, however, the minimal results led to discontinuation of this project in favour of more chemically accessible systems (**Chapters 4-5**).

3.5 Anomalous NPoM Spectral Shift

Although AuNP aggregation and NPoM SERS gas sensing were not realised with BPC*, reproducible NPoM fabrication was readily achieved. Upon λ_C measurement of >2000 NPoMs over multiple BPC* NPoM samples for each Ln, an anomalously large $\overline{\lambda}_C$ redshift ($\Delta\overline{\lambda}_C$) was observed with decreasing r_{Ln}^{-1} (**Figure 3.14a**). While some redshift is expected, the observed spectral tuning is far stronger than predicted by either the LCR circuit model^{76,102} (**Section 1.3.1**) or finite-difference time domain (FDTD) numerical simulations¹ for the expected $\Delta d = 0.02$ nm (**Section 2.1.4**).

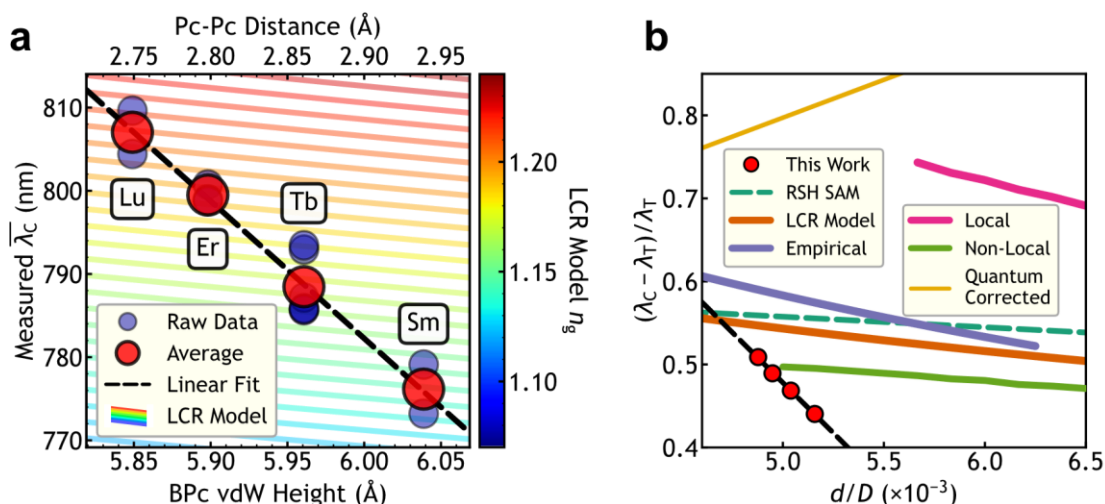


Figure 3.14. (a) $\overline{\lambda}_C$ for LnPc^*_2 ($\text{Ln} = \text{Sm}, \text{Tb}, \text{Er}, \text{Lu}$) NPoMs ($D = 80$ nm) plotted against d_{vdW} (bottom axis) and $d_{\text{Pc-Pc}}$ (top axis); d measured as in **Section 2.1.4**. Blue data points are $\overline{\lambda}_C$ values of separate NPoM samples (each with $\sim 10^2$ - 10^3 NPoM spectra); red points are averages per Ln. Coloured background lines are λ_C vs d traces calculated using the LCR model^{76,102} for a range of n_g (see colourbar) with $D = 80$ nm, $w = 20$ nm, $G = 0$. Experimental $\overline{\lambda}_C$ shift is far larger than expected in all cases. Absolute n_g values are underestimated due to non-classical effects.⁷⁴ (b) Comparison of relative $\overline{\lambda}_C$ shift gradient with literature plasmon ruler data, normalised to AuNP size: alkanethiol SAM on TSG (extrapolated),⁹³ empirical plasmon ruler equation,¹⁶⁵ local/nonlocal analytical models^{74,83} and a quantum-corrected model.¹⁷⁰ Here, $d = (d_{\text{Pc-Pc}} + d_{\text{vdW}})/2$ for illustrative purposes.

Classical electrodynamic simulations are unsuitable for modelling plasmonic response when $d < 1$ nm, leading to singular behaviour as $d \rightarrow 0$ ¹⁶⁶ and requiring non-local and/or quantum corrections for accurate theoretical treatment^{74,170} (**Section 1.4.1**). Comparison with relevant theoretical and experimental literature data is possible via normalisation of $\overline{\lambda}_C$ to λ_T and d to D ,^{156,165} yielding tuning rate $\frac{\partial \lambda_r}{\partial x}$, where $\lambda_r = \frac{\overline{\lambda}_C - \lambda_T}{\lambda_T}$ and $x = \frac{d}{D}$.¹ **Figure 3.14b** illustrates a clear decrease in $-\frac{\partial \lambda_r}{\partial x}$ magnitude when nonlocal corrections are applied (pink/green traces).^{74,83} For $d \lesssim 0.5$ nm, electron tunnelling becomes non-negligible as d approaches the electron spillout length and charge-transfer modes appear as effective G increases, manifesting as a λ_C blueshift and reversal of the sign of $\frac{\partial \lambda_r}{\partial x}$ (yellow trace).¹⁷⁰

The experimental $\frac{\partial \lambda_r}{\partial x}$ observed here is an order of magnitude larger than predicted even by the least “realistic” classical models. This result demonstrates the importance of subtle

physicochemical changes when calibrating $\lambda_C(d)$, particularly for small absolute d . The anomalous $\Delta\overline{\lambda}_C$ is most likely caused by the variation of BPc* electronic structure and/or BPc*-Au interaction with Ln, implying continuous variation of one or more nanocavity properties with $d_{\text{Pc-Pc}} (\propto r_{\text{Ln}})$.

In addition to d , λ_C is affected by n_g and G (**Section 1.3.1; Figure 1.11**), as well as the local electron density of Au.^{52,74,102} The possibility of nonzero G is considered in **Section 3.5.1**, and perturbation of local Au electron density upon BPc* absorption (aka the “pillow effect”^{152,432}) is discussed in **Appendix 8.2.4**. Prediction of n_g (the most likely factor) is more complex for BPc and depends on both molecular packing density and molecular polarisability normal to the substrate (α_{zz}). Due to the strong Pc-Pc orbital overlap and electronic coupling, α_{zz} is easily perturbed by changes in molecular geometry, peripheral functionality, surface binding and oxidation state. These factors are explored in **Sections 3.5.2-3.5.5** using DFT.

These DFT calculations revealed a large systematic shift in the wavelength-dependent $\alpha_{zz}(\lambda)$ curve of [BPc*]⁻ around the λ_C region as Ln is varied, consistent with the magnitude and direction of $\Delta\overline{\lambda}_C$; no systematic shift in $\alpha_{zz}(\lambda)$ was calculated for [BPc*]⁰. Chemical reduction of BPc* is therefore proposed as the explanation for the observed $\Delta\overline{\lambda}_C$, discussed further in **Sections 3.5.6-3.5.7**.

3.5.1 Conductance

Given the various possible tunnelling pathways through unoccupied BPc* molecular orbitals (MOs), molecular conductance is non-trivial to quantify.^{26,433} Qualitatively, for Ln-dependent G variation to cause the observed $\Delta\overline{\lambda}_C$, a positive correlation between d and G is required. Using the analytical LCR model,^{76,102} G was allowed to vary as a polynomial function of d for a range of n_g and L_g . Reproduction of the observed $\frac{\partial\overline{\lambda}_C}{\partial d}$ required unrealistic G and $\partial G/\partial d$, on the order of 10^8 – 10^9 G_0 in all cases. Further modelling of coherent electron transport would require a more thorough quantum mechanical treatment of BPc*-Au interactions²⁷ and is beyond the scope of this work.

While BPcs do exhibit semiconducting behaviour, most studies involve extended molecular wires or thin films and focus on DC conductance via BPc redox and charge hopping. For NPoMs with monolayer-thickness BPc* junctions, the relevant property is ballistic, optical frequency AC conductance. Redox-based BPc* conductance occurs over much longer timescales than the ~femtosecond optical periods involved here, and should therefore have little effect on $\overline{\lambda}_C$. This is consistent with incoherent, hopping-like charge transport previously observed¹⁷⁶ for BPc@AuNP aggregates (Ln = Tb, Lu), which imply little BPc-AuNP covalency and negligible conductivity difference between LuPc₂ and TbPc₂ systems. As such, molecular conductance was not considered further as a cause of the anomalously large $\Delta\overline{\lambda}_C$.

3.5.2 DFT Estimation of d

For many SAMs, understanding of plasmon ruler behaviour has increased the utility of NPoM as a nanometrology device.^{17,83} Because BPc* NPoMs deviate from expected λ_C and I_C/I_T behaviour, $\partial\lambda_C/\partial d$ estimation requires independent measurement of Δd as Ln is varied. Direct measurement of BPc height on Au often requires UHV-based techniques like STM and non-contact AFM, which yield apparent heights of $\sim 0.4 \pm 0.1$ nm but not necessarily the true size of a BPc* NPoM cavity. Additionally, the uncertainty of these techniques precludes measurement of sub-angstrom Δd . Ellipsometry similarly lacks the sensitivity for quantitative thickness measurements of sub-nm monolayers with $\Delta d < 0.1$ nm, and measurement attempts were inconclusive.

DFT offers a complementary toolbox for exploring size and polarisability variations at the molecular scale. While the approximate nature of the technique and wide variety of exchange-correlation functionals can lead to variable accuracy, useful qualitative trends can still be extracted. Initial estimates of Δd were based on preliminary DFT geometry optimisations of unfunctionalised BPc. However, the effects of alkylthio substituents and BPc*-Au covalency on Δd require investigation to ensure the correct distance range is being considered.

Geometry optimizations and polarisability calculations were performed for the oxidised, neutral and reduced states of LnPc_2 , LnPc'_2 and $\text{Ln}(\text{Pc}'\text{Au})_2$ with Ln = Sm, Tb, Er, Lu and Pc' = *octakis*-(methylthio)Pc (**Figure 3.15**); *n*-dodecylthio groups were replaced with methylthio to reduce computational expense. Optimisation of unsubstituted BPc-Au₂ complexes failed to converge, suggesting increased BPc*-AuNP covalency in the *n*-dodecylthio substituted NPoMs. The same functional (B3LYP), basis sets (Def2SVP + Stuttgart) and dispersion corrections (GD3-BJ) were used for all calculations (**Methods 3.7.3**). Pc Z-profiles were extracted to explore the effects of metal centre, oxidation state and functionalisation on Pc-Pc distance and deformation (**Figure 3.16**).

Azimuthal Pc-Pc angles of 45° were observed in all cases, in agreement with crystallographic^{413,423} and theoretical^{215,225} literature data. Unsubstituted BPc exhibits significant outward Pc doming (**Figure 3.16c**), whereas BPc' exhibits increased Ln-Pc bond length, decreased doming of the central π system and a significant downturn of the fused outer benzene rings (**Figure 3.16d**). These geometric effects are further exaggerated by external Pc-Au coordination (**Figure 3.16e**).

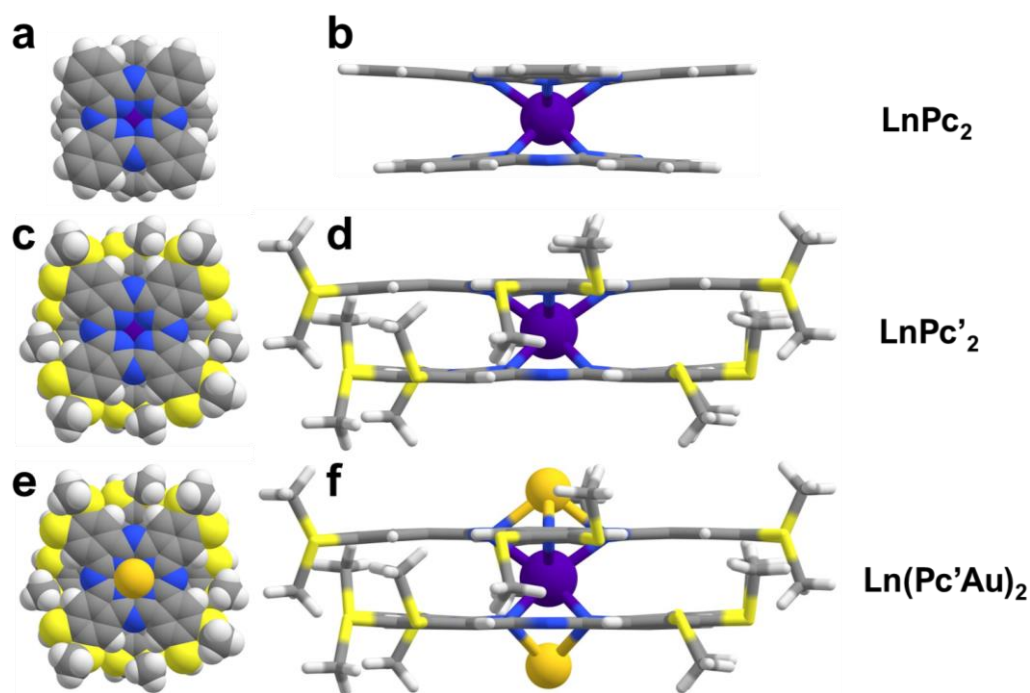


Figure 3.15. Top views (left) and isometric side views (right) of geometry optimised structures of (a, b) ErPc_2 , (c, d) ErPc'_2 and (e, f) $\text{Er}(\text{Pc}'\text{Au})_2$. vdW spheres have been included in (a, c, e) but omitted for clarity in (b, d, f). Pc' denotes Pc ligand octa-peripherally functionalised with SMe groups to emulate the electronic effects of the *n*-dodecylthio groups of BPC*. Atom colours: C (grey), H (white), N (blue), Er (purple), Au (gold).

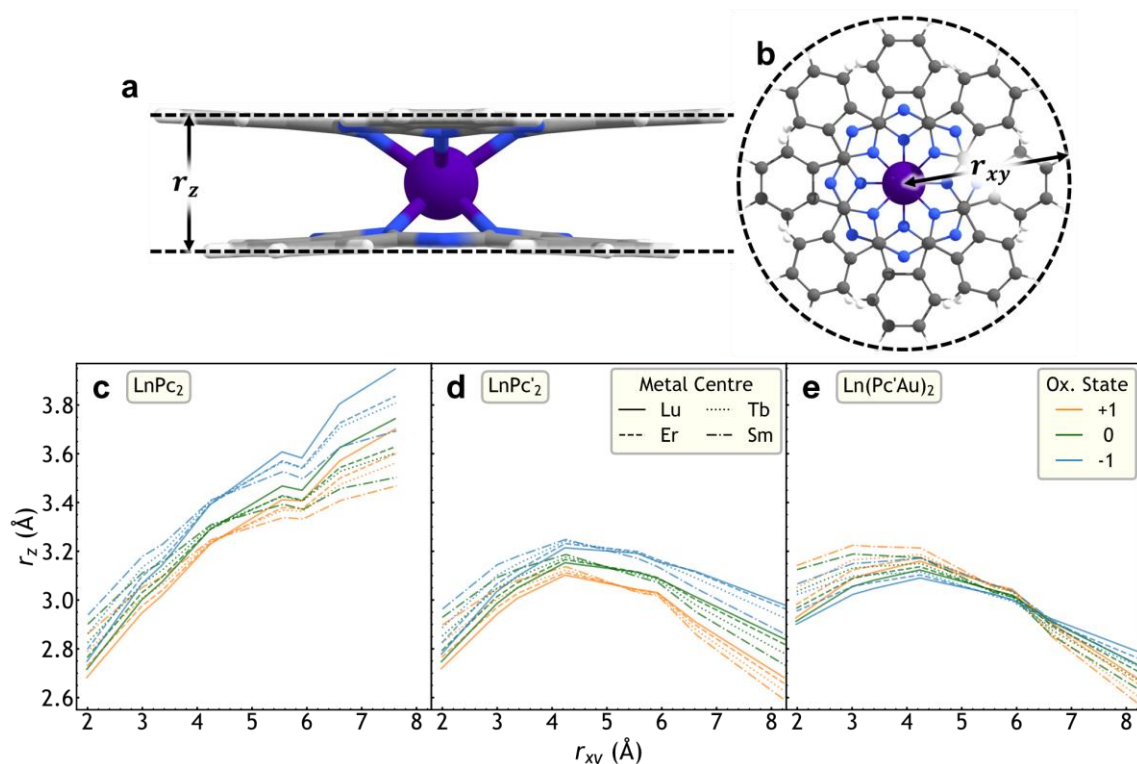


Figure 3.16. Illustration of BPC ligand non-planarity and influence of peripheral functionalisation and Au ligation. (a, b) DFT-optimized ErPc_2 structures (isometric view) displaying measurement metrics used in (c-e). Here, average Pc-Pc distance (r_z) and average lateral distance from central symmetry axis (r_{xy}) are illustrated for the outermost hydrogen atoms. (c-e) Average Pc plane cross sections (stretched in z direction for clarity) for all (c) BPC, (d) BPC' and (e) $\text{Au}_2\text{BPC}'$ structures, based on r_z and r_{xy} of each atomic environment as measured in (a, b).

The Z-profile shapes (**Figure 3.16**) arise from a combination of attractive and repulsive Pc-Pc interactions.²¹⁴ Ln ligation binds the Pc rings together, leading to bonding/antibonding interactions between the two 18-electron π -systems.^{196,214,215,219} Occupied antibonding orbitals cause the Pc rings to dome outward; this deviation from planarity is mitigated somewhat by vdW attraction between the electron-rich outer benzene π -systems. The electronic nature of the Pc-Pc repulsion is illustrated by the increased doming in LuPc_2 - in which r_{Ln} is smallest and π - π coupling is strongest - compared to the more weakly-coupled SmPc_2 .

Peripheral functionalisation with electron-rich SMe groups (**Figure 3.15c,d**) increases the attractive vdW interaction between the Pc extremities. Omitting dispersion corrections from the geometry optimisation drastically increases the doming angle of both BPc and BPc' (**Figure A11**). An increase in Ln-Pc bond length upon addition of electrons, SMe groups or external Au atoms reflects the antibonding nature of the BPc SOMO.^{434,435} The trend is reversed for BPc'Au₂ redox, however, indicating significant perturbation of the BPc' electronic structure by Au in these systems.

This deviation from planarity complicates the estimation of d . Assuming zero compression of Pc rings by AuNP-Au vdW forces (i.e., measurement of the largest Pc-Pc distance, r_z^{max}) yields an increase in d from Sm to Lu for unsubstituted BPc (**Figure 3.16c**). For the BPc' system, r_z^{max} occurs closer to the centre and d increases from Lu to Sm, as expected (**Figure 3.16d**). For BPc'Au₂, the xy position at r_z^{max} varies with metal centre, but d also increases from Lu to Sm in all cases (**Figure 3.16e**).

To investigate the interaction of BPc* with an extended Au surface, geometry optimisations were performed for LuPc_2 and LuPc'_2 on an Au slab (**Figure A12**). The Pc ring in contact with the Au became planar in both cases, demonstrating significant interaction between the molecule and substrate. This Pc flattening is assumed to occur at both Au surfaces of the nanocavity, implying that $d_{\text{Pc-Pc}}$ (**Figure 2.6a**) is a suitable measurement for determining relative Δd between SmPc'_2 and LuPc'_2 .

Absolute d_{gap} values will be larger than $d_{\text{Pc-Pc}}$ and depend on the degree of overlap between the BPc vdW loci and the Au surface. The absence of systematic λ_c spectral splitting (**Figure 3.5**) indicates absence of tunnelling-based charge transfer plasmons to which the antenna mode can couple. Such behaviour was observed at $d = 0.34$ nm for a graphene monolayer NPoM⁷⁷ which implies $d > 0.34$ nm for BPc*, consistent with apparent STM heights of ~ 0.3 - 0.5 nm.¹⁹⁴

Discotic liquid crystals of BPc* (columnar, cofacially stacked molecular wires) exhibit an average Ln-Ln distance of 0.7 nm,²⁰² which roughly agrees with r_z^{max} of BPc' (~ 0.31 nm; **Figure 3.16a**) plus the carbon vdW diameter ($2r_{\text{vdW}}(\text{C}) = 0.34$ nm; $r_z^{\text{max}}(\text{BPc}') + 2r_{\text{vdW}}(\text{C}) = 0.65$ nm). However, such liquid crystals exhibit increased BPc*-BPc* separation due to thermal, “trampoline-like” movement, even at low temperatures. While such vibrations may well occur

in the NPoM cavity, the strong Pc-Au and AuNP-Au vdW interactions are likely to inhibit the geometric effect of this motion.

BPc* NPoM gap sizes therefore lie between $0.4 \leq d < 0.7$ nm. Combining the central pyrrole N distance with the nitrogen vdW diameter yields $0.588 \leq d_{\text{vdW}} \leq 0.606$ ($\Delta d = 0.018$) nm for BPc' and $0.600 \leq d_{\text{vdW}} \leq 0.616$ ($\Delta d = 0.016$) nm for BPc'Au₂. The stable Pc-Au coordination of the BPc'Au₂ structure suggests nonzero BPc*-Au covalency, in which case the above values represent an upper limit for d . While quantum tunnelling is unlikely to be significant, electron nonlocality is clearly important. The pseudo-adatom formation upon BPc*-Au ligation may also perturb the effective value of d and/or contribute to the large SERRS signals reported in **Section 3.3.2**, although the extent of these effects is currently unknown.

3.5.3 DFT Estimation of n_g

Distance-dependent π - π coupling is expected to perturb molecular polarisability (α) and therefore n_g as r_{Ln} is varied. For this to cause the observed $\Delta\bar{\lambda}_C$ would require an increase in n_g with decreasing r_{Ln} . The system's unpredictable I_C/I_T behaviour, deviation from classical theory and small d all preclude spectral measurement of n_g using either ellipsometry or DF NPR spectroscopy.¹⁷ However, the out-of-plane relative permittivity $\varepsilon_{\perp}$ (and therefore n_g) can be approximated from molecular z-polarisability (α_{zz} ; calculated with DFT), monolayer thickness ($\sim d$) and 2D lattice spacing b using a modified Clausius-Mosotti-like relation for a pseudo-2D monolayer:⁴³⁶

$$n_g^2 \approx \varepsilon_{\perp}(\omega) \approx \frac{1 + 2\pi\rho\alpha_{\perp}(\omega)\xi}{1 + 2\pi\rho\alpha_{\perp}(\omega)(\xi - 2\zeta)} \quad (5)$$

where $\alpha_{\perp}(\omega) \approx \alpha_{zz}(\omega)$ is the frequency-dependent out-of-plane molecular polarisability, $\rho = b^{-2}$ is the number of molecules per unit area and $\xi \approx \rho^{1/2}$, $\zeta \approx d^{-1}$ are the average in-plane and out-of-plane linear molecular densities; this treatment is valid for $b \gg d$. Assuming a full monolayer with $b = 3.0$ nm²⁴¹ (**Figure 3.1b** in **Section 3.1.2**), **Equation (5)** allows qualitative comparison of $\partial n_g / \partial r_{\text{Ln}}$ and $\partial \lambda_C / \partial d$ for the three oxidation states of BPc, BPc' and BPc'Au₂.

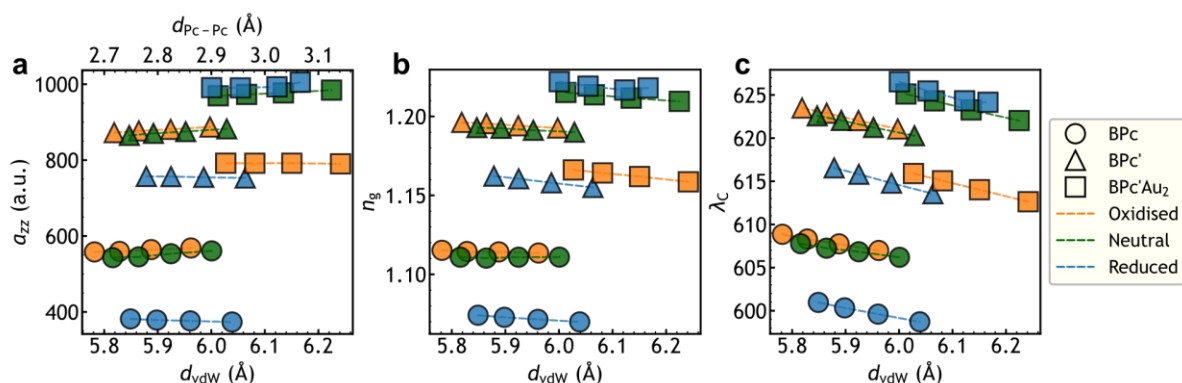


Figure 3.17. Calculated variation of (a) molecular z-polarisability, (b) n_g and (c) λ_C with d_{vdW} for BPc, BPc' and BPc'Au₂. Largest predicted $|\Delta\lambda_C| = 3.26$ nm.

The wavelength-independent α_{zz} varies only slightly from Lu to Sm in all cases (**Figure 3.17a**). The largest calculated $-\partial\alpha_{zz}/\partial r_{Ln}$ shift is $\sim 2\%$, for unsubstituted $[BPc]^-$. However, the $d^{-1/2}$ dependence of **Equation (5)** creates a slight increase in n_g from Sm to Lu for all systems (**Figure 3.17b**). While this does translate to a slightly increased $\Delta\lambda_C$ (using the LCR model¹⁰²) compared to the constant n_g curves in **Figure 3.14a**, the largest predicted $\Delta\lambda_C$ here is 3.3 nm (**Figure 3.17c**), far smaller than the ~ 35 nm shift observed experimentally.

Use of d_{Pc-Pc} instead of d_{vdW} in **Equation (5)** generates far larger shifts in both n_g and λ_C (**Figure A13**). However, small d values imply unphysically large ζ in **Equation (5)**, with singular $\partial n_g/\partial d$ behaviour as $d \rightarrow \Delta d$. This method should therefore be treated with caution and, like the LCR model¹⁰² and I_C/I_T analysis,¹⁷ is less reliable for small d . Unless BPc* NPoM gap sizes truly are in the unphysical range described by d_{Pc-Pc} , changes in static molecular α_{zz} are insufficient to explain the anomalous spectral shift.

3.5.4 Pc-Pc Skew Angle

As with Pc-Pc distance, small changes in Pc-Pc azimuthal angle (θ_{BPc}) can significantly perturb the BPc* electronic structure,^{196,215} which may affect α_{zz} and n_g . Solid-state X-Ray crystallography studies report that, under certain conditions, $\theta_{[BPc]^-}$ decreases with increasing r_{Ln} , such that $\theta_{[LuPc_2]^-} \approx 45^\circ$ and $\theta_{[NdPc_2]^-} \approx 0^\circ$, while $\theta_{[BPc]^0} \approx 45^\circ$ for all Ln.^{437,438} The effect depends on the local environment,⁴³⁸ and gas-phase DFT geometry optimisations (here and elsewhere²¹⁵) predict only $\theta_{BPc} \approx 45^\circ$, regardless of metal centre or oxidation state. However, the Pc-Pc libration rate is known to increase with r_{Ln} .^{194,199} This manifests as a broadening of the Q band in **Figure 3.3** from $LuPc^*_2$ (FWHM = 26 nm) to $SmPc^*_2$ (30 nm), consistent with greater average deviation from $\theta_{BPc} \approx 45^\circ$ in the latter.

BPc*-Au binding may perturb this behaviour. In addition to geometry changes predicted by DFT (**Figures 3.15e-f; A12**), BPc is reduced by Au under certain conditions²²⁹ and exhibits redox-dependent chiral switching or θ_{BPc} changes on various substrates.^{196,197,439,440} While BPc reduction may not occur spontaneously,¹⁷⁶ comparison of SUMO energies (**Figure A14**) suggests greater electron affinity of BPc* compared to BPc, and therefore increased likelihood of BPc* reduction on Au. Surface-bound BPc* may also be reduced by aqueous citrate during AuNP deposition¹³ and/or electron transfer from the photoexcited NPoM.²⁷

The effects of θ_{BPc} on α_{zz} were explored for unsubstituted BPc (Ln = Sm, Tb, Er, Lu). Geometry optimizations and polarisability calculations were performed for $[BPc]^0$ and $[BPc]^-$ over a range of fixed θ_{BPc} (**Figure 3.18**). As expected, all systems exhibit an energy minimum at or near $\theta_{BPc} = 45^\circ$; a local minimum is also observed at $\theta_{BPc} = 0^\circ$ for $ErPc_2$ and $SmPc_2$. The rotational energy barrier (E_{rot}) decreases both upon reduction and as r_{Ln} increases, consistent with literature X-ray studies^{437,438} and the Q-band broadening in **Figure 3.3**. The lowered E_{rot} for reduced $[BPc]^-$ suggests increased reduction probability for $\theta_{BPc} \neq 45^\circ$, as observed by Komeda *et al.*¹⁹⁶

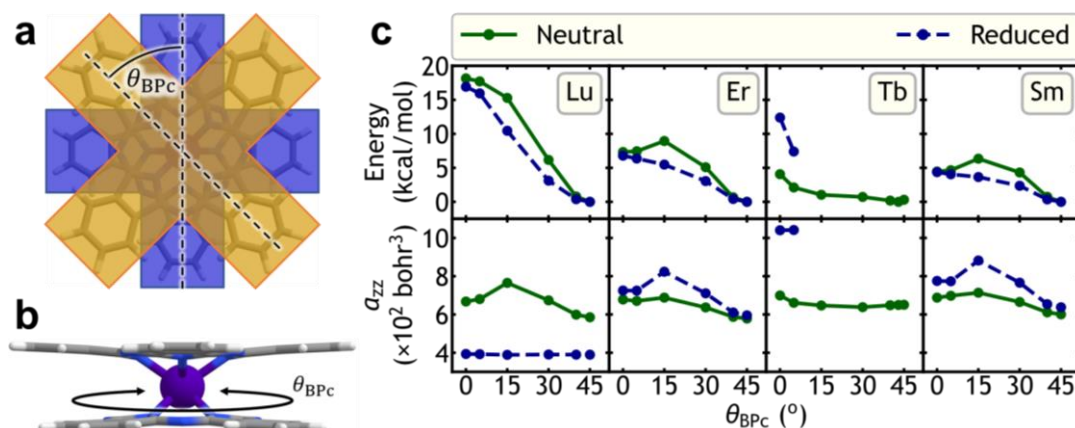


Figure 3.18. (a, b) Schematic of BPc molecule illustrating Pc-Pc skew angle θ_{BPc} . (c) Relative energies and z-polarisabilities calculated for unsubstituted $LnPc_2$ and $[LnPc_2]^-$ at a range of skew angles for $Ln = Lu, Er, Tb, Sm$. Energies are relative to $\theta_{BPc} = 45^\circ$ for each Ln . Calculations were performed by Istvan Szabo (Department of Physics, University College London). Tb dataset is incomplete due to unsuccessful DFT geometry optimisation convergence.

α_{zz} also varies with θ_{BPc} , with absolute and local minima at 45° and 0° and higher α_{zz} at intermediate θ_{BPc} . The change in α_{zz} with Ln is small for $[BPc]^0$, but varies considerably for $[BPc]^-$ with an increase in average α_{zz} observed from Lu to Sm. The significant drop in α_{zz} for diamagnetic $[LuPc_2]^-$ indicates some paramagnetic contribution to α_{zz} in the other systems.

The lowest E_{rot} here is ~ 5 kcal/mol (210 meV), far higher than the available thermal energy at room temperature (25 meV). However, local plasmonic heating is expected to increase the average deviation from $\theta_{BPc} = 45^\circ$, which increases both the likelihood of reduction and average polarisability in most cases. Because of the lower rotational barrier for larger r_{Ln} , this increase in overall polarisability will be strongest for $SmPc_2$, creating a λ_C redshifting effect from Lu to Sm. Therefore, if θ_{BPc} significantly affected λ_C , $\Delta\lambda_C$ would be smaller than the static n_g scenario, again contrary to the result in **Figure 3.14a**.

3.5.5 Wavelength-Dependent n_g

All preceding n_g predictions were based on wavelength-independent α_{zz} . However, the BPc* UV-Vis spectrum indicates a significant wavelength dependence of n_g at optical frequencies. Experimental data for multilayer $TbPc_2$ films^{198,430} indicates $\partial n(\lambda)/\partial \lambda < 0$ when $\lambda > \lambda_Q$. The λ_Q blueshift from Sm to Lu (**Figure 3.3**) implies a similar shift in $n(\lambda)$ (due to Kramers-Kronig relations⁴⁴¹) and therefore a lower n_g for smaller r_{Ln} . This is illustrated and confirmed in **Appendix 8.2.5** and elsewhere¹ by incorporating the experimental $n(\lambda)$ (extrapolated using λ_Q for Lu, Er, Sm) to the into the LCR model (**Equation (2)**). Again, this yields a smaller relative $\Delta\lambda_C$ than the static n_g case, contrary to **Figure 3.14**.

$[BPc^*]^-$, however, exhibits different spectral variation with Ln (**Figure 3.19a**) due to electrochemical activation of Pc-Pc charge transfer states that are dark in the neutral system.^{214,216–218,221} Configuration interaction (CI) between the lowest excitonic and charge transfer states splits the Q band into two strong absorption peaks (with wavelengths $\lambda_{Q1} <$

λ_{Q2}); coupling strength scales inversely with Pc-Pc distance, leading to an increased splitting from Sm to Lu accompanied by a large (~ 28 nm) λ_{Q2} redshift.

Therefore, unlike the neutral system, the $[\text{BPc}^*]^-$ spectra exhibit a strong absorption peak that redshifts from Sm to Lu, with the same direction and magnitude as the experimental $\Delta\lambda_C$. This redshift in absorption may well translate to a $n_g(\lambda)$ shift large enough to explain the magnitude of $\Delta\lambda_C$. While experimental $n(\lambda)$ has not been measured for $[\text{BPc}]^-$, a qualitative comparison can be made using wavelength-dependent $\alpha_{zz}(\lambda)$ (DFT; **Methods 3.7.3**).

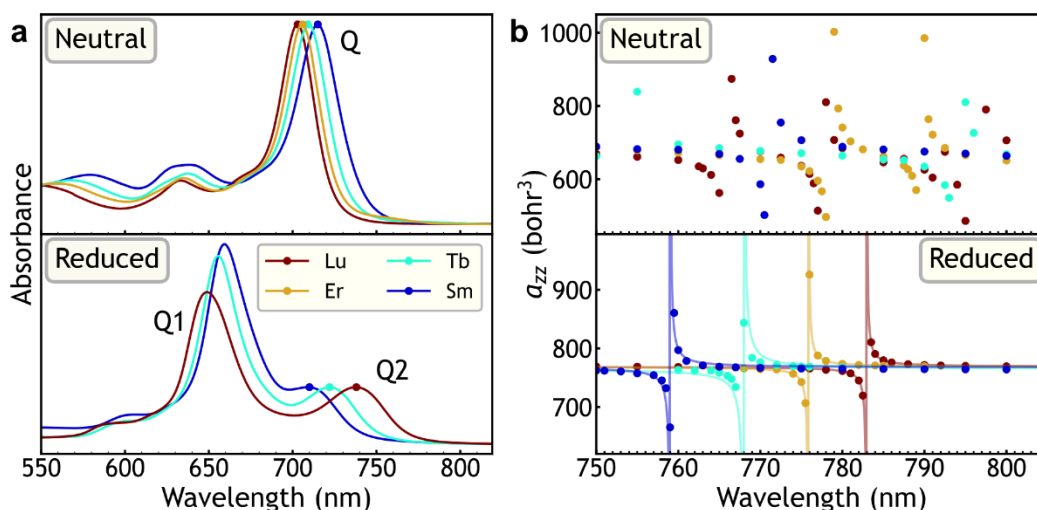


Figure 3.19. (a) UV-Vis absorption spectra (Q band only; normalised) for $[\text{BPc}^*]^\circ$ in CHCl_3 (top) and $[\text{BPc}^*]^-$ in THF (+ NaBH_4) (bottom). (b) $\alpha_{zz}(\lambda)$ calculated for $[\text{BPc}^*]^\circ$ (top) and $[\text{BPc}^*]^-$ (bottom) for $750 \leq \lambda \leq 805$ nm. Solid lines in bottom plot are Breit-Wigner-Fano⁴⁴² fits. Note the difference in x-axis scale between (a) and (b).

Both $\alpha_{zz}(\lambda)$ (**Figure 3.19b**) and the corresponding $n_g(\lambda)$ (estimated via **Equation (5)**; **Figure A16b**) for $[\text{BPc}^*]^-$ exhibit distinct Fano-shaped⁴⁴² peaks that redshift smoothly from SmPc'_2 to LuPc'_2 . Similar peaks in $\alpha_{zz}(\lambda)$ are also visible for $[\text{BPc}^*]^\circ$ (**Figure 3.19b**, top), although the behaviour is more complex and the same systematic shift from Sm to Lu is not observed. Fitting the $[\text{BPc}^*]^-$ data in **Figure A16b** to Breit-Wigner-Fano functions⁴⁴² yields analytical expressions for $n_g(\lambda)$, which can be incorporated into **Equation (2)** as before (**Appendix 8.2.5**). Evaluating the real, positive roots of the resulting quartic expressions for SmPc_2 to LuPc_2 reproduces, for the first time, a smooth λ_C redshift from Sm to Lu in agreement with the experimentally observed $\Delta\lambda_C \approx 30$ nm (**Figure A17**). As before, absolute λ_C values are significantly overestimated by this method and non-classical corrections to the LCR model, together with improvements to **Equation (5)**, would be required for greater absolute accuracy. However, this result represents the first significant predicted increase in $-\partial\lambda_C/\partial d$ observed in this investigation.

3.5.6 New Experimental Data

Repetition of the BPc^* NPoM DF measurements three years later yielded a significantly different result (**Figure 3.20**). The measured $\overline{\lambda}_C$ values of the new datasets were blueshifted

from the original results (**Figure 3.14**) by 10-50 nm and $\Delta\bar{\lambda}_C$ was notably decreased from $\Delta\bar{\lambda}_C(2017) \approx 30$ nm to $\Delta\bar{\lambda}_C(2020) < 10$ nm. Within experimental error, the new result agrees with $\partial\lambda_C/\partial d$ predicted by the LCR model^{76,102} in the explored Δd range, consistent with expected neutral BPc* behaviour (**Sections 3.5.1-3.5.5**).

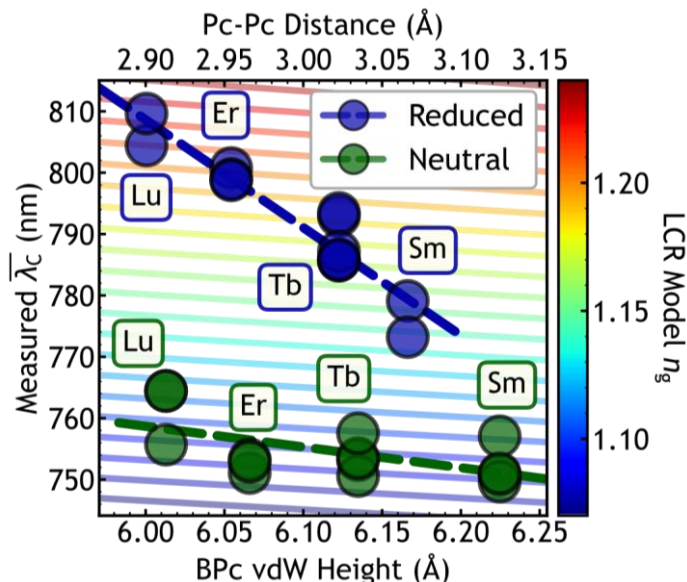


Figure 3.20. BPc* NPoM ($D = 80$ nm) DF $\bar{\lambda}_C$ values measured in 2017 (“reduced”, blue) and again in 2020 (“neutral”, green). Coloured lines are LCR model^{76,102} predictions, as in **Figure 3.14**, with absolute n_g values again underestimated due to nonlocal effects.⁷⁴ As labelled, difference between the two datasets is attributed to the BPc* monolayer oxidation state.

Several reasons for this disparity were considered, including BPc* contamination/degradation, difference in AuNP formulation and changes to the Au substrate. No changes in UV-Vis, FTIR or EA data were observed for BPc* after >3 years’ storage, and degradation was therefore deemed unlikely. The exact AuNP chemical formulation is undisclosed by the supplier,¹³ and the AuNP surface chemistry may have changed. However, as AuNP ligand displacement is expected upon NPoM formation,⁵⁷ the surface chemistry should not significantly affect $\bar{\lambda}_C$. Changes in AuNP shape,¹⁶ facet size⁷⁶ and surface defects^{52,53} may change λ_C , but the effects would be systematic, and evident in the shape of DF spectra or λ_C frequency distributions. Therefore, differences in AuNP formulation were also not considered further.

A key experimental difference observed during NPoM sample preparation indicates that changes to the Au substrate may be responsible. The template-stripping procedure (**Scheme 3.4**) was inconsistently successful in 2017; the lift-off step was often hampered by excessive Au-Si adhesion, indicating contamination of the Au with chromium, which is often used for Si-Au adhesion of other samples using the same apparatus. During preparation of more recent NPoM samples, greater care was taken to avoid Cr contamination, and sample lift-off was consequently easier and more consistently successful.

Cr is a more powerful reducing agent than Au⁴⁴³ and, if present, will increase the likelihood of BPc* SAM reduction.^{193,197,439} Consistent with this, samples prepared in 2017 often required

60-120 s AuNP deposition times. This is longer than normally required for a neutral SAM,^{26,50,51} indicating electrostatic AuNP-substrate repulsion and therefore a negatively charged BPC* layer. In contrast, the more recent NPoM samples required shorter AuNP deposition (15 - 30 s), indicating an uncharged BPC* SAM. As discussed in **Section 3.5.5**, BPC* reduction is likely responsible for the large experimental $\Delta\bar{\lambda}_C$ in **Figure 3.14**, while the more recent NPoM samples evidently contain neutral BPC* spacer layers.

Future experiments may test this hypothesis via DF and SERS analysis combined with recently developed electrochemical techniques.^{97,434} Another method would be to monitor the position of λ_C as capacitive charge is added to the substrate.⁴³⁴ Aberration-corrected DF spectroscopy of many NPoMs may be precluded by sample degradation upon repeated electrochemical cycling; this could be bypassed by large-area spectroscopy of NPoM samples with higher AuNP densities, which would remove single-cavity information but allow more rapid $\bar{\lambda}_C$ measurement. Echem-SERS⁹⁷ would reveal SERS spectra of the different BPC* oxidation states, which could then be correlated with DF position. Both of these techniques should also reveal the currently unknown effect of BPC* SAM oxidation on λ_C .

If the hypothesis is correct, Δn_g can now be estimated for neutral and reduced BPC* NPoMs using the LCR model. Assuming $d_{\text{gap}} \approx d_{\text{vdW}}$ and $\partial G/\partial r_{\text{Ln}} = 0$, n_g varies from $n_g([\text{SmPc}^*_2]) = 1.15$ to $n_g([\text{LuPc}^*_2]) = 1.21$ for reduced $[\text{BPC}^*]$ while remaining almost constant ($n_g \approx 1.1$) for neutral $[\text{BPC}^*]^0$. These values are most likely underestimates due to the semi-classical nature of the LCR model and subsequent overestimation of λ_C for $d < 1$ nm. Inclusion of non-classical effects^{167,444} into **Equation (2)** will therefore be required for more accurate estimates of n_g .

3.5.7 Final Comments on $\Delta\bar{\lambda}_C$

The observation of such a large λ_C shift across a small d range highlights the extreme sensitivity of the NPoM geometry to small variations in BPC* height, via changes in n_g and oxidation state as well as d . Many geometric and physicochemical simplifications used for NPoM systems evidently become less valid in the sub-nanometre regime. While the complex electronic structure of BPC* represents an exceptional case, caution should be exercised when assuming static $\partial n_g/\partial d$ and $n_g(\lambda)$ behaviour for nominally similar molecular spacers, particularly when $d < 1$ nm.

For this result to be useful in plasmon ruler and nanometrology applications, NPR-based analyses¹⁷ should be re-calibrated with non-classical corrections to improve the sub-nm accuracy of the technique. The validity of the Clausius-Mosotti-like relation for estimation of n_g from α_{zz} (**Equation (5)**)⁴³⁶ is questionable for such small SAM thickness, where small Δd leads to a significant change in n_g due to the $d^{-1/2}$ dependence. More accurate NPR d and n_g

measurements would improve the experimental benchmark for refinement of this relationship between molecular polarisability and n_g for SAMs with sub-nm thickness.

Understanding of experimental results is also complicated by increased sensitivity to geometric variation (e.g. AuNP shape, faceting, surface roughness) as d approaches the plasmonic limit.^{76,77} Broad assumptions involving spherical AuNPs^{26,102} and circular facets⁷⁶ are again less valid for the NPoM systems in this work, and greater precision in AuNP synthesis and Au substrate preparation is required for further calibration and understanding of the plasmonic response for $d < 1$ nm.

Nevertheless, the results of this chapter represent another piece of the theoretical puzzle. The sensitivity of λ_C to BPc* oxidation state hints at the possibility of optical devices with low switching powers and $\Delta\lambda(\text{on/off})$ tuneable via Ln centre. The apparent sensitivity of BPc* oxidation state to substrate doping may also facilitate optical assessment of Au contamination in the future.

3.6 BPc Conclusion & Outlook

BPc was chosen as a novel molecular spacer for its accessible redox states, chemical stability and tailorability, gas sensing activity, large optical absorption and Raman cross-sections, together with its ability to form SAMs on Au and introduce metal centres into the plasmonic hotspot. These extra physicochemical degrees of freedom were envisioned to build on the success of existing self-assembled plasmonic nanostructures for improved plasmonic sensing, catalysis and reaction monitoring applications, particularly those involving gas-phase analytes.

The goal was to fabricate BPc-based NPoMs for analysis of light-matter and BPc-analyte interactions at the single-cavity and few-molecule level, and BPc@AuNP aggregates for improved gas sensing applications. Chemical functionality was successfully added to improve BPc solubility and facilitate NPoM fabrication, although the resulting nanostructures were found to be incompatible with available optical gas sensing apparatus. BPc@AuNP aggregates were successfully assembled using unmodified BPcs and exposed to VOCs, but no SERS sensing activity was evidenced.

In the BPc* NPoM systems, an anomalous $\overline{\lambda_C}$ shift was observed that surpassed all theoretical estimations of $-\partial\lambda_C/\partial d$. Several possible origins for this were explored, and the most likely explanation was proposed to be a redox-induced shift in n_g from reduction of the BPc* SAM. Further calibration and control of this system may yield advances in both nanometrology and nanophotonic display applications.

It is clear that the initial assumption of chemical equivalence across the LnPc₂ series was not universally valid. While the hard-sphere model of Ln implies size to be the only difference between the BPc* compounds here, the accompanying variation in Pc-Pc distance has significant implications for the electronic structure, molecular polarisability and resultant $n_g(\lambda)$

of the spacer layer. This result highlights the need for caution when making assumptions about the physical properties of molecular junctions and challenges the validity of bulk quantities at the nanoscale. The knowledge gained in this chapter will become increasingly important for future study of plasmonic nanocavities with molecular spacers containing metal centres.^{97,120}

Closely probing the behaviour of a system near the plasmonic limit naturally reveals gaps in the current understanding of the system. While recent data (**Figure 3.20**) has improved understanding of the previously unexplained anomalous spectral shift,¹ many uncertainties still remain regarding the concept of refractive index and importance of molecule-surface interactions for such thin spacer layers.

Despite these uncertainties, the ease of fabrication of these self-assembled systems, combined with their high environmental sensitivity, demonstrates the potential for future plasmonic applications. While VOC sensing was unsuccessful, the apparent sensitivity of BPc* oxidation state to substrate impurities nevertheless indicates some capacity for environmental sensing and device diagnostics at the few-molecule limit. Conversely, this redox sensitivity may also facilitate few-molecule electrochromic switching with fine control over a moderate wavelength range, in a device geometry compatible with printable plasmonic displays.^{434,435}

Building on this work, several future BPc/BPc* NPoM experiments are recommended. As mentioned in **Section 3.5.6**, the effects of applied electrochemical potential,⁹⁷ capacitive charging⁴³⁴ and through-gap bias²⁵ on λ_C , I_C/I_T and SERS signatures should be explored. Complementary calculations using a nonlocal or quantum-corrected plasmonic dimer response model are also strongly recommended. While the analytical LCR model is quick, convenient and easy to implement, the omission of non-classical effects limits the applicability for understanding the spectral behaviour and effective n_g of sub-nm plasmonic nanocavities. Such experimental and theoretical results would further refine understanding of the nanoscale relationship⁴³⁶ between α_{zz} and n_g for thin molecular layers, particularly if more BPc derivatives and Ln centres are used.

From a molecular electronics and information processing perspective, current-dependent chiral switching^{196,197,199} should also be explored with SERS, via application of bias across the nanocavity.²⁵ The recent developments regarding far-field optical manipulation of BPc 4f magnetic moments^{210–212} is also worth exploring, particularly given the call for improved devices allowing spin-resolved plasmonic incoupling.²¹³

Additional future experiments may benefit from more well-defined Au substrates (e.g. annealed Au with a single, flat crystal plane exposed) and AuNPs with more precise shape, whether ultra-spherical for easier modelling, or of well-defined non-spherical geometry to explore influence of AuNP faceting. Single-nanocavity gas sensing may still be possible, but would require a device geometry suitable for imaging of NPoMs through a coverslip with high collection angle,⁹⁷ and exploration of a greater range of analytes and BPc derivatives. Use of triple-decker Ln_2Pc_3 derivatives may increase chemical accessibility and therefore sensing

activity of the system, although increased gap sizes would decrease the SERS enhancement. Actinide BPcs (UPc₂, ThPc₂) may also exhibit improved analyte interactions, and possibly catalytic activity, via the more diffuse and chemically accessible 5f orbitals.⁴⁴⁵

An alternative route is to use a different molecular spacer system entirely. While BPc* spacers yielded interesting results from a nanophotonics perspective, the original vision of plasmonic sensing and catalysis was not realised experimentally. The sub-nm NPoM cavity, although yielding extraordinarily high SER(R)S signals, likely severely limits the chemical accessibility of the hotspot. Even if this is not the case, the most reactive sites on the BPc molecule are blocked by the Au surfaces.

Chapter 4 therefore explores a completely new molecular spacer system, involving new redox-active molecules with high chemical tuneability, whose orientation and coupling within the gap are controllable via host-guest interactions with CB[n]. **Chapter 5** then combines this functionality with macrocyclic metal-ligating moieties (inspired by BPc) to introduce chemically accessible transition metal centres into the hotspot.

3.7 BPc Methods

3.7.1 Synthesis

See **Chapter 7** for materials and instrumentation.

4,5-bis(*n*-dodecylthio)phthalonitrile

4,5-dichlorophthalonitrile (5.295 g, 26.88 mmol) and 1-dodecanethiol (15.5 mL, 64.7 mmol) were added to stirred anhydrous DMSO (125 mL) and purged with N₂ at 100 °C for 15 min. Finely powdered anhydrous K₂CO₃ (35 g, 250 mmol) was then added in 7g portions every 5 min. The mixture was stirred at 100 °C for a further 30 min, then cooled to room temperature, diluted with deionised water (300 mL) and extracted with CHCl₃ (5 × 100 mL). The combined organic extract was washed with deionised water (3 × 170 mL) and dried over MgSO₄. After solvent removal, the crude product was purified by column chromatography [silica gel; DCM/40-60 petroleum ether (60:40 v/v)] and recrystallized twice from *n*-hexane to yield 4,5-bis(*n*-dodecylthio)phthalonitrile (11.62 g, 81.75%) as fluffy, off-white, plate-like crystals.

¹H-NMR (CDCl₃) δ 0.90 (t, *J* = 7.0 Hz, 6H, CH₃), 1.80-1.25 (m, 40H, CH₂), 3.03 (t, *J* = 7.2 Hz, 4H, S-CH₂), 7.43 (s, 2H, Ph). Anal. Calc.: C, 72.67; H, 9.91; N, 5.30. Found: C, 72.79; H, 9.91; N, 5.35.

Lutetium bis((*op*-*n*-dodecylthio)phthalocyanine) (LuPc*₂)

4,5-bis(*n*-dodecylthio)phthalonitrile (1.38 g, 2.61 mmol), lutetium acetate hydrate (0.137 g, 0.389 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (143 μL, 0.956 mmol) were refluxed together under N₂ in stirred 1-hexanol (30 mL) for 20 h. The green/black solution was

cooled to room temperature, precipitated with MeOH and filtered. The crude product was purified thrice by column chromatography [silica gel; DCM/40-60 petroleum ether (30:70 v/v); second fraction] and recrystallized four times from EtOAc. The product was dried under vacuum, with heating, yielding waxy black/green LuPc^{*}₂ solid (251 mg, 17.5%).

IR $\nu_{\max}$ (cm⁻¹) 2918, 2850 (CH₂), 1592 (Ph), 751 (S-CH₂). Anal. Calc.: C, 69.78; H, 9.52; N, 5.09. Found: C, 69.94; H, 9.43; N, 5.20. MALDI-TOF m/z : 4405.9 (M⁺). NMR characterisation was not performed due to ligand paramagnetism.

Erbium bis((*op*-*n*-dodecylthio)phthalocyanine) (ErPc^{*}₂)

4,5-bis(*n*-dodecylthio)phthalonitrile (2.01 g, 3.80 mmol), erbium acetate hydrate (0.199 g, 0.477 mmol) and DBU (287 μ L, 1.92 mmol) were refluxed under N₂ in stirred 1-hexanol (30 mL) for 16.5 h. The product was purified as above, yielding waxy black/green ErPc^{*}₂ solid (360 mg, 17.2%).

IR $\nu_{\max}$ (cm⁻¹) 2920, 2851 (CH₂), 1591 (Ph), 750 (S-CH₂). Anal. Calc.: C, 69.91; H, 9.53; N, 5.10. Found: C, 69.73; H, 9.46; N, 5.31. MALDI-TOF m/z : 4397.8 (M⁺). NMR characterisation was not performed due to ligand paramagnetism.

Terbium bis((*op*-*n*-dodecylthio)phthalocyanine) (TbPc^{*}₂)

4,5-bis(*n*-dodecylthio)phthalonitrile (1.59 g, 3.01 mmol), terbium acetate hydrate (0.163 g, 0.485 mmol) and DBU (216 μ L, 1.44 mmol) were refluxed under N₂ in stirred 1-hexanol (30 mL) for 5.5 h. More terbium acetate hydrate (0.161 g, 0.479 mmol) and DBU (0.216 mL, 1.44 mmol) were then added and the mixture was refluxed for another 16 h. The product was purified as above, yielding waxy black/green TbPc^{*}₂ solid (524 mg, 31.7%).

IR $\nu_{\max}$ (cm⁻¹) 2919, 2850 (CH₂), 1591 (Ph), 750 (S-CH₂). Anal. Calc.: C, 70.04; H, 9.55; N, 5.09. Found: C, 70.12; H, 9.59; N, 5.13. MALDI-TOF m/z : 4389.9 (M⁺). NMR characterisation was not performed due to ligand paramagnetism.

Samarium bis((*op*-*n*-dodecylthio)phthalocyanine) (SmPc^{*}₂)

4,5-bis(*n*-dodecylthio)phthalonitrile (1.53 g, 2.89 mmol), samarium acetate hydrate (0.116 g, 0.354 mmol) and DBU (217 μ L, 1.45 mmol) were refluxed under N₂ in stirred 1-hexanol (30 mL) for 20 h. The product was purified as above, yielding waxy black/turquoise SmPc^{*}₂ solid (134 mg, 8.46%).

IR $\nu_{\max}$ (cm⁻¹) 2919, 2850 (CH₂), 1591 (Ph), 748 (S-CH₂). Anal. Calc.: C, 70.18; H, 9.57; N, 5.11. Found: C, 70.37; H, 9.65; N, 5.11. MALDI-TOF m/z : 4382.8 (M⁺). NMR characterisation was not performed due to ligand paramagnetism.

3.7.2 Nanostructure Fabrication & Analysis

TSG and NPoM substrates were fabricated as in **Methods 7.1**. Unsubstituted BPc was deposited from toluene (0.5 mM) or CHCl₃ (1 mM) for 10-30 min or 12-24 h. AuNPs (D = 80 nm) were deposited for 30-120 sec. Substituted BPc^{*} was deposited from hexane or heptane

(1 mM) for 15-60 min and AuNPs were deposited for 60-120 sec (2017 experiments) or 15-30 sec (2020 experiments).

BPc@AuNP aggregates were fabricated by exposing aqueous colloidal AuNPs ($D = 16, 40, 50, 60, 80$ nm) to equal volume of unsubstituted BPc/ CHCl_3 solution (1 mM). The two solutions were mixed in a glass vial, allowed to settle and left at room temperature for up to 24 h. Extinction spectra of the aqueous layer were monitored over time using a quartz cuvette (1 cm) (**Methods 7.4.3**).

For TEM measurements (**Methods 7.2**), 2 μL of the aqueous layer was extracted from a ($D = 60$ nm) sample after 15 min, deposited on a TEM grid (3 mm; holey carbon/300 mesh Cu) and allowed to dry. VOC SERS sensing experiments were performed using a custom PTFE gas cell (**Figure 3.7**) with syringe-connected inlets/outlets and exchangeable 2x2 cm glass slide viewing window. For VOC sensing, 20 μL was extracted from the aqueous AuNP layer ($D = 16$ nm) and allowed to dry on a 2x2 cm glass slide, which was inverted and used as the gas cell viewing window. Imaging and SERS measurements (**Methods 7.4.4**) were performed with a 50x objective and 633 nm excitation at a range of powers between 10 - 2200 μW with 0.1 - 10 s exposure time. Samples were exposed to VOCs by adding 30 μL of solvent to a separate glass slide inside the sealed gas cell and allowing it to evaporate. SERS measurements were performed during evaporation and equilibration for up to 1 h after addition of solvent.

3.7.3 Computational Details

Gas-phase DFT calculations were performed using the B3LYP^{446,447} hybrid generalized gradient approximation (GGA) exchange-correlation functional, augmented with Grimme's D3 dispersion correction with Becke-Johnson damping (GD3BJ).⁴⁴⁸ The Def2SVP basis set was employed for all light atoms, plus Au (for which a Def2SVP pseudopotential was used). Stuttgart large-core relativistic effective core potentials (LCRECPs) and corresponding basis sets^{449–452} were used for the Ln atoms. This treatment implicitly includes the 4f electrons within the core due to their chemical inaccessibility. Explicit treatment of these electrons using the small-core RECPs^{453–455} made little difference to the geometry in preliminary calculations and was not used further due to the significantly (~ 40 x) longer computational time. All calculations were implemented by myself (unless otherwise indicated) using an ultrafine integration grid in Gaussian 09 Rev. E.⁴⁵⁶

DFT modelling of LuPc_2 and LuPc'_2 complexes on an Au surface was performed by Istvan Szabo* using the Siesta package⁴⁵⁷ with the PBE generalized gradient approximation⁴⁵⁸ Nuclei and core electrons were approximated with norm-conserving pseudopotentials via the modified scheme of Troullier and Martins.⁴⁵⁹ The numerical pseudo-atomic orbitals (PAOs) were of double- ζ quality, except the 4f, 5d, 6s, and 6p orbitals of Lu, where triple- ζ quality was required. Free LuPc'_2 conformers were preoptimized with Siesta⁴⁵⁷ using a cubic supercell of

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30.0 Å; the LuPc₂ starting structure was taken from the Gaussian geometry optimization. The Au(111) surfaces were modelled as three-layer periodic slabs with 144 Au atoms per layer generated with the ASE Python package.⁴⁶⁰ To represent the density on a fine grid a mesh cutoff of 200 Ry was used. The Brillouin zone sampling was limited to the Gamma point only. No restraints were applied on the Au layers during geometry relaxation.

4. $\text{ArV} \subset \text{CB}[n]$

4.1 $\text{ArV} \subset \text{CB}[n]$ Introduction

This chapter explores the use of multi-component supramolecular spacers in plasmonic nanocavity self-assembly, demonstrating the potential for more advanced hotspot functionality. The supramolecular systems consist of rod-like ArV scaffolds non-covalently encapsulated by $\text{CB}[n]$ at either end, forming monomeric $\text{ArV} \subset \text{CB}[7]_2$ or dimeric $(\text{ArV})_2 \subset \text{CB}[8]_2$ inclusion complexes, depending on the $\text{CB}[n]$ homologue. The two $\text{CB}[n]$ molecules encapsulate the ends of the structure and can bind to various surfaces via the terminal carbonyl-lined portals^{302,305} (**Figure 4.1**). The exposed central part of the ArV scaffold can be expanded to introduce various functional groups into the system, including fluorophores,^{260,261} molecular switches⁴⁶¹ and metal centres.³²⁸ This opens routes to powerful new chemonanophotonic applications if $\text{ArV} \subset \text{CB}[n]$ supramolecular structure can be retained within plasmonic hotspots upon $\text{ArV} \subset \text{CB}[n] @ \text{AuNP}$ self-assembly.

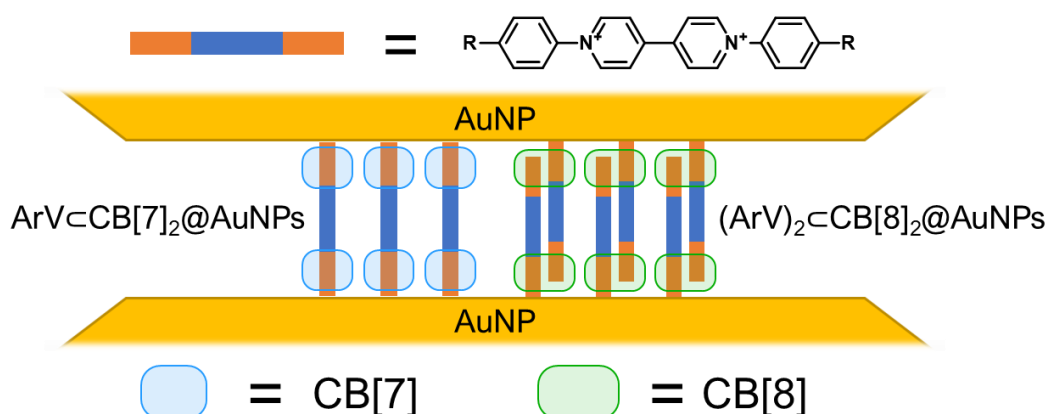


Figure 4.1. Predicted binding geometry of $\text{ArV} \subset \text{CB}[7]_2$ and $(\text{ArV})_2 \subset \text{CB}[8]_2$ complexes within a plasmonic hotspot. $\text{CB}[n]$ aligns the ArV long axis normal to the Au surface, parallel to the plasmonically enhanced optical field. $\text{CB}[7]$ isolates individual ArV molecules and blocks intermolecular interactions, while $\text{CB}[8]$ enforces ArV dimerisation and intracomplex π - π coupling.

The purpose of this chapter is to investigate the possibility of AuNP self-assembly using these complexes and explore the conditions required for retention of $\text{ArV} \subset \text{CB}[n]$ supramolecular structure during the process. Achieving this sets a future precedent for introducing a wider range of chemical functionality into plasmonic hotspots without requiring the typically employed thiol functionalisation. The cationic arylpyridinium groups also impart water solubility, while the $\text{CB}[n]$ tethering group controls molecular alignment, intermolecular coupling, chemical accessibility and molecule-surface interactions in the nanocavity. This creates a toolbox for a range of advanced functional nanophotonic devices with possible applications including molecular switches, sensors, quantum emitters and electron transfer catalysts, the behaviour and properties of which are tuneable via size, shape and functionality of the ArV scaffold.

4.1.1 Objectives & Hypotheses

All ArV and CB[n] molecules had been previously synthesised, and supramolecular assembly behaviour characterised with NMR spectroscopy and isothermal titration calorimetry (ITC).² Aqueous solutions of CB[7], CB[8] and ArV dichlorides were provided by Guanglu Wu^{2,261} and Zehuan Huang,^{275,286} with concentrations pre-calibrated via NMR and/or ITC. Therefore, unlike **Chapters 3 & 5**, no further molecular design or synthesis was required and the objectives began directly with AuNP self-assembly.

The first objective was to optimise NPoM assembly using ArV $\subset$ CB[n] and spectroscopically characterise the plasmonic structures. The effects of terminal ArV functionality upon self-assembly were explored using three different ArV derivatives (**Figure 4.2**).

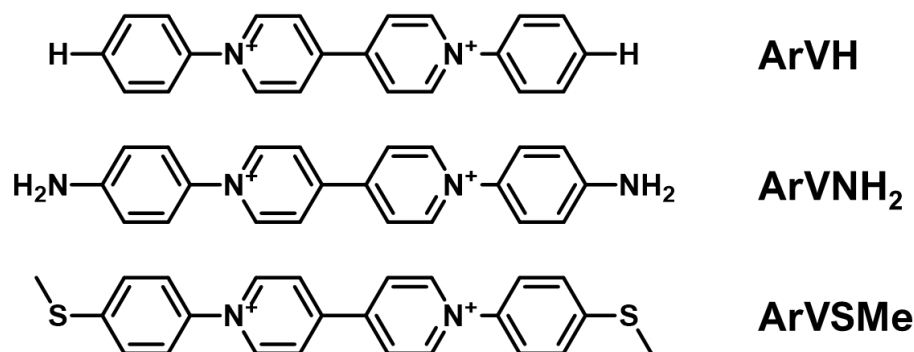


Figure 4.2. Structures of the ArV complexes used in this chapter. ArVNH₂ was quickly found to be incompatible with the Au substrate used here. As such, only results from ArVH and ArVSMMe are reported. All compounds were received as aqueous dichloride salts (anions omitted here for clarity).

Unlike BPCs, ArV $\subset$ CB[n] complexes are water soluble and can be added directly to colloidal AuNPs as aqueous solutions. Consequently, the next objective was to characterise the AuNP aggregation behaviour and hotspot-bound supramolecular structure of ArV $\subset$ CB[n] via extinction spectroscopy (**Section 1.3.3**) and SERS. ArV $\subset$ CB[n] complexes are stable over NMR timescales, with no appreciable concentration of free ArV or CB[n] in solution at the appropriate (1:2 or 2:2) stoichiometry.^{2,260,261,275} However, the reversibility of ArV $\subset$ CB[n] complexation may be problematic during the longer timescales of AuNP assembly, with possible disruption of supramolecular structure within the hotspot at certain ArV $\subset$ CB[n] concentrations. Therefore, AuNP aggregation was performed using a range of ArV $\subset$ CB[n] concentrations for each ArV:CB[n] stoichiometry.

This chapter begins with several hypotheses. ArV $\subset$ CB[7]₂ and ArV₂ $\subset$ CB[8]₂ are predicted to bind Au surfaces via the CB[n] carbonyl portals and self-assemble under typical SAM deposition conditions with retention of supramolecular structure. The complexes may or may not retain their structure during rinsing/drying and AuNP deposition; the presence of positively charged ArV should be evidenced by shorter required AuNP deposition times due to AuNP-SAM electrostatic attraction. As $d \geq 0.9$ nm is generally expected, success of self-assembly may be determined using NPR spectroscopy via $\overline{\lambda}_C$ and I_C/I_T measurement. NPoM SERS spectra, if stable, may reveal ArV $\subset$ CB[n] stoichiometry and orientation in the hotspot.

As the complexes are water soluble, aqueous AuNP aggregation will be easier than with BPc and should exhibit concentration-dependent RLCA/DLCA behaviour.^{59,107,109} Retention of ArV₂CB[n] structure upon AuNP aggregation is expected at certain concentrations, identifiable by λ_{dim} position and relative SERS intensities.

4.2 NPoM: DF NPR Characterisation

NPoMs were prepared (**Methods 4.7.1**) using ArVH, ArVNH₂, ArVSMe, CB[7] and CB[8], plus ArV₂CB[7]₂ and ArV₂CB[8]₂ complexes for each ArV. In water, each ArV (~2 mM) was mixed with sufficient CB[7] (1.0 mM) or CB[8] (0.1 mM) solution to yield ArV₂CB[7]₂ or ArV₂CB[8]₂ stoichiometry without further dilution. SAMs were initially deposited for 4-6 h, based on existing procedures for CB[7].^{17,462} For ArV₂CB[n] samples, AuNP deposition times of ~15 s were required for reasonable coverage, compared to 15-20 s for CB[n] alone, and 5-10 s for uncomplexed ArVSMe. NPR analysis revealed broad λ_{C} and $I_{\text{C}}/I_{\text{T}}$ distributions for all ArV₂CB[n] NPoMs (**Figures A18-A19**). λ_{C} deviated somewhat from the uncomplexed CB[7] data, indicative of some ArV inclusion, but significant $I_{\text{C}}/I_{\text{T}}$ variability precluded reliable estimation of d and n_{g} , and ArV₂CB[n] structural retention was not confirmed.

Repeating the experiments with 24 h deposition times yielded sharper λ_{C} and $I_{\text{C}}/I_{\text{T}}$ distributions (FWHM 30-40 nm; **Figure A19**), with reasonable d and n_{g} values that match those expected for ArVH₂CB[n] and ArVSMe₂CB[n] systems (**Figure 4.3**), in some cases. Only 5-10 s AuNP deposition times were required, indicating positively charged, ArV-containing SAMs. ArVNH₂ samples still exhibited broad, variable λ_{C} and $I_{\text{C}}/I_{\text{T}}$ distributions, with increased Au surface damage evident for longer SAM depositions (**Figure A20**); ArVNH₂ systems were therefore not investigated further.

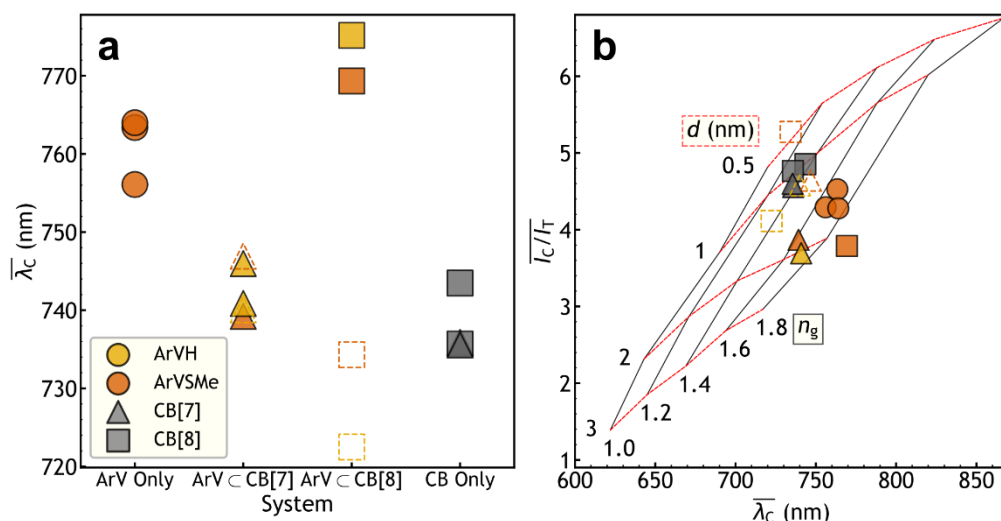


Figure 4.3. (a) λ_{C} values for various ArV and CB[n] combinations. (b) $I_{\text{C}}/I_{\text{T}}$ vs λ_{C} for the same systems. Slanted background grid indicates theoretical values¹⁷ for a range of d (red dashed lines) and n_{g} (grey solid lines). Markers with solid/broken edges suggest retention/loss of ArV₂CB[n] supramolecular structure. Data points present in (a) but not (b) are λ_{C} from experiments with misaligned optical collection, for which λ_{C} remains reliable, but $I_{\text{C}}/I_{\text{T}}$ data does not.

ArV₂CB[8]₂ NPoMs exhibited $\overline{\lambda}_C$ values distinct from ArVSMes or CB[8] alone, while $\overline{\lambda}_C$ of ArV₂CB[7]₂ samples did not vary significantly from the CB[7] case (**Figure 4.3a**). However, NPR analysis of $\overline{I}_C/\overline{I}_T$ vs $\overline{\lambda}_C$ data (**Figure 4.3b**) indicates distinct n_g and d for ArV₂CB[7]₂, despite this $\overline{\lambda}_C$ similarity. The d (0.9-1 nm) and n_g (1.3-1.4) values predicted for CB[7] and CB[8] approximately agree with CB[7] literature data.¹⁷ Deviation from the expected $d = 0.9$ nm may be due to impurities within CB[n], as well as the high sensitivity of NPR analysis to small differences in nanostructure geometry and optical alignment (**Section 1.3.2**).

The thioether groups of ArVSMes evidently facilitate Au binding and SAM assembly, based on the uniform λ_C distributions (**Figure A21**), with $d \approx 1.7$ nm and $n_g \approx 1.7$. This implies a molecular tilt of $\phi = \cos^{-1}\left(\frac{(d-r_{SAu})}{l}\right) \approx 38^\circ$ from normal (**Figure 4.4**) for molecule length $l = 1.9$ nm and S-Au bond length $r_{SAu} = 0.23$ nm (**Figure A22**). Approximating out-of-plane polarisability as $\alpha_\perp \approx \alpha_{zz} \cos \phi + \frac{1}{2}(\alpha_{xx} + \alpha_{yy}) \sin(\phi)$, where z is the ArVSMes long axis, **Equation (5)** (**Section 3.5.3**) yields $n_g \approx 1.66$ for this tilt angle, assuming an insulating, close-packed monolayer of rod-like molecules freely rotating about the long molecular axis, and negligible contribution of non-diagonal α tensor components ($\alpha_{i \neq j}$).

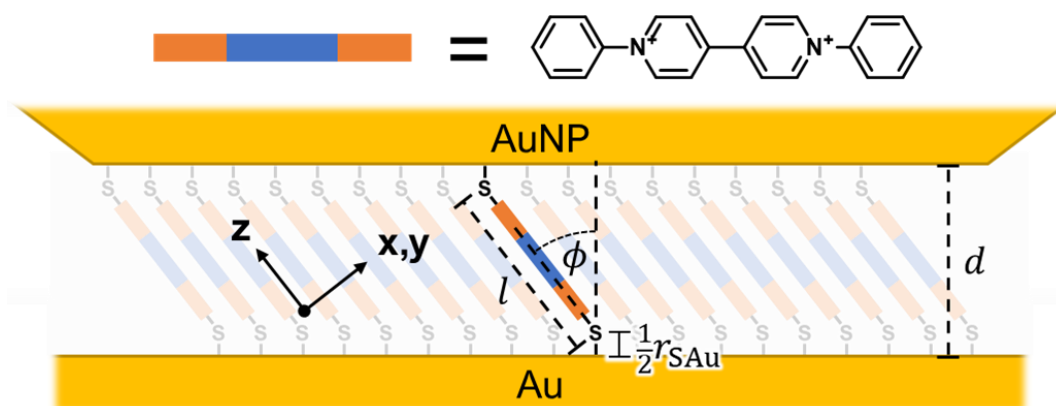


Figure 4.4. Proposed binding geometry of close-packed ArVSMes in NPoM cavity with $\phi = 38^\circ$.

In some cases (**Figure 4.3**, solid markers), ArV₂CB[n] complexes yielded $d \approx 2$ nm, consistent with a CB[n] bilayer and $1.6 < n_g < 1.8$, implying vertically oriented ArV ($\alpha_\perp$ increases due to higher α_{zz} contribution) with lower ArVSMes density (n_g decreases due to smaller ξ ; **Equation (5)**) than the ArVSMes-only SAM. ArV₂CB[8]₂ is predicted to exhibit higher n_g than ArV₂CB[7]₂ due to electronic coupling within the ArV dimer, which redshifts the optical absorption spectrum - and therefore $n_g(\lambda)$ - relative to the monomer.^{2,260,261}

For SAMs that were rinsed excessively, d and n_g deviated significantly from the expected values (**Figure 4.3**, broken-edge markers), implying dissociation of the surface-bound ArV₂CB[n] complexes upon prolonged contact with fresh water. For dissociated ArV₂CB[7]₂ samples, the data (**Figure 4.3b**) indicates retention of CB[7] on the sample surface and removal of ArV. The dissociated ArV₂CB[8]₂ data was less predictable, and more data is required to understand this behaviour.

Therefore, while evidence exists for retention of ArV $\subset$ CB[n] structure within NPoM cavities in certain cases, further optimisation of the fabrication procedure is required for controlled, reliable assembly. Future experiments should include NPoM PL measurements (*cf.* **Section 5.8.3**), which would evidence hotspot-bound ArV $\subset$ CB[8]₂ via redshifted emission of the coupled ArV dimers. SERS measurements were attempted for initial NPoMs with 3-6 h SAM deposition times, but instrumental difficulties led to inconclusive results. Future NPoM DF characterisation should be complemented with more comprehensive SERS measurements.

4.3 AuNP Aggregates: Extinction Spectroscopy

NMR analysis of the ArV $\subset$ CB[n] systems used here indicates ArV $\subset$ CB[n] lifetimes of $\gg 3$ ms and negligible aqueous concentration of free ArV or CB[n].² Retention of ArV $\subset$ CB[n] structure was therefore predicted to be more likely in AuNP aggregates than in NPoM cavities. ArV and CB[n] were combined (*cf.* **Section 4.2**) to yield aqueous ArV $\subset$ CB[n]. AuNP aggregation ($D = 60$ nm) was performed (**Methods 4.7.3**) for several dilutions of each ArV, CB[n] and ArV $\subset$ CB[n] system to explore the effects of aggregant concentration upon plasmonic evolution and supramolecular structure within the nanocavities.

Extinction spectra were recorded at 0.5-1 s intervals (**Methods 7.4.3**) and analysed as in **Section 1.3.3 (Figure 4.5a,b)**. Based on the evolution of λ_{agg} and its integrated sum (**Figure 4.5e-g**), nearly all systems exhibited DLCA aggregation kinetics.⁵⁹ As the goal of this section is to explore ArV $\subset$ CB[n] hotspot orientation via λ_{dim} at short aggregation times, the measurement timescales here are 10-100 $\times$ shorter than previous reports,⁵⁹ the AuNP/spacer concentration ratios are far higher, and RLCA behaviour was not explored.

To avoid over-reliance on approximate bi-Lorentzian fits, λ_{dim} was estimated for each sample via the spectral maximum (after subtracting the single AuNP contribution) of the earliest possible extinction spectrum (**Figure 4.5c,d**). While λ_{dim} is affected by d and n_g similarly to λ_c , the behaviour may deviate somewhat due to lower spacer packing density and higher n_m (=1.33 for water). The AuNP/aggregant ratios here ($1:10^5 - 10^7$) imply $>100\%$ surface coverage. However, as only extremely sparse coverage is required to induce AuNP aggregation,⁵⁹ AuNPs are likely to aggregate before all citrate ligands are displaced and $<100\%$ surface coverage is expected in the cavity. Consequently, the relative influence of molecular polarisability (α) on n_g and λ_{dim} is expected to be lower than for analogous full-monolayer NPoM systems.

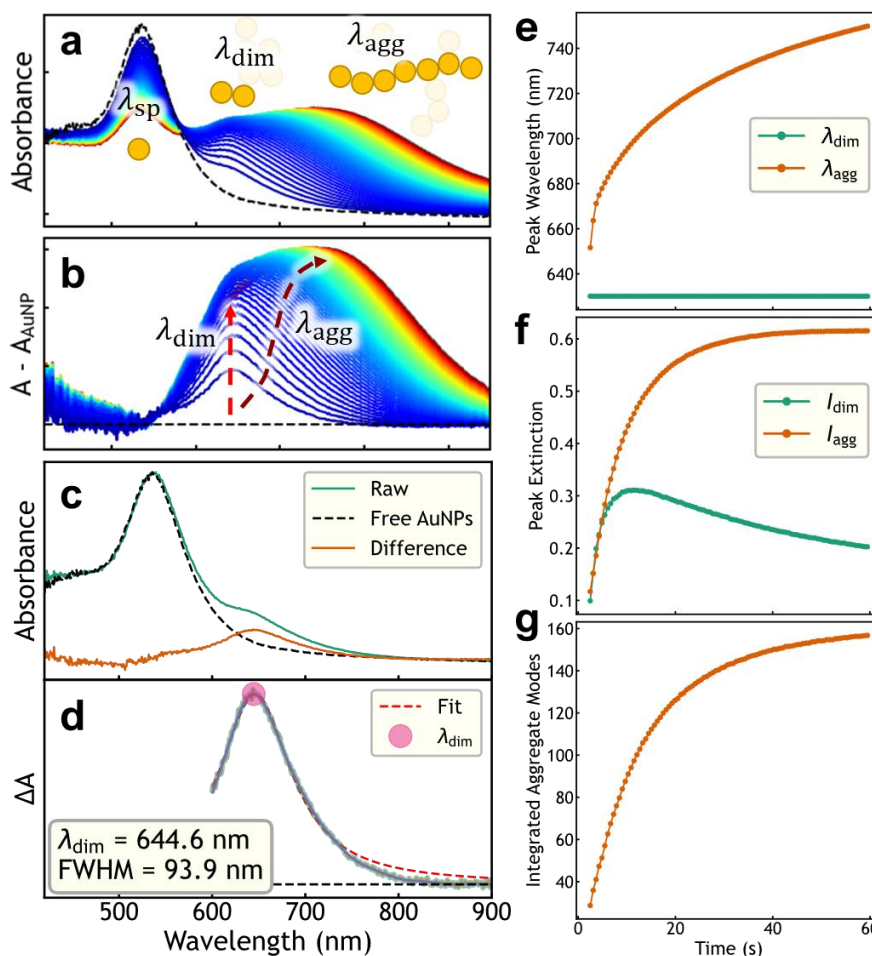


Figure 4.5. Typical plasmonic evolution of AuNP ($D = 60$ nm) aggregation, illustrated here with ArVSMcCB[7]₂ spacer (4×10^{-4} μ M; AuNP/spacer ratio 1:10⁷). **(a)** Time resolved extinction spectra of aggregating AuNPs measured at 0.5 s intervals. Inset schematics illustrate the AuNP arrangements responsible for λ_{sp} , λ_{dim} and λ_{agg} . Monomeric AuNP ($t = 0$) spectrum shown as dashed black trace. **(b)** Difference spectra obtained from **(a)** by subtracting monomeric AuNP contribution. Progression of λ_{dim} and λ_{agg} modes (obtained by fitting each spectrum to a pair of Lorentzian functions) illustrated with bright and dark red dashed arrows. **(c, d)** Illustration of λ_{dim} measurement using earliest possible spectrum exhibiting a dimer resonance. **(e, f)** Results of bi-Lorentzian fits: **(e)** Variation of λ_{agg} over time, exhibiting a smooth redshift from fixed λ_{dim} . **(f)** Variation of λ_{dim} and λ_{agg} intensities (I_{dim} , I_{agg}) over the same period; I_{agg} steadily increases while I_{dim} quickly plateaus. **(g)** Integrated sum of spectra in **(b)** ($525 < \lambda < 900$ nm) over time, exhibiting DLCA kinetics.⁵⁹

4.3.1 Hypothesised Spectral Behaviour

As in **Section 4.2**, expected differences in Au binding between ArVSMc and ArVH should yield distinct differences in d and therefore λ_{dim} . ArVSMc is more likely to stand upright on an Au surface (due to S-Au coordination), with d dependent on bond angle; ArVH-Au binding should be less well-defined without discrete binding groups, most likely adsorbing laterally to the AuNP surface via π -Au interactions, yielding variable d values that are nonetheless smaller than for ArVSMc. This should yield a redshifted λ_{dim} and less well-defined spectral shape for AuNPs aggregated with ArVH only (ArVH@AuNPs) compared to those aggregated with ArVSMc (ArVSMc@AuNPs). Additionally, the higher Au affinity expected of ArVSMc should cause higher aggregation rates than ArVH and a lower aggregation threshold concentration.

If ArV⊂CB[n] structure is retained upon assembly, this should yield larger d than for CB[n] alone and therefore a blueshifted λ_{dim} . The positive charge of the ArV-containing systems should also increase aggregation rate and lower the aggregation threshold concentration relative to CB[n], due to increased charge screening and colloidal destabilisation. If molecular packing density (and therefore n_g perturbation) is small, λ_{dim} of CB[n]@AuNP aggregates is expected to lie between $\lambda_{\text{dim}}(\text{ArVSMe})$ and $\lambda_{\text{dim}}(\text{ArVH})$. Conversely, $\lambda_{\text{dim}}(\text{CB}[n]) < \lambda_{\text{dim}}(\text{ArVSMe})$ would therefore indicate significant molecular packing and n_g perturbation.

4.3.2 Results

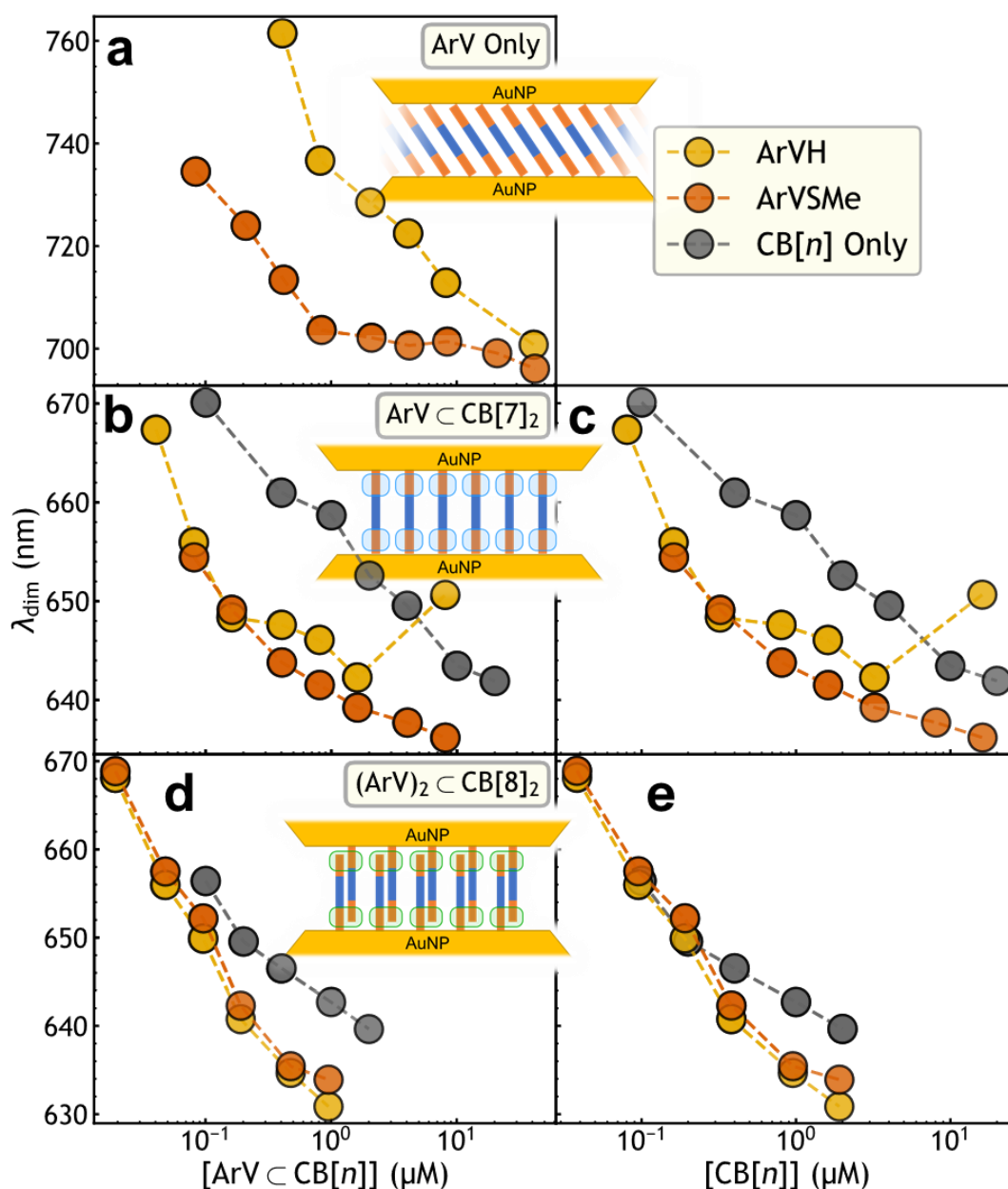


Figure 4.6. λ_{dim} vs aggreant concentration for the various ArV, CB[n] and ArV⊂CB[n] AuNP aggregate systems (insets illustrate interparticle gap contents; not to scale; structures are as labelled in **Figure 4.1**). (a) ArVSMe and ArVH systems without CB[n]. (b, c) ArV⊂CB[7]₂ systems, with CB[7]@AuNP data included for comparison. (d, e) ArV₂⊂CB[8]₂ systems, plus CB[8] data. Data in (c, e) is identical to (b, d) but plotted against absolute CB[n] concentration rather than expected ArV⊂CB[n] concentration.

The λ_{dim} vs aggregate concentration data summarised in **Figure 4.6** supports some, but not all, of the hypotheses in **Section 4.3.1**. Immediately apparent is a significant and unexpected λ_{dim} redshift as aggregate concentration decreases, observed for all systems; possible reasons for this are discussed in **Section 4.4**. First, however, the hypotheses are discussed, and systematic differences between λ_{dim} of the various systems are analysed, to investigate supramolecular structure and orientation within the hotspots.

As predicted, λ_{dim} of ArVH@AuNPs is systematically redshifted from that of ArVSMe (Figures 4.6a; 4.7); this redshift is not uniform, however, and increases as aggregate concentration drops. This non-uniformity may be caused by differences in ArV-Au affinity and/or displacement of citrate ligands (**Section 4.4**). Assuming $d = 1.7$ nm for ArVSMe (**Section 4.2**) and $d = 0.34$ - 0.65 nm for ArVH (based on lateral adsorption with various possible conformations), a minimum systematic λ_{dim} difference of ~ 80 nm is expected between the two systems (via the LCR model;¹⁰² $D = 60$ nm, $n_g = n_m = 1.333$). The smaller experimental difference (~ 45 nm on average) indicates that perturbation of n_g by molecular polarizability (α) is still significant. ArVSMe is most polarisable along its long axis which, assuming ArVSMe stands $\sim$ upright within the gap, may yield higher n_g than ArVH. However, a smaller cavity means that nonlocal effects may also affect λ_{dim} for ArVH@AuNPs; the relative contribution of this requires further investigation.

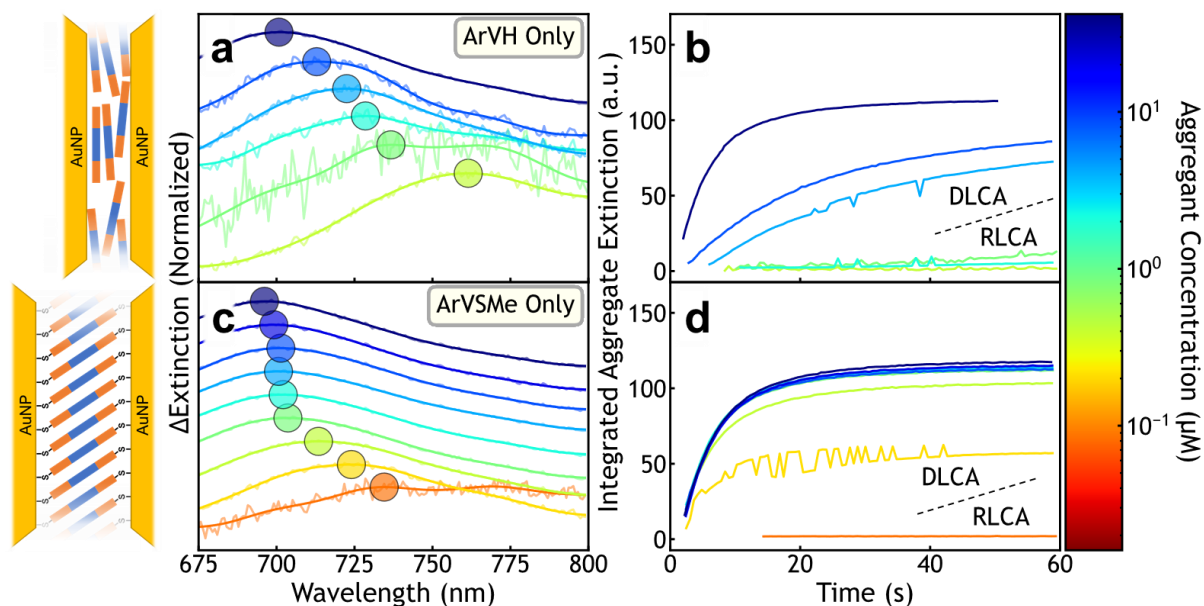


Figure 4.7. (a, c) Initial dimer peaks for ArVSMe@AuNP and ArVH@AuNP aggregates, with λ_{dim} positions highlighted. (b, d) Temporal evolution of integrated spectral sum ($525 < \lambda < 900$ nm as in **Figure 4.5g**). Schematics on left-hand side illustrate hypothesised arrangement of molecular spacers within the hotspots.

Analysis of the individual dimer peaks (**Figure 4.7a,c**) reveals better-defined extinction spectra for ArVSMe@AuNPs than ArVH@AuNPs, with a much lower aggregation threshold concentration, as hypothesised. Irregular peak shapes indicate variable gap geometry in ArVH@AuNPs, while smooth, Lorentzian-shaped peaks for ArVSMe@AuNPs imply more

uniform hotspots. ArVSM exhibits DLCA kinetics (characterised by a sharp initial increase in spectral integration⁵⁹) in most cases except for the lowest concentration tested (**Figure 4.7d**). ArVH causes RLCA-like behaviour at higher concentrations than ArVSM (**Figure 4.7b**), indicating lower AuNP aggregation ability, concurrent with lower Au affinity.

CB[7]@AuNPs (**Figures 4.6b,c; 4.8a**) exhibit a blue-shifted λ_{dim} compared to either CB-free ArV@AuNPs system (**Figures 4.6a; 4.7**). While a blueshift from ArVH@AuNPs ($0.34 < d < 0.65$ nm) is qualitatively expected based on d alone ($d_{CB} = 0.9$ nm), the significant blueshift (50-60 nm) from ArVSM@AuNPs ($d \approx 1.7$ nm) implies a large n_g difference between the CB[7] and ArVSM systems (LCR model calculates $\Delta\lambda_{dim} = 50$ nm for $n_g(CB[7]) = 1.3$, $n_g(ArVSM) = 1.7$) and therefore non-negligible surface coverage in the hotspot at these aggregant concentrations.

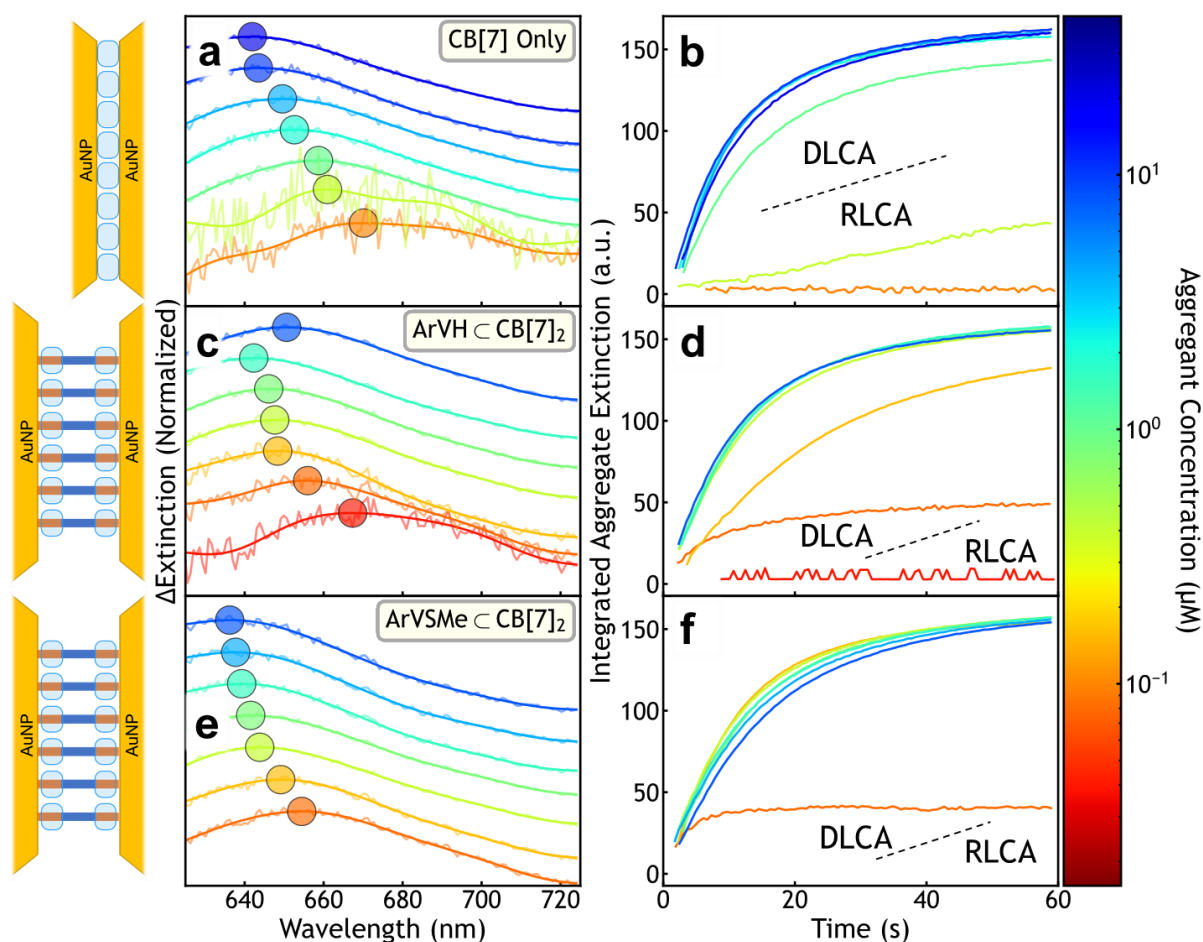


Figure 4.8. (a, c, e) Initial dimer peaks CB[7]@AuNP ArV $\subset$ CB[7]₂@AuNP and aggregates, with λ_{dim} positions highlighted. (b, d, f) Temporal evolution of integrated spectral sum ($525 < \lambda < 900$ nm as in **Figure 4.5g**). Schematics on left-hand side illustrate hypothesised arrangement of molecular spacers within the hotspots.

Both ArV $\subset$ CB[7] systems (**Figures 4.6b,c; 4.8c,e**) exhibit moderately blueshifted λ_{dim} (15-20 nm) relative to CB[7] alone, indicating larger gaps. Assuming similar surface coverage between the three systems, the presence of ArV (aligned perpendicular to the AuNP surface by CB[7]) should increase n_g and offset the λ_{dim} blueshift somewhat. Using $n_g(CB[7]) = 1.3$, as above,

$\Delta\lambda_{\text{dim}} = 20$ nm can be reproduced with $d(\text{ArV}_2\text{CB}[7]_2) = 2$ nm and $n_g(\text{ArV}_2\text{CB}[7]_2) = 1.47$; this is consistent with lower ArV density than the ArVSM_e-only system, although smaller than the $n_g(\text{ArV}_2\text{CB}[7]_2) \approx 1.6$ implied by the NPoM NPR results (**Figure 4.3b**).

The λ_{dim} data in **Figure 4.6b** is plotted against the expected ArV₂CB[7]₂ concentration, equal to half the total CB[7] concentration. To ensure the apparent blueshift is not an artefact of this, the same data is plotted (**Figure 4.6c**) against absolute CB[7] concentration, demonstrating that both ArV₂CB[7]₂@AuNP systems exhibit distinct λ_{dim} behaviour from CB[7]@AuNPs, indicating presence of both ArV and CB[7] in the hotspot.

While these results appear to support ArV₂CB[7]₂ structural retention, the complex may be dissociating to form CB[7]-bridged hotspots ($d = 0.9$ nm) with lower CB[7] density, interspersed with ArV molecules parallel to the surface. Indeed, $\Delta\lambda_{\text{dim}} = -20$ nm can be reproduced with $n_g(\text{ArV} + 2\text{CB}[7]) = 1.23$, which is plausible given that the calculated $\alpha_{xx}(\text{ArVSM}_e)$ (=250 au) is lower than $\alpha_{zz}(\text{CB}[7])$ (=843 au). Both possibilities are explored with SERS in **Section 4.5**.

The DLCA/RLCA concentration threshold (**Figure 4.8b,d,f**) of ArV₂CB[7]₂@AuNPs is lower than either ArV or CB[7] alone, indicating synergistic destabilisation of the AuNP colloid. The initial aggregation rates of ArVSM_eCB[7]₂@AuNPs are higher than ArVH₂CB[7]₂@AuNPs, indicating additional contribution of S-Au coordination to the aggregation process.

CB[8]@AuNPs (**Figures 4.6d,e; 4.9a**) exhibit a blueshifted λ_{dim} ($\Delta\lambda_{\text{dim}} \approx -10$ nm) relative to CB[7]@AuNPs. This is consistent with identical d and smaller n_g , resulting from similar α_{zz} but lower surface density due to the larger CB[8] diameter. The DLCA/RLCA concentration threshold of CB[8]@AuNPs is lower than for CB[7], likely due to HCl impurities in CB[8].⁴⁶³

As with the ArV₂CB[7]₂ systems, ArV and CB[8] combine synergistically to cause aggregation at lower concentrations than either component alone (**Figure 4.9**). The λ_{dim} curves of (ArVH)₂CB[8]₂@AuNPs and (ArVSM_e)₂CB[8]₂@AuNPs (**Figure 4.6d,e**) are less blueshifted ($\Delta\lambda_{\text{dim}} = 5$ -15 nm) from CB[8]@AuNPs than for the analogous ArV₂CB[7]₂ systems (**Figure 4.6b,c**), consistent with a similar increase in d upon ArV incorporation (expected for vertically-aligned ArV₂CB[8]₂) and similar n_g , given the lower n_g of the CB[8]@AuNP gap. $\Delta\lambda_{\text{dim}} = 9$ nm can be reproduced by $n_g(\text{CB}[8]) = 1.2$, $n_g(\text{ArV})_2\text{CB}[8]_2 = 1.4$, significantly lower than predicted by NPoM NPR analysis (**Figure 4.3b**), possibly due to differences in packing density.

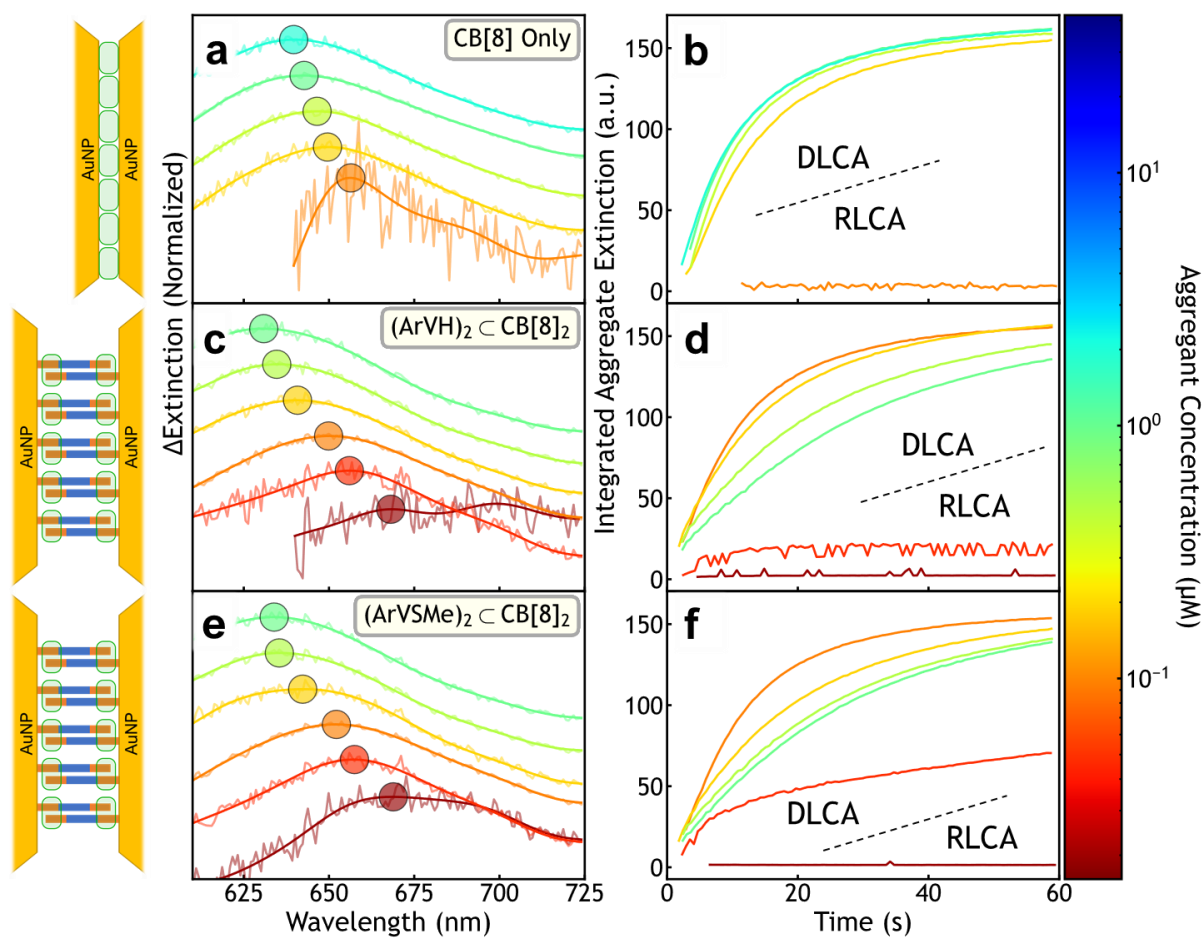


Figure 4.9. (a, c, e) Initial dimer peaks CB[8]@AuNP ArV₂CB[8]₂@AuNP and aggregates, with λ_{dim} positions highlighted. (b, d, f) Temporal evolution of integrated spectral sum ($525 < \lambda < 900$ nm as in **Figure 4.5g**). Schematics on left-hand side illustrate hypothesised arrangement of molecular spacers within the hotspots.

Unlike the ArV₂CB[7]₂ system, the λ_{dim} curves do overlap if plotted against absolute CB[8] concentration (**Figure 4.6e**). However, based on the above discussion, the hotspots do contain a mixture of ArV and CB[8], and it is likely that ArV₂CB[8]₂ supramolecular structure is retained in most cases.

4.4 Aggregate Extinction: Another Anomalous Spectral Shift

As mentioned in **Section 4.3**, the general trend for all systems in **Figure 4.6** reveals a significant λ_{dim} redshift ($\dot{\lambda}_{\text{dim}} = \partial \lambda_{\text{dim}} / \partial c$ for aggregate concentration c) as spacer concentration decreases ($\dot{\lambda}_{\text{dim}} < 0$ in all cases). While this result was not reported previously, it is worth reiterating that the aggregate concentrations used here are much higher, and the spectral acquisition much faster, than in the experiments of Taylor *et al.*,⁵⁹ implying that appreciable nonzero $\dot{\lambda}_{\text{dim}}$ only occurs at these higher spacer/AuNP ratios.

Section 4.4.1 explores the possibility of concentration-dependent changes in the usual gap properties (d , n_g , G) and the plasmonic consequences thereof. Geometry-related possibilities

are then discussed in **Section 4.4.2**, including variations in chain length, AuNP polydispersity and nanocavity/dimer geometry. The leading hypothesis for the observed λ_{dim} proposes a continuous change in average facet overlap (and therefore gap capacitance C_g) as spacer concentration is varied.

4.4.1 Gap & Surface Properties

Molecular density within AuNP aggregate hotspots is predicted to be lower than in NPoM gaps (**Section 4.3.1**). However, as the amount of aggregant present in solution is sufficient to completely cover the combined AuNP surface area, the possibility of an aggregant bilayer in the cavity should also be considered. The consequently larger gap would manifest as a second, blueshifted λ_{dim} and would be more likely at higher aggregant concentrations. Convolution of the two peaks with steady variation of relative intensity may lead to an apparent continuous λ_{dim} shift.

This was tested for CB[7] ($d = 0.9$, $n_g = 1.3$), ArVSMc ($d = 1.7$, $n_g = 1.7$) and ArVSMc₂CB[7]₂ ($d = 2$, $n_g = 1.47$) using the LCR model.¹⁰² λ_{dim} was calculated using d and $2d$ for each system, broadened with otherwise identical Lorentzian functions and superimposed. The calculated $\Delta\lambda_{\text{dim}} = 52\text{-}58$ nm is within the experimental range (λ_{dim} range = 30-60 nm in **Figure 4.6**), and of the correct sign. However, the superimposition of two peaks is clearly visible for this $\Delta\lambda_{\text{dim}}$ using the typical peak FWHM (80-100 nm; ~ 90 nm in **Figure 4.5d**) observed here (**Figure 4.10**).

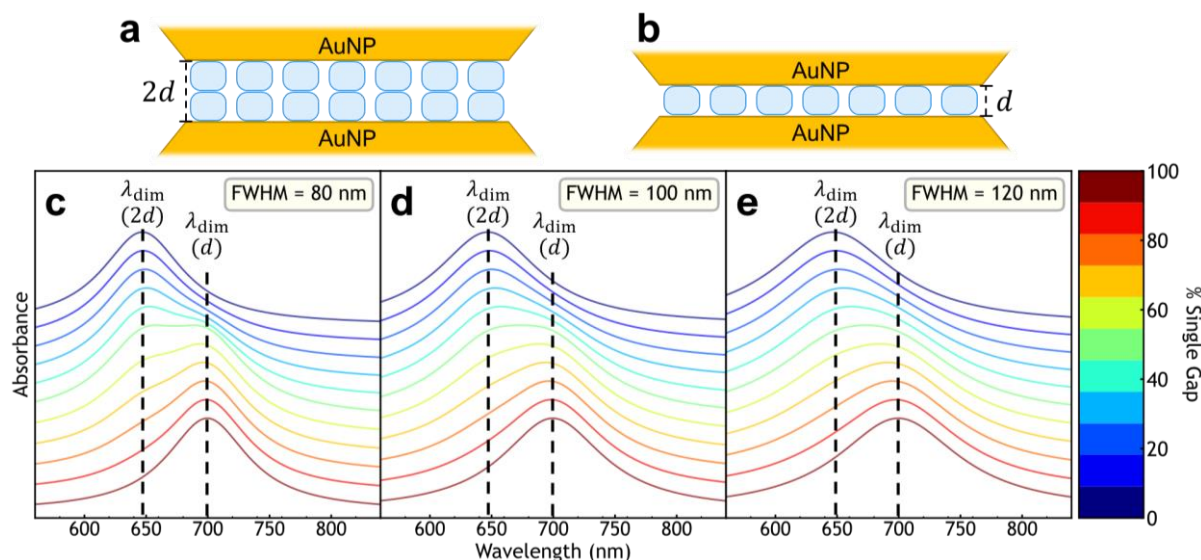


Figure 4.10. (a, b) Schematics illustrating interparticle gaps (not to scale) created by (a) double- and (b) single-thickness layers of CB[7]. (c) for each gap, λ_{dim} was calculated ($d = 0.9$ nm and $2d = 1.8$ nm; $D = 60$ nm, $w = 15$ nm, $n_g = 1.3$, $n_m = 1.333$) and broadened with a Lorentzian function (FWHM = 80 nm). The resulting pair of Lorentzian functions were then summed with a range of weights (coloured traces, offset for clarity; see colour bar for weighting). (d, e) show the same calculated λ_{dim} data as in (c), but instead broadened with FWHM of (d) 100 or (e) 120 nm. The two broadened λ_{dim} signals are clearly distinct in (c) when FWHM = 80 nm, but far less so in (e) when FWHM = 120 nm.

For $\Delta\lambda_{\text{dim}} = 30$ nm and/or FWHM > 120 nm, the asymmetry is less visible and this explanation is plausible (**Figure A23a**). Additionally, the large experimental λ_{dim} range of ArVH@AuNPs is accompanied by broad peak shapes, indicative of multiple resonances. However, the double resonance is clearly theoretically visible for $\Delta\lambda_{\text{dim}} = 40$ nm; FWHM = 100 nm (**Figure A23b**), yet no evidence for this is observed experimentally (e.g. ArVSM@AuNPs; **Figures 4.7; A24**).

If n_g is responsible for the observed $\dot{\lambda}_{\text{dim}} < 0$, this requires n_g to increase as surface coverage decreases. For this to be true, a full molecular monolayer must have $n_g < n_m$. The maximum theoretical λ_{dim} shift due to n_g can be calculated (using the LCR model) by comparing λ_{dim} when $n_g = n(\text{spacer})$ and $n_g = n_m$. In this way, $\Delta\lambda_{\text{dim}} = 28$ nm can be reproduced for CB[7]@AuNPs with reasonable values of $n(\text{CB}[7]) \approx 1.24$ and $n_m(\text{citrate/water}) = 1.333$. However, to similarly reproduce $\Delta\lambda_{\text{dim}} = 40$ nm for ArVSM@AuNPs (assuming $d = 1.7$ nm), a lower value of $n(\text{ArVSM}) = 1.15$ is required. While the exact $n(\text{ArVSM})$ is unknown, **Sections 4.2-4.3** clearly suggest that $n(\text{ArVSM}) > n_m$ and $n(\text{ArVSM}) > n(\text{CB}[7])$. If variation of n_g with surface coverage were to significantly affect λ_{dim} , the sign of $\dot{\lambda}_{\text{dim}}$ would be reversed for the ArVSM system. Concentration-dependent n_g is therefore unlikely to cause the observed behaviour of $\dot{\lambda}_{\text{dim}}$.

Similarly, for coverage-dependent variation of gap conductance (G) to cause a redshift with decreasing spacer concentration ($\dot{\lambda}_{\text{dim}} < 0$), optical-frequency AC conductance of a full monolayer must be higher than for a water/citrate layer of the same thickness. This would manifest spectrally as a larger shift for more conductive spacers, with λ_{dim} blueshifting as water/citrate is replaced and G increases; less conductive spacers would exhibit a less negative or sign-reversed $\dot{\lambda}_{\text{dim}}$.

A difference in G may indeed explain the $\dot{\lambda}_{\text{dim}}$ difference between the aliphatic CB[n] and conjugated, Au-bound ArVSM systems. The large $|\dot{\lambda}_{\text{dim}}|$ of ArVH@AuNPs is less consistent with this hypothesis, as the poorly defined adsorption geometry and expected lack of ArVH-Au covalency implies low G . However, the small d expected for ArVH may increase the AC tunnelling current, as could any $(\eta^2-\pi)$ -Au coordination. A more diverse range of spacers would be required to explore this hypothesis further.

Another explanation is the “pillow effect”,¹⁵² whereby a higher surface coverage of electron-rich molecules lowers the Au work function⁴³² (**Appendix 8.2.4**). This may increase the effective G and therefore $|\dot{\lambda}_{\text{dim}}|$, as described above. However, the opposite is observed experimentally, with larger $|\dot{\lambda}_{\text{dim}}|$ observed instead for the electron-deficient ArV-only systems.

The Au surface charge delocalisation may be restricted by covalency between the spacer and Au. As light only appreciably penetrates ~3 nm into the Au surface, covalent binding of all surface atoms could restrict motion of up to 10% of the optically interacting electron density.^{27,52} The subsequent λ_p decrease would blueshift λ_{dim} (**Equation (2); Section 1.3.1**) as spacer coverage increases.

If this effect causes the observed λ_{dim} , increased spacer-Au covalency would generate a larger shift. Again, higher covalency is expected for $ArVSM_e$ than $CB[n]$, concurrent with the relative λ_{dim} ranges observed, but the degree of $ArVH$ -Au covalency is unknown, as are the consequences of electron nonlocality on this behaviour for smaller d . This hypothesis therefore requires more investigation.

4.4.2 AuNP Aggregation Geometry

AuNP aggregation involves greater geometric variability than NPoM assembly. In addition to gap properties and individual AuNP/facet geometry, the plasmonic response is affected by AuNP chain length, aggregate shape, facet overlap, and dimerisation geometry.

The AuNP aggregate λ_{max} depends on the position and intensity of both λ_{dim} and the various λ_{agg} chain modes.⁶² As λ_{dim} measurement is based on λ_{max} at the earliest possible t (**Figure 4.5c,d**), the spectral influence of longer-chain resonances at small t should be considered. For chain length to cause the observed λ_{dim} implies the presence of longer AuNP chains at earlier t for lower aggregant concentrations. While this may be counterintuitive at first, DLCA conditions yield fast, widespread dimerisation, with obvious λ_{max} at $t = 0.5$ s, whereas longer wait times are required for λ_{max} visibility in the RLCA case, which may provide time for longer chains to form. Additionally, larger AuNP clusters are more likely to capture free AuNPs under RLCA conditions, which may increase relative spectral contribution of λ_{agg} to the “initial” λ_{max} .

To test this, the relative spectral response of an AuNP trimer ($D = 60$ nm, $d = 0.9$ nm, $n_g = 1.4$, $n_m = 1.333$) was calculated for close-packed and linear geometries (**Figure 4.11**). The trimer resonance (λ_{trimer}) is virtually identical to λ_{dim} in the close-packed scenario, but redshifts by 80 nm for the linear trimer; intermediate λ_{trimer} wavelengths are expected for geometries between these two extremes.

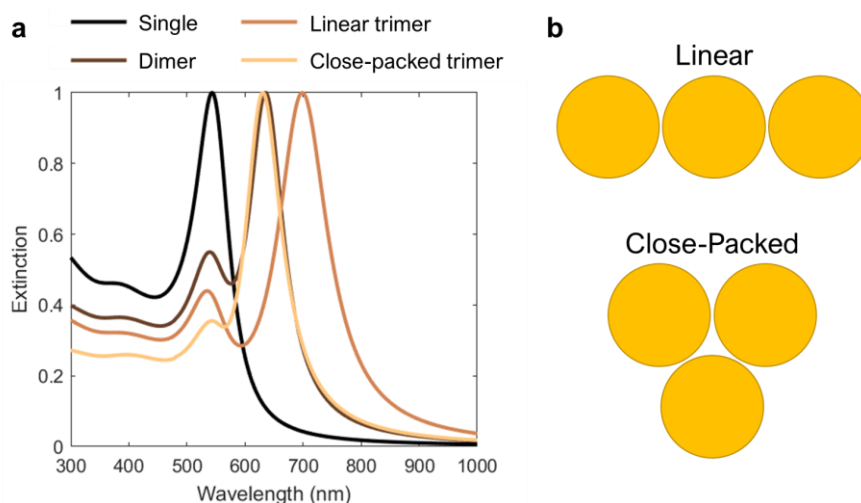


Figure 4.11. (a) Calculated optical response of single AuNP, AuNP dimer and the AuNP trimer geometries illustrated in (b). $D = 60$ nm, $w = 0$, $d = 0.9$ nm, $n_g = 1.3$, $n_m = 1.333$. Calculations were performed by Aoife Gregg (Department of Physics, University of Cambridge) using the open-source multiple sphere T-matrix (MSTM) Fortran code of Mackowski & Mishchenko.⁴⁶⁴

As RLCA favours maximised interparticle contact, close-packed trimers should dominate at low aggregant concentrations and λ_{trimer} is unlikely to cause a λ_{max} redshift. Conversely, more open AuNP chains form quickly at higher aggregant concentrations and DLCA spectral evolution is observed^{59,62} (**Section 1.3.3**). Overall, any contribution of λ_{trimer} to λ_{max} should be negligible under RLCA conditions, while under DLCA conditions, longer λ_{trimer} resonances contribute instead to the observed plasmonic evolution of λ_{agg} ; longer chains are therefore unlikely to cause the observed $\Delta\lambda_{\text{dim}}$.

The normal distribution of NPoM λ_{C} values reflects the polydispersity of colloidal AuNPs used in this work. According to the manufacturer,¹³ D has standard deviation $\sigma_D = 4.8$ nm, implying a size range of $D = \bar{D} \pm 3\sigma_D$ present in solution (46-74 nm for $\bar{D} = 60$ nm), assuming $D \sim N(\bar{D}, \sigma_D)$. This polydispersity is reflected in the λ_{dim} peak width, but individually represents a maximum $\Delta\lambda_{\text{dim}}$ of 80 nm across the size range. This may affect λ_{dim} if aggregation rate varies significantly with D .

To explore this, λ_{dim} was calculated (LCR model: $d = 0.9$ nm, $w = 15$ nm, $n_g = 1.4$, $n_m = 1.333$ for CB[7]@AuNPs) for 1000 AuNP dimers with $D \sim N(\bar{D}, \sigma_D)$. Each result was broadened with a Lorentzian function (FWHM = 90 nm), yielding a spectral sum over all dimers with FWHM ≈ 100 nm (**Figure 4.12a**). Enforcing a lower size limit (D_{min}) for which only $D > D_{\text{min}}$ are included in the spectral sum leads to an apparent redshift of $\Delta\lambda_{\text{max}} = 44 \pm 3$ nm for $\bar{D} \leq D \leq \bar{D} + 3\sigma_D$ (**Figure 4.12b**). Similarly, an upper size limit yields a blueshift of the same magnitude. The magnitude of this shift is similar to the experimentally observed λ_{dim} ranges, but does not vary significantly with different n_g or d .

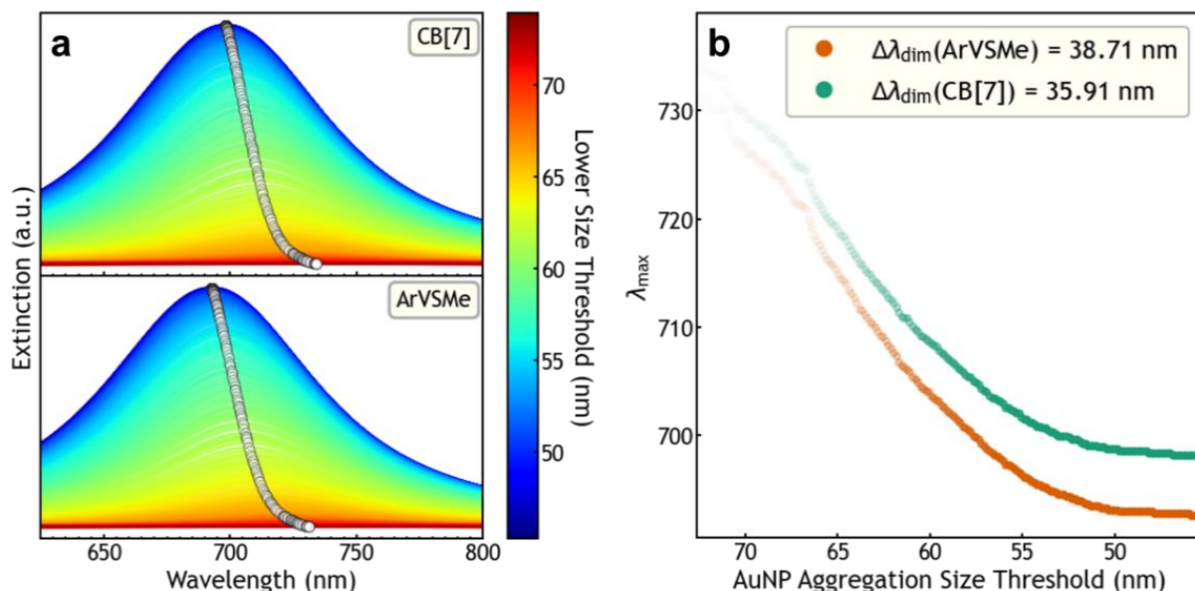


Figure 4.12. (a) AuNP dimer spectra for size distribution of $D(\text{nm}) \sim N(60, 4.8)$ and $n_m = 1.333$, $w = 15$ nm with lower AuNP size thresholds for aggregation of $36 < D < 74$ nm, calculated for CB[7] ($n_g = 1.3$, $d = 0.9$) and ArVSMc ($n_g = 1.66$, $d = 1.7$). (b) Apparent λ_{max} vs size threshold, with opacity scaled according to peak intensity.

For this size-dependent aggregation to cause the observed λ_{dim} implies an increase in D_{min} as aggregant concentration decreases. Experimentally, this could be tested using AuNPs with identical surface chemistry but different $\bar{D}$ and σ_D . $|\lambda_{\text{dim}}|$ would increase along with σ_D , and the DLCA/RLCA concentration threshold would decrease as $\bar{D}$ increases. Such experiments are currently being planned, but are beyond the scope of this work.

Theoretically, the effects of AuNP size, surface charge and spacer coverage upon the aggregation energy barrier may be approximated using DLVO theory.^{58,465} However, this predicts an activation barrier that increases with D (**Appendix 8.3.3**), according to which any λ_{dim} should be of opposite sign to the experimental results. Size-selective aggregation is therefore unlikely to cause the observed λ_{dim} .

So far, this discussion has assumed spherical AuNPs. However, aggregation geometry and facet overlap are also very important in solution. Dimerisation may not always occur with flat facet-to-facet contact and, where it does, facet overlap is rarely perfect. Dimerisation geometry significantly affects gap capacitance C_g , such that λ_{dim} redshifts as geometry approaches complete facet-facet overlap⁶⁵ (**Figure 4.13**).

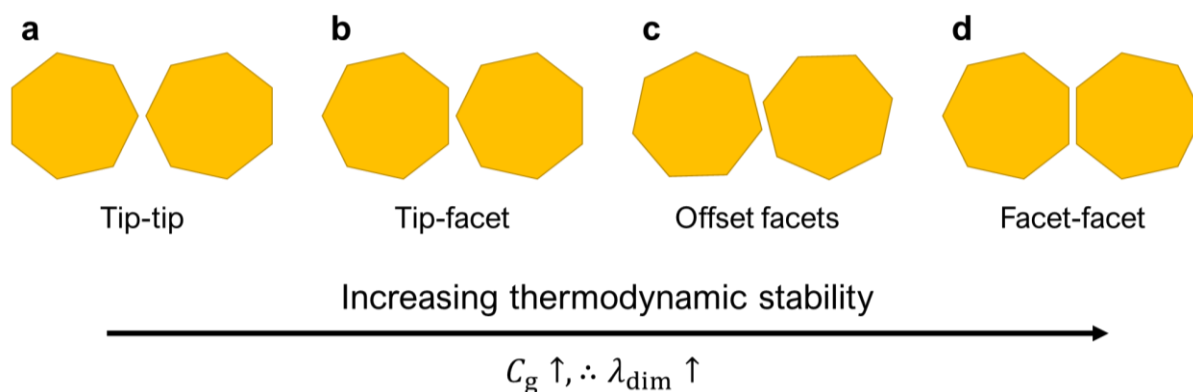


Figure 4.13. Possible non-spherical AuNP dimerisation geometries in ascending order of thermodynamic stability. Gap capacitance (C_g) increases from (a-d) with increasing facet-facet overlap, and λ_{dim} redshifts. Low aggregant concentrations (RLCA regime) lead to higher population of thermodynamically relaxed dimers (c, d), while probability of kinetic trapping of dimer structures (a) and (b) increases with aggregant concentration.

As reported previously,⁵⁹ RLCA conditions yield close-packed AuNP aggregates (**Figure 1.14e-f**), while DLCA conditions yield kinetically-trapped open, extended structures. The current hypothesis for the observed λ_{dim} posits that a similar process occurs with AuNP dimerisation geometry. Kinetic trapping of less thermodynamically favourable structures (**Figure 4.13a,b**) becomes more likely as aggregant concentration increases; for RLCA, the more thermodynamically relaxed dimer geometries in **Figure 4.13c,d** are favoured. As discussed, this behaviour should redshift λ_{dim} as aggregant concentration decreases. The continuous nature of such a λ_{dim} may also convolute the λ_{dim} curves in **Figure 4.10** and conceal the double peak; the possibility of both single and double gap spacings should therefore not be overlooked.

Confirmation of this would require TEM or SEM imaging of dried AuNP aggregates⁵⁹ or gel-quenched dimers⁶⁵ for the aggregant concentration ranges used here. The plasmonic response of the geometries in **Figure 4.13** should also be calculated numerically. The hypothesis could also be experimentally tested using ultra-spherical AuNPs⁴⁶⁶ to minimise the spectral effects of AuNP/facet geometry.

4.5 Aggregate SERS

Aqueous SERS measurements were performed for the ArV, CB[n] and ArV $\subset$ CB[n] AuNP aggregate systems explored in **Sections 4.3-4.4** over similar aggregant concentration ranges. For each sample, aqueous AuNPs ($D = 60$ nm; $333 \mu\text{L}$) were mixed with aggregant solution ($6.8 \mu\text{L}$) in a multi-well plate (vol = $340 \mu\text{L}$) and incubated for 1 min, after which SERS spectra were collected ($\lambda_{\text{ex}} = 785$ nm; **Methods 7.4.4**). To probe (supra)molecular spacer orientation within the hotspot, x/y/z components of the calculated Raman activities were extracted to simulate the polarised local excitation field (**Methods 4.7.1**). Relative peak intensities within the experimental and calculated spectra were then compared, as illustrated for CB[7] in **Figure 4.14**.

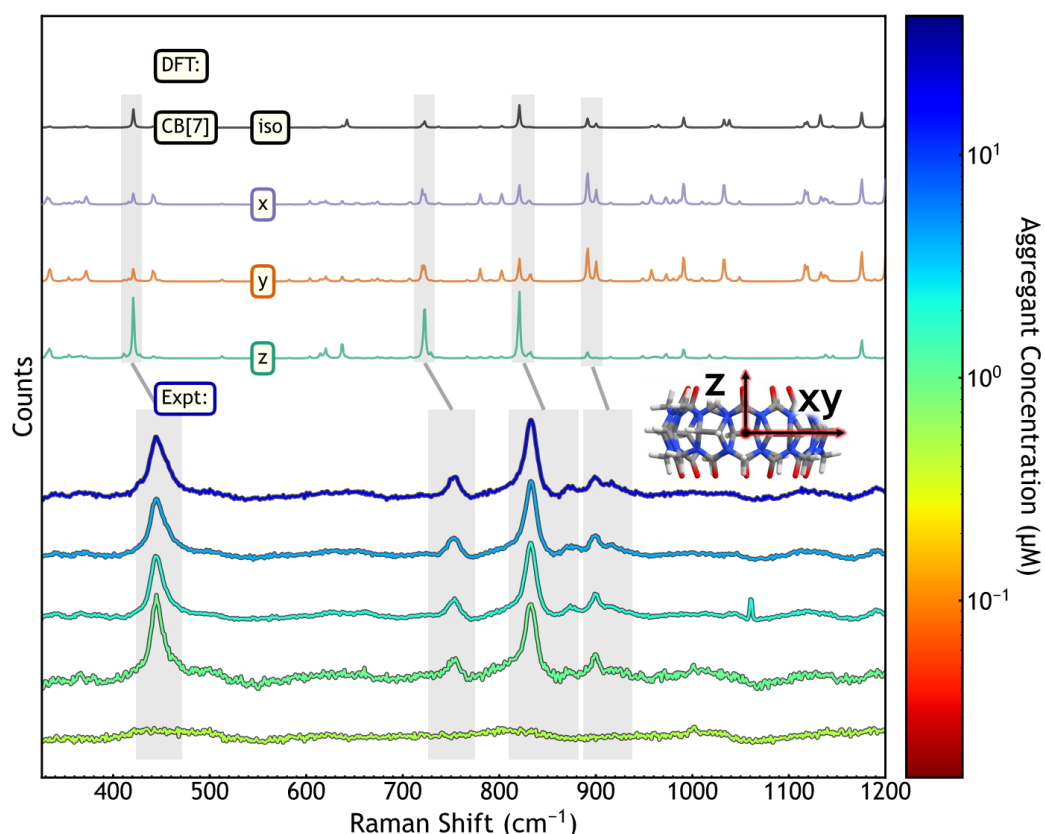


Figure 4.14. Top: DFT Raman spectra calculated for CB[7] with either isotropic excitation field (black trace) or excitation polarised along x, y or z directions (indicated on CB[7] structure inset) scaled in wavenumber by a factor of 0.9671. Bottom: experimental SERS spectra of aqueous CB[7]@AuNP aggregates at a range of concentrations, background-subtracted using adaptive least-squares fitting and normalised to the resonance at 833 cm^{-1} . Grey shaded areas indicate corresponding predicted and experimental peaks. Atom colours: C (grey), H (white), N (blue), O (red).

The isotropic DFT Raman spectrum of CB[7] predicts several more peaks than are observed experimentally. However, due to the expected CB[7] orientation within the hotspot,^{6,59,96} the x/y-polarised vibrational signals are suppressed and the z-polarised calculation agrees well with the experimental SERS. The relative intensities of the observed modes do not vary significantly with CB[7] concentration, concurrent with the rigidity of CB[7] and geometric uniformity of CB[7]@AuNP nanocavities.

ArVSM@AuNPs (without CB[n]) exhibit more complex concentration dependence (**Figure 4.15**). Normalisation of spectra to the resonance at 814 cm⁻¹ reveals an increase in relative intensity of all other resonances with increasing ArVSM concentration. Given the strong x-polarisation of said resonance, this behaviour indicates variation of ArVSM orientation, with ϕ (angle from surface normal) decreasing as ArVSM surface coverage increases. This should increase d with concentration, consistent with the larger $|\lambda_{\text{dim}}|$ of the ArVSM system than for CB[n] or ArV $\subset$ CB[n] (**Section 4.3.2**).

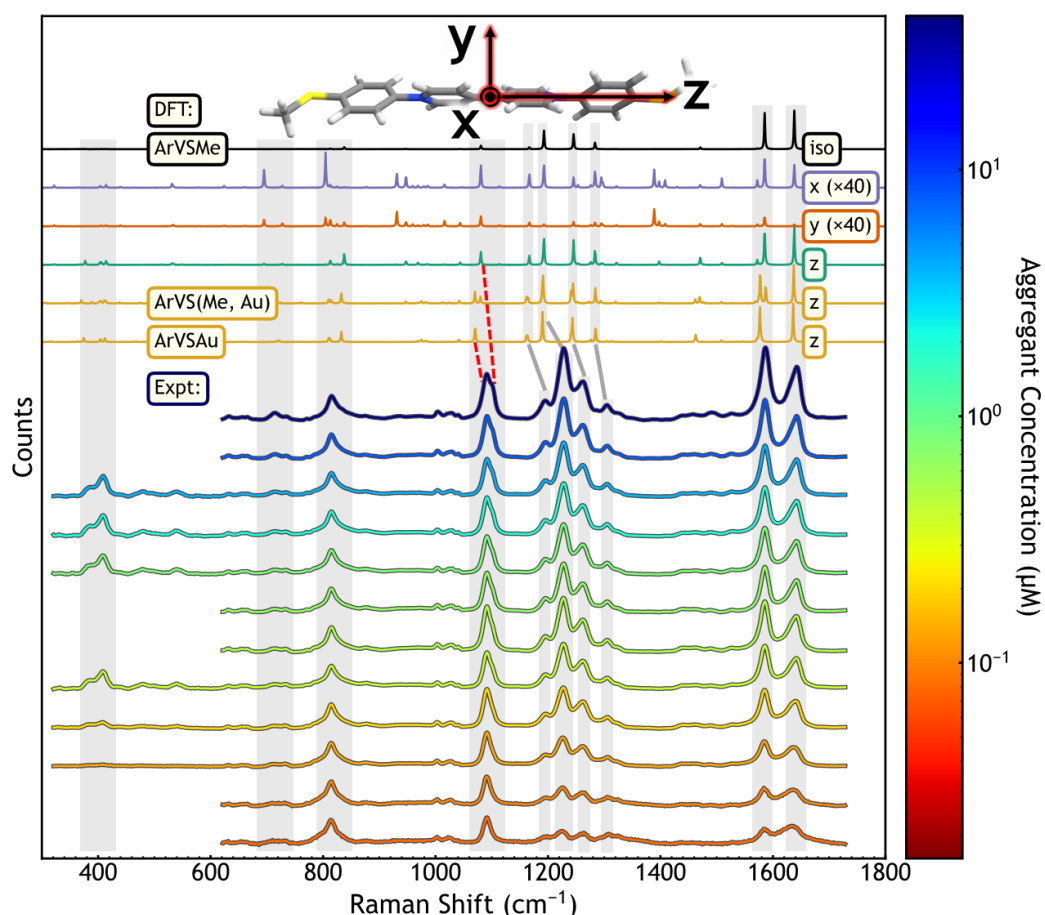


Figure 4.15. Top: DFT Raman spectra calculated for ArVSM with isotropic and polarised excitation (axes indicated on ArVSM structure inset) as in **Figure 4.14**. Note the required magnification of the x/y-polarised spectra. Also included (yellow traces) are z-polarised DFT Raman spectra calculated for ArVSM with one or both terminal methyl groups replaced with a fixed Au atom to simulate ArVSM-Au surface bond. Bottom: experimental SERS spectra of aqueous ArVSM@AuNP aggregates at a range of concentrations, background-subtracted and normalised to the resonance at 814 cm⁻¹. Grey shaded areas indicate corresponding predicted and experimental peaks. Red dashed lines highlight the presence of both S-Me and S-Au stretches around 1100 cm⁻¹. Atom colours: C (grey), H (white), N (blue), S (yellow).

Again, this may be tested experimentally via SEM or TEM imaging of interparticle gap geometries for various ArVSM e concentrations. Alternatively, use of ultra-spherical AuNPs should lower this geometric variability and therefore variability of the S-Me/S-Au intensity ratio. Measurement of S-Au bond incidence may also be complemented with STEM-EELS to probe the different chemical environments in and around the hotspot with sub-nm resolution.⁴⁶⁷

ArVH@AuNP aggregates exhibit more complex SERS behaviour (**Figure 4.17**). The relative intensities of many vibrations change with ArVH concentration, indicating significant variation in molecular orientation within the hotspots. While each group of resonances variously resembles either the x, y or z-polarised DFT predictions, characterisation of the spacer orientation is complicated by additional resonances in the experimental spectra.

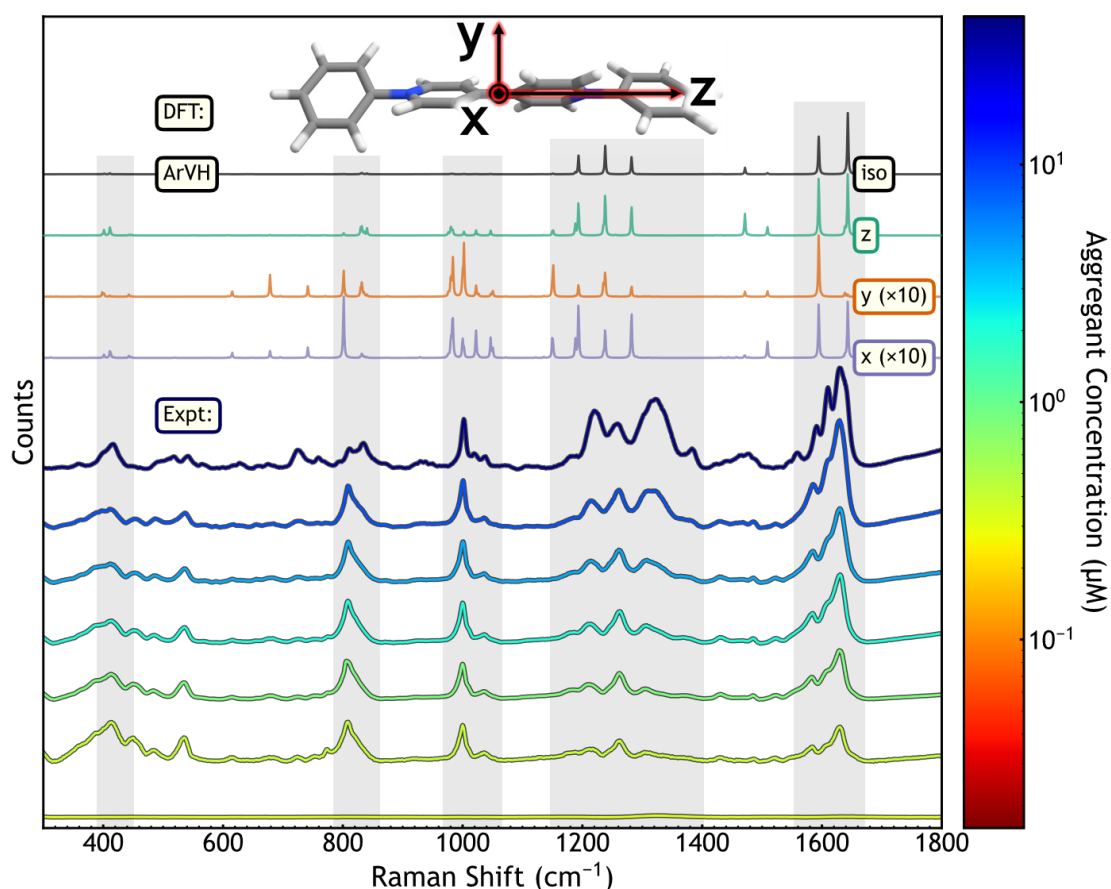


Figure 4.17. Top: DFT Raman spectra calculated for ArVH with isotropic and polarised excitation (axes indicated on ArVH structure inset) as in **Figure 4.14**. Note the required magnification of the x/y-polarised spectra. Bottom: experimental SERS spectra of aqueous ArVH@AuNP aggregates at a range of concentrations, normalised to the resonance at 1000 cm⁻¹. Grey shaded areas indicate corresponding predicted and experimental peak regions. Atom colours: C (grey), H (white), N (blue).

For example, the evolution of peak intensities in the ~800 cm⁻¹ wavenumber region suggests ArVH x/y-alignment at low concentrations, progressing to greater x- or even z-alignment at the highest concentration. Conversely, the ~1200-1400 cm⁻¹ spectral region appears x-polarised at high ArVH concentration, but y/z-like at lower concentration. Furthermore, the peak shapes and spacing indicate additional resonances in the experimental spectra, making direct comparison difficult. This, together with additional peaks at ~400-600 and ~1500-1700 cm⁻¹,

implies perturbation of ArVH vibrational structure by the nanocavity. Possible causes include changes in intramolecular dihedral angles, π -Au coordination or chemical reduction by citrate or photoexcited electrons.^{27,31}

The experimental spectra appear consistent with some ArVH in the hotspots, while the spectral variability indicates poorly-defined spacer orientation and surface binding, as predicted. Comparison of ArVSM@AuNPs (**Figure 4.15**) and ArVH@AuNPs (**Figure 4.17**) SERS spectra indicates more well-defined spacer orientation and environment in the former.

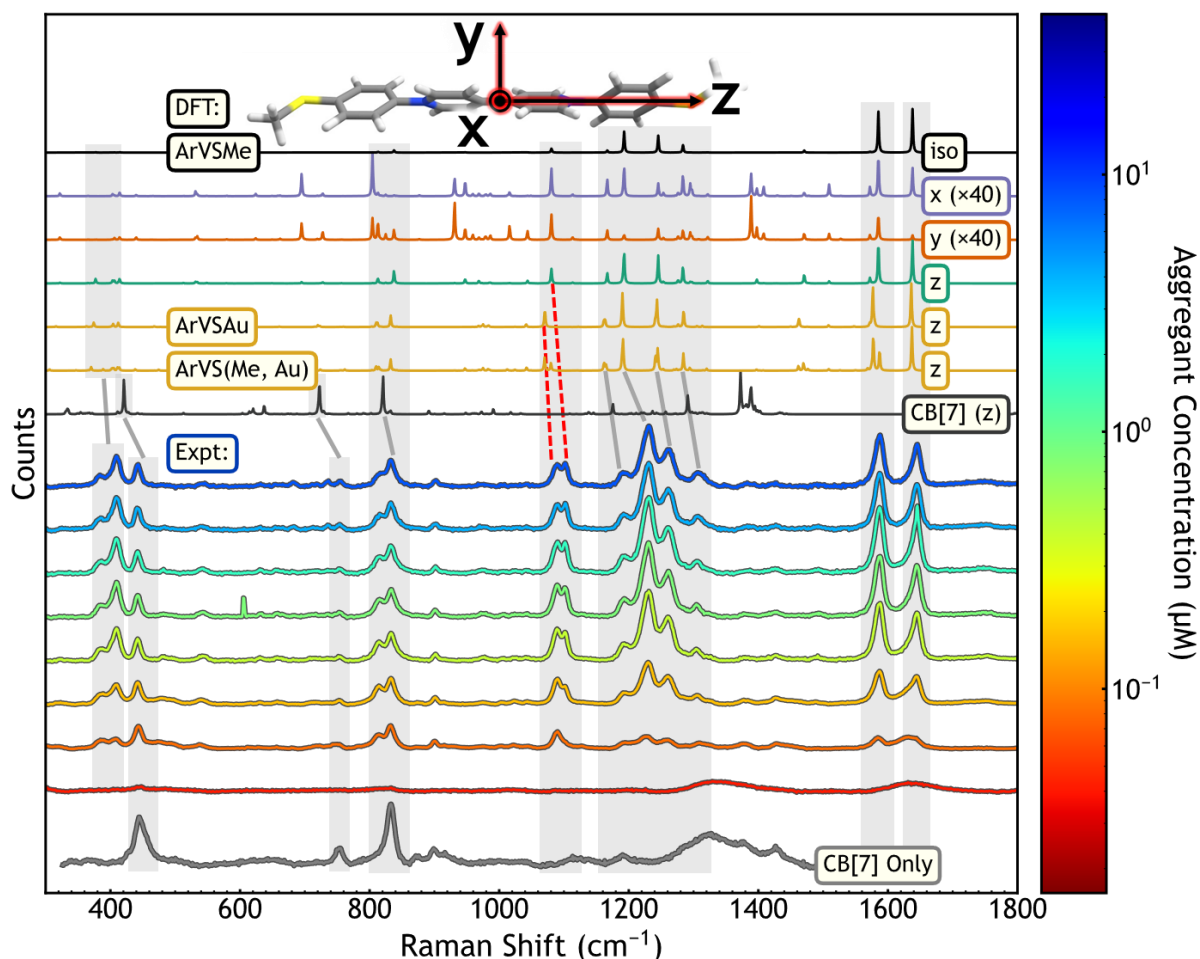


Figure 4.18. Top: DFT Raman spectra calculated for ArVSM with isotropic and polarised excitation (axes indicated on ArVSM structure inset) as in **Figure 4.14**, plus z-polarised spectrum for CB[7]. Note the required magnification of the x/y-polarised spectra. Yellow traces are z-polarised DFT Raman spectra of ArVSM(Au) and ArVSAu, as before. Bottom: experimental SERS spectra of aqueous ArVSM@CB[7]₂@AuNP aggregates at a range of concentrations, normalised to the CB[7] resonance at 444 cm^{-1} . Grey shaded areas indicate corresponding predicted and experimental peaks. Red dashed lines highlight the presence of both C-S-Me and C-S-Au stretches around 1100 cm^{-1} . Atom colours: C (grey), H (white), N (blue), S (yellow).

ArVSM@CB[7]₂@AuNPs yielded clear, stable SERS spectra (**Figure 4.18**) with relatively little variation in peak intensity ratios at higher concentrations ($>0.15 \mu\text{M}$), indicating consistent spacer structure and orientation. The 1160-1330 cm^{-1} band intensity (relative to the 814 and 1100 cm^{-1} resonances) is greater than observed at the high concentration (small ϕ) limit of ArVSM@AuNPs (**Figure 4.15**), indicating stronger alignment of the ArVSM z-axis with the

hotspot field when CB[7] is present. Negligible concentration dependence of the ArVSMc peak intensities when normalised to the 444 cm^{-1} CB[7] resonance suggests a constant ArVSMc/CB[7] ratio in the hotspots for [ArVSMc $\subset$ CB[7] $_2$] > 0.15 μM . This combined evidence indicates structural retention of the ArVSMc $\subset$ CB[7] $_2$ complex at higher concentrations.

The relative peak intensities change at lower concentrations (<0.15 μM), indicating a change in ArVSMc/CB[7] ratio and/or ArVSMc orientation. Relative to the CB[7] peaks, the ArVSMc bands at ~ 400 , 1250, 1600 cm^{-1} all decrease in intensity as [ArVSMc $\subset$ CB[7] $_2$] drops, while the bands at ~ 815 , 1100 cm^{-1} decrease less. The strong x/y component present for these latter resonances suggests an increase in ϕ for ArVSMc, while the consistent relative intensity of the CB[7] peaks implies CB[7] orientation remains unchanged. This change in relative orientation and concentration of ArVSMc and CB[7] within the hotspot implies ArVSMc $\subset$ CB[7] $_2$ dissociation at lower concentrations.

For [ArVSMc $\subset$ CB[7] $_2$] > 0.15 μM , the C-S-Me and C-S-Au resonances at ~ 1100 cm^{-1} appear consistently similar in intensity, suggesting $\sim 50\%$ of SMe groups are unbound (again assuming similar Raman cross-sections). This suggests that the ArVSMc $\subset$ CB[7] $_2$ structure prevents ArVSMc from binding to Au at both ends, either due to unfavourable C-S-Au bond angle ($\approx 108^\circ$ in the gas phase; **Figure A29c**) or changes in supramolecular structure upon S-Au coordination.

Either way, this behaviour would enforce one unbound SMe group per ArVSMc molecule, whether ArVSMc $\subset$ CB[7] $_2$ is dangling or bridging. As such, the S-Me/S-Au intensity ratio is indeed expected to remain constant across the different gap geometries in **Figure 4.16**. At lower concentrations, the bound S-Au resonance dominates, indicating doubly bound ArVSMc and coexistence of separate CB[7] and ArVSMc bridging the hotspot.

The ArVH $\subset$ CB[7] $_2$ @AuNPs spectra are markedly different (**Figure 4.19**), and characterisation of ArVH orientation is difficult with the sparse information available. CB[7] dominates the experimental spectra at all concentrations, while the ArVH signals are significantly weaker than in ArVH@AuNPs (**Figure 4.17**). The ArV/CB[7] spectral intensity ratio is also far smaller than for ArVSMc $\subset$ CB[7] $_2$ @AuNPs. This may be caused by the lower polarisability of ArVH ($\alpha_{zz}(\text{ArVH}) = 555$ au; $\alpha_{zz}(\text{ArVSMc}) = 1564$ au), implying high ArVH density in the CB-free ArVH@AuNPs hotspots.

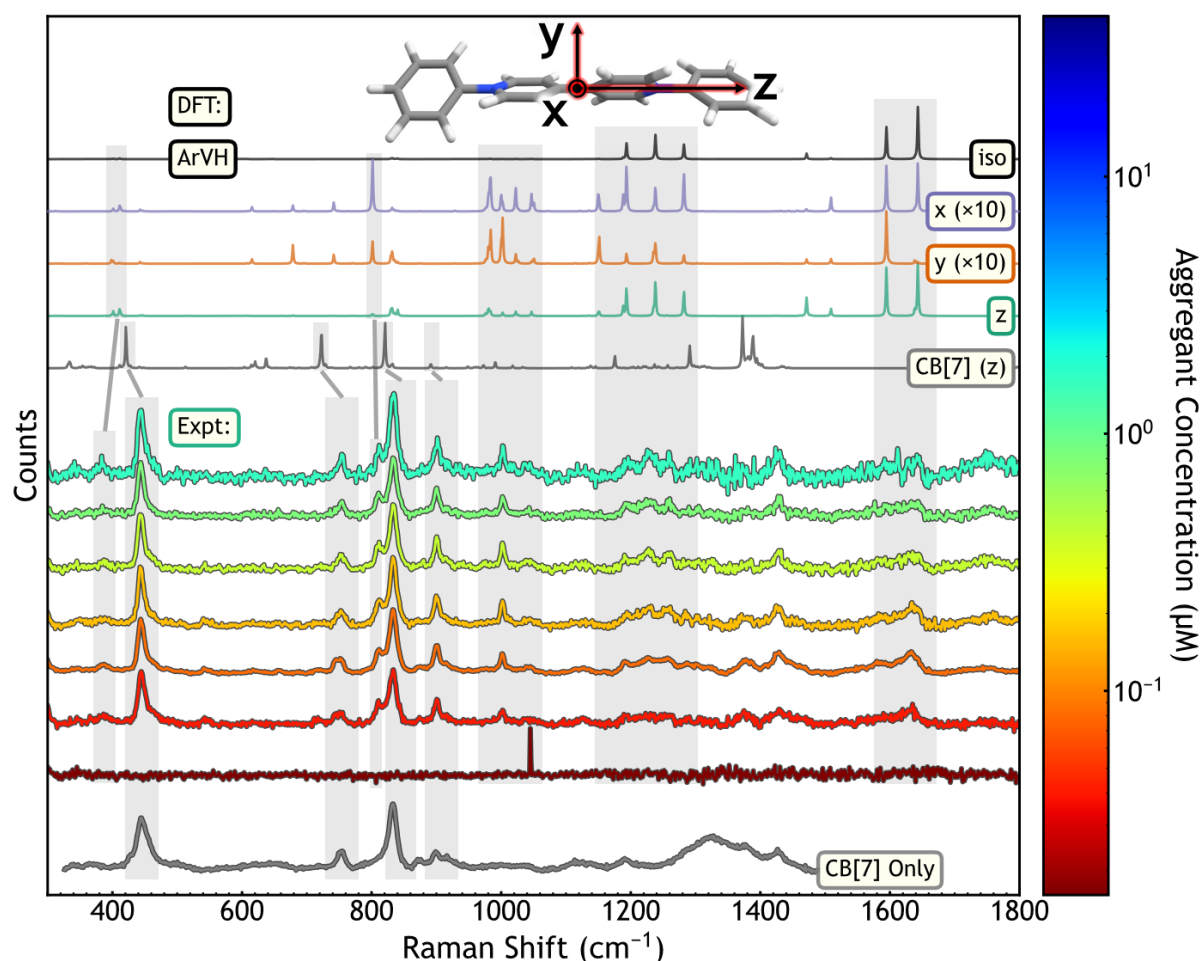


Figure 4.19. Top: DFT Raman spectra calculated for ArVH with isotropic and polarised excitation (axes indicated on ArVH structure inset) as in **Figure 4.14**, plus z-polarised spectrum for CB[7]. Note the required magnification of the x/y-polarised spectra. Bottom: experimental SERS spectra of aqueous ArVH₂CB[7]₂@AuNP aggregates at a range of concentrations, normalised to the CB[7] resonance at 444 cm⁻¹. Grey shaded areas indicate corresponding predicted and experimental peaks. Atom colours: C (grey), H (white), N (blue).

The high intensities of the ~800, 1000 cm⁻¹ ArVH bands (relative to the ~1200, 1600 cm⁻¹ bands) suggest x/y-alignment of ArVH with the hotspot field. Conversely, the overall ArVH spectral shape differs from that of ArVH@AuNPs, implying different ArVH orientation than the x/y-alignment expected for the ArVH only case. The ArVH/CB[7] spectral intensity ratio also remains fairly constant, implying that ArVH₂CB[7]₂ structure is either always retained, or never. This data is therefore less conclusive than for ArVSM@AuNPs. Characterisation is complicated further by the low spectral SNR; more confident analysis would require longer integration times.

The (ArVSM)₂CB[8]₂@AuNPs SERS spectra (**Figure 4.20**) somewhat resemble those of ArVSM@AuNPs. The primary difference is the ArVSM/CB[8] spectral intensity ratio; normalisation to the 440 cm⁻¹ CB[8] resonance reveals approximately double the ArVSM/CB[n] intensity ratio of ArVSM@AuNPs (**Figure 4.18**), indicating retention of (ArVSM)₂CB[8]₂ stoichiometry in the hotspot.

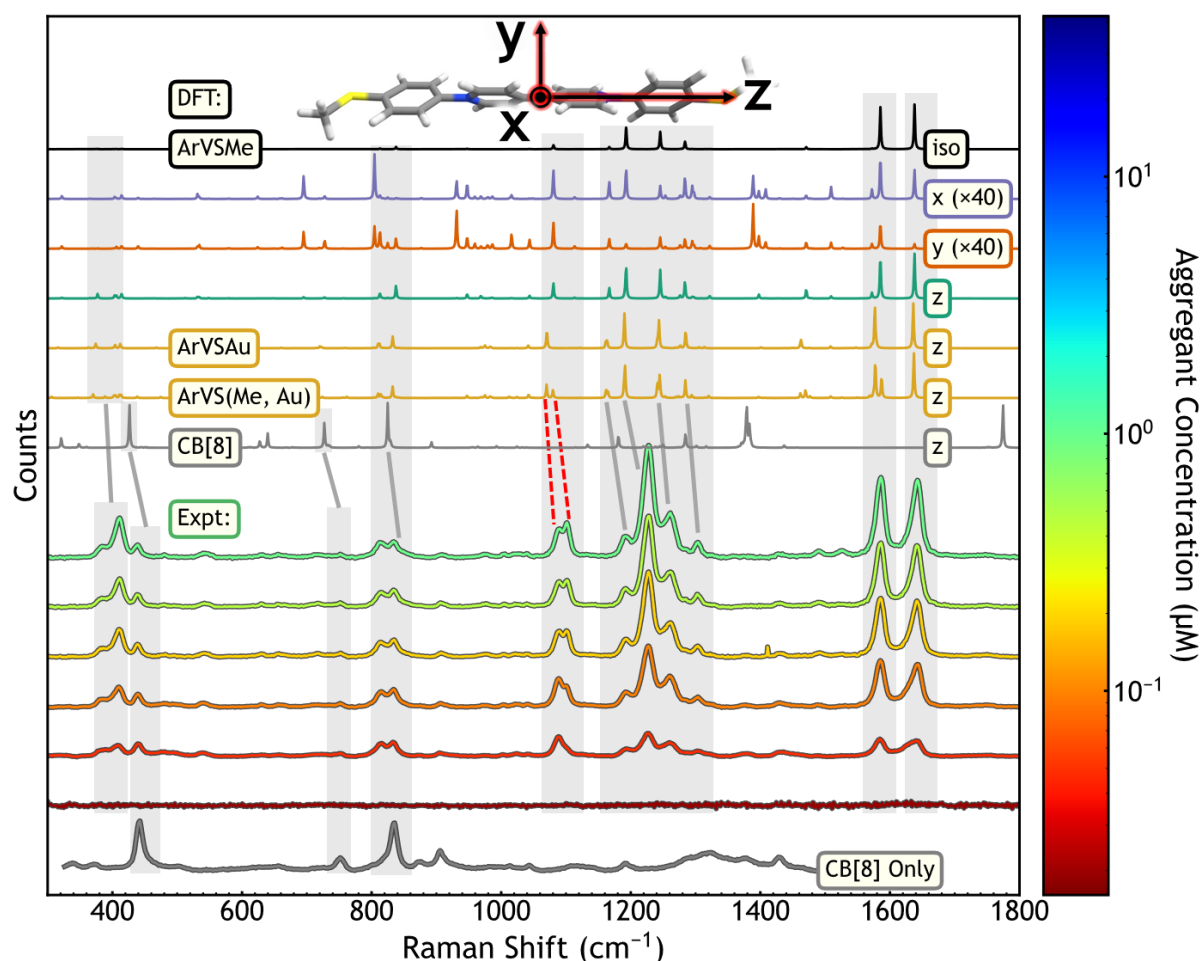


Figure 4.20. Top: DFT Raman spectra calculated for ArVSMes with isotropic and polarised excitation (axes indicated on ArVSMes structure inset) as in **Figure 4.14**, plus z-polarised spectrum for CB[8]. Note the required magnification of the x/y-polarised spectra. Yellow traces are z-polarised DFT Raman spectra for ArVS(Me, Au) and ArVSAu, as before. Bottom: experimental SERS spectra of aqueous (ArVSMes)₂@CB[8]₂@AuNP aggregates at a range of concentrations, normalised to the CB[8] resonance at 440 cm⁻¹. Grey shaded areas indicate corresponding predicted and experimental peaks. Red dashed lines highlight the presence of both C-S-Me and C-S-Au stretches around 1100 cm⁻¹. Atom colours: C (grey), H (white), N (blue), S (yellow).

The ArVSMes spectral shape resembles the high-concentration limit of ArVSMes@AuNPs and ArVSMes@CB[7]₂@AuNPs, again indicating ArVSMes z-alignment with the hotspot field and retention of (ArVSMes)₂@CB[8]₂ supramolecular structure. As with ArVSMes@CB[7]₂@AuNPs, (ArVSMes)₂@CB[8]₂ seems to dissociate at lower concentrations (<0.15 μM), evidenced by a decrease in ArVSMes signal intensity around ~400, 1200 and 1600 cm⁻¹, but less of a decrease for the more xy-polarised modes at ~815 and 1100 cm⁻¹. This is supported by the C-S-Au/C-S-Me stretch behaviour, with C-S-Au (1090 cm⁻¹) dominating at lower concentrations indicating a gap bridged by both ArVSMes (with large ϕ) and CB[8].

Another spectral difference of (ArVSMes)₂@CB[8]₂@AuNPs is the intensity of the C-S-Me stretch (1100 cm⁻¹) exceeding that of C-S-Au at higher concentrations. This is rationalised similarly to the ArVSMes@AuNPs system, based on dimerisation geometry (**Figure 4.13**). If (as hypothesised for ArVSMes@CB[7]₂) CB[8] encapsulation prevents bidentate Au-ArVSMes-Au

bridging, this should yield equal S-Au and SMe concentration if all $(\text{ArVSM}e)_2 \subset \text{CB}[8]_2$ bridge the gap (**Figure 4.21a**). This is consistent with the linearly offset geometry within the ArVSM e dimer,^{2,260,261} with only one thioanisyl moiety accessible either end.

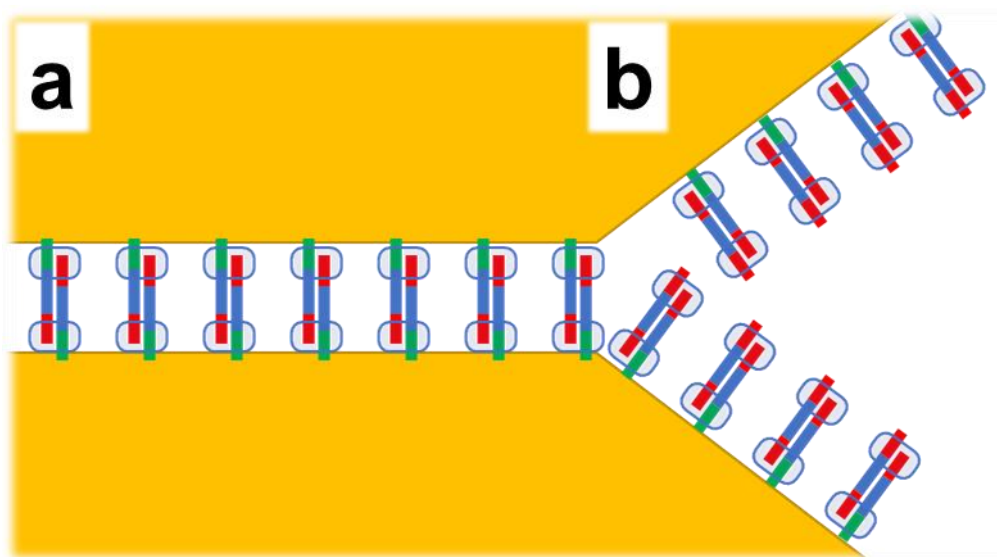


Figure 4.21. Schematic of hypothesised binding geometry of $(\text{ArVSM}e)_2 \subset \text{CB}[8]_2$ between two AuNPs, with S-Au and SMe groups highlighted as green and red, respectively (*cf.* **Figure 4.16**). **(a)** $(\text{ArVSM}e)_2 \subset \text{CB}[8]_2$ complexes that bridge the hotspot are predicted to have one SMe and one S-Au group per ArVSM e molecule due to the linearly offset ArVSM e dimer geometry. **(b)** Dangling $(\text{ArVSM}e)_2 \subset \text{CB}[8]_2$ complexes would have one S-Au group for the same reason, and three unbound SMe.

Consequently, unlike the $\text{ArVSM}e \subset \text{CB}[7]_2$ case, each dangling $(\text{ArVSM}e)_2 \subset \text{CB}[8]_2$ should contain one S-Au group and three unbound SMe (**Figure 4.21b**). Therefore, at higher $(\text{ArVSM}e)_2 \subset \text{CB}[8]_2$ concentrations, the unbound SMe (1100 cm^{-1}) intensity should increase further as the fraction of dangling spacers increases (*cf.* **Figure 4.16a-d**). These experiments were limited by the aqueous solubility of CB[8] ($\sim 0.1\text{ mM}$ ^{248,286}); the high-concentration limit of **Figure 4.20** likely represents the lower-concentration limit of this behaviour.

Again, the analogous $(\text{ArVH})_2 \subset \text{CB}[8]_2 @ \text{AuNPs}$ system (**Figure 4.22**) exhibits weaker ArV signals, with lower SNR than $(\text{ArVSM}e)_2 \subset \text{CB}[8]_2 @ \text{AuNPs}$. However, normalisation to the 440 cm^{-1} CB[8] resonance again yields double the relative ArVH spectral intensity compared to $\text{ArVH} \subset \text{CB}[7]_2 @ \text{AuNPs}$ (**Figure 4.19**), consistent with the $(\text{ArVH})_2 \subset \text{CB}[8]_2$ stoichiometry. The spectral shape of the $\sim 1200\text{--}1300\text{ cm}^{-1}$ band resembles that of $\text{ArVSM}e \subset \text{CB}[7]_2$, possibly implying vertical ArVH orientation and therefore retention of $(\text{ArVH})_2 \subset \text{CB}[8]_2$ structure. If so, this may also suggest structural retention of $\text{ArVH} \subset \text{CB}[7]_2$, based on the similar spectral shapes and stoichiometry-consistent ArVH/CB[n] intensity ratios.

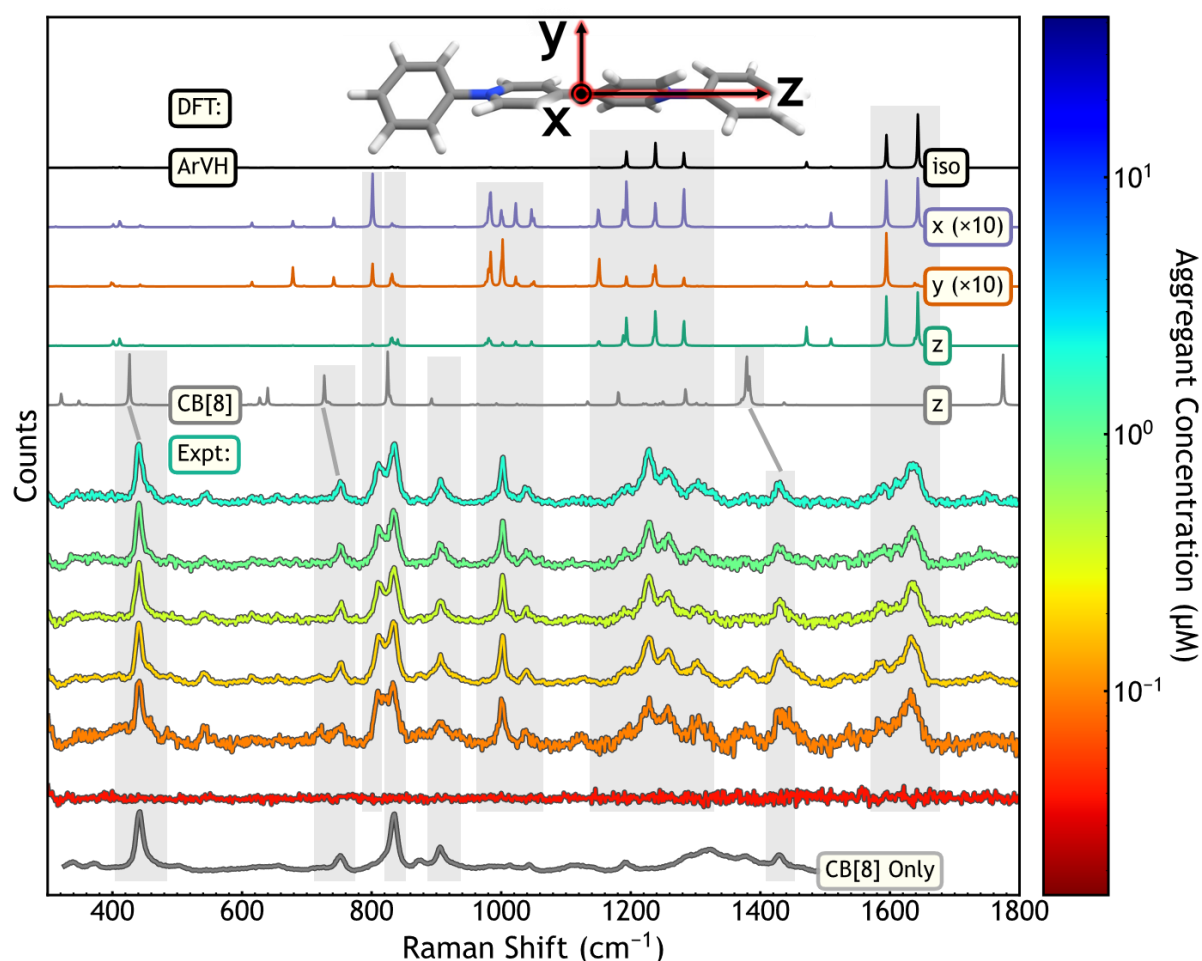


Figure 4.22. Top: DFT Raman spectra calculated for ArVH with isotropic and polarised excitation (axes indicated on ArVH structure inset) as in **Figure 4.14**, plus z-polarised spectrum of CB[8]. Note the required magnification of the x/y-polarised spectra. Bottom: experimental SERS spectra of aqueous $(\text{ArVH})_2\subset\text{CB}[7]_2\text{@AuNP}$ aggregates at a range of concentrations, normalised to the CB[8] resonance at 440 cm^{-1} . Grey shaded areas indicate corresponding predicted and experimental peaks. Atom colours: C (grey), H (white), N (blue).

Together, the experimental SERS data and polarised DFT Raman calculations demonstrate retention of $\text{ArVSMecCB}[n]$ supramolecular structure upon AuNP aggregation, provided $[\text{ArVSMecCB}[n]] > 0.15 \text{ mM}$. Similar evidence was obtained for analogous $\text{ArVH}\subset\text{CB}[n]\text{@AuNPs}$ systems, albeit with low SNR and questionable spectral agreement between theory and experiment. The $\text{ArVH}\subset\text{CB}[n]$ measurements should therefore be repeated with optimised incubation and/or integration times to improve spectral clarity before structural retention can be confirmed.

Comprehensive characterisation of each system would require complementary analysis techniques. TEM/SEM should help reveal AuNP gap geometry and/or d ; while inconclusive for BPc@AuNPs (**Section 3.4.2; Figure 3.11**), the large Δd expected between $\text{CB}[n]\text{@AuNPs}$ and $\text{ArV}\subset\text{CB}[n]\text{@AuNPs}$ should allow distinction between AuNP aggregates with and without $\text{ArV}\subset\text{CB}[n]$ structural retention. As discussed, quantitative XPS and/or STEM-EELS would help confirm the relative S-Me/S-Au hotspot populations. These techniques may also distinguish

between free and Au-coordinated carbonyl oxygens. If so, retention of $\text{ArV} \subset \text{CB}[n]$ structure may be detected via an excess of unbound carbonyls, as the inward-facing $\text{CB}[n]$ portals of the complexes are not expected to bind to Au.

4.6 $\text{ArV} \subset \text{CB}[n]$ Conclusion & Outlook

As a precursor to functional, modular supramolecular plasmonic spacers, this chapter explored nano self-assembly properties of $\text{ArV} \subset \text{CB}[n]$ complexes ($\text{ArV} = \text{ArVH}$, ArVSMe ; $n = 7, 8$; all previously synthesised²), and of the individual ArV and $\text{CB}[n]$ components. NPoM assembly was investigated using DF NPR spectroscopy,¹⁷ but SERS and PL behaviour were not explored. Aqueous AuNP aggregation was monitored with extinction spectroscopy, and solution-phase SERS was used to characterise binding and orientation of ArV and/or $\text{CB}[n]$ within the interparticle junctions. The AuNP aggregation experiments indicated some control over supramolecular structure within the hotspots, via aggregant concentration, for the $\text{ArV} \subset \text{CB}[n]$ systems.

The $\text{ArV} \subset \text{CB}[n]$ water solubility greatly simplified AuNP aggregation experiments compared to BPc. The thioether functionality of ArVSMe facilitated controlled plasmonic self-assembly with or without $\text{CB}[n]$, while $\text{ArV} \subset \text{CB}[n]$ assembly provided supramolecular control over molecular orientation within the cavity, paving the way for more complex systems.

Overall, the combination of NPoM DF/NPR, AuNP aggregate extinction and aggregate SERS data indicates that $\text{ArV} \subset \text{CB}[n]$ supramolecular structure can be retained upon AuNP self-assembly, under the right conditions. While $\text{CB}[n]$ may impart Au affinity to otherwise Au-inert molecules, incorporation of terminal SMe moieties appears to improve supramolecular stability within plasmonic hotspots. To reinforce conclusions and confirm hypotheses drawn in this chapter, several complementary experiments are recommended. First, $\text{ArV} \subset \text{CB}[n]$ NPoM assembly should be repeated to understand/optimize the effects of post-deposition SAM washing. NPoM DF NPR analysis should also be augmented with both PL and SERS measurements.

AuNP aggregate extinction and SERS data can be complemented with SEM or TEM to visualise nanocavity and aggregation geometry, providing evidence for both spacer geometry and concentration-dependent variation of interparticle facet overlap. Experiments are currently underway using ultra-spherical AuNPs and different AuNP size distributions to explore the effects of AuNP geometry and polydispersity on λ_{dim} . AuNP geometry investigations would also benefit from numerical FDTD simulations. Characterisation of ArVSMe -Au binding may be augmented with XPS and/or STEM-EELS measurements to provide ensemble and/or nanoscale information on the relative S-Au/S-Me bond populations. Depending on instrument sensitivity and C=O--Au coordination strength, these techniques

may also evidence ArV $\subset$ CB[n] structural retention or dissociation based on the fraction of carbonyl portals coordinated to Au.

So far, these experiments have focused mainly on nanostructure characterisation. Now that ArV $\subset$ CB[n]@AuNP self-assembly is within reach, several opportunities exist to explore the properties of this new system with experiments similar to those in **Section 1.4.1**. ArVs can be extended with myriad central moieties, which raises the possibility of similar scaffold-like systems containing molecular switches or electron transfer catalysts. Just as ArVH and ArVSMe served as model systems for exploring viologen $\subset$ CB[n]@AuNP assembly, they may also provide a knowledge base for the electrochemical, charge transport and charge transfer behaviour of encapsulated and/or dimerised functional extended viologens in plasmonic hotspots.

For example, Au connectivity differences between ArVH and ArVSMe should affect hot electron transport behaviour, as previously observed with NPoM SERS using smaller molecular spacers.²⁷ Exploring this behaviour for ArV $\subset$ CB[n] NPoMs should yield similar results regarding tunnel junction coherence and presence of electron-deficient heteroatoms, but would also uncover effects of intermolecular coupling by direct comparison of monomeric ArV $\subset$ CB[7]₂ and dimeric (ArV)₂ $\subset$ CB[8]₂ spacers. The redox and electron transport properties of the various ArV $\subset$ CB[n]@Au systems may be characterised even further using recently developed spectroelectrochemical⁹⁷ and junction bias²⁵ NPoM techniques.

However, given this new ability to self-assemble AuNPs with ArV $\subset$ CB[n] spacers, the next objective of this work is to incorporate chemical functionality into the ArV structure. **Chapter 5** explores the design, synthesis, supramolecular assembly and nano self-assembly properties of a functional, tetradentate ArV derivative, extended with a metal-ligating porphyrin core.

4.7 ArV $\subset$ CB[n] Methods

4.7.1 Computational Details

Gas-phase DFT calculations were performed using B3LYP^{446,447} with GD3BJ⁴⁴⁸ dispersion and Def2SVP basis set (including Def2SVP pseudopotential for Au atoms). Calculations were implemented (by myself) using an ultrafine integration grid in Gaussian 09 Rev. E.⁴⁵⁶ Directional components of DFT-calculated Raman spectra were extracted from the polarisability tensor as described elsewhere,⁴⁶⁸ using Python code written by David-Benjamin Gryns.⁵⁷

4.7.2 NPoM Assembly

Aqueous ArV (ArVH 2.05 mM; ArVSMe 2.10 mM; ArVHN₂ 1.98 mM) and CB[n] (CB[7] 1.0 mM; CB[8] 0.1 mM) solutions were prepared previously by Guanglu Wu^{2,261} and Zehuan Huang;^{275,286} concentrations were calibrated with ¹H-NMR and/or ITC. ArV $\subset$ CB[n] solutions were prepared by mixing ArV and CB[n] solutions in appropriate amounts to yield ArV $\subset$ CB[7]₂ and

$(\text{ArV})_2 \subset \text{CB}[8]_2$ stoichiometry, without further dilution. For preparation of single-component ArV or $\text{CB}[n]$ NPoMs, spacer solutions were used as received.

For each sample, fresh TSG was immersed in spacer solution for either 1-8 h or 24-48 h. For the latter, $\text{CB}[n]$ -free and $\text{CB}[7]$ -containing systems were incubated for 24 h; $\text{CB}[8]$ -containing systems required 48 h. AuNP ($D = 80$ nm) deposition was performed for 5-10 (ArV only) 15 ($\text{ArV} \subset \text{CB}[n]$) or 15-20 ($\text{CB}[n]$ only) seconds. See **Methods 7.2** for more details.

4.7.3 AuNP Aggregation

Aqueous ArV , $\text{CB}[n]$ and $\text{ArV} \subset \text{CB}[n]$ solutions (**Methods 4.7.2**) were diluted by factors of 1-500 to yield a logarithmic aqueous concentration series for each system. For each measurement, a small aliquot (10 μL for extinction spectroscopy (**Methods 7.4.3**); 6.8 μL for SERS (**Methods 7.4.4**)) of analyte solution was added to a 1 mL polystyrene cuvette (extinction) or 340 μL polypropylene multi-well plate (SERS). To this, AuNP solution (49:1 v/v) was added rapidly to ensure mixing, and spectra were collected either immediately (extinction) or after 60 s incubation (SERS).

5. M-TAPP $\subset$ CB[n]

5.1 M-TAPP $\subset$ CB[n] Introduction

The molecular spacers in this chapter combine insights from macrocyclic, metal-ligating BPCs (**Chapter 3**) and water-soluble, supramolecular ArV $\subset$ CB[n] complexes (**Chapter 4**). The new spacers (TAPP; **Figure 5.1**) are porphyrins augmented with *N*-(4-thioanisyl)pyridinium moieties, which form non-covalent CB[n] complexes similarly to ArVs/EVs and can ligate various transition metals. Terminal 4-thioanisyl functionality was chosen to facilitate M-TAPP@Au coordination, based on the ArVSMe behaviour in **Chapter 4**. TAPP is one example of a bespoke, EV-like molecular spacer capable of introducing advanced optoelectronic and chemical functionality into a plasmonic hotspot.

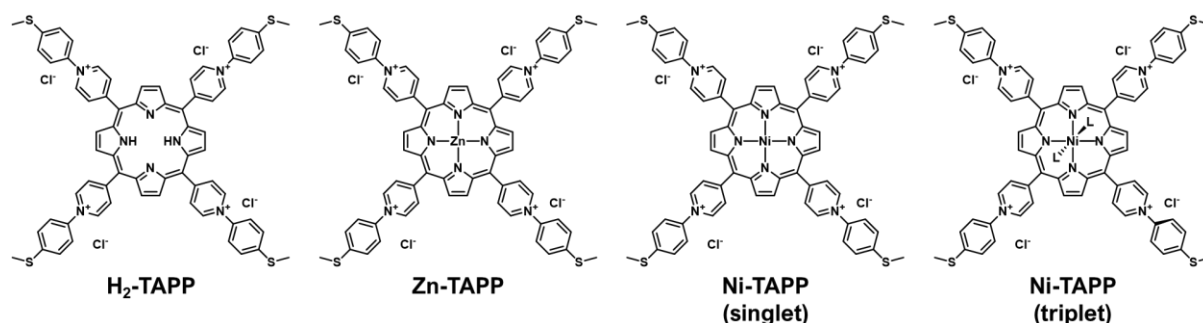


Figure 5.1. M-TAPP chemical structures used in this work.

The chapter first develops a synthetic route to TAPP and its metal complexes (M-TAPP; M = 2H, Ni, Zn; **Figure 5.1**). Aqueous stability, solvchromism and CB[n] complexation of M-TAPP is then investigated with liquid chromatography/mass spectrometry (LCMS) and NMR, UV-Vis and PL spectroscopy. Finally, M-TAPP $\subset$ CB[n] NPoM assembly is characterised with DF, PL and SERS. AuNP aggregation (*cf.* **Sections 4.2-4.5**) has not yet been performed and is the next step for plasmonic characterisation of this system.

Section 2.3 envisages an electrocatalyst whose reactivity can be influenced with supramolecular chemistry and plexcitonic coupling. Moving forward, future experiments should begin with spectroelectrochemical characterisation of M-TAPP and M-TAPP $\subset$ CB[n] to understand the optical absorption of the various complexes and their available redox states. The effects of AuNP geometry and applied potential upon the spectral response of M-TAPP($\subset$ CB[n]) NPoMs should then be explored to reveal the necessary conditions for plexcitonic coupling. Following this, the electrocatalytic behaviour of M-TAPP($\subset$ CB[n]) should be explored using model reactions (e.g., CO₂ reduction), both in solution and M-TAPP($\subset$ CB[n])@AuNP nanostructures, to explore effects of plexcitonic coupling upon transition metal catalysis.

5.1.1 Objectives & Hypotheses

M-TAPP was designed based on certain hypotheses, inspired by the properties of ArVs/EVs^{2,260,261,275} and cationic porphyrins.^{313,469–471} The four arylpyridinium groups should impart aqueous solubility and allow CB[n] complexation, while the porphyrin core is expected to ligate transition metals. The molecular rigidity should favour discrete (M-TAPP)₂ $\subset$ CB[8]₄ complexation, rather than the extended assembly observed for compounds with greater conformational entropy^{314–316,406} (**Scheme 2.5b**). The terminal SMe groups will likely improve M-TAPP-Au coordination (yielding well-defined nanocavities) and stabilise the positively-charged (M-TAPP)₂ $\subset$ CB[8]₄ dimer via electron donation.² The symmetric porphyrins should exhibit readily interpretable optical absorption/emission,^{357,472} aiding characterisation of M-TAPP $\subset$ CB[n] complexes and their orientation, structure and bonding within self-assembled plasmonic nanocavities.

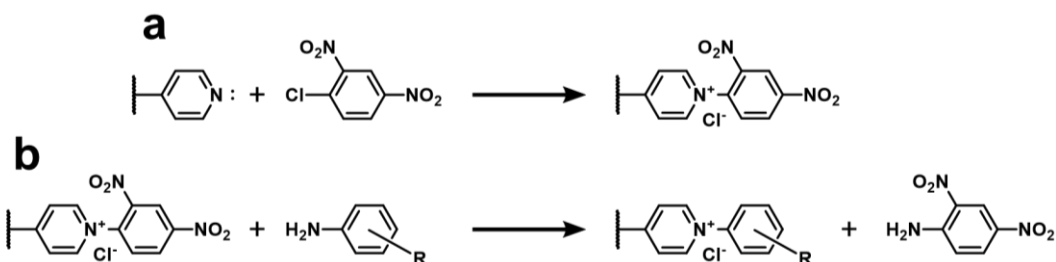
The first objective was to synthesise freebase H₂-TAPP from TPYP (**Figure 2.14d**) via the Zincke reaction (**Section 5.1.2**). The first synthetic step already existed,³⁴⁶ but no reports existed for the second. The initial objectives were therefore to reproduce the first step, then devise reaction conditions for the second. The final synthetic objective was to metallate H₂-TAPP and isolate the final M-TAPP products. The arylation and metallation procedures were expected to resemble existing EV syntheses^{260,261} and cationic porphyrin metallations.^{471,473,474}

The second goal was to confirm the hypothesised M-TAPP $\subset$ CB[7]₄ and (M-TAPP)₂ $\subset$ CB[8]₄ supramolecular structures, using NMR to probe the geometry, stoichiometry and internal dynamics of the complexes.^{260,261,275} Next, calibrated M-TAPP stock solutions were needed to reproduce the appropriate M-TAPP $\subset$ CB[n] stoichiometries, requiring NMR-based concentration measurements using an internal standard. The intense optical absorption expected of M-TAPP should allow UV-Vis calibration for faster subsequent concentration measurements.

Assuming reproducible M-TAPP $\subset$ CB[n] assembly, any consequent perturbation of the M-TAPP electronic structure may be probed with UV-Vis and PL spectroscopy. Based on similar ArV/EV $\subset$ CB[n] experiments,^{2,260,261,275} CB[7] should increase the PL QY of M-TAPP, while UV-Vis and PL redshifts are expected for (M-TAPP)₂ $\subset$ CB[8]₄. The final objective was to explore and characterise M-TAPP $\subset$ CB[n]@AuNP self-assembly (*cf.* **Chapter 4**), with additional PL and SERS measurements performed for the NPoM structures.

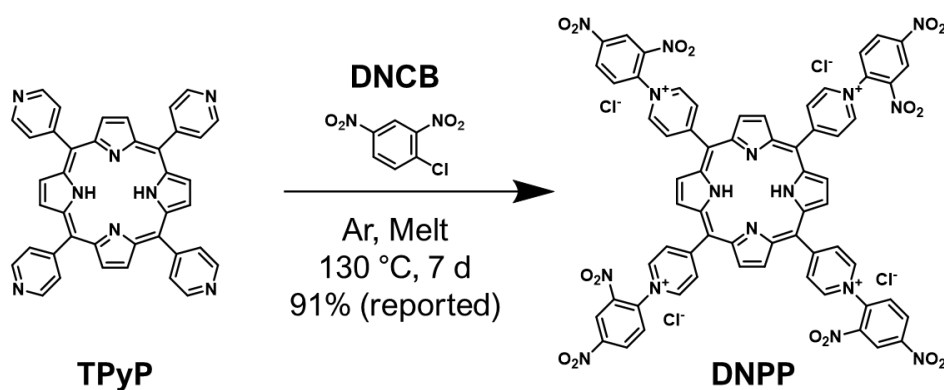
5.1.2 Synthetic Plan

ArVs/EVs are commonly synthesised via the Zincke reaction,^{475–477} which converts pyridyl groups to quaternary pyridinium salts via *N*-(2,4-dinitrophenyl)pyridinium intermediates (**Scheme 5.1**). First, 2,4-dinitrochlorobenzene (DNCB) and the pyridyl moiety react via nucleophilic aromatic substitution (S_N^{Ar}), yielding the *N*-(2,4-dinitrophenyl)pyridinium chloride (**Scheme 5.1a**). Subsequent treatment with a primary amine, e.g. an aniline (**Scheme 5.1b**), leads to nucleophilic attack on the pyridinium ring, sigmatropic rearrangement and elimination of 2,4-dinitroaniline (**Scheme A30**) to yield the *N*-arylpyridinium chloride.^{477,478}



Scheme 5.1. General form of the two-step Zincke reaction for synthesis of *N*-arylpyridinium compounds. **(a)** Pyridyl moiety is converted to *N*-(2,4-dinitrophenyl)pyridinium intermediate via S_N^{Ar} . **(b)** 2,4-dinitrophenyl group is replaced with an arbitrary aryl group using the appropriate aniline derivative. Both steps commonly take place in polar solvent under reflux. See **Scheme A30** for detailed mechanism.

This procedure is compatible with various aromatic functionality and appears suitable for creating TAPP. However, only one study³⁴⁶ reports synthesis of the 5,10,15,20-*tetrakis*(*N*-(2,4-dinitrophenyl)pyridinium-4-yl)porphyrin (DNPP) intermediate (**Scheme 5.2**); no previous reports exist for any other *tetrakis*(*N*-arylpyridinium)porphyrin species.

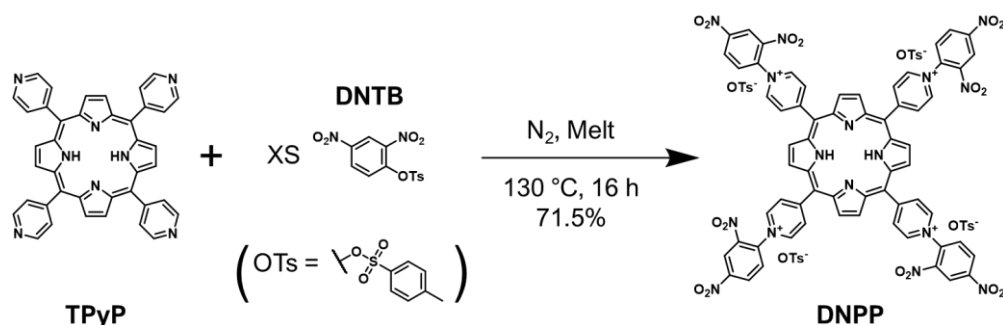


Scheme 5.2. Synthesis of 5,10,15,20-*tetrakis*(*N*-(2,4-dinitrophenyl)pyridinium-4-yl)porphyrin (DNPP), reported by Bříza *et al.*³⁴⁶ A high temperature, airless, solvent-free environment is required due to low pyridyl nucleophilicity and strongly electron withdrawing *N*-(2,4-dinitrophenyl)pyridinium groups.

For many ArVs/EVs, **Scheme 5.1a** uses relatively mild conditions (e.g. refluxing EtOH²⁶¹). However, for electron-deficient pyridyl precursors, the pyridyl nucleophilicity is lowered and harsher conditions are required.⁴⁷⁹ Here, Bříza *et al.*³⁴⁶ report a high-temperature (130 °C), solvent-free synthesis in a sealed vessel, likely necessitated by pyridyl nucleophilicity that decreases with each successive *N*-(2,4-dinitrophenyl)pyridinium formation. To avoid the need for separation of multiple cationic products, full conversion to *tetrakis*-DNPP is desired.

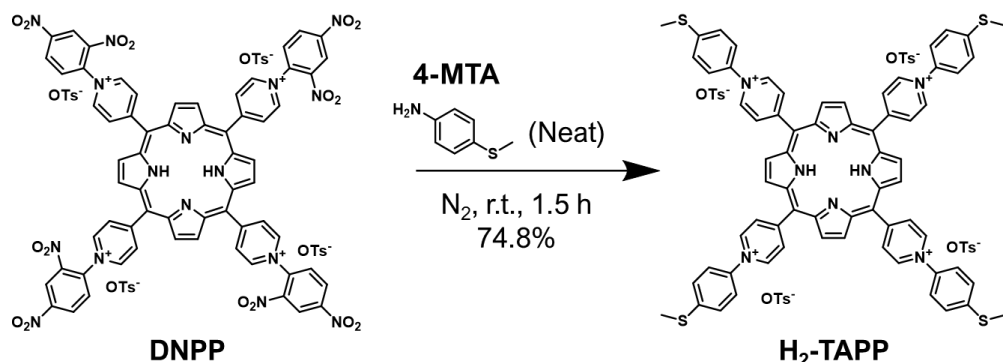
Otherwise, separation should be attempted via recrystallisation or, if unsuccessful, reverse-phase chromatography or high-performance liquid chromatography (HPLC).

Several DNPP synthesis attempts were performed using a glass pressure vessel, none of which yielded *tetrakis*-DNPP. DNCB was therefore replaced with 2,4-dinitrotosyloxybenzene (DNTB), a reactive DNCB analogue with a superior *p*-toluenesulfonate (tosylate; OTs) leaving group. An increased DNTB excess was also required to offset the viscosity increase caused by DNPP precipitation. Under these conditions (**Scheme 5.3**), full conversion occurs overnight at atmospheric pressure.



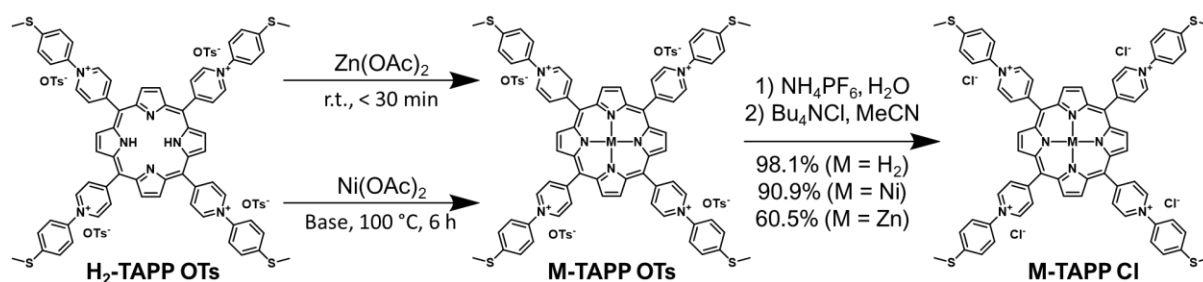
Scheme 5.3. Modified synthesis of DNPP using DNTB, a tosylated DNCB analogue. Superior leaving group and greater excess of DNTB yields a faster reaction at atmospheric pressure.

The second step (**Scheme 5.1b**) converts the 2,4-dinitrophenyl groups to 4-thioanisyl by addition of 4-methylthioaniline (4-MTA), the required conditions for which were previously unknown. After several attempts with different polar solvents and temperatures, solvent-free conditions were again superior; the reaction proceeded rapidly at room temperature in neat 4-MTA (**Scheme 5.4**).



Scheme 5.4. Synthesis of H₂-TAPP from DNPP and 4-methylthioaniline (4-MTA). Reaction proceeds rapidly in neat 4-MTA at room temperature.

The final step is ligation of transition metals; Ni and Zn were used as examples for this work. Zn, while less chemically interesting as a porphyrin centre, was chosen for its low metallation energy barrier;⁴⁷¹ Ni was selected for its stronger metal-porphyrin bond and chemically accessible 3*d* electrons.^{351,473,480,481} Metallation is achieved relatively simply by combining H₂-TAPP with M(II) salt (**Scheme 5.5**). Zn metallation occurs at room temperature, while Ni-TAPP requires basic conditions and elevated temperatures. Excess unreacted metal salt is then removed via ion exchange.^{470,471,474,480}



Scheme 5.5. Metallation of M-TAPP with M(II) acetate salt, followed by anion exchange from tosylate to chloride. Here, M = Ni, Zn.

Ion exchange was also required to improve M-TAPP water solubility, via conversion to the chloride salt. This was achieved by precipitation of M-TAPP with aqueous ammonium hexafluorophosphate (NH_4PF_6) to yield water-insoluble M-TAPP PF_6 , followed by precipitation from acetonitrile (MeCN) with tetrabutylammonium chloride (Bu_4NCl), yielding the corresponding water-soluble M-TAPP chlorides. This also removed unreacted metal salt from Ni-TAPP and Zn-TAPP.

5.1.3 Supramolecular and Nano Self-Assembly

Having established a synthetic route to M-TAPP, the next objective was to investigate $M\text{-TAPP} \subset \text{CB}[n]$ complexation using NMR spectroscopy. This is achieved²⁶¹ by titration of M-TAPP into $\text{CB}[n]$ in D_2O , which causes shifting/splitting of the $\text{CB}[n]$ ^1H resonances indicative of the complexed species. Provided $\text{CB}[n]$ remains in excess throughout, all M-TAPP molecules are expected to exist as $M\text{-TAPP} \subset \text{CB}[n]$. Therefore, using a known $\text{CB}[n]$ concentration, integration of the M-TAPP and complexed/uncomplexed $\text{CB}[n]$ signals allows determination of $M\text{-TAPP} \subset \text{CB}[n]$ stoichiometry and M-TAPP stock concentration. Comparing ^1H chemical shifts of complexed/uncomplexed M-TAPP and $\text{CB}[n]$ allows characterisation of $M\text{-TAPP} \subset \text{CB}[n]$ supramolecular geometry, while temperature-dependent signal broadening and splitting allow study of the intracomplex dynamics.

Intramolecular CT states of M-TAPP are influenced by the rotational freedom and surrounding environment of the pyridinium groups.³⁸⁶ Therefore, in addition to the expected PL QY changes and/or spectral shifts upon $\text{CB}[n]$ complexation, complementary optical reporting of $M\text{-TAPP} \subset \text{CB}[n]$ geometry and dynamics is possible via PL spectral shape. This information also aids PL analysis of $M\text{-TAPP} \subset \text{CB}[n]$ NPoMs, whereby deviation from the solution phase behaviour may reveal supramolecular geometry perturbation, M-TAPP-Au interactions and/or external heavy atom effects.^{119,120}

$M\text{-TAPP} \subset \text{CB}[n]$ NPoMs are prepared similarly to $\text{ArV} \subset \text{CB}[n]$ NPoMs (**Chapter 4**), using comparable SAM and AuNP deposition procedures. Care should be taken to avoid prolonged contact with fresh water during SAM rinsing. AuNP aggregation experiments, while not yet conducted, should be performed next and may be analysed similarly to the $\text{ArV} \subset \text{CB}[n]$ systems.

5.2 M-TAPP Synthesis

This section summarises development of a synthetic route to M-TAPP (see **Methods 5.10.1**, **Appendix 8.4.2** for full details). **Section 5.2.1** describes attempts to reproduce the DNPP synthesis of Bříza *et al.*,³⁴⁶ followed by improvement/optimisation of the procedure. **Section 5.2.2** outlines development of a synthetic method for conversion of DNPP to TAPP, beginning with known conditions for analogous ArV systems.^{2,260,261} As these experiments were performed in parallel, initial TAPP syntheses were performed with various mixtures of *mono*-, *bis*-, *tris*- and/or *tetrakis*-DNPP obtained from preliminary DNPP synthesis attempts. Lastly, a pathway to TAPP metallation with Ni and Zn was developed, together with an optimised anion exchange procedure (**Section 5.2.3**).

5.2.1 DNPP

Several issues were experienced during attempts to reproduce the reaction³⁴⁶ in **Scheme 5.2**. TPyP and excess DNCB were added to a heavy-walled glass reaction tube in a N₂ glovebox, and sealed. The mixture was then stirred for 7 days at 130 °C in a blast-containment fumehood. After cooling, the mixture was dispersed with acetone and filtered/washed. Bříza *et al.*³⁴⁶ report using this product without further purification.

Experimentally, the acetone wash was insufficient to purify the sticky, amorphous solid, and the opaque red/brown filtrate indicated significant loss of product. ¹H-NMR analysis of the remaining red/brown precipitate revealed DNCB contamination even after multiple washes (**Figure 5.2**).

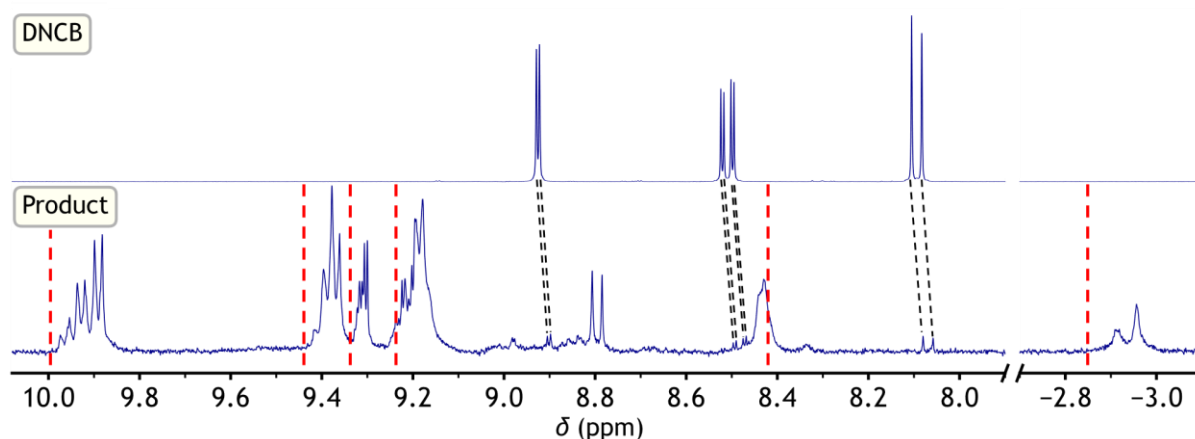


Figure 5.2. ¹H-NMR spectra of first DNPP synthesis product (bottom) and DNCB precursor (top) in d₆-DMSO. Black dashed lines indicate DNCB peak positions in DNPP product spectrum; red dashed lines show DNPP peak positions reported by Bříza *et al.*³⁴⁶

While the aromatic ($8.4 < \delta < 10$ ppm) ¹H multiplet positions almost agree with the existing report,³⁴⁶ the two resonances at negative ppm indicate otherwise. The core NH protons of freebase porphyrins lie inside the aromatic 18-electron π -system and are shifted significantly upfield (to negative δ) due to strong effective shielding by the diamagnetic ring current.⁴⁸² The

NH resonances in this uncrowded spectral region allow characterisation of subtle ring current perturbations from, e.g., the number of cationic *N*-(2,4-dinitrophenyl)pyridinium groups. The presence of multiple peaks in this region therefore indicates a mixture of porphyrin species.

To identify the degree of DNPP pyridyl conversion, LCMS analysis was performed (**Methods 5.10.2**). Two distinct chromatogram peaks were observed (**Figure 5.3a**), the mass spectra of which indicate *bis*- and *tris*-DNPP (**Figure 5.3b**). FTIR analysis confirmed presence of NO₂ groups in the product (**Figure A31**).

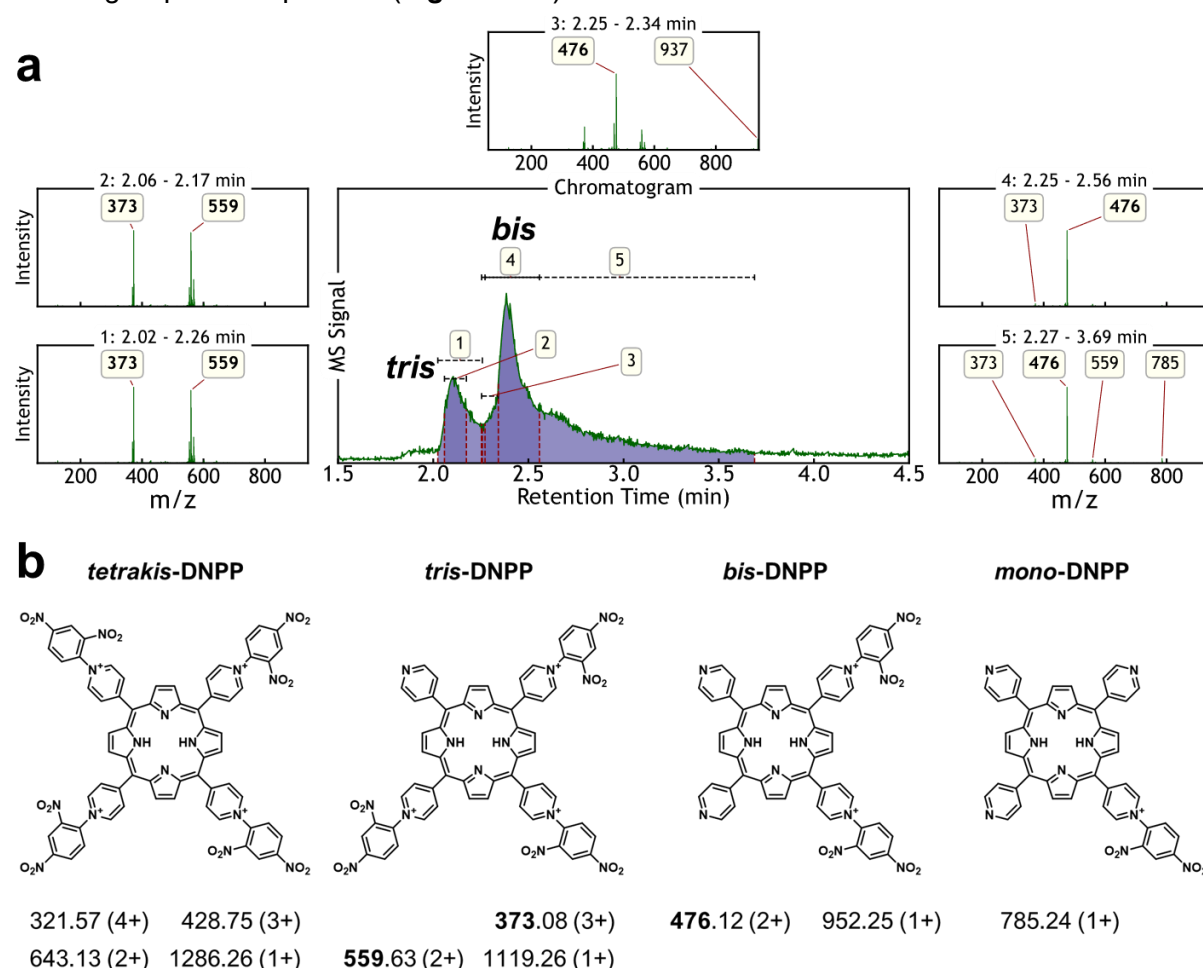


Figure 5.3. (a) Experimental LCMS data for the first DNPP synthetic attempt. Central plot is the chromatogram, surrounding plots are mass spectra integrated over the time ranges indicated. (b) *m/z* values for the different possible charge states of the possible DNPP product structures, predicted using ChemDraw Professional 16.0 (for clarity, only one isomer of *bis*-DNPP is displayed).

To increase conversion, the synthetic procedure was modified slightly. TPyP was first melted together with an increased excess of pre-dried DNCP and cooled/solidified under N₂ flow, after which the reaction vessel was transferred to a glovebox and sealed as before. The reaction setup was enveloped in foil to minimise heat loss. After 7 days at 130 °C, the mixture was dispersed in acetone, and centrifuged instead of filtered. Acetone washing/centrifugation was repeated until the supernatant contained no DNCP, confirmed with thin layer chromatography (TLC).

This procedure improved the DNPP yield, but had little effect on conversion, with NMR (**Figure 5.4**) and LCMS (**Figures A32, A34**) results indicating similar proportions of *bis*- and *tris*-DNPP. MeCN recrystallisation (**Figure 5.4c,d**) increased the relative *tris*-DNPP yield but spectral broadening (**Figure A35**) indicated DNPP instability under recrystallisation conditions. Trituration with cold MeCN had no effect.

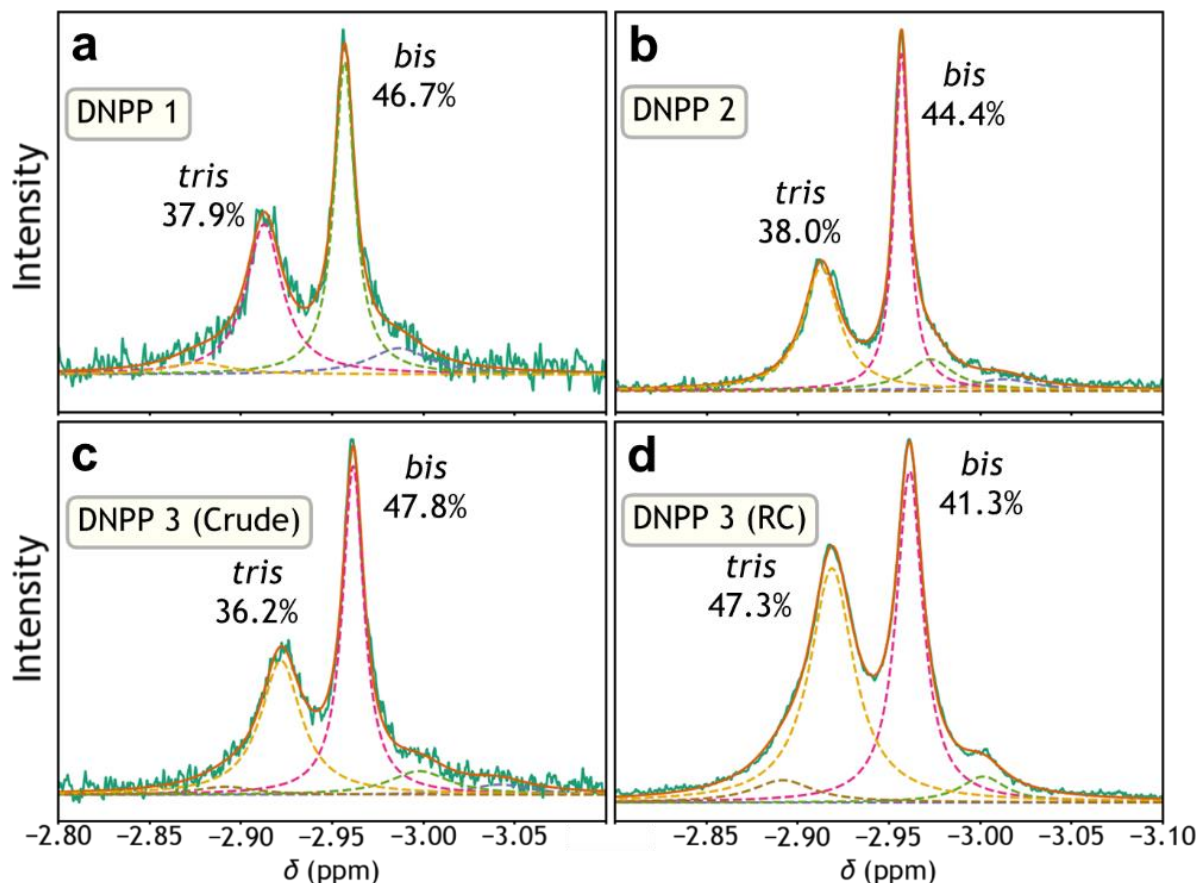
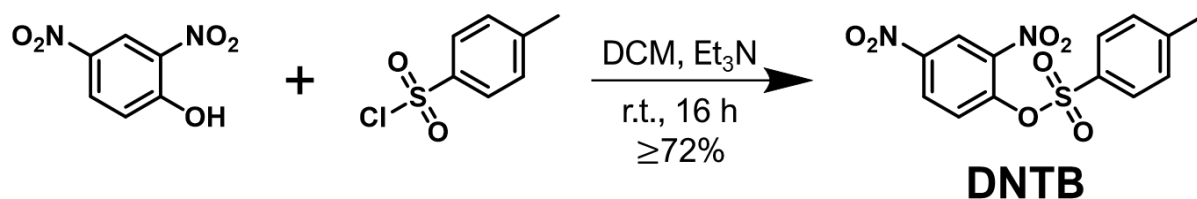


Figure 5.4. ^1H -NMR spectra (truncated to porphyrin core NH δ region) of attempted DNPP synthetic products 1, 2 and 3 (**a-c**). MeCN-recrystallised (RC) DNPP #3 spectrum (**d**) is also shown. Percentages based on integrated component areas of multi-Lorentzian fit.

The existing procedure therefore appeared unsuitable for full conversion of TPyP to *tetrakis*-DNPP, regardless of care taken to eliminate air/water from the reaction. The harsh conditions and long reaction times required for **Scheme 5.2** indicate low TPyP/DNCB reactivity. Quaternisation of the pyridyl groups creates an electron-withdrawing effect that decreases the porphyrin core basicity⁴⁸³ and therefore, most likely, the nucleophilicity of the remaining unreacted pyridyl moieties.

The solvent-free reaction conditions already represent the highest possible DNCB concentration. Increasing the temperature or pressure further may increase reaction rate, but this also raises safety concerns. To increase the reaction rate therefore requires an increase in nucleophilicity or electrophilicity of TPyP or DNCB, respectively. Attempts to increase TPyP nucleophilicity via deprotonation with DBU generated multiple unknown side products and were quickly discontinued. Increasing the electrophilicity of DNCB was far more successful;

replacing the chloride leaving group with tosylate yields the more reactive DNTB (**Scheme 5.3**).^{311,479} This was synthesised using a literature procedure⁴⁷⁹ (**Scheme 5.6**) and recrystallised from EtOAc (**Methods 5.10.1**).



Scheme 5.6. DNTB synthesis from 2,4-dinitrophenol and tosyl chloride in DCM with non-nucleophilic base triethylamine (Et₃N).

Subsequent reactions of TPyP (or *bis/tris*-DNPP mixtures from earlier attempts) with molten DNTB at 130 °C (**Scheme 5.3**) were performed under N₂ flow (rather than a sealed vessel) and yielded significant amounts of *tetrakis*-DNPP after 16 h (**Figures 5.5a, A36**). Continuing the reaction for 6 days, while increasing the *tetrakis*-DNPP yield, still yielded significant amounts of *bis/tris*-DNPP (**Figures 5.5b, A38**). Room-temperature trituration of the mixture from *N,N*-dimethylacetamide (DMAc) solution into MeCN slightly decreased the proportion of *bis*-DNPP, although not substantially (**Figure 5.5c**).

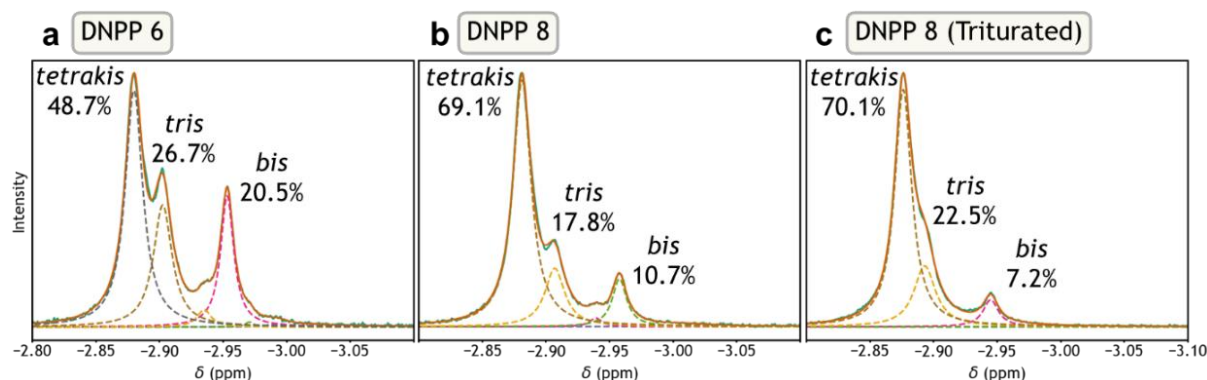


Figure 5.5. ¹H-NMR spectra (porphyrin core NH region) of (a) DNPP #6 (16 h reaction), (b) crude DNPP #8 (6 d reaction) and (c) DNPP #8 after room-temperature trituration from DMAc into MeCN. See **Figures A36, A38** for corresponding LCMS data.

This indicates that full conversion may simply require a longer reaction. Experiments were therefore planned with different reaction times to determine the necessary time for 100% conversion to *tetrakis*-DNPP. However, after 6 h reaction time, precipitation of DNPP was found to increase the reaction mixture viscosity and prevent stirring, despite the large DNTB excess. This was previously unnoticed due to the opaque foil cladding used for insulation. Adding 50% more DNTB to the melt allowed effective stirring, and complete conversion of TPyP to *tetrakis*-DNPP was achieved overnight.

The optimised general synthesis is as follows. TPyP and DNTB (1:60 mol/mol) are crushed together and dried under vacuum for 24 h. In a Schlenk flask, the powder is purged (repeated vacuum/refill) with N₂, heated to 130 °C and stirred overnight as a melt. The mixture is cooled, dissolved in DMAc and filtered; the stirred filtrate is then precipitated with dropwise addition

of acetone. The suspension is centrifuged and the precipitate washed with acetone via repeated agitation and centrifugation. The precipitate is then dissolved in MeOH/MeCN (1:1 v/v), precipitated with diethyl ether (Et₂O) and centrifuged/washed several times as above. The precipitate is dried under vacuum for 12-24 h to yield dark red DNPP tosylate. LCMS data is shown in **Figure 5.6**; see **Section 5.3** for ¹H-NMR spectrum and **Methods 5.10.1** for full synthetic details.

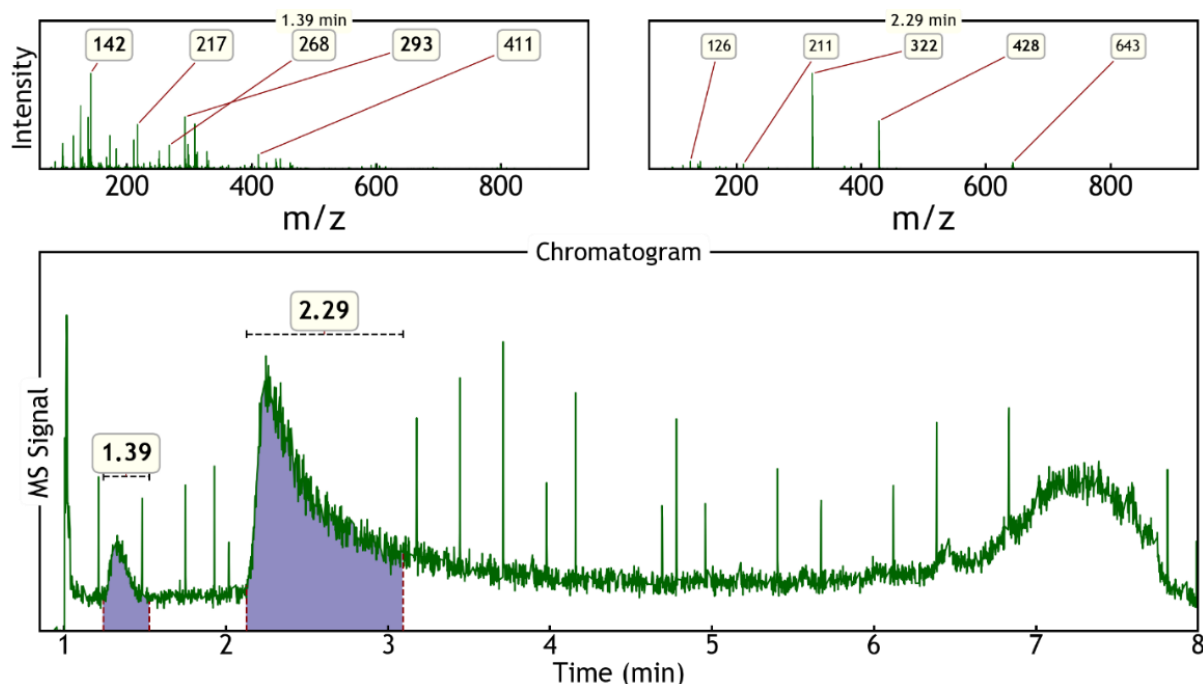


Figure 5.6. *tetrakis*-DNPP LCMS data. *m/z* 322 (DNPP⁴⁺), 428 (DNPP³⁺), 643 (DNPP²⁺). Peak at 1.39 min attributed to residual column contamination based on clean ¹H-NMR spectrum of product (**Section 5.3**). No *mono*-, *bis*-, or *tris*-DNPP were detected. The sharp signal spikes in the chromatogram are caused by a detector error, but do not otherwise affect the accuracy of the data.

5.2.2 TAPP

Parallel to the DNPP synthesis experiments, attempts were made to convert the DNPP mixtures into the corresponding TAPP compounds using 4-MTA (**Scheme 5.4**). The first attempts, based on existing ArV/EV syntheses,^{2,260,261} involved reflux of **DNPP #2** mixture with 4-MTA in MeOH or EtOH under N₂. However, the expected 2,4-dinitroaniline side product^{477,478} was not observed with TLC, and NO₂ groups were still present in the FTIR spectrum (**Figure A47a**) of the product (obtained by precipitation with THF or Et₂O).

The reaction was repeated at 135 °C and 180 °C in DMAc. 2,4-dinitroaniline was observed via TLC for the latter after 20 h, NO₂ peaks were absent from the product FTIR spectrum (**Figure A47b**), and the UV-Vis spectrum exhibited a new thioanisyl absorption² around 250 nm (**Figure A48**). LCMS analysis indicated presence of *bis/mono*-TAPP, along with several other products (**Figure 5.7**). This is inconsistent with the *tris/bis*-DNPP starting material, indicating some *N*-arylpyridinium decomposition and unwanted side products, supported by three broad peaks in the low- δ porphyrin NH ¹H-NMR region (**Figure A47c**).

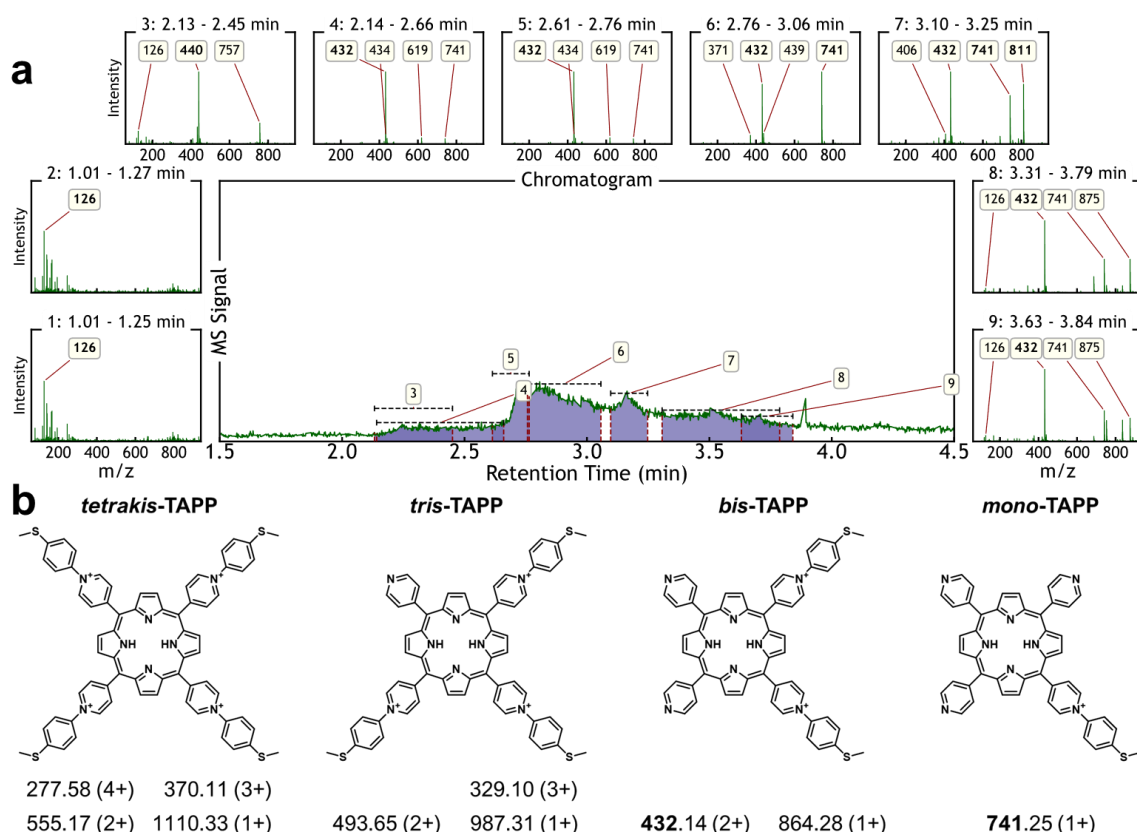


Figure 5.7. (a) LCMS data for **TAPP #1** synthesis attempt (using **DNPP #2** as a precursor). (b) Structures and predicted m/z values for various charge states of the possible TAPP product structures. Data indicates a mixture of *mono*- and *bis*-TAPP (masses indicated in bold in (b)), indicating product decomposition given the *bis*- and *tris*-DNPP starting mixture.

Conversion of DNPP to TAPP is therefore possible, although stability is affected by high temperatures and long reaction times. The reaction was repeated several times (**Appendix TAPP #4 - TAPP #8**) at 120 °C, with increasing care taken to minimise air/water/light exposure. Aliquots were extracted regularly, quenched in cold MeOH and analysed with UV-Vis. Variable spectral shifts were observed over time, and LCMS & $^1\text{H-NMR}$ results indicated mixed synthetic success. LCMS revealed mixed *mono*-, *bis*-, *tris*- and/or *tetrakis*-TAPP species (depending on the DNPP starting mixture used) contaminated with unknown side products; the $^1\text{H-NMR}$ spectra were often indecipherable.

Predictably, exclusion of air and water improved product yield and purity, although not reproducibly. More important, however, appeared to be the order of mixing of reactants and solvent. Specifically, exposure of crude DNPP solid to neat 4-MTA before dissolution yielded the most recognisable products. Inspired by the solvent-free DNPP synthesis (**Section 5.2.1**), subsequent TAPP syntheses were performed in neat 4-MTA. Stirring powdered crude (*bis/tris/tetrakis*)-DNPP in 4-MTA under N_2 for 2 hours at room temperature, followed by Et_2O trituration/centrifugation, yields LCMS data consistent with a (*bis/tris/tetrakis*)-TAPP mixture (**Figure 5.8**).

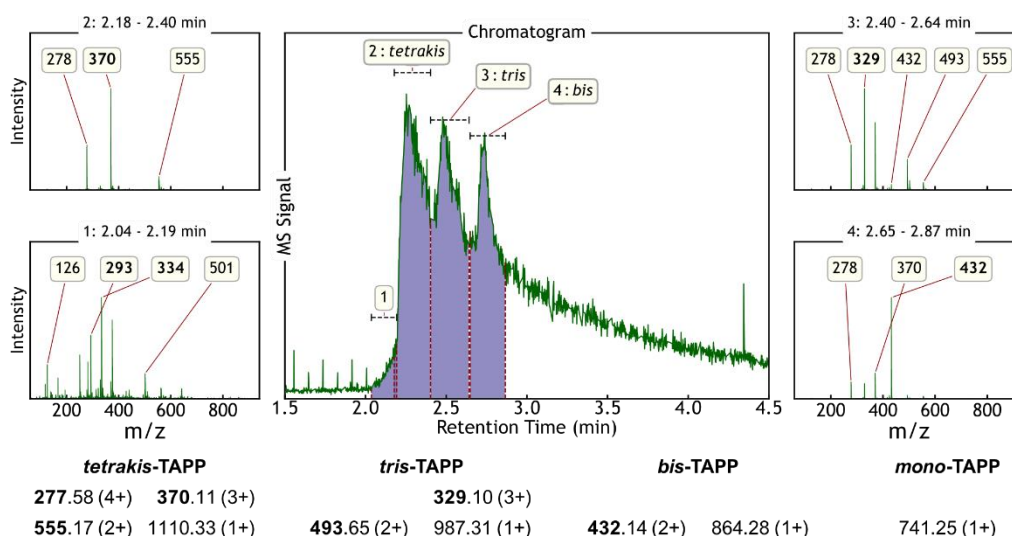


Figure 5.8. LCMS data for **TAPP #10**. Room-temperature reaction of **DNPP #8** with 4-MTA yields corresponding mixture of *tetrakis*-, *tris*- and *bis*-TAPP, with minimal side products detected.

The ^1H -NMR spectra (**Figures A65, A67**) exhibit clear, sharp resonances and splitting patterns consistent with *tetrakis*-TAPP, plus smaller multiplets from *bis*/*tris*-TAPP. Analysis of the low- δ core NH region (**Figure A68**) reveals a dominant (>80%) *tetrakis*-TAPP resonance with a small (10%) neighbouring signal from *bis*- and/or *tris*-TAPP.

Repeating this reaction with pure *tetrakis*-DNPP from the final optimised synthesis in **Section 5.2.1** yielded the corresponding pure *tetrakis*-TAPP tosylate. Again, the optimised synthesis is as follows (see **Methods 5.10.1, Section 5.3** for full details and characterisation). In a Schlenk flask, gently stirred powdered *tetrakis*-DNPP is purged with N_2 , then covered with neat 4-MTA (~1 mL per 200 mg DNPP). The mixture is stirred for 1-2 h, then dissolved in minimum DMAc and filtered. The filtrate is precipitated slowly with Et_2O and centrifuged. The precipitate is washed several times with Et_2O , redissolved in DMAc and precipitated/centrifuged/washed again with Et_2O . The precipitate is dried to yield crude *tetrakis*-TAPP as a red solid. The main contaminant (DMAc) is used during subsequent metallation and ion-exchange steps (**Section 5.2.3**); the crude product was therefore used immediately without further purification.

5.2.3 Metallation and Ion Exchange

Following successful *tetrakis*-TAPP synthesis, the next objective was metallation. While a wider range of metal centres can and should be explored, Ni and Zn-TAPP were chosen as examples here. Porphyrin metallation with Zn is usually straightforward and offers a closed-shell, diamagnetic product for easy NMR and UV-Vis characterisation.^{471,484,485} Zn porphyrins often appear green in colour, exhibiting redshifted optical absorption with significant extinction above 600 nm. Zn-TAPP is therefore a promising candidate for achieving plexcitonic nanocavity-porphyrin coupling with the AuNP nanostructures in this work.¹²⁰

Ni-TAPP is more complex, containing an open-shell metal centre with different available spin/oxidation states, chemically accessible 3d electrons and variable spectroscopic behaviour^{470,473,481,486} (**Sections 5.3-5.8**). The strong Ni-porphyrin bond is accompanied by a higher metallation activation energy, requiring harsher reaction conditions than Zn-TAPP.⁴⁷¹

Zn-TAPP is synthesised by exposing freebase TAPP (hereafter denoted H₂-TAPP) to a slight excess of Zn(II) salt in solution; metallation was performed for 30 min in warm DMAc immediately prior to ion exchange (described below). Contrastingly, Ni-TAPP synthesis required a 10x excess of Ni(II) salt, elevated temperatures (~100 °C), basic conditions and 6 h reaction time to achieve full metallation.⁴⁸⁰ See **Methods 5.10.1** for details.

In both cases, removal of excess metal salt was required to obtain pure M-TAPP products. As aqueous solubility is desirable for CB[n] complexation and future AuNP assembly, the sparingly water-soluble M-TAPP tosylate was converted to the more hydrophilic chloride salt. While ion exchange resins exist for this,^{313,386,487} another simple method involves sequential precipitation using aqueous NH₄PF₆^{311,480} followed by Bu₄NCl. This method has been used to remove excess metal salt after M-TMPyP synthesis^{470,471,480} and should be applicable here.

A general anion exchange procedure is as follows. A concentrated aqueous⁴⁸⁰ or methanolic³¹¹ solution of the tosylate salt is precipitated by dropwise addition of concentrated aqueous NH₄PF₆. The precipitate is filtered, washed with water and redissolved in MeCN. This solution is then precipitated by dropwise addition of concentrated Bu₄NCl in MeCN and filtered to yield the solid chloride salt, which is then washed with MeCN and dried.

As M-TAPP tosylates have poor aqueous solubility, initial anion exchange attempts used MeOH as the starting solvent. The above procedure yielded products with decreased d₆-DMSO solubility and barely improved aqueous solubility compared to the tosylate starting materials. Despite absence of ³¹P or ¹⁹F NMR signals in the d₆-DMSO supernatant after attempted product dissolution, residual MeCN solubility of the remaining solid implied incomplete anion exchange. To minimise co-precipitation of different counterions, a modified method was developed. See **Methods 5.10.1** for full details.

For each system, ~2% v/v of saturated aqueous NH₄PF₆ was added to a warm (45 °C), stirred M-TAPP/DMAc solution over 10 min. The solution was precipitated gradually with deionised water, centrifuged, and the precipitate washed several more times with water. This step was performed twice, followed by redissolution in DMAc and further precipitation, centrifugation and washing with water. The procedure was then repeated, this time using saturated Bu₄NCl in MeCN (again performed twice), followed by MeCN precipitation from DMAc, centrifugation and washing. To remove DMAc, the precipitate was redissolved in MeOH/MeCN (1:1 v/v), precipitated/centrifuged/washed with Et₂O, then dried under vacuum overnight to yield the M-TAPP chloride.

The final products were soluble in d₆-DMSO and characterised with ³¹P, ¹⁹F and ¹H-NMR, which confirmed removal of tosylate, PF₆⁻ and tetrabutylammonium ions (**Figures A69, A70**).

Addition of aqueous NH₄PF₆ and water to control solutions of M(II) acetate in warm DMAc did not cause precipitation; contamination of M-TAPP products with unreacted metal salt is therefore unlikely. The M-TAPP chlorides exhibit higher water and MeOH solubility than H₂-TAPP tosylate, and similar solubility in DMAc and DMSO. The compounds are completely insoluble in neat MeCN, but extremely soluble in MeOH/MeCN or H₂O/MeCN mixtures containing 10-90% MeCN (v/v); replacing MeCN with acetone yields similar results. M-TMPyPs behave similarly, likely due to cooperative solvation of the amphiphilic porphyrin structure.⁴⁷⁰ Also in agreement with literature is the higher water solubility of Zn-TAPP than H₂-TAPP or Ni-TAPP.⁴⁷¹

5.3 Characterisation & Calibration

This section summarises and discusses DNPP, H₂-TAPP and M-TAPP characterisation data. For full details, see **Methods 5.10.1 & Appendix 8.4.2**. The ¹H-NMR, UV-Vis and PL spectra reported in this section were recorded in organic solvents. Different spectral behaviour was observed in water and is discussed in **Sections 5.4-5.5**.

The LCMS data of the final products indicates full conversion of TPyP to *tetrakis*-DNPP, full replacement of all 2,4-dinitrophenyl groups with 4-thioanisyl in H₂-TAPP and complete metallation of Ni- and Zn-TAPP, with no H₂-TAPP remaining. All ¹H-NMR spectra (in d₆-DMSO) exhibit chemical shifts and spectral splitting consistent with a single APP species in solution. Concurrently, the DNPP and H₂-TAPP spectra each contain one resonance in the $\delta < 0$ porphyrin region, the absence of which for Ni- and Zn-TAPP indicates complete metallation. Finally, the optical absorption and emission spectra (in 1:1 MeOH/MeCN) exhibit behaviour characteristic of freebase, Zn and Ni porphyrins. Observed spectral variations are attributed to intramolecular CT, metal spin state and/or dark excited states.

5.3.1 LCMS

DNPP tosylate and H₂-TAPP chloride exhibit one main LC peak (**Figures 5.6, 5.9a**), the integrated mass spectrum of which corresponds only to the *tetrakis* compound in both cases. Addition of Zn or Ni is reflected in the mass spectra, and no LC peak is observed for non-metallated H₂-TAPP in either case (**Figure 5.9**). A secondary LC peak with shorter retention time was observed for all M-TAPP chloride systems, indicating a more polar compound (based on the non-polar LC column; **Methods 7.2**). Certain porphyrins photocatalyse oxidation of thioethers to sulfoxides,⁴⁸⁸ and the mass spectra of the contaminants here indicate oxidation of one SMe group (i.e. M-TAPP + O). This LC signal increases in intensity in the order Ni < H₂ < Zn, which correlates with the relative photosensitising power expected of each.⁴⁸⁹ This is explored further in **Section 5.5**.

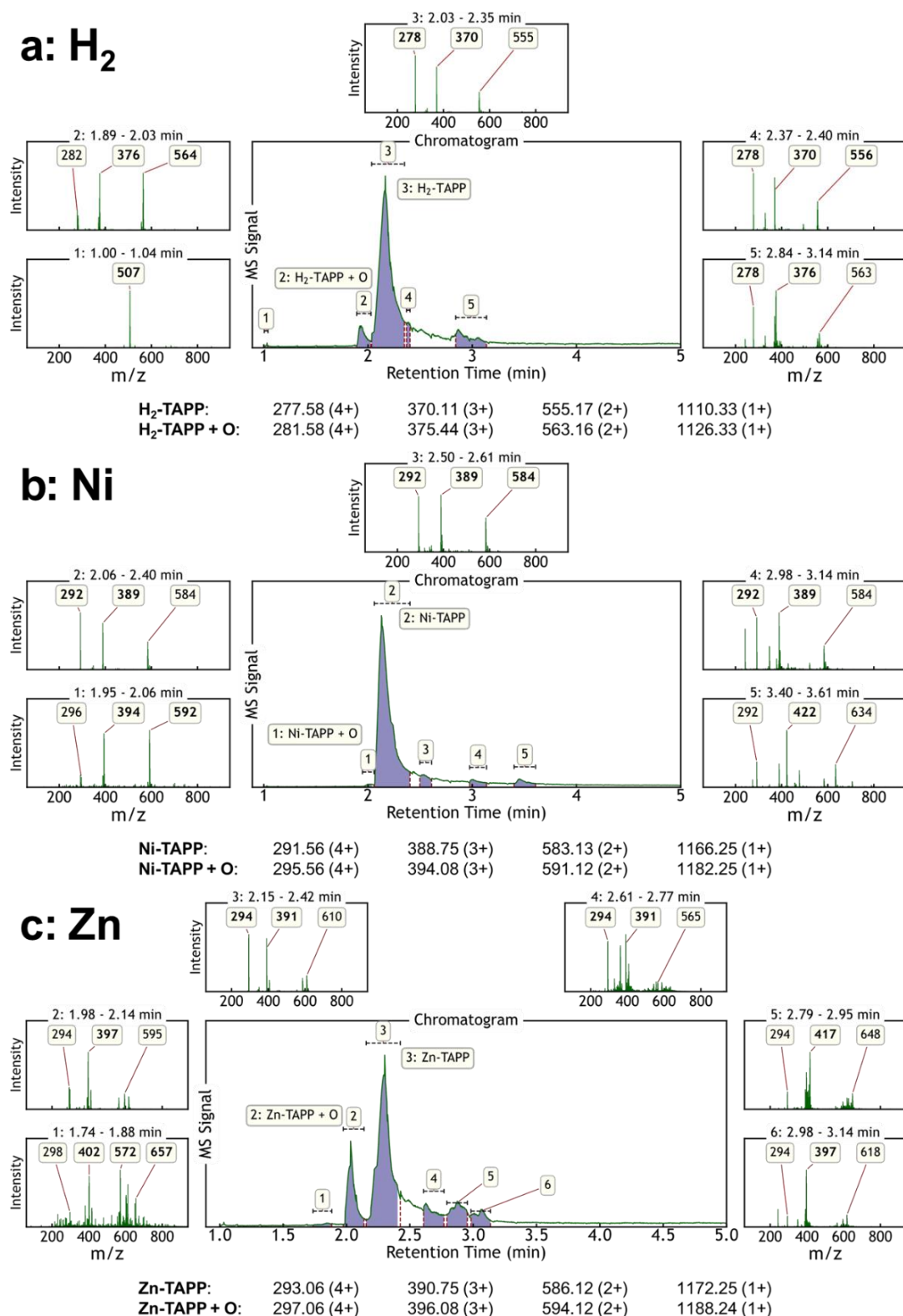


Figure 5.9. LCMS data for (a) H₂-TAPP, (b) Ni-TAPP and (c) Zn-TAPP (all chloride salts), indicating successful metallation in the latter two. Zn-TAPP exhibits a significant secondary peak at shorter retention times, with m/z values consistent with one extra oxygen atom per molecule (i.e. oxidation of SMe to S(=O)Me). The same peak is present, but less intense for H₂- and Ni-TAPP.

5.3.2 NMR

The ¹H-NMR spectra (in d₆-DMSO) exhibit clear, sharp resonances for all DNPP and TAPP compounds (**Figure 5.10**), with chemical shifts and splitting patterns consistent with APP compounds uncontaminated by other aromatic or porphyrinoid species. For DNPP, this contrasts with the multiplets in the aromatic region reported by Bříza *et al.*,³⁴⁶ which indicate a mixture of partially-converted DNPP products (*cf.* **Figure A39**), in contrast to the pure *tetrakis*-DNPP reported here.

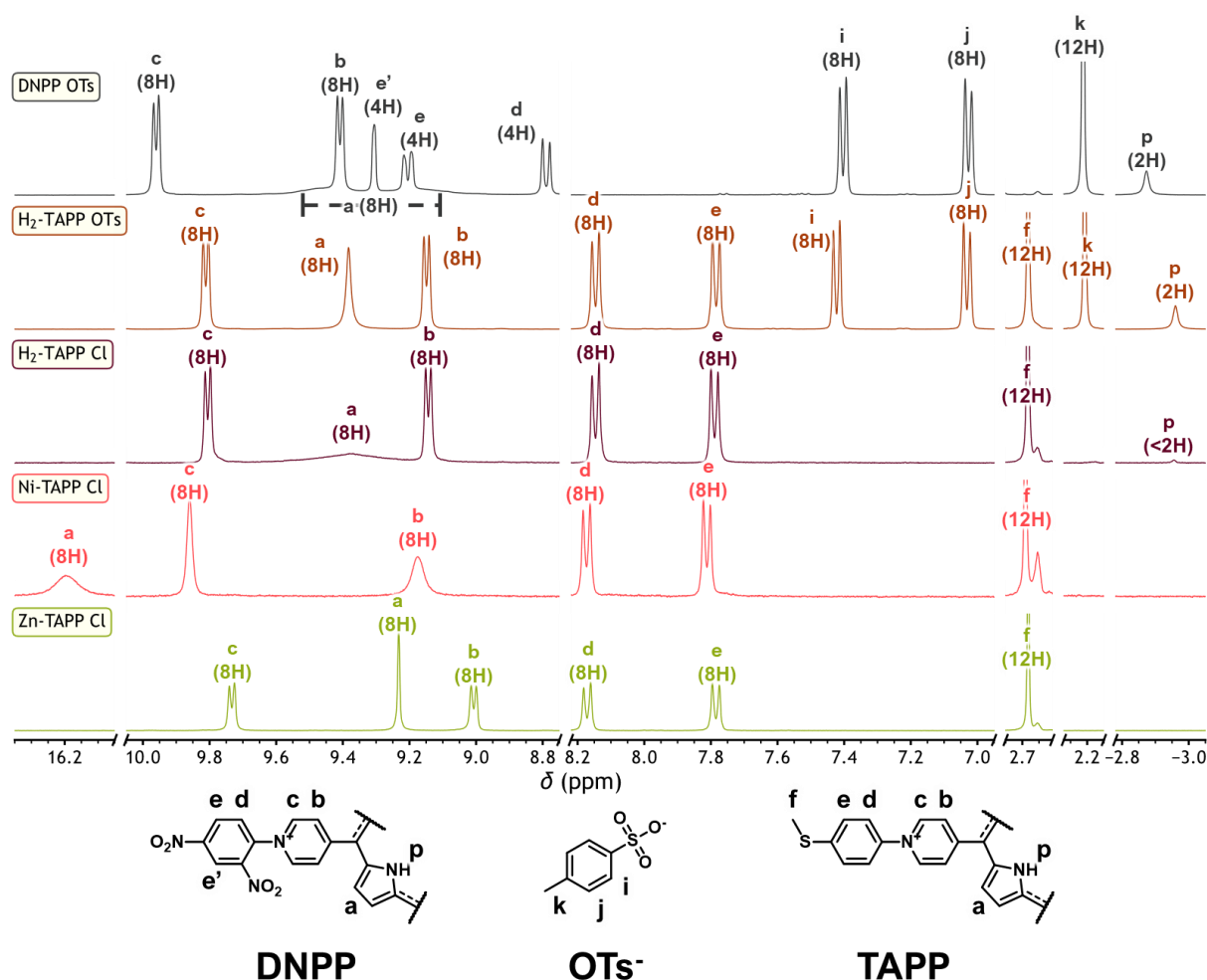
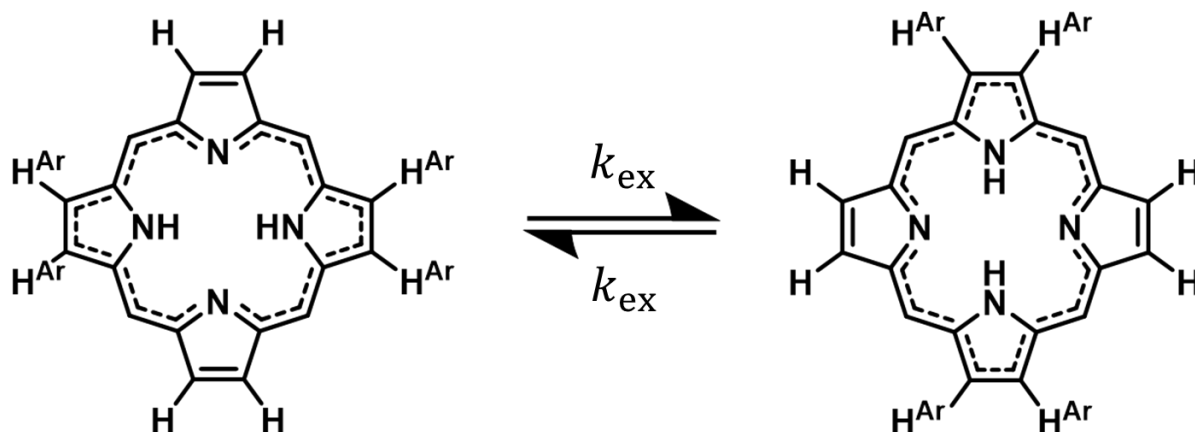


Figure 5.10. ¹H-NMR spectra and assignment of the major DNPP and TAPP products in d₆-DMSO. Solvent/aliphatic region omitted for clarity. 12H integration of resonance (f) includes secondary peak, which varies in height and is attributed to interaction with residual MeOH, water and/or MeCN; further investigation is required. For full spectra, see **Methods 5.10.1**.

The single, Lorentzian-shaped δ < 0 NH resonance (p) for DNPP and H₂-TAPP OTs confirms that each exists as a single porphyrin species, while the 2H relative integration indicates minimal exchange between the NH protons and the deuterated solvent. Conversion of DNPP to H₂-TAPP is evidenced by appearance of the SMe proton singlet (f) at 2.68 ppm and fewer aromatic resonances (due to symmetry). All aromatic resonances are shifted slightly upfield by the electron-donating SMe group in H₂-TAPP, relative to the effect of the electron-withdrawing NO₂ groups in DNPP.

The pyrrole proton resonance (**a**) appears as a slightly broadened singlet for H₂-TAPP OTs, but is significantly broadened and split for DNPP OTs. Due to the D_{2h} symmetry of freebase porphyrins, the outer pyrrole protons are inequivalent (**Scheme 5.7**). The rate (k_{ex}) of NH proton tautomerisation (relative to the chemical shift difference ($\Delta\nu$) between the two resulting pyrrole environments) determines whether the signal appears as a single resonance ($k_{\text{ex}} \gg \Delta\nu$) or a pair ($k_{\text{ex}} \ll \Delta\nu$)^{394,490,491} (**Figure 5.11**).



Scheme 5.7. Tautomerisation of porphyrin core NH protons and aromatic π -system (indicated as dashed bonds) with exchange rate k_{ex} (occurring over timescale $\tau_{\text{ex}} = k_{\text{ex}}^{-1}$). “Ar” subscript indicates protons directly adjacent to aromatic system. Arylpyridinium substituents have been omitted for clarity.

This leads to the concept of “NMR timescale” (τ_{NMR}), which effectively describes the temporal resolution of a spectrometer regarding chemical exchange.^{491,492} This timescale depends on the spectrometer strength and $\Delta\nu$, and is on the order of milliseconds with $\tau_{\text{NMR}} = \sqrt{2}/\pi\Delta\nu = \sqrt{2}/\pi\nu_0\Delta\delta$, where ν_0 is the ¹H magnetic moment precession frequency at $\delta = 0$ ppm (here, $\nu_0 = 400$ MHz; **Methods 7.2**) and $\Delta\delta$ is the separation (in ppm) between the two resonances at the slow exchange limit (when $k_{\text{ex}} < \pi\Delta\nu/\sqrt{2}$). For the DNPP pyrrole ¹H resonance pair (**a**) in **Figure 5.10**, $\Delta\delta \approx 9.44 - 9.18 = 0.26$ ppm, therefore $\Delta\nu \approx 104$ Hz and $\tau_{\text{NMR}} \approx 4.3$ ms.

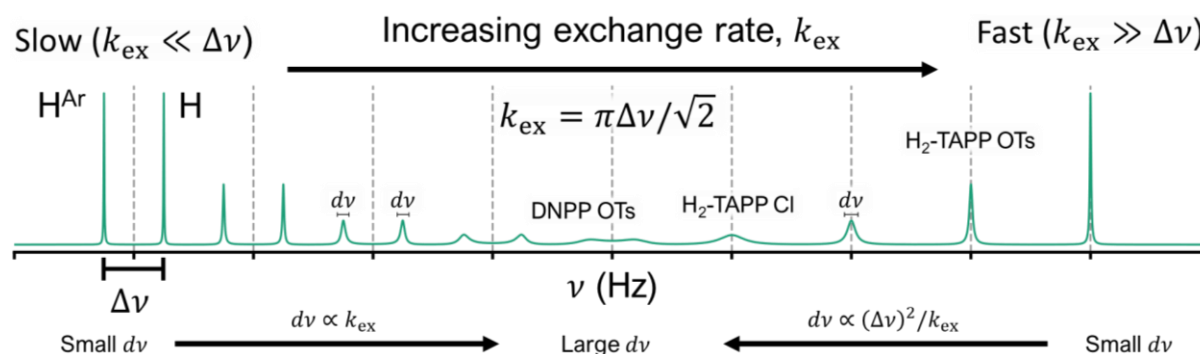


Figure 5.11. Effects of chemical exchange (e.g. tautomerisation) on ¹H-NMR resonances, simulated using lineshape⁴⁹² in **Appendix 8.5**. Chemical exchange occurs at rate k_{ex} between two different proton environments (e.g. H and HAr in **Scheme 5.7**) with ¹H-NMR chemical shifts separated by $\Delta\nu$ and resonance width $d\nu$. Slow exchange ($k_{\text{ex}} \ll \Delta\nu$) results in two sharp peaks, which broaden, coalesce and sharpen again as exchange rate increases, manifesting as a single sharp peak at the fast exchange limit ($k_{\text{ex}} \gg \Delta\nu$). Here, DNPP and H₂-TAPP labels indicate the relative pyrrole proton tautomerisation and/or exchange rates, based on the shape of resonance (**a**) for each compound in **Figure 5.10**.

The single, slightly broadened pyrrole resonance of H₂-TAPP OTs indicates NH tautomerisation occurring over shorter timescales than τ_{NMR} , meaning $k_{\text{ex}} > 231$ Hz. Similarly, $k_{\text{ex}} \approx 231$ Hz for DNPP OTs; this means that $k_{\text{ex}}(\text{H}_2\text{-TAPP OTs}) > k_{\text{ex}}(\text{DNPP OTs})$, implying slower NH tautomerisation (and a higher exchange energy barrier) when stronger electron-withdrawing groups (2,4-dinitrophenyl vs. 4-thioanisyl) are present. Proton exchange with the solvent may also perturb the peak shape, but is unlikely for the OTs compounds based on the unperturbed NH (**p**) signal intensity. Further analysis of tautomerisation kinetics is possible with variable-temperature NMR (VT-NMR),^{261,491} but is not investigated here.

Next, successful ion exchange is evidenced by the absence of tosylate resonances (**i-k**) in the H₂-TAPP chloride spectrum (**Figure 5.10**). This is accompanied by a broadened pyrrole resonance (**a**) relative to H₂-TAPP OTs, indicating slower core NH tautomerisation (**Figure 5.11**). The decreased intensity, but not disappearance, of the core NH resonance (**p**) implies gradual proton/deuteron exchange with the solvent, likely accompanied by various hydrogen bonding configurations which contribute to broadening of pyrrole resonance (**a**). This difference in behaviour implies disruption of porphyrin-solvent interactions by tosylate anions in H₂-TAPP OTs, consistent with the lower aqueous solubility of H₂-TAPP OTs than H₂-TAPP chloride.

Upon metallation of TAPP with Ni or Zn, the core NH resonance (**p**) disappears, as expected. Thioanisyl proton resonances (**d, e, f**) are not significantly shifted by metallation, while changes are more noticeable for the pyridinium (**b, c**) and pyrrole (**a**) resonances closer to the porphyrin core. The Zn-TAPP pyrrole resonance (**a**) is now a sharp singlet due to the square planar (D_{4h}) Zn-TAPP symmetry and consequent equivalence of all pyrrole protons. The Zn-TAPP (**a, b, c**) resonances are shifted upfield from their H₂-TAPP positions due to the electron-rich 3d¹⁰ Zn(II) centre.⁴⁰⁹

Conversely, the Ni-TAPP pyridinium (**b, c**) resonances are shifted slightly downfield, implying a slight electron-withdrawing effect, while pyrrole resonance (**a**) is shifted dramatically downfield. Additionally, all three peaks are increasingly broadened with proximity to Ni, while the thioanisyl resonances (**d, e, f**) are much less affected. These effects all suggest Ni paramagnetism.

To understand this, the Ni(II) electronic structure must be considered. The spin state of 3d⁸ Ni(II) (two electrons short of a filled 3d shell) is determined by the relative energies of the two highest-energy 3d orbitals. Electrons in partially-filled degenerate orbitals typically favour unpaired, spin-parallel configurations, which maximise electronic angular momentum and minimise Coulombic repulsion;⁴⁴³ the Ni²⁺ free ion therefore exists as a triplet (**Figure 5.12a**). However, nearby ligands can break the 3d degeneracy, with significant, symmetry-dependent consequences on the orbital population and spin state (**Figure 5.12b,c**).

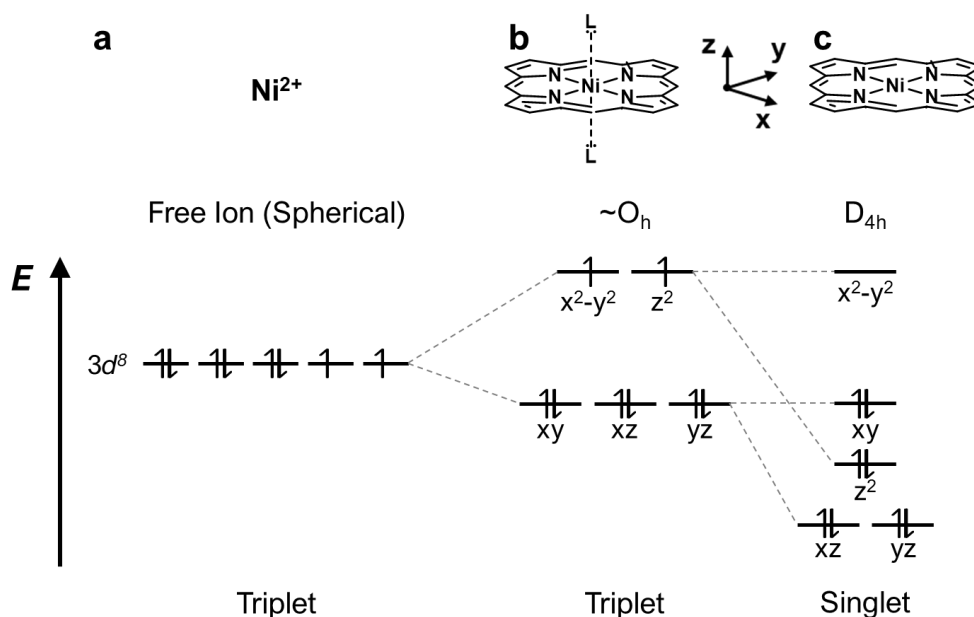


Figure 5.12. Qualitative 3d orbital energy level splittings for a d^8 transition metal (e.g. Ni^{II}) in several ligand field symmetries. **(a)** Ni^{2+} free ion 3d orbitals are degenerate, and a triplet state is adopted to minimise electron-electron repulsion. **(b)** Degeneracy is broken in a pseudo-octahedral ($\sim O_h$) ligand field (e.g. a porphyrin plus two axial ligands); for a d^8 system, six electrons pair in the lower, triply-degenerate energy level and the remaining two again adopt a parallel, unpaired conformation in the upper, doubly-degenerate level. **(c)** Removal of axial ligands creates D_{4h} ligand field symmetry and lowers the energy of all orbitals with a z-component. The resulting energy gap between the two highest-energy orbitals outweighs the electron pairing energy penalty; the high-energy $d_{x^2-y^2}$ orbital therefore remains vacant and a diamagnetic singlet state is favoured.

Square planar $3d^8$ metalloporphyrins are mostly diamagnetic due to the D_{4h} ligand field (**Figure 5.12c**), which destabilises the $d_{x^2-y^2}$ orbital such that electron pairing in a lower-energy orbital is favoured. However, axial ligand coordination raises the energy of the d_{z^2} orbital (**Figure 5.12b**); if this perturbation is strong enough, the energy gap between the $d_{x^2-y^2}$ and d_{z^2} orbitals becomes smaller than the repulsive electron pairing energy, and an unpaired, spin-parallel triplet conformation is favoured.

The spin state of a Ni(II) porphyrin in solution is therefore dependent on axial ligation. Generally, Ni(II) porphyrins are weak Lewis acids and only ligate strong Lewis bases (e.g. pyridine).^{351,493} However, electron-withdrawing porphyrin substituents (e.g. quaternary pyridinium groups^{470,473}) increase the Ni(II) Lewis acidity, which increases axial ligation probability and triplet Ni(II) population.

Consequently, the Ni-TAPP chemical shifts in **Figure 5.10** are likely caused by ligation of water present in the NMR solvent, facilitated by increased Ni(II) Lewis acidity due to the electron-deficient arylpyridinium groups. The signal broadening, but not splitting, of proton environments closest to the Ni(II) centre indicates fast equilibrium ($k_{\text{ex}} > \pi\Delta\nu/\sqrt{2}$) between singlet (non-ligated D_{4h}) and triplet (ligated pseudo- O_h) conformations, of which the observed chemical shifts are averages. Therefore, if water is the dominant ligand, repeating the NMR measurements in D_2O should shift the observed pyrrole (a) resonance further downfield; this is explored more in **Section 5.4.1**.

5.3.3 UV-Vis & PL

Porphyrinoid optical absorption is dominated by configuration interaction (CI) between the two lowest excited states of the aromatic π -system.^{357,472,485,494} Briefly, the relevant frontier orbitals of a square planar metalloporphyrin (ignoring contribution from metal orbitals) are the nearly-degenerate $1a_{1u}(\pi)/3a_{2u}(\pi)$ HOMO/HOMO-1 pair and the doubly degenerate $4e_g(\pi^*)$ LUMO, (**Figure 5.13**).^{494,495} CI occurs between the $4e_g(\pi^*) \leftarrow 1a_{1u}(\pi)$ and $4e_g(\pi^*) \leftarrow 3a_{2u}(\pi)$ excited states due to their similar energy and matching symmetry; constructive and destructive CI yields, respectively, an intense, near-UV absorption band (Soret band; ~ 400 - 500 nm in **Figure 5.14**) and a weaker redshifted absorption (Q band; >500 nm). Higher-energy bands also exist, but are less relevant to this work and not discussed here.

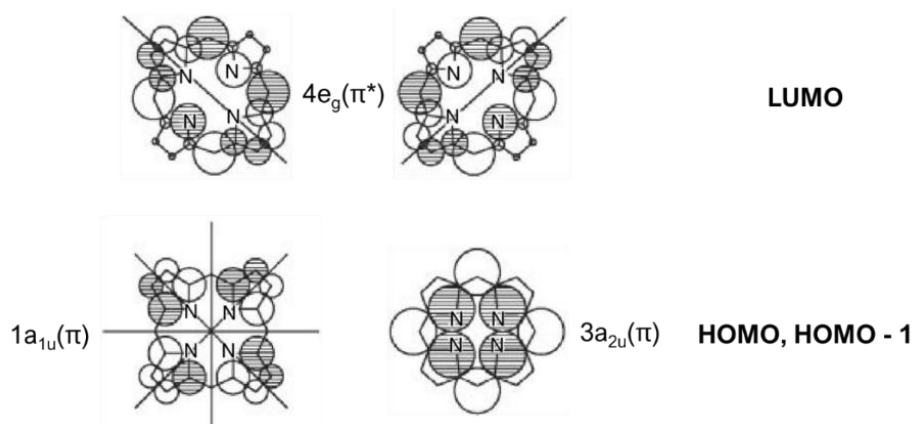


Figure 5.13. Frontier orbitals responsible for the porphyrin UV-Vis absorption bands discussed here.

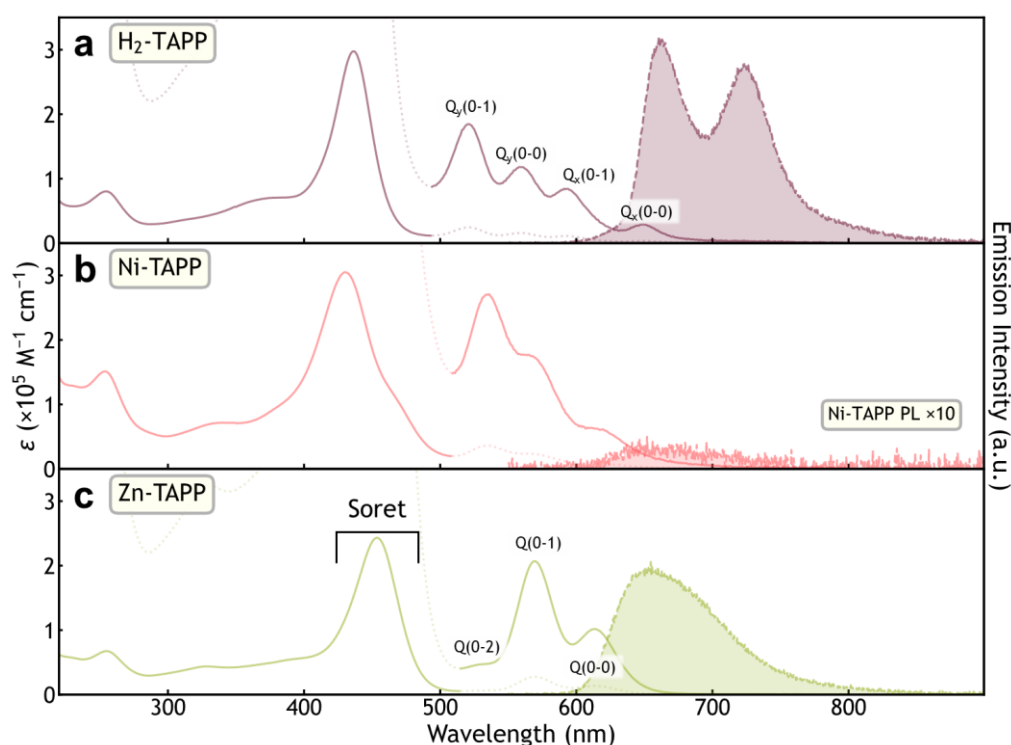


Figure 5.14. UV-Vis absorption (solid/dotted traces, left axis; Q band magnified 7.5x for clarity) and PL (dashed traces with filled area, right axis) spectra of M-TAPP chloride compounds synthesised here. M = H₂, Ni, Zn. Solvent = 1:1 MeOH/MeCN (v/v).

The Q band has a distinct vibronic structure, commonly manifesting for metalloporphyrins as two or three peaks (**Figure 5.14b,c**). The lower (D_{2h}) symmetry of freebase porphyrins (e.g. H_2 -TAPP) breaks the $e_g(\pi^*)$ degeneracy; this splits the Q band in two (four vibronic transitions in total), while the Soret band is unchanged^{485,496} (**Figure 5.14a**). Conventionally, the low- and high-energy components of the Q band are labelled Q_x and Q_y , respectively.

The H_2 -TAPP UV-Vis spectrum is characteristic of a freebase porphyrin, exhibiting a four-peaked Q band corresponding to the first and second vibronic states of the Q_x and Q_y transitions. The Soret band is redshifted by 15 nm from that of the analogous H_2 -TMPyP,⁴⁹⁰ while the Q band redshifts only by 3 nm. This decreased energy separation between the two bands indicates weaker CI between the lowest excited states and therefore a larger HOMO/HOMO-1 energy gap in H_2 -TAPP than in H_2 -TMPyP. As the $1a_{1u}(\pi)$ MO has zero π -electron density at the *meso* substituent positions (**Figure 5.13**), this CI destabilisation is likely due to an increase in $3a_{2u}(\pi)$ HOMO energy by electron donation from the thioanisyl groups.⁴⁸⁵ Metallation with Zn redshifts the whole spectrum and further decreases the energy and intensity difference between the Soret and Q bands. This indicates additional destabilisation of the $3a_{2u}(\pi)$ HOMO by nonzero Zn p_π electron density which, again, decreases the HOMO/HOMO-1 near-degeneracy and therefore the CI strength.³⁵⁷

This effect is not observed for Ni-TAPP, due to a lower p_π population. Instead, the Ni-TAPP Soret absorption is slightly blueshifted from that of H_2 -TAPP, possibly indicating lower π -electron density.⁴⁸⁵ This is consistent with the observed 1H chemical shifts (**Figure 5.10**) and smaller Soret redshift of Ni-TAPP from the corresponding Ni-TMPyP ($\Delta Soret = 12.5$ nm)⁴⁷³ than observed for H_2 -TAPP/ H_2 -TMPyP. Conversely, the Zn-TAPP spectrum exhibits a much larger redshift from Zn-TMPyP ($\Delta Soret = 20$ nm), suggesting increased π -electron density and conjugation across the structure.

Metallation with Ni also broadens the Soret band and introduces a shoulder at longer wavelengths. This is also observed for aqueous Ni-TMPyP,^{351,471,486,497} in which a double Soret peak indicates a mixed singlet/triplet population in solution, with the singlet state absorbing at shorter wavelengths. Here (Ni-TAPP in MeOH/MeCN), the singlet dominates due to preferential MeCN solvation of the hydrophobic porphyrin core, which discourages ligation of MeOH or H_2O with Ni and stabilises the diamagnetic D_{4h} structure⁴⁷³ (**Figure 5.12c**). The triplet state population should therefore increase in H_2O (investigated in **Section 5.4**).

The emission spectra of H_2 -TAPP and Zn-TAPP are redshifted from their lowest-energy absorption bands (following excitation at the Soret wavelength), indicating fast nonradiative relaxation (NRR) to the lowest excited state, from which emission then occurs (Kasha's rule).^{484,498} Ni-TAPP does not emit due to low-lying triplet excited states, between which fast intersystem crossing is facilitated by increased spin-orbit coupling, quenching radiative emission.^{481,486,499–501}

The H₂-TAPP emission has two clear peaks, typical of many freebase and metalloporphyrins; the peaks are vibronic and not related to the Q_x/Q_y energy split.⁴⁸⁴ Zn-TAPP emission appears as one broad, asymmetric peak, indicating numerous emissive excited states of varying energy. Observed previously for M-TMPyP compounds, this is caused by intramolecular CT states between the porphyrin core and the pyridinium π -systems;³⁸⁶ which couple to the porphyrin S₁ excited state. The energies of these coupled, and emissive, excited states depend on the dihedral angle between the two π -systems, while the stability and coupling strength of the states are increased by greater π -conjugation across the structure. Fast NRR between these coupled states also decreases PL intensity. Consequently, rapid pyridinium libration in solution manifests as weaker, broadened emission, but only when these CT states are stabilised; the difference in PL between H₂-TAPP and Zn-TAPP is therefore consistent with higher π -conjugation when Zn is present.

5.3.4 Stock Solution Preparation & Concentration Calibration

Calibrated M-TAPP stock solutions are required for reproducible stoichiometric M-TAPP_cCB[n] assembly. However, M-TAPP hygroscopicity precludes accurate mass measurement due to non-negligible water content in the solid. Instead, the solution concentration of M-TAPP is measured using ¹H-NMR against a known internal standard. The general procedure is outlined below (see **Methods 5.10.2** for full details).

For each compound, concentrated M-TAPP/d₆-DMSO solution was prepared, and the M-TAPP concentration measured precisely ($\pm 3\%$) with ¹H-NMR against an internal standard. Accurate dilutions ($\pm 0.5\%$) of this solution in 1:1 MeOH/MeCN were then used to prepare a UV-Vis calibration curve based on the Soret peak absorbance. This allows fast optical measurement of M-TAPP concentration (via dilution in MeOH/MeCN) with 5-10% uncertainty when preparing fresh aqueous solutions for M-TAPP_cCB[n] analysis (**Section 5.7**) and NPoM self-assembly (**Section 5.8**).

5.4 Solvochromism

During characterisation and calibration, solvochromism was observed in both NMR and optical spectra. Therefore, before investigating M-TAPP_cCB[n] complexation and AuNP self-assembly, the spectroscopic effects of aqueous M-TAPP solvation were explored using ¹H-NMR, UV-Vis and PL spectroscopy. The main consequences of aqueous solvation were increased stability of intramolecular porphyrin-pyridinium CT states and broadened, lower-intensity PL spectra,³⁸⁶ increased Ni-TAPP triplet population due to axial water ligation,⁴⁷³ and increased thioanisyl oxidation. For improved solvochromic comparisons in future, additional ¹H-NMR analysis should be performed in d₄-MeOH/d₃-MeCN, and UV-Vis/PL analysis in DMSO.

5.4.1 NMR

The M-TAPP ^1H -NMR spectra in D_2O (**Figure 5.15**) exhibit similar chemical shifts and splitting patterns to the d_6 -DMSO spectra in **Figure 5.10**, with some key differences. First, due to rapid exchange between the porphyrin NH core protons and the solvent deuterons, the corresponding $\delta < 0$ ^1H resonance is now invisible (and excluded from **Figure 5.15**). The H_2 -TAPP pyrrole resonance (a) is significantly broadened in D_2O compared to d_6 -DMSO, indicative of an increased number of hydrogen bonding configurations and/or intermediate NH proton tautomerisation rate.

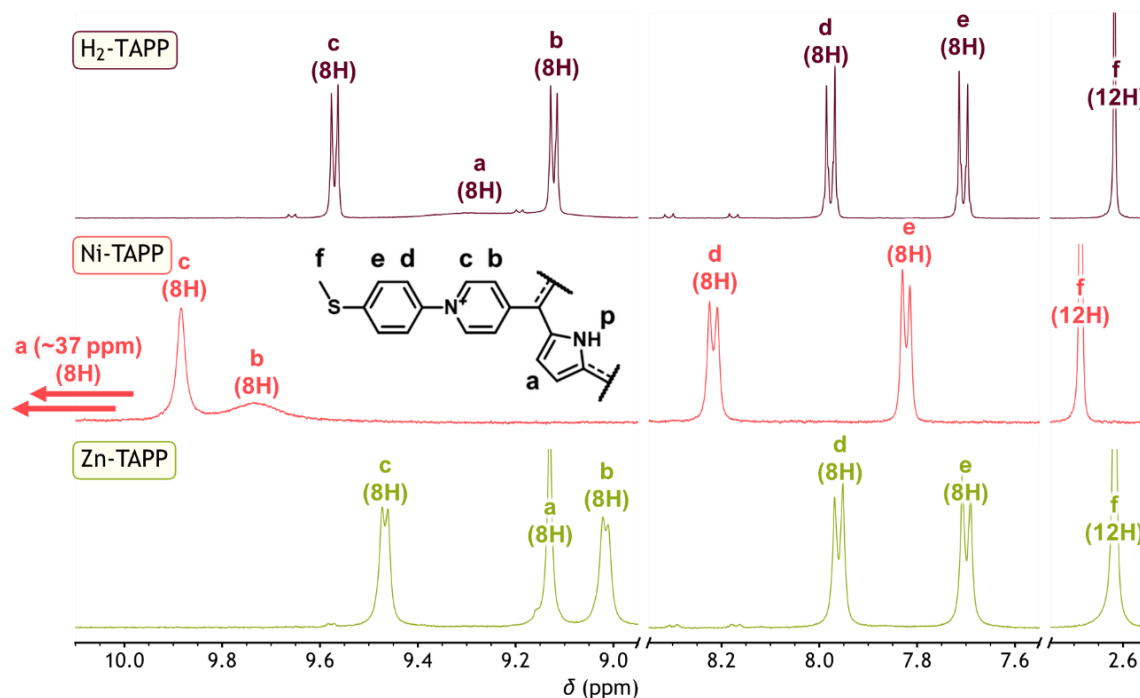


Figure 5.15. ^1H -NMR Spectra of M-TAPP Cl (M = H_2 , Ni, Zn) in D_2O . Core NH ($\delta < 0$) and solvent peak regions have been omitted.

The Ni-TAPP resonances changed significantly in D_2O , with more pronounced signal broadening and proton deshielding that increases with proximity to Ni. Pyrrole resonance (a), in particular, shifted downfield to +37 ppm, indicating a higher Ni-TAPP triplet population than in d_6 -DMSO due to increased $\text{H}_2\text{O}/\text{D}_2\text{O}$ axial ligation. Finally, for both H_2 -TAPP and Zn-TAPP a new, downshifted set of resonances appears and grows over time, accompanied by a broadening of the existing resonances; this is attributed to terminal thioether oxidation and discussed in **Section 5.5**.

5.4.2 UV-Vis/PL

The M-TAPP compounds exhibit similar UV-Vis solvochromism (**Figure 5.15**) to their M-TMPyP analogues when comparing aqueous and organic solvation.³⁸⁶ Changing the solvent from MeOH/MeCN to H_2O has little effect on the Soret band position of either H_2 - or Zn-TAPP. A very slight broadening and redshift, more pronounced for Zn, is observed, consistent with

the results of Vergeldt *et al.*³⁸⁶ This behaviour implies slight, but minimal, M-TAPP aggregation in water, consistent also with the results of Pasternack *et al.*^{471,483,497} and the linear Beer-Lambert behaviour observed during calibration (**Methods 5.10.2**).

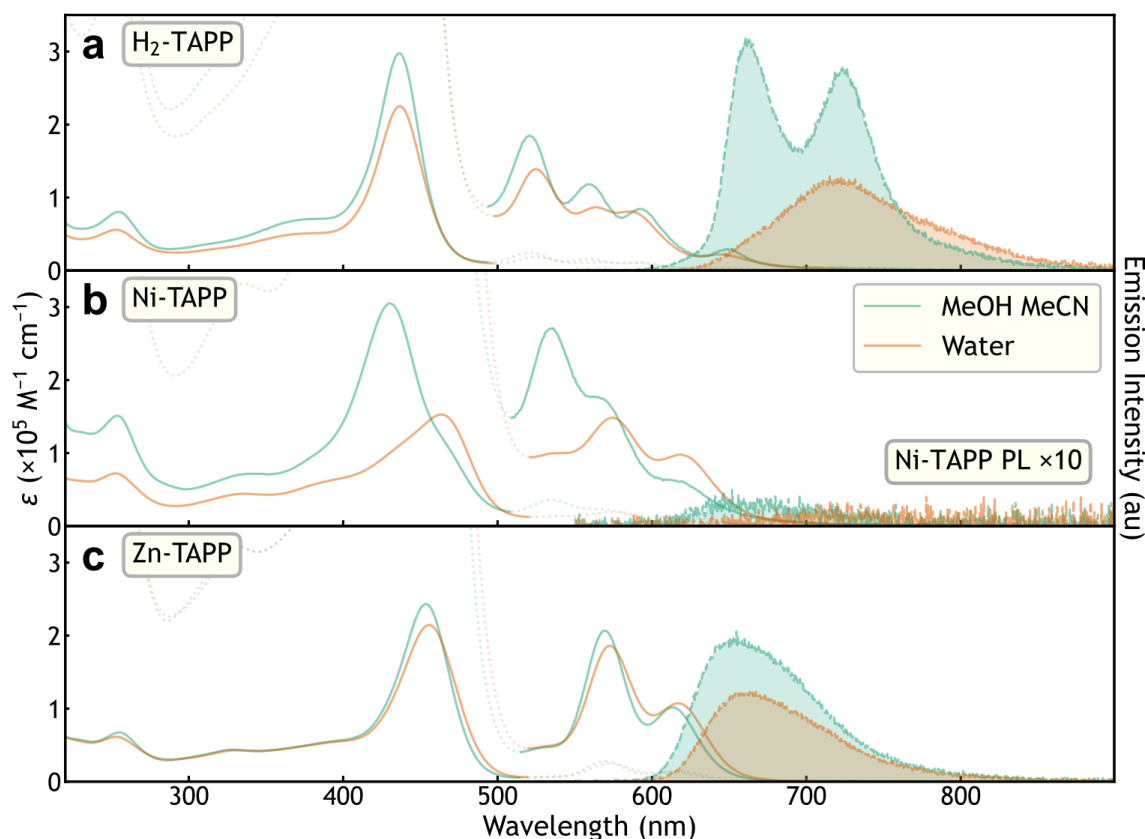


Figure 5.16. UV-Vis and PL spectra (formatted as in **Figure 5.14**) of M-TAPP (M = H₂, Ni, Zn) in water and 1:1 MeOH/MeCN. All measurements were taken at $1 \pm 0.1 \mu\text{M}$ and excited at Soret λ_{max} .

Contrastingly, aqueous Ni-TAPP exhibits a large Soret redshift ($\Delta\text{Soret} = 50 \text{ nm}$) and decreased absorbance compared to the organic solution. As before, the Soret peak appears asymmetric due to superimposition of singlet and triplet Ni-TAPP absorption. The new aqueous Soret position appears similar to the position of the low-energy (triplet state) shoulder in organic solution. A shoulder now exists at higher energy, loosely corresponding to the singlet-state Soret position in the organic solvent. This is consistent with a higher Ni-TAPP triplet state population in water due to increased Ni axial ligation,⁴⁷³ concurrent with the large downfield ¹H-NMR shifts in **Figure 5.15**.

Similarly, the Q band changes slightly for H₂/Zn-TAPP, but significantly for Ni-TAPP. For H₂-TAPP, the Q_x/Q_y bands become closer in energy, as reported for H₂-TMPyP.³⁸⁶ As before, the Zn-TAPP Q band is slightly redshifted and broadened, while the Ni-TAPP Q-band peak positions remain the same, but change in relative intensity. While only three Ni-TAPP vibronic peaks are visible for the two spin states, deconvolution (beyond the scope of this work) will likely yield more complex spectral features.^{496,502}

As mentioned earlier (**Section 5.3.3**), the H₂-TAPP Q band shape reflects the D_{2h} symmetry of the core NH proton arrangement. A decreased Q_x/Q_y energy split here is consistent with increased H-bonding between the porphyrin and solvent. The NH groups act as hydrogen bond donors, decreasing the N-H bond strength; conversely, the basic N atoms act as acceptors and increase in NH character. The increased chemical similarity in the x/y directions is likely responsible for the smaller Q_x/Q_y energy separation, while the slight broadening reflects increased H-bonding conformational entropy in water.³⁸⁶

The effects of aqueous solvation upon the PL spectra similarly agree with observed M-TMPyP solvochromism.^{386,503} The most notable perturbation is the H₂-TAPP PL shape, exhibiting two clear vibronic peaks in MeOH/MeCN but one broad, convoluted peak in water. As discussed in **Section 5.3.3**, this broadening indicates coupling between the porphyrin excited state and intramolecular porphyrin-to-pyridinium CT states. These highly polar excited states are stabilised by the higher dielectric constant of water, yielding broad emission and decreased PL intensity.³⁸⁶ The increased NRR responsible for the latter is encouraged further by the H-bonding described above.⁵⁰³ Consequently, the Zn-TAPP spectral shape changes little, and the intensity decrease is less pronounced. Again, Ni-TAPP emission is negligible in both solvents due to increased NRR via low-lying excited states and increased spin-orbit coupling in the open-shell 3d⁸ Ni centre.^{481,486,499–501}

To explore this behaviour further would require further UV-Vis, PL and ¹H-NMR analyses using a wider range of solvents with different H-bonding and metal-ligating behaviour. The data would benefit from time-correlated single-photon counting (TCSPC) and integration sphere measurements to determine the effects of solvent on excited state lifetimes and PL QY.

5.5 Aqueous Oxidative Stability

During M-TAPP characterisation and solvochromic analysis, concerns were raised regarding oxidative stability of the thioanisyl moieties. Therefore, before exploring M-TAPP $\subset$ CB[n] complexation and AuNP self-assembly, M-TAPP aqueous stability was investigated.

5.5.1 NMR

While apparently stable in the solid state and in d₆-DMSO solution, H₂-TAPP and Zn-TAPP exhibited significant temporal spectral evolution during ¹H-NMR analysis in D₂O. Noted in **Section 5.4.1**, new, downshifted ¹H-NMR resonances appear quickly in D₂O solution. Repeated preparation of D₂O solutions from solid-state M-TAPP always yielded similarly small peaks, which then grew over time. To investigate this, freshly prepared D₂O solutions of H₂-TAPP (**Figure 5.17a**) and Zn-TAPP (**Figure 5.17b**) were stored under ambient conditions and monitored with ¹H-NMR over several days. Ni-TAPP (**Figure A71**) was also analysed but exhibited no spectral changes after 306 h in D₂O.

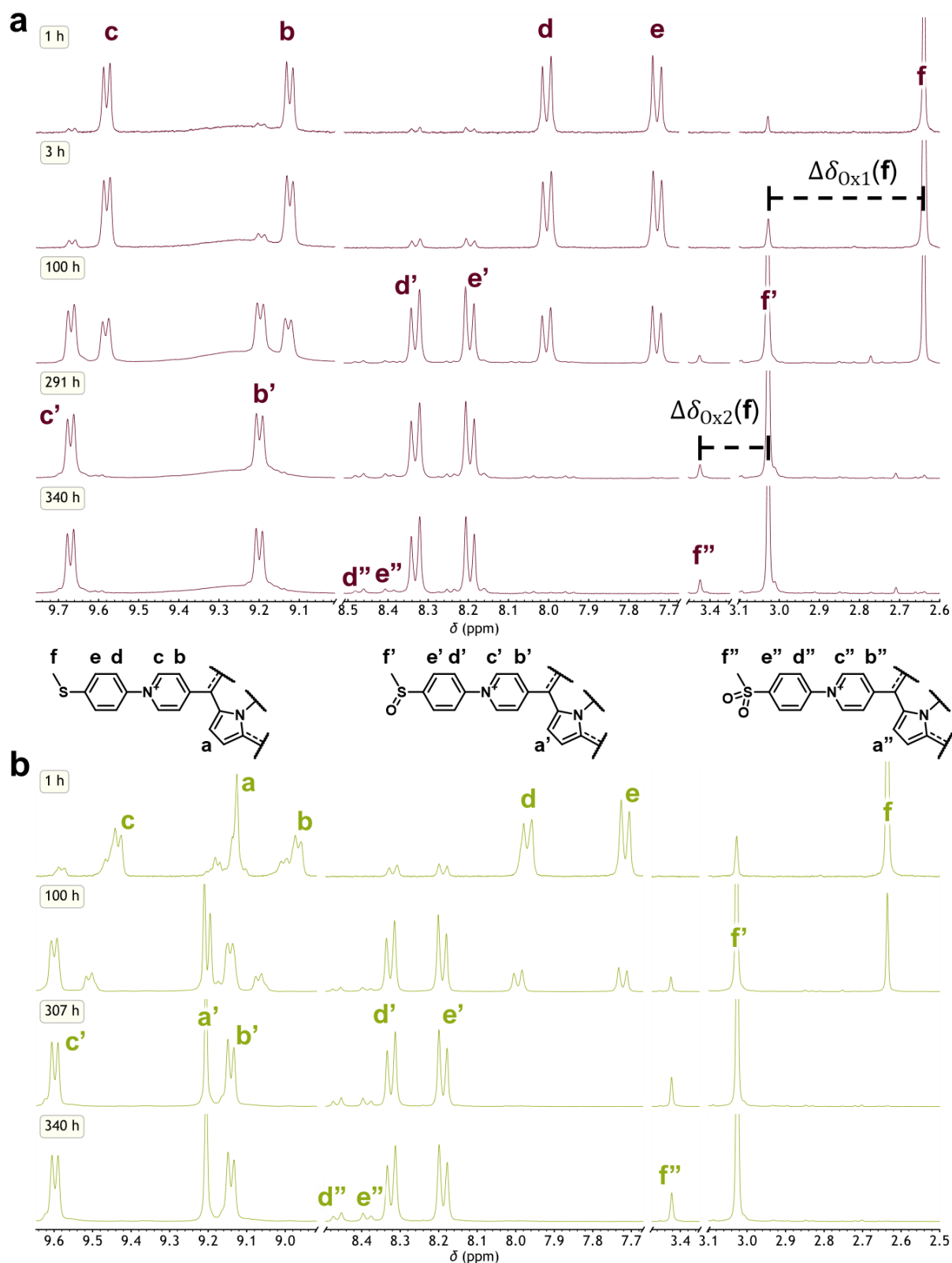


Figure 5.17. Temporal evolution of ¹H-NMR spectra of **(a)** H₂-TAPP and **(b)** Zn-TAPP in D₂O. Quantities $\Delta\delta_{\text{ox1}}$ and $\Delta\delta_{\text{ox2}}$ are illustrated in **(a)** for resonance (f) and denote the chemical shift difference ($\Delta\delta$) of each proton environment upon single and double oxidation, respectively.

For both H₂- and Zn-TAPP, downfield-shifted counterparts (**a'**, **b'**, **c'**, ...) of each proton resonance appear and increase in intensity over time. The new signal growth is much faster for Zn-TAPP than H₂-TAPP, and the downfield shift is larger. After 100 h, a third set of resonances (**a''**, **b''**, **c''**, ...) appear further downfield again; the successive change in chemical shift is smaller than the first, and the intensities increase more slowly.

The simultaneous appearance and concerted intensity increase of resonances (**a'**, **b'**, **c'**, ...), then (**a''**, **b''**, **c''**, ...), suggest that each set belongs to a single, modified M-TAPP species. The new resonances (**a'**, **b'**, **c'**, ...) are downshifted from their original (**a**, **b**, **c**, ...) counterparts by decreasing amounts with increasing proximity to the porphyrin core, indicating electron-withdrawing chemical modification at the terminal sulfur atoms. The aliphatic SMe ¹H resonance shift ($\Delta\delta_{\text{Ox1}}(\mathbf{f}) = \delta(\mathbf{f}') - \delta(\mathbf{f})$) is smaller than that of the nearest aromatic proton ($\Delta\delta_{\text{Ox1}}(\mathbf{e}) = \delta(\mathbf{e}') - \delta(\mathbf{e})$), despite a similar through-bond distance from S, indicating significant mesomeric communication of this chemical change across the molecule. The appearance of a third set of resonances (**a''**, **b''**, **c''**, ...), downshifted again, indicates that this chemical modification can occur twice, in the same place.

These observations are consistent with the SMe oxidation indicated by LCMS (**Section 5.3.1**). This again implies photosensitising behaviour, as with M-TMPyPs, which generate singlet oxygen⁴⁸⁹ and catalyse thioether oxidation^{504,505} when photoexcited under aerobic conditions. Here, D₂O boosts photocatalytic activity by extending the solution lifetime of singlet oxygen.^{489,506} The absence of Ni-TAPP self-photooxidation correlates with its negligible PL intensity, as both phenomena are precluded by fast internal NRR (**Sections 5.3.3, 5.4.2**). As a control, the mass spectrum of ArVSMes (**Figure A72**) was recorded after >2 years' ambient aqueous storage; no SMe oxidation was evidenced in the absence of porphyrin sensitiser.

The Zn-TAPP downfield region (8.90 < δ < 9.65 ppm) exhibits additional complex behaviour, with multiple intermediate resonances for the (**a**, **b**, **c**) protons closest to the porphyrin core, which collapse into (**a'**, **b'**, **c'**) once all SMe groups have been oxidised. In parallel, thioanisyl resonances (**d**, **e**) are broadened slightly before disappearing. The H₂-TAPP pyridinium (**b**, **c**) and thioanisyl (**d**, **e**) resonances exhibit broadening only, the degree of which increases with proximity to the porphyrin core. This behaviour is attributed to perturbation of non-oxidised 4-thioanisylpyridinium resonances by distant S(O)Me oxidation on the same molecule.

The effects of SMe oxidation are evidently felt more widely across the Zn-TAPP molecule than in H₂-TAPP, again consistent with higher π -delocalisation in the former (**Sections 5.3.3, 5.4.2**). **Figure 5.18** illustrates the successive chemical shift difference ($\Delta\delta$) of each proton environment upon single ($\Delta\delta_{\text{Ox1}}$) and double ($\Delta\delta_{\text{Ox2}}$) oxidation (illustrated for resonance (**f**) in **Figure 5.17a**), plotted against average through-bond distance from the nearest sulfur atom ($|r_{\text{S}}|$); measured using DFT-optimised H₂-TAPP (**Figure A73**) and Zn-TAPP (**Figure A74**) geometries.

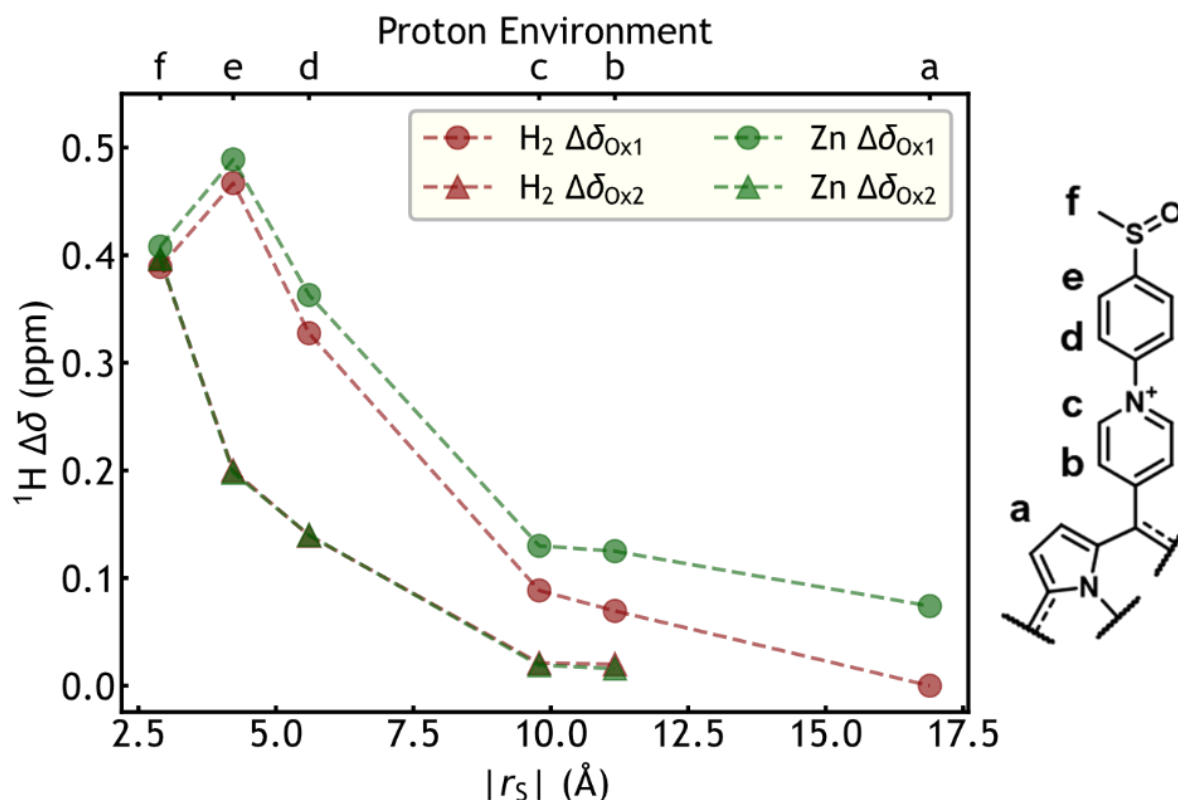


Figure 5.18. ^1H -NMR chemical shift differences ($\Delta\delta$) resulting from the first ($\text{R-SMe} \rightarrow \text{R-S(O)Me}$; $\Delta\delta_{ox1}$; circles) and second ($\text{R-S(O)Me} \rightarrow \text{R-S(OO)Me}$; $\Delta\delta_{ox2}$; triangles) oxidations at the SMe group of Zn-TAPP (green) and H₂-TAPP (red) against average centre-centre through-bond distance between each proton environment and the nearest S atom ($|r_s|$).

For both compounds, $\Delta\delta_{ox1}$ decreases with $|r_s|$, as expected, except in the case of $\Delta\delta_{ox1}(\text{f})$ due to the aliphatic character of the (f) protons. Zn-TAPP exhibits larger $\Delta\delta_{ox1}$ than H₂-TAPP for all protons; this is particularly noticeable for larger $|r_s|$, again indicating higher π -conjugation in Zn-TAPP. The second oxidation ($\text{S(O)Me} \rightarrow \text{S(O}_2\text{)Me}$) yields smaller $\Delta\delta_{ox2}$ values that are virtually identical for H₂-TAPP and Zn-TAPP. Unlike $\Delta\delta_{ox1}$, a smooth $\Delta\delta_{ox2}$ vs $|r_s|$ correlation is observed. This indicates a primarily inductive electron withdrawing effect from the second S=O.

5.5.2 LCMS

Initially, M-TAPP LCMS analysis yielded one main chromatogram peak plus an additional sub-peak at shorter retention time. The additional peak was larger for Zn-TAPP than for H₂-TAPP, and almost negligible for Ni-TAPP. The m/z values of this peak were consistent with M-TAPP + O. After six months in aqueous solution, LCMS analysis was repeated for all three compounds. No significant change was observed for Ni-TAPP (**Figure A75**). For H₂-TAPP (**Figure 5.19**), while the secondary peak grew with solution age, the pristine main signal still dominated. A third, smaller peak also appeared at shorter retention time, consistent with H₂-TAPP + 2O. This contrasts with the rapid SMe oxidation evidenced in **Figure 5.17a**, indicating relative oxidative stability in H₂O compared with significantly faster oxidation in D₂O^{489,506} (**Section 5.5.1**).

The aged Zn-TAPP solution, consistent with the results of **Figure 5.17b** and Zn-TMPyP PDT studies,⁴⁸⁹ contained more oxidation products, with *m/z* data indicating up to 5 additional oxygen atoms per molecule (**Figure 5.20**). As with H₂-TAPP, however, the pristine M-TAPP peak still dominated. To further explore and quantify M-TAPP oxidative (in)stability would require deeper systematic investigation into the effects of air, light and H₂O/D₂O exposure. Overall, however, the effects of M-TAPP oxidation appear minimal, provided solutions are freshly prepared (without D₂O) before use.

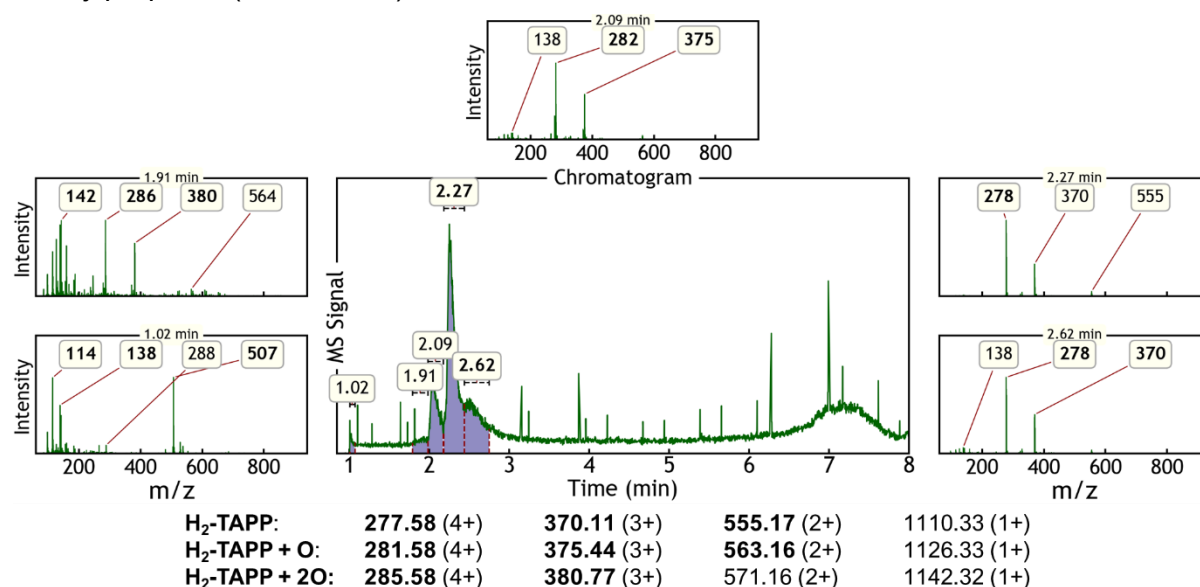


Figure 5.19. LCMS data for H₂-TAPP after 6 months in aqueous solution. While increased amounts of partially oxidised H₂-TAPP (+1O, +2O per entire molecule) are present compared to **Figure 5.9a**, the majority of the compound remains pristine and unoxidized.

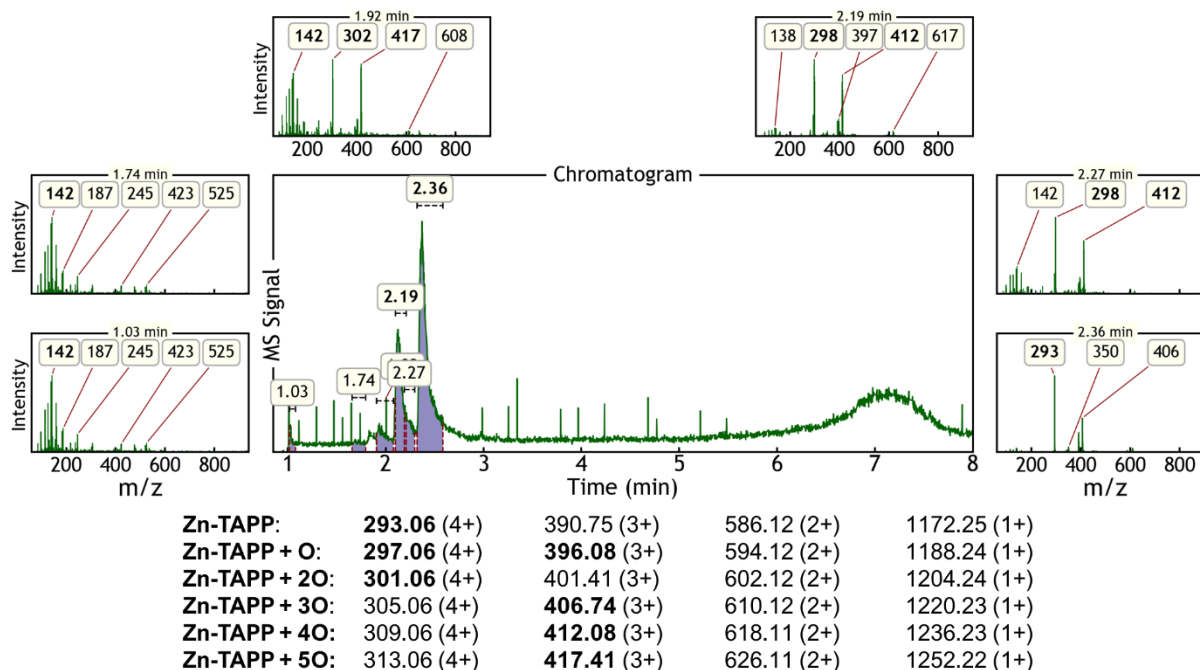


Figure 5.20. LCMS data for Zn-TAPP after 6 months in aqueous solution. A higher fraction of partially oxidised Zn-TAPP is present than before. However, the un-oxidised compound remains dominant. Some evidence for up to 5 oxidations is present, but similar retention times preclude quantification.

5.6 M-TAPP $\subset$ CB[n] ^1H -NMR Analysis

The stability of solid-state M-TAPP allowed investigation of M-TAPP $\subset$ CB[n] assembly in D_2O using freshly prepared M-TAPP solutions. Based on the four *N*-arylpyridinium groups and absence of aliphatic conformational entropy, M-TAPP and CB[n] were expected to form discrete M-TAPP $\subset$ CB[7]₄ and (M-TAPP)₂ $\subset$ CB[8]₄ complexes in aqueous solution. To quantify this, M-TAPP was titrated into CB[n] (both in D_2O) and the mixture analysed using a 500 MHz ^1H -NMR cryoprobe spectrometer (**Methods 7.2**) for improved spectral resolution, SNR and integration time, relative to the 400 MHz spectrometer used for **Sections 5.2-5.5**.

Fresh M-TAPP solutions (~0.5-1 mM; 90:5:5 v/v/v $\text{D}_2\text{O}/\text{d}_4\text{-MeOH}/\text{d}_3\text{-MeCN}$) were added in small (10-50 μL) aliquots to CB[7] (1 mM; D_2O) or CB[8] (165 μM ; 0.1 mM DCl/ D_2O). Again, pre-calibrated CB[n] solutions were provided by Guanglu Wu and Zehuan Huang.^{261,275,286}

M-TAPP $\subset$ CB[7] titration was performed first, and ^1H signal integrations of complexed M-TAPP, complexed CB[7] and free CB[7] were used to confirm M-TAPP $\subset$ CB[7]₄ stoichiometry and initial M-TAPP concentration. M-TAPP $\subset$ CB[8] titration was then performed, and (M-TAPP)₂ $\subset$ CB[8]₄ stoichiometry was confirmed using the known M-TAPP concentration plus the free and complexed CB[8] ^1H signal integrations. In all cases, ^1H signal splittings, integrations and diffusion-oriented spectroscopy (DOSY) coefficients were consistent with discrete, long-lived M-TAPP $\subset$ CB[7]₄ and (M-TAPP)₂ $\subset$ CB[8]₄ complexes. Additional 2D ^1H -NMR experiments (NOESY, COSY) have not yet been performed, but should complement the M-TAPP $\subset$ CB[n] characterisation.

As observed for EV $\subset$ CB[8] systems,^{260,261} M-TAPP $\subset$ CB[8] signal broadening evidenced restricted intramolecular and/or intracomplex motion. Preliminary VT-NMR analysis suggests multiple distinct intracomplex motions with different activation energies that vary with M-TAPP metal centre. To understand and quantify this behaviour, analysis over a wider temperature range with additional intermediate data points should be performed in future.

5.6.1 M-TAPP $\subset$ CB[7]

M-TAPP $\subset$ CB[7] complexation yields less complex ^1H -NMR spectra than the M-TAPP $\subset$ CB[8] systems and is used here to introduce the necessary concepts. As oxidative stability concerns necessitate the use of freshly prepared M-TAPP solutions, no time was available to pre-calibrate M-TAPP concentrations. Fortunately, the sharp M-TAPP $\subset$ CB[7] ^1H resonances and known CB[7] concentration allowed in-situ calibration of both M-TAPP concentration and M-TAPP $\subset$ CB[7] stoichiometry during titration (illustrated for Zn-TAPP $\subset$ CB[7] in **Figure 5.21**).

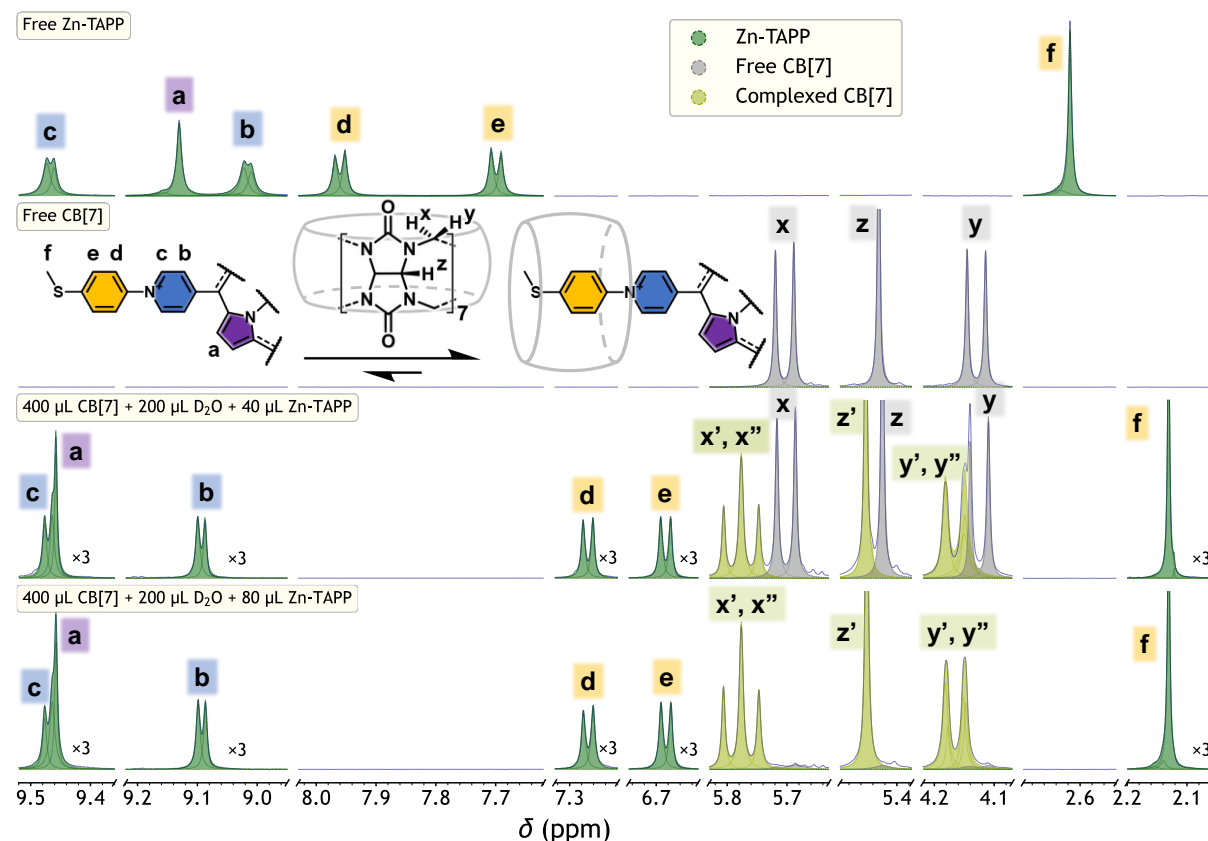


Figure 5.21. Titration of Zn-TAPP into CB[7], monitored by ^1H -NMR. Inset: schematic illustrating $M\text{-TAPP} \subset \text{CB}[7]$ complexation equilibrium and approximate geometry, plus M-TAPP and CB[7] proton environment labels. Different M-TAPP aromatic groups have been colour-coded to aid comparison. Zn-TAPP spectral intensities have been magnified 3x for visibility.

Guest $\subset$ CB[n] complexation and intracomplex dynamics can be precisely probed with NMR.^{260,261} Three ^1H chemical environments (**x**, **y**, **z**) exist for free CB[n] (**Figure 5.21**) all with integrals of $2n\text{H}$ ($=14\text{H}$ for CB[7]). The equatorial protons (**z**) manifest as one singlet, while the chemically inequivalent inward- & outward-facing portal protons (**x**, **y**) couple to form two doublets; resonance (**x**) is downshifted from (**y**) by the neighbouring inward-facing, carbonyl groups^{489,506} (see CB[n] geometry in **Figure 2.7**). Addition of Zn-TAPP to excess CB[7] yields a single set of shifted Zn-TAPP resonances (**a-f**), together with new CB[7] resonances (**x'/x''**, **y'/y''**, **z'**).

The free and complexed CB[7] resonances are distinct and comparably sharp. The new (**x'/x''**, **y'/y''**, **z'**) resonances are all downshifted from (**x**, **y**, **z**), indicating an electron deficient guest. While resonance (**z'**) remains a singlet, resonances (**x'/x''**, **y'/y''**) each appear as two overlapping doublets of equal intensity, consistent with the chemical inequivalence of the two portals upon $M\text{-TAPP} \subset \text{CB}[7]$ complexation. The inner (**x'/x''**) protons are closer to the cationic guest; consequently, both their splitting and resonance shift upon complexation exceed those of the outer (**y'/y''**) protons. The clear spectral resolution and narrow linewidths of (**x'/x''**, **y'/y''**) demonstrate relatively slow association & dissociation in solution (complex lifetime $\gg 3$ ms; **Section 5.3.2**, **Figure 5.11**), indicating strong non-covalent $M\text{-TAPP} \subset \text{CB}[7]$ binding.²⁶¹

The single set of shifted Zn-TAPP resonances indicates complete, symmetric encapsulation of all *N*-arylpyridinium groups within CB[7], with no free Zn-TAPP remaining. The absence of Zn-TAPP resonance broadening/splitting indicates unhindered, independent rotation of CB[7] and the thioanisyl & pyridinium moieties. Typically, encapsulation has a shielding effect on guest protons inside the electron-rich CB[n] cavity, while guest protons just outside the cavity are deshielded by the nearby carbonyl portals.^{260,261,267} Here, the upfield shift ($\Delta\delta_{\text{CB}[7]}$) of resonances (**d**, **e**, **f**) indicates encapsulation of the thioanisyl group inside CB[7]; $|\Delta\delta_{\text{CB}[7]}|$ increases in the order (**f**) < (**d**) < (**e**), implying proton environment (**e**) lies nearest the cavity centre, on average (**Figure 5.22**). Conversely, resonance (**a**) is shifted significantly downfield, (**b**) less so, and (**c**) not at all. This implies that environment (**a**) lies outside the cavity and near the carbonyl portal, while (**c**) sits at an intermediate position where the shielding and deshielding effects balance out.

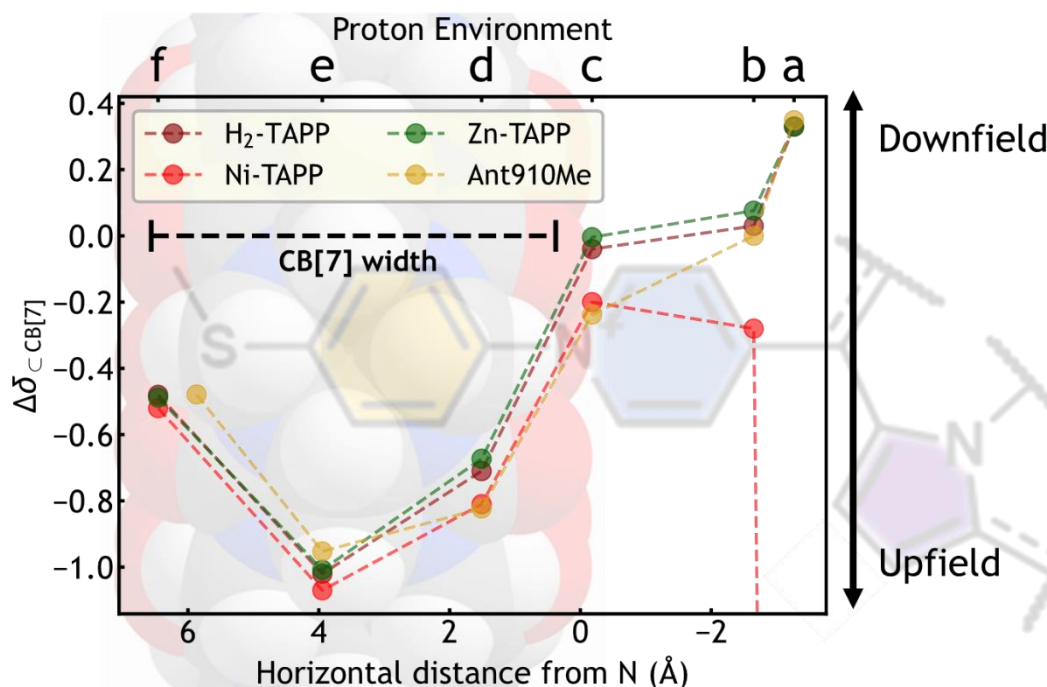


Figure 5.22. Difference between M-TAPP ^1H chemical shifts before (δ_{Free}) and after ($\delta_{\text{CB}[7]}$) complexation with CB[7] ($\Delta\delta_{\text{CB}[7]} = \delta_{\text{CB}[7]} - \delta_{\text{Free}}$) for different proton environments of H₂-, Zn- and Ni-TAPP, plotted against horizontal distance from pyridinium nitrogen (calculated for H₂-TAPP using DFT), plus Ant910Me data reported by Wu *et al.*²⁶¹ Plot has been superimposed with approximate position of CB[7] (inc. vdW radii) and truncated M-TAPP structure. Ant910Me structure has not been included here, but spatial positions of proton environments (**a-e**) are approximately the same. Difference in shape of M-TAPP and Ant910Me curves indicates different CB[7] equilibrium position along the *N*-arylpyridinium axis due to different steric bulk of anthracene and porphyrin cores, plus nearby perpendicular CB[7] molecules in the M-TAPP case. CB[7] atom colours: C (grey), H (white), N (blue), O (red).

In the $\text{CB}[7]$ complex of the smaller EV species Ant910Me^{261} (**Figure 2.10**), environment (c) lies inside $\text{CB}[7]$, while environment (b) sits at the intermediate position. In $\text{Zn-TAPP}\subset\text{CB}[7]_4$, $\text{CB}[7]$ evidently sits further out along the N -arylpyridinium axis due to steric repulsion from the large porphyrin core and neighbouring perpendicular $\text{CB}[7]$ molecules, not present in $\text{Ant910Me}\subset\text{CB}[7]_2$.

Overall, the data indicates discrete $\text{Zn-TAPP}\subset\text{CB}[7]_4$ complexation, with one $\text{CB}[7]$ molecule per N -arylpyridinium arm, encapsulating the thioanisyl group. The 1:4 stoichiometry is confirmed via the integrated peak areas of complexed $\text{CB}[7]$ and Zn-TAPP . The same information is used to determine the initial Zn-TAPP concentration. In **Figure 5.21**, addition of 40 μL Zn-TAPP was sufficient to complex 50% of the available $\text{CB}[7]$, based on the equal areas of complexed/uncomplexed $\text{CB}[7]$ resonances. Calculating the total moles of $\text{CB}[7]$ present ($1\text{ mM} \times 400\text{ }\mu\text{L} = 0.4\text{ }\mu\text{mol}$) reveals the moles of Zn-TAPP added ($0.5 \times 0.4/4 = 0.05\text{ }\mu\text{mol}$) and therefore the initial Zn-TAPP concentration ($0.05\text{ }\mu\text{mol} / 40\text{ }\mu\text{L} = 1.25\text{ mM} \pm 5\text{-}10\%$; uncertainty derived from initial $\text{CB}[7]$ concentration). This information was then used during $\text{Zn-TAPP}\subset\text{CB}[8]$ titration (**Appendix 8.5.4**) to confirm the $(\text{Zn-TAPP})_2\subset\text{CB}[8]_4$ stoichiometry.

Similar titrations were performed with $\text{H}_2/\text{Ni-TAPP}$ into $\text{CB}[7]$ and $\text{CB}[8]$ (**Figures A77-A81**). The final $M\text{-TAPP}\subset\text{CB}[n]$ ^1H -NMR spectra are summarised in **Figure 5.23** overleaf. The rest of this section discusses the spectral behaviour of $\text{H}_2/\text{Ni-TAPP}\subset\text{CB}[7]_4$; $(M\text{-TAPP})_2\subset\text{CB}[8]_4$ spectra are then discussed in **Section 5.6.2**.

Spectroscopically, $\text{H}_2\text{-TAPP}\subset\text{CB}[7]_4$ behaves similarly to $\text{Zn-TAPP}\subset\text{CB}[7]_4$, while significant differences are observed for $\text{Ni-TAPP}\subset\text{CB}[7]_4$. The downfield shifts and splittings of the ($\mathbf{x'}/\mathbf{x''}$, $\mathbf{y'}/\mathbf{y''}$) resonances of $\text{H}_2\text{-TAPP}\subset\text{CB}[7]_4$ match those of $\text{Zn-TAPP}\subset\text{CB}[7]_4$, as outlined earlier. The $\text{H}_2\text{-TAPP}$ $\Delta\delta_{\text{CB}[7]}$ curve shape (**Figure 5.22**) indicates that $\text{CB}[7]$ lies, on average, marginally closer to the porphyrin core than in $\text{Zn-TAPP}\subset\text{CB}[7]_4$, consistent with a slightly bulkier, more electron-rich porphyrin in the latter.

The width of $\text{H}_2\text{-TAPP}$ resonance (a) decreases upon $\text{H}_2\text{-TAPP}\subset\text{CB}[7]_4$ complexation, indicating increased core NH tautomerisation rate and/or lower H-bonding conformational entropy. This implies steric and/or non-classical hydrophobic (*cf.* **Scheme 2.1**) protection of the porphyrin core from the aqueous environment by $\text{CB}[7]$.

$\text{CB}[7]$ resonances ($\mathbf{x'}/\mathbf{x''}$, $\mathbf{y'}/\mathbf{y''}$) are shifted further downfield in $\text{Ni-TAPP}\subset\text{CB}[7]_4$ than for $\text{H}_2/\text{Zn-TAPP}$, as expected, given the systematically downshifted Ni-TAPP proton resonances observed so far. Not expected, however, is the $\text{Ni-TAPP}\subset\text{CB}[7]_4$ ($\mathbf{x'}/\mathbf{x''}$, $\mathbf{y'}/\mathbf{y''}$) splitting behaviour. Here, ($\mathbf{x'}/\mathbf{x''}$) is split less than ($\mathbf{y'}/\mathbf{y''}$), not more, suggesting lower $\text{CB}[7]$ portal asymmetry than for the other $M\text{-TAPP}\subset\text{CB}[7]_4$ complexes, and possibly a different $\text{CB}[7]$ position along the N -arylpyridinium axis.

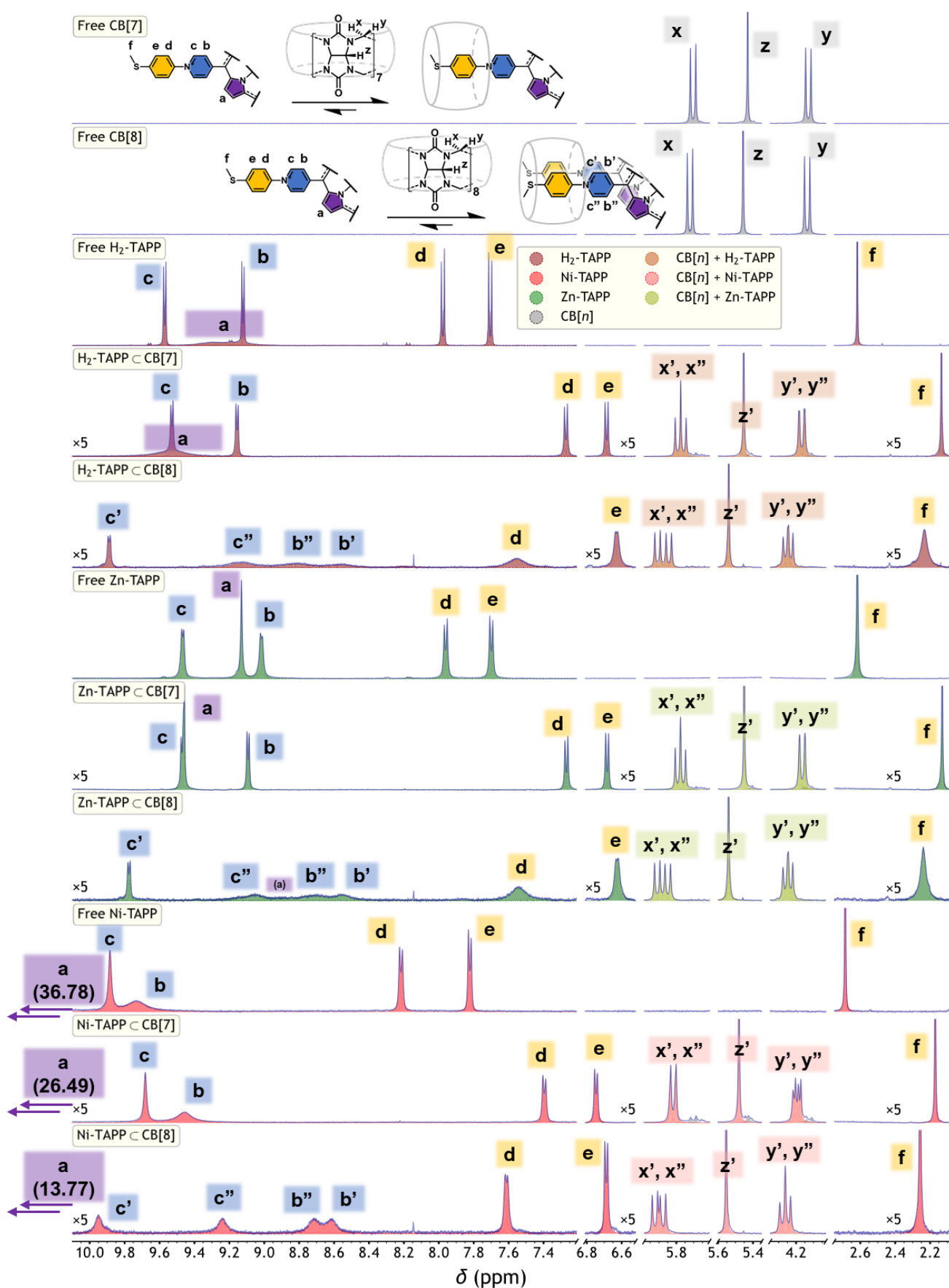


Figure 5.23. ^1H -NMR spectra of all *M*-TAPP $\subset$ CB[*n*] complexes in D_2O . ppm values for resonance (a) in Ni-TAPP systems also given.

Analysis of the Ni-TAPP proton shifts does reveal significantly upshifted $\Delta\delta_{\text{CB}[7]}$ compared to $\text{H}_2/\text{Zn-TAPP}$ (**Figure 5.22**). However, based on the dramatic upshift in pyrrole resonance (a) ($\Delta\delta_{\text{CB}[7]} = -10.29$ ppm) upon complexation, encapsulation of Ni-TAPP within CB[7] evidently decreases the triplet state population, indicating less axial water ligation. This again implies protection of the porphyrin core from the solvent by CB[7], as with $\text{H}_2\text{-TAPP}\subset\text{CB}[7]_4$. Given the resultant systematic $\Delta\delta_{\text{CB}[7]}$, the overall curve shape for Ni-TAPP in **Figure 5.22** does not indicate a sufficient difference in CB[7] axial binding position to explain the anomalous (x'/x'' , y'/y'') splittings.

DFT geometry optimisations (**Methods 5.10.3**) indicate square planar structures for $\text{H}_2\text{-TAPP}$, Zn-TAPP and triplet Ni-TAPP, but a non-planar, saddled structure for singlet Ni-TAPP (**Figures A73a, A74a, A76**), consistent with literature reports.⁵⁰⁷ The sharp CB[7] resonances and absence of further splitting in the Ni-TAPP $\subset$ CB[7]₄ $^1\text{H-NMR}$ spectra (**Figure 5.23**) indicate fast interconversion between the two different spin states and/or geometries. This may cause the anomalous (x'/x'' , y'/y'') splitting behaviour, but the mechanism is currently unknown. Further DFT and NOESY investigations would be required to explore this.

Overall, the NMR titration data indicates similar supramolecular binding geometry and identical stoichiometry for all three M-TAPP $\subset$ CB[7]₄ systems. Analysis of relative M-TAPP and CB[7] integrals (as described earlier) allowed calculation of M-TAPP stock concentrations and confirmed the 1:4 stoichiometry of all M-TAPP $\subset$ CB[7]₄. Additionally, DOSY measurements were performed for all M-TAPP $\subset$ CB[7]₄; the measured diffusion coefficients were smaller than for existing²⁶¹ EV $\subset$ CB[7]₂ systems (**Table A82**), consistent with a larger M-TAPP $\subset$ CB[7]₄ structure.

5.6.2 M-TAPP $\subset$ CB[8]

Titration of M-TAPP into CB[8] (**Figures A79-A81**) yielded quantitative conversion of free CB[8] resonances (x , y , z) into their complexed counterparts (x'/x'' , y'/y'' , z') at 1:2 M-TAPP/CB[8] stoichiometry, consistent with the predicted $(\text{M-TAPP})_2\subset\text{CB}[8]_4$ structure. In all cases, the $(\text{M-TAPP})_2\subset\text{CB}[8]_4$ spectra deviate significantly from the free M-TAPP and M-TAPP $\subset$ CB[7]₄ systems. The complexed CB[8] resonances behave more simply than those of complexed M-TAPP and will be discussed first.

As with CB[7], titration of M-TAPP into CB[8] solution splits and downshifts the (x , y) resonances, consistent with an asymmetric, electron-deficient guest. The sharp, well-defined (x'/x'' , y'/y'') signals again indicate long (>3 ms) lifetime of the $(\text{M-TAPP})_2\subset\text{CB}[8]_4$ complex in solution. Due to the relative size of the *N*-arylpyridinium moiety and the CB[8] cavity, such slow dynamics indicates strong binding of two guests per CB[8] molecule. The (x'/x'' , y'/y'') splitting and downfield shifts are larger than with M-TAPP $\subset$ CB[7]₄, consistent with the larger deshielding effect of two *N*-arylpyridinium guests.

Additionally, the observed chemical shifts and splitting behaviour of complexed M-TAPP eliminate the possibility of discrete M-TAPP $\subset$ CB[8]₂ or M-TAPP $\subset$ CB[8]₄ structures. If the 1:2 stoichiometry truly reflected a M-TAPP $\subset$ CB[8]₂ structure, the poor *N*-arylpyridinium/CB[8] size complementarity would yield faster complexation dynamics and broadened CB[8] resonances.² Alternatively, a mixture of free M-TAPP and M-TAPP $\subset$ CB[8]₄, in addition to this broadening, would also exhibit free M-TAPP resonances, which are not observed here. Elongated polymeric (M-TAPP)_n $\subset$ CB[8]_{2n} structures can also be excluded, as the head-to-tail binding geometry would yield symmetric portal environments,⁵⁰⁸ inconsistent with the observed (x'/x'' , y'/y'') splitting.

The M-TAPP/CB[8] stoichiometry and CB[8] ^1H splitting patterns therefore demonstrate formation of discrete (M-TAPP)₂ $\subset$ CB[8]₄ complexes, consistent with previously reported (EV)₂ $\subset$ CB[8]₂ dimers.^{2,260,261,275} This is supported by smaller DOSY diffusion coefficients than for M-TAPP $\subset$ CB[7]₄ (**Table A82**), indicating a larger supramolecular structure.

Preliminary geometry optimisations were also performed* using Grimme's semiempirical GFN2-xTB method⁵⁰⁹ (**Figure A88**), the results of which support the stability of discrete M-TAPP $\subset$ CB[7]₄ and (M-TAPP)₂ $\subset$ CB[8]₄ structures. Additional DFT analysis of the (M-TAPP)₂ $\subset$ CB[8]₄ geometry and dynamics would be beneficial, but the high computational expense renders this beyond the scope of this work.

The M-TAPP proton resonance behaviour in (M-TAPP)₂ $\subset$ CB[8]₄ is considerably more complex than in M-TAPP $\subset$ CB[7]₄. The tightly clamped M-TAPP dimers experience significantly restricted intracomplex motion, manifesting spectrally as broadened and/or split ^1H -NMR signals. To understand these dynamics first requires knowledge of the various energetic minima of the (M-TAPP)₂ $\subset$ CB[8]₄ supramolecular geometry between which chemical exchange occurs.

Previous reports of (ArV/EV)₂ $\subset$ CB[8]₂ systems found that the confined *N*-arylpyridinium moieties are linearly offset (**Figure 5.24a**).^{2,260} There, the relative spatial arrangement of the various proton environments was confirmed with NOESY analysis and agrees with the preferred stacking geometry of π -systems in general.⁵¹⁰ Dynamic interconversion between the resultant degenerate pair of offset conformations is usually rapid enough for each proton environment to manifest as a single resonance ($k_{\text{ex}} \gg \Delta\nu$; cf. **Figure 5.11**). Due to molecular rigidity along the *N*-arylpyridinium axis, any hindrance to this motion results in uniform temperature-dependent broadening of all guest proton resonances.

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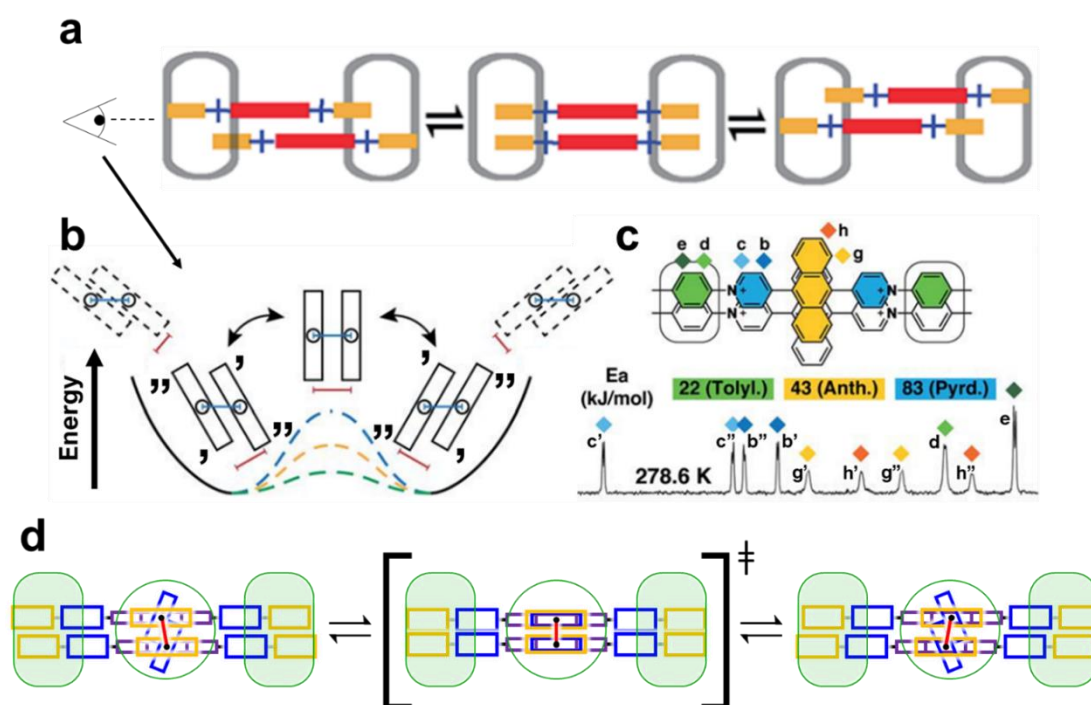


Figure 5.24. (a, b) Schematics illustrating dynamic interconversion between degenerate pairs of (a) linearly²⁶⁰ and (b) laterally²⁶¹ offset conformations within (EV)₂⊂CB[8]₂ complexes. (c) Structure and example NMR spectrum of (Ant910Me)₂⊂CB[8]₂ (500 MHz, 278.6 K) illustrating the effects of restricted librational motion.²⁶¹ Pyridinium resonances (b, c) are split and sharp (relative positions of (', ") environments indicated in (b)), indicating severely restricted motion with large activation energy of interconversion (represented by blue curve in (b)). Toly. resonances (d, e) are not split, indicating free libration with low activation energy (green curve in (b)). Anthracenylene resonances (g, h) (analogous to resonance (a) of M-TAPP) are split and broadened due to more restricted motion than (d, e) but faster libration than (b, c), indicating an intermediate activation energy (yellow curve in (b)). Linear interconversion occurs at much faster timescales and does not lead to additional broadening in (Ant910Me)₂⊂CB[8]₂. Schematics and spectrum adapted from [260,261]. (d) Schematic illustrating partial interdependence of linear and librational interconversion for the 2D (M-TAPP)₂⊂CB[8]₄ systems. Green outlines in (d) represent CB[8]; aromatic groups are represented by rectangles following the colour scheme of chemical structures in Figures 5.21, 5.23.

Analysis of more sterically hindered systems (e.g. Ant910Me) also reveals dynamic interconversion between equivalent laterally offset conformations²⁶¹ (Figure 5.24b). Due to tight lateral confinement within CB[8], this interconversion occurs via libration, rather than translation. The rotational independence of the different aromatic groups within each guest molecule introduces additional degrees of freedom, and temperature-dependent broadening/splitting of the ^1H -NMR resonances reveals independent activation energies of interconversion for proton environments on different aromatic rings.

In (Ant910Me)₂⊂CB[8]₂,²⁶¹ intramolecular steric clash between the pyridinium and anthracenyl protons is amplified by the confined, offset dimer geometry, and libration of both groups is restricted. This manifests as spectral splitting of the pyridinium and anthracenyl resonances (Figure 5.24c). The split anthracenyl resonances are broad, indicating moderately slow exchange ($k_{\text{ex}} < \pi\Delta\nu/\sqrt{2}$ @ 278 K); the split pyridinium resonances are very sharp, indicating much slower interconversion ($k_{\text{ex}} \ll \pi\Delta\nu/\sqrt{2}$) due to additional steric confinement by the surrounding CB[8] portal.

In comparison, the Ant910Me tolyl resonances (analogous to the M-TAPP thioanisyl resonances here) are not split and broaden only at lower temperatures, indicating relatively unrestricted pairwise libration ($k_{\text{ex}} \gg \pi\Delta\nu/\sqrt{2}$) inside the more spacious CB[8] cavity. Analysis of the temperature-dependent broadening of each resonance allows extraction of the activation energy of librational interconversion²⁶¹ (**Section 5.6.3**), revealing energy barriers that are near-identical for protons on the same parent ring, but different for separate rings (**Figure 5.24b**). For less sterically hindered systems (e.g., Ph13Me; **Figure 2.10**), no such broadening/splitting is observed.

The current understanding of (EV) $_2\subset$ CB[8] $_2$ intracomplex dynamics will now be applied to the M-TAPP proton resonance behaviour in (M-TAPP) $_2\subset$ CB[8] $_4$. For (Ph13Me) $_2\subset$ CB[8] $_2$, (Ant910Me) $_2\subset$ CB[8] $_2$ and other (EV) $_2\subset$ CB[8] $_2$ complexes, linear shuttling (**Figure 5.24a**) is relatively unhampered by CB[8], occurs much faster than lateral twisting and does not cause spectral broadening, even at lower temperatures.²⁶¹ For (M-TAPP) $_2\subset$ CB[8] $_4$, however, the perpendicular *N*-arylp pyridinium guest moieties lead to two-dimensional restriction of motion upon CB[8] clamping, and linear/lateral motions may no longer be independent (**Figure 5.24d**). Consequently, broadening and/or splitting results from both localised libration and system-wide linear shuttling, evidenced by the temperature-dependent peak width of each resonance (**Section 5.6.3**).

In **Figure 5.23**, thioanisyl resonances (**d, e, f**) of all (M-TAPP) $_2\subset$ CB[8] $_4$ systems (assigned based on position, integrals and (Ni-TAPP) $_2\subset$ CB[8] $_4$ COSY analysis (**Figure A83**)) are shifted upfield from their free M-TAPP positions, indicating encapsulation within CB[8]. The three resonances are broadened, but not split, by this confinement, indicating moderately fast interconversion ($k_{\text{ex}} > \pi\Delta\nu/\sqrt{2}$) in linear (**Figure 5.24a**) and/or lateral (**Figure 5.24b**) directions. This broadening indicates that thioanisyl motion is more restricted in (M-TAPP) $_2\subset$ CB[8] $_4$ than the tolyl motion in (Ant910Me) $_2\subset$ CB[8] $_2$.²⁶¹

The linear offset of the *N*-arylp pyridinium pair causes proton environments (**d, f**) to lie further from the centre of CB[8], on average (**Figure 5.25**), than in the CB[7] case (**Figure 5.22**); smaller upfield shifts are therefore observed. Environment (**d**) experiences an additional decrease in upfield shift from its proximity to the electron-deficient pyridinium nitrogen of the neighbouring guest. Conversely, resonance (**e**) experiences a larger upshift, due to the shielding effect of the aromatic ring currents near the centre of the neighbouring thioanisyl group.

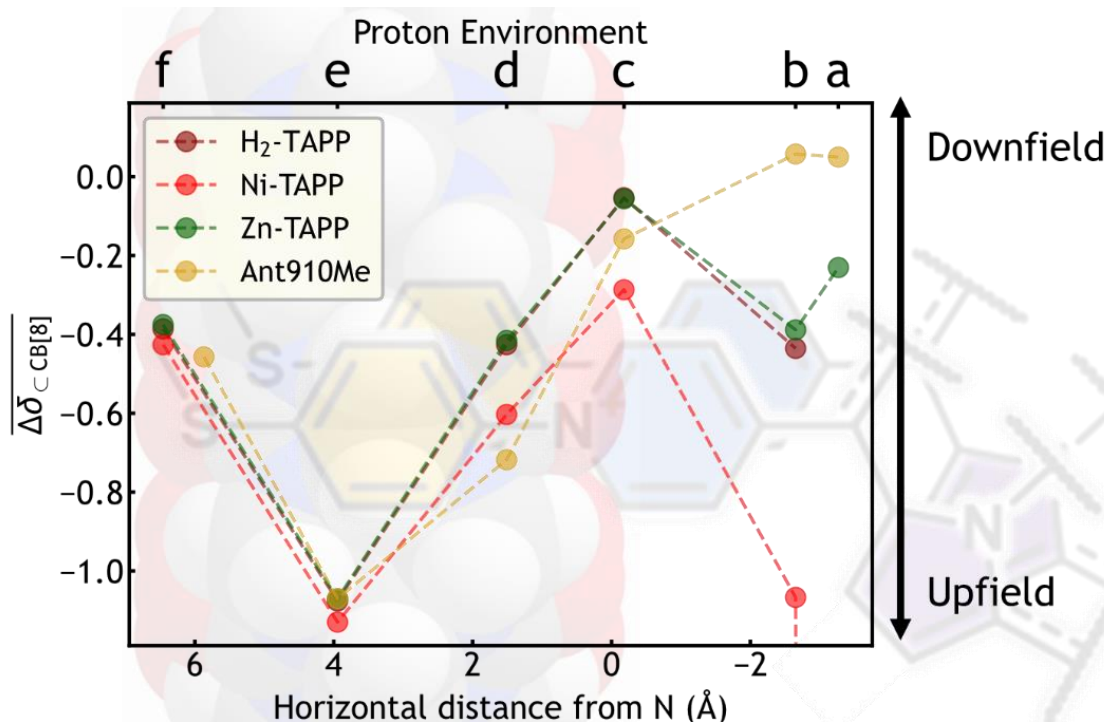
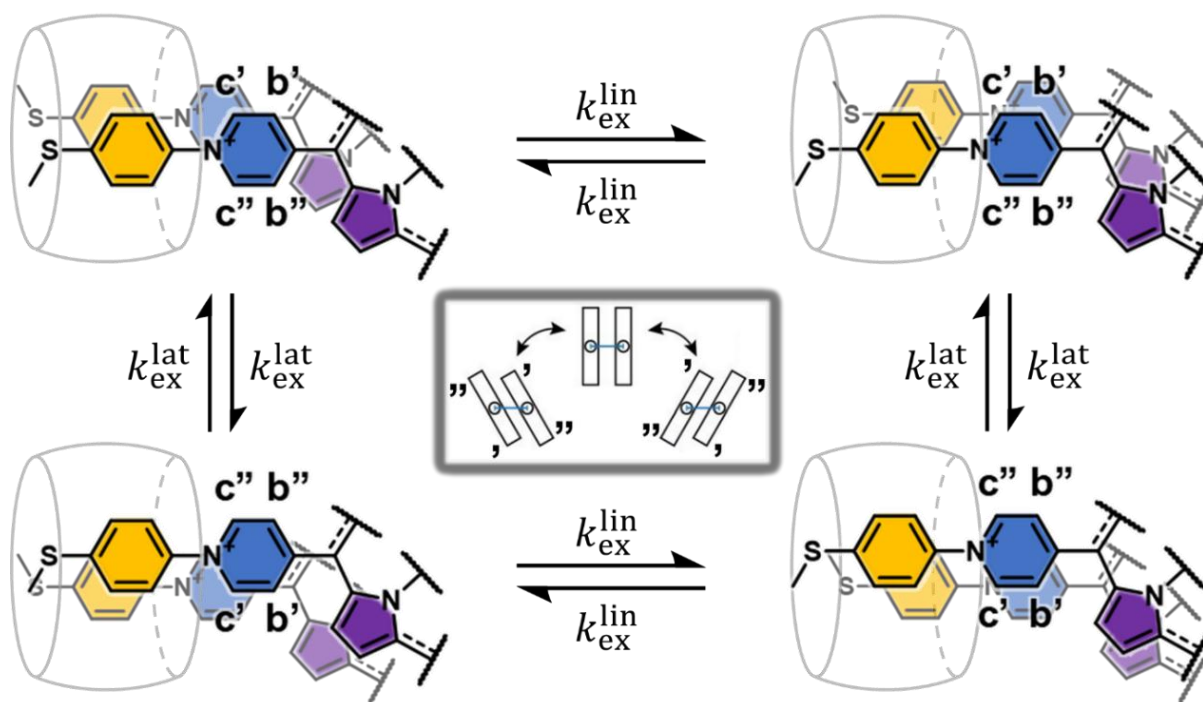


Figure 5.25. Average differences in M-TAPP ^1H chemical shifts upon complexation with CB[8] ($\overline{\Delta\delta_{\text{CB}[8]}}$) for different proton environments of Ant910Me²⁶¹ and M-TAPP, plotted against horizontal distance from pyridinium nitrogen (calculated for H₂-TAPP using DFT). Plot has been superimposed with approximate position of CB[8] (with vdW radii) and truncated M-TAPP structures. Note that M-TAPP offset positioning here represents one of several intracomplex conformations (**Scheme 5.8** overleaf). Ant910Me structure has not been included here, but spatial positions of protons (**a-e**) are approximately the same. Only average chemical shifts of resonances (**b**, **c**) are displayed here. For alternative figure with explicit $\Delta\delta_{\text{CB}[8]}$ (**c'**, **c''**, **b''**, **b'**) values, see **Figure A84**. CB[8] atom colours: C (grey), H (white), N (blue), O (red).

In the fast-exchange regime ($k_{\text{ex}} > \pi\Delta\nu/\sqrt{2}$), peak width ($d\nu$) varies as $d\nu \propto (\Delta\nu)^2/k_{\text{ex}}$.^{491,492} Resonances (**d**, **e**) are therefore broadened unequally despite their similar k_{ex} , due to different values of $\Delta\nu$ upon interconversion. To understand which intracomplex motion (linear or lateral) causes this broadening, the behaviour of the other proton resonances must first be considered.

Pyridinium resonances (**b**, **c**) are each split into (**b'/b''**, **c'/c''**), as observed²⁶¹ for (Ant910Me)₂CB[8]₂ (**Figure 5.24c**). Additional structure in the broad (**c''**, **b''**, **b'**) region of (Zn-TAPP)₂CB[8]₄ (**Figure 5.23**) is likely due to pyrrole resonance (**a**); this becomes more apparent later, at higher temperature (**Section 5.6.3**). Here, (**b'**, **c'**) indicate the protons pointing towards the neighbouring aromatic ring, while (**b''**, **c''**) point outward (**Figure 5.24b,c**; **Scheme 5.8**). This splitting is not observed for thioanisyl resonances (**d**, **e**, **f**) and is therefore due to restricted pyridinium libration (rather than linear shuttling), exacerbated by the steric bulk of the porphyrin core.



Scheme 5.8. Dynamic interconversion between degenerate N -arylpyridinium dimer conformations in $(M\text{-TAPP})_2 \subset \text{CB}[8]_4$. Only one N -arylpyridinium pair has been shown for clarity. Proton environments that exhibit splitting (i.e. (**b**, **c**)) have been labelled. Linear interconversion (left-to-right; rate $k_{\text{ex}}^{\text{lin}}$) is relatively fast and does not cause spectral splitting. Rate of lateral interconversion (top-to-bottom here; rate $k_{\text{ex}}^{\text{lat}}$) differs for each parent moiety. Proton environment label annotations (', ') correspond to the lateral offset positions labelled in **Figure 5.24b** (shown here in truncated form as inset). Here, pyridinium libration results in slow chemical exchange between inward-facing (**b'**, **c'**) and outward-facing (**b''**, **c''**) proton environments; $k_{\text{ex}}^{\text{lat}}$ is small for these resonances, and spectral splitting is observed.

For all $M\text{-TAPP}$, the (**c'/c''**) resonance pair is split more than the corresponding (**b'/b''**) pair ($\Delta\nu(\text{c}) > \Delta\nu(\text{b})$). This is caused by relative proximity of inward-pointing environment (**c'**) to the significantly electron-withdrawing pyridinium nitrogen of the neighbouring guest (**Scheme 5.8**), which evidently outweighs the shielding effect of the pyridinium ring current; the (**c''**) protons point outwards, with an upfield shift from the free $M\text{-TAPP}$ case, indicating partial encapsulation inside $\text{CB}[8]$.

The (**b'/b''**) pair splitting is reversed, with the inward-facing protons experiencing a greater upshift. Here, both resonances are shifted upfield from the free $M\text{-TAPP}$ case by the aromatic ring currents of the adjacent pyridinium ring and of the neighbouring, non-coplanar porphyrin π -system.⁵¹⁰ The outward-facing (**b''**) protons are closer to the nearby $\text{CB}[8]$ portal than their inward-facing (**b'**) counterparts and therefore experience a smaller upfield shift.²⁶¹

The widths of the two (**b'/b''**) resonances are approximately equal, as expected for proton resonances undergoing slow chemical exchange ($d\nu \propto k_{\text{ex}}$ when $k_{\text{ex}} < \pi\Delta\nu/\sqrt{2}$).^{491,492} Based on this resonance pair alone, such broadening would imply a lower activation barrier (larger k_{ex}) for pyridinium libration here than in $(\text{Ant910Me})_2 \subset \text{CB}[8]_2$.

However, while this equal broadening also occurs for the (**c'/c''**) pair of $(\text{Ni-TAPP})_2 \subset \text{CB}[8]_4$, a significant disparity in peak width is observed between (**c'**) and (**c''**) in the $(\text{H}_2/\text{Zn-}$

TAPP)₂CB[8]₄ systems. If (**c'**/**c''**) broadening was caused only by the same slow exchange process responsible for the splitting (i.e. $d\nu \propto k_{\text{ex}}$), their identical k_{ex} would yield comparable peak widths (cf. (Ant910Me)₂CB[8]₂ resonances (**g**, **h**) in **Figure 5.24c** and temperature-dependence thereof²⁶¹). However, in the fast exchange regime ($k_{\text{ex}} > \pi\Delta\nu/\sqrt{2}$; $d\nu \propto (\Delta\nu)^2/k_{\text{ex}}$), peak width is also affected by $\Delta\nu$.^{491,492} The fact that $d\nu(\mathbf{c}') < d\nu(\mathbf{c}'', \mathbf{b}'', \mathbf{b}')$ indicates, therefore, a second, simultaneous interconversion process in the fast exchange regime, with $\Delta\nu(\mathbf{c}') < \Delta\nu(\mathbf{c}'', \mathbf{b}'', \mathbf{b}')$.

As mentioned earlier, this dynamic exchange process likely involves linear shuttling, restricted by the perpendicular, CB[8]-clamped *N*-alkylpyridinium groups (**Figure 5.24d**). The small $d\nu(\mathbf{c}')$ suggests that pyridinium libration is severely restricted in (H₂/Zn-TAPP)₂CB[8]₄, and that the (**c''**, **b''**, **b'**) broadening is due to moderately restricted linear motion. The broadening of (**d**, **e**, **f**) without splitting indicates that linear interconversion, while restricted, still occurs in the fast-exchange regime.

Proton environments (**c**, **b**) lie, on average, at the intermediate region between the shielding CB[n] cavity and deshielding carbonyl portals (**Figure 5.22**), the effects of which are amplified for the outward-pointing protons.²⁶¹ Linear oscillation along the *N*-arylpyridinium axis (**Scheme 5.8**) could therefore cause a large $\Delta\nu(\mathbf{c}'', \mathbf{b}'')$. Inward pointing environment (**b'**) is hypothesised to oscillate in proximity between the neighbouring electron-deficient pyridinium nitrogen and electron-rich porphyrin π -system, leading to similar broadening.

Environment (**c'**), on the other hand, appears to oscillate about the neighbouring, electron-deficient pyridinium nitrogen with slight (but similar) shielding effects from the pyridinium ring current at one end, and the thioanisyl π -system at the other, yielding a small $\Delta\nu(\mathbf{c}')$. These hypotheses should be tested with NOESY analysis at the slow-exchange limit of $k_{\text{ex}}^{\text{lin}}$ (i.e., lower temperature and/or higher spectrometer field; **Section 5.6.3**) to reveal the relative spatial arrangement of protons in the temporally resolved offset geometries.

In (Ni-TAPP)₂CB[8]₄, resonance (**c'**) is broader than in the other (M-TAPP)₂CB[8]₄ systems and (**c''**, **b''/b'**) are sharper, yielding uniform $d\nu(\mathbf{c}'/\mathbf{c}'', \mathbf{b}''/\mathbf{b}')$. This is consistent with a higher k_{ex} of both pyridinium libration and linear shuttling, which simultaneously increase ($d\nu \propto k_{\text{ex}}$ for slow pyridinium exchange) and decrease ($d\nu \propto 1/k_{\text{ex}}$ for fast linear exchange) the peak width, respectively. Concurrently, resonances (**d**, **e**, **f**) of (Ni-TAPP)₂CB[8]₄ appear sharper than in (H₂/Zn-TAPP)₂CB[8]₄, indicating faster linear interconversion and less restricted intracomplex motion overall. To further investigate the interplay between lateral and linear interconversion for each (M-TAPP)₂CB[8]₄, preliminary variable temperature (VT) NMR measurements were performed.

5.6.3 VT-NMR

To better understand the intracomplex dynamics and kinetics thereof, ¹H-NMR analysis was repeated at lower (278 K) and higher (317 K) temperature for each (M-TAPP)₂CB[8]₄ in D₂O. For a typical chemical exchange process, k_{ex} varies with temperature according to the Arrhenius equation:

$$k_{\text{ex}} = Ae^{\frac{-E_a}{RT}}$$

Here, A is a pre-exponential constant and E_a is the activation energy of interconversion. This temperature dependence of k_{ex} manifests spectrally as broadening and/or splitting (*cf.* **Figure 5.11**) of certain proton resonances as temperature is varied.^{261,491,492} Resonances of proton environments undergoing slow exchange ($k_{\text{ex}} < \pi\Delta\nu/\sqrt{2}$; e.g., pyridinium libration) broaden as temperature increases ($d\nu \propto k_{\text{ex}}$; $\ln(d\nu) \propto -E_a/RT$), eventually coalescing into a single resonance when $k_{\text{ex}} \geq \pi\Delta\nu/\sqrt{2}$. Conversely, resonances of fast-exchange processes ($k_{\text{ex}} > \pi\Delta\nu/\sqrt{2}$; e.g. thioanisyl libration, linear shuttling) broaden as temperature *decreases* ($d\nu \propto (\Delta\nu)^2/k_{\text{ex}}$; $\ln(d\nu) \propto E_a/RT$), eventually splitting when $k_{\text{ex}} \leq \pi\Delta\nu/\sqrt{2}$. In both cases, the temperature dependence of $d\nu$ allows estimation of E_a via the slope of a linear $\ln(d\nu)$ vs. $1/T$ Arrhenius plot.²⁶¹

The current (M-TAPP)₂CB[8]₄ VT-NMR dataset is limited, and a wider range of temperature measurements will be required for quantitative analysis of (M-TAPP)₂CB[8]₄ dynamics. Nevertheless, the high/low-temperature measurements here allow qualitative appraisal of the dominant (M-TAPP)₂CB[8]₄ intracomplex motions.

¹H VT-NMR spectra of the three (M-TAPP)₂CB[8]₄ systems are shown in **Figures 5.26-5.28**. Inspection of the complexed CB[8] signals (**Figures A85-A87**) reveals that (M-TAPP)₂CB[8]₄ association/dissociation remains in the slow-exchange limit ($k_{\text{ex}} \ll \Delta\nu$) up to 317 K. Thioanisyl peak widths $d\nu(\mathbf{d}, \mathbf{e}, \mathbf{f})$ decrease as temperature increases for all systems; $d\nu(\mathbf{d}, \mathbf{e}, \mathbf{f})$ exhibit similar temperature dependence between (H₂/Zn-TAPP)₂CB[8]₄, but are systematically sharper at all temperatures for (Ni-TAPP)₂CB[8]₄, indicating a lower activation energy for the same dynamic process in the latter.

The faster (Ni-TAPP)₂CB[8]₄ intracomplex motion indicates lower steric hindrance, possibly due to lower π -electron density (**Section 5.3**). The motion may also be affected by the saddled geometry of singlet Ni-TAPP⁵⁰⁷ (**Figure A76a**), whose increased population in (Ni-TAPP)₂CB[8]₄ is evidenced by the upfield shift of pyrrole resonance (**a**) from both the free Ni-TAPP and Ni-TAPP₂CB[7]₄ cases. This increased singlet population may be caused by steric blocking of the inward-facing Ni-TAPP faces (restricting axial ligation) and/or reduced steric clash between adjacent CB[8] molecules due to the saddled structure.

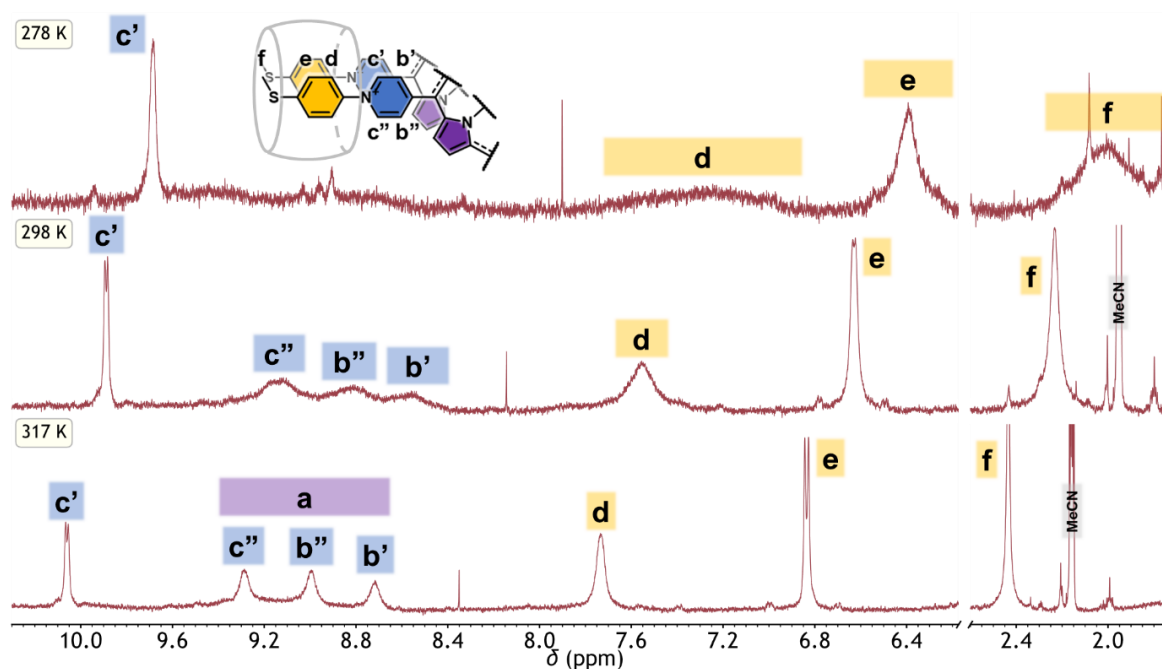


Figure 5.26. ^1H VT-NMR spectra of $(\text{H}_2\text{-TAPP})_2\text{CB}[8]_4$ in D_2O at 278, 298 and 317 K.

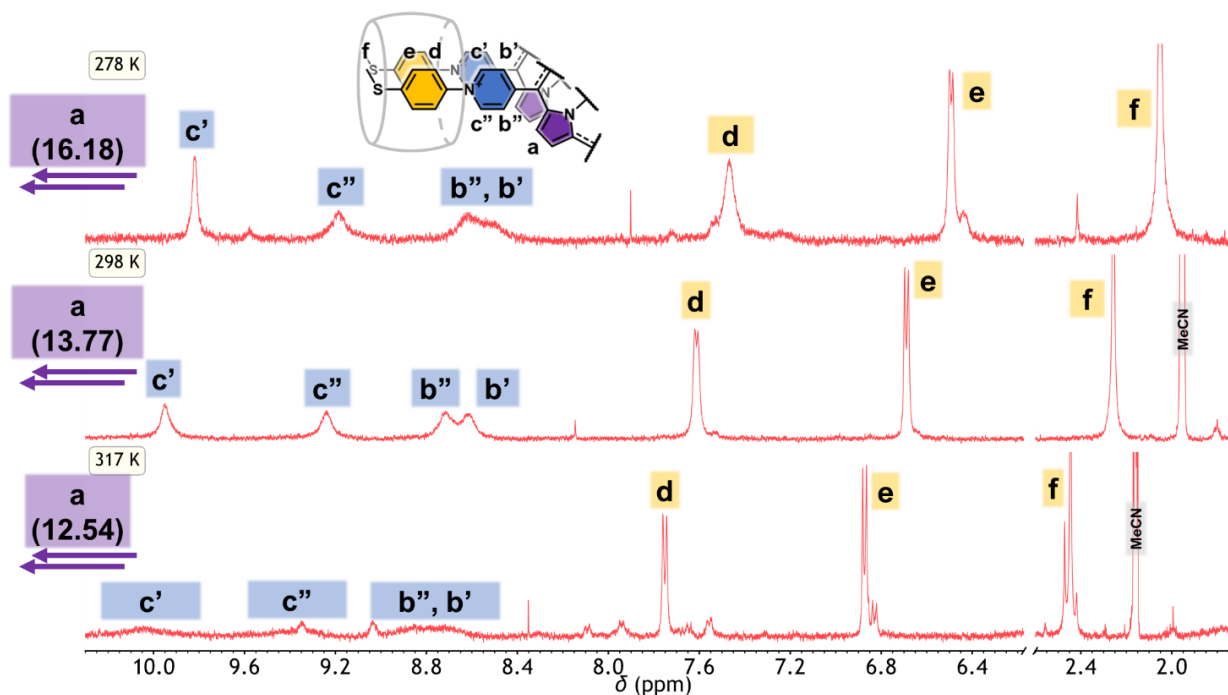


Figure 5.27. ^1H VT-NMR spectra of $(\text{Ni-TAPP})_2\text{CB}[8]_4$ in D_2O at 278, 298 and 317 K. Additional small peaks are likely due to breakdown products, indicating instability of $(\text{Ni-TAPP})_2\text{CB}[8]_4$ in the acidic $\text{DCI}/\text{D}_2\text{O}$ solution at 317K.

The effect of saddling upon internal $(\text{Ni-TAPP})_2\text{CB}[8]_4$ dynamics is currently unknown. One hypothesis is that intracomplex motion is assisted by fast dynamic switching (and geometric oscillation) between the saddled singlet and planar triplet states. The distinct broadening and downfield shift of pyrrole resonance (**a**) with decreasing temperature (**Figure A86**) indicates that the two species may be spectrally resolved at lower temperatures. While the melting point of D_2O (277 K) limits lower-temperature analysis, temporal resolution can alternatively be

controlled via the spectrometer field.^{261,491} With respect to chemical exchange, a higher field strength is spectrally analogous to a lower sample temperature; the desired temporal and spectral resolution might therefore be achieved in future using a higher-field (600 or 700 MHz) spectrometer.

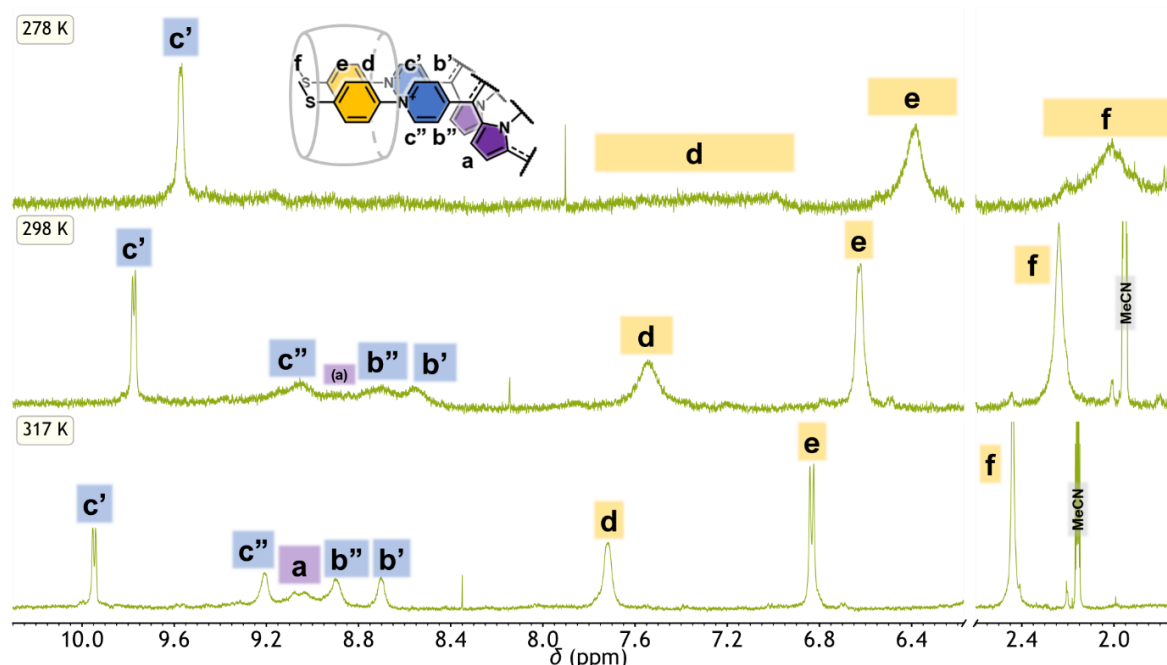


Figure 5.28. ^1H VT-NMR spectra of $(\text{Zn-TAPP})_2\text{CB}[8]_4$ in D_2O at 278, 298 and 317 K.

The pyridinium resonance widths $\delta\nu(\mathbf{c}', \mathbf{c}'', \mathbf{b}'', \mathbf{b}')$ of $(\text{H}_2/\text{Zn-TAPP})_2\text{CB}[8]_4$ exhibit similar temperature dependence to $\delta\nu(\mathbf{d}, \mathbf{e}, \mathbf{f})$, with a spectrum-wide decrease in $\delta\nu$ observed with increasing temperature. This indicates moderately fast linear exchange along the *N*-arylpyridinium axis. If so, all resonances should split simultaneously if the measurements are repeated at a sufficiently higher field (lower effective temperature). The persistence of $(\mathbf{c}'/\mathbf{c}'', \mathbf{b}''/\mathbf{b}')$ splitting reveals that pyridinium libration remains in the slow exchange limit at 317 K for both systems. These resonances are expected to eventually broaden and coalesce at higher temperature and/or lower spectrometer field, as observed for $(\text{Ant910Me})_2\text{CB}[8]_2$.²⁶¹

A small doublet (~ 9.05 ppm) appears for $(\text{Zn-TAPP})_2\text{CB}[8]_4$ at 317 K; based on its absence in the $(\text{H}_2\text{-TAPP})_2\text{CB}[8]_4$ spectrum, this is likely pyrrole resonance (**a**), shifted upfield from its free Zn-TAPP position by ring currents of the neighbouring porphyrin π -system.⁵¹⁰ The broad, weak increase in background signal in this spectral region of $(\text{H}_2\text{-TAPP})_2\text{CB}[8]_4$ may be due to the same pyrrole resonance, broadened by core NH proton dynamics (**Section 5.3.2**). Higher temperature measurements and/or a lower spectrometer field²⁶¹ would be required to confirm this.

At 298 K, pyridinium resonances $(\mathbf{c}', \mathbf{c}'', \mathbf{b}'', \mathbf{b}')$ of $(\text{Ni-TAPP})_2\text{CB}[8]_4$ are similar in width, yet much broader than thioanisyl resonances (**d, e, f**). This difference is amplified at 317 K, with significantly larger $\delta\nu(\mathbf{c}', \mathbf{c}'', \mathbf{b}'', \mathbf{b}')$ and smaller $\delta\nu(\mathbf{d}, \mathbf{e}, \mathbf{f})$. The decrease in $\delta\nu(\mathbf{d}, \mathbf{e}, \mathbf{f})$ with increasing temperature indicates fast-exchange ($\delta\nu \propto 1/k_{\text{ex}}$) libration and/or linear

shuttling of the thioanisyl groups, while the increase in $d\nu(\mathbf{c}', \mathbf{c}'', \mathbf{b}'', \mathbf{b}')$ indicates slow-exchange ($d\nu \propto k_{\text{ex}}$) pyridinium libration. As temperature increases (and/or spectrometer field is lowered), the $(\text{Ni-TAPP})_2\subset\text{CB}[8]_4$ pyridinium resonances are expected to coalesce and sharpen sooner than those of $(\text{H}_2/\text{Zn-TAPP})_2\subset\text{CB}[8]_4$. The increased pyridinium libration rate is again consistent with increased freedom of motion in $(\text{Ni-TAPP})_2\subset\text{CB}[8]_4$.

As before, the strongest evidence for two coexistent intracomplex exchange processes is the disparity between $d\nu(\mathbf{c}')$ and $d\nu(\mathbf{c}'', \mathbf{b}'', \mathbf{b}')$. This divergence is particularly apparent for $(\text{Ni-TAPP})_2\subset\text{CB}[8]_4$ at 278 K. If slow pyridinium libration was the only chemical exchange process occurring here, a decrease in temperature (and therefore k_{ex}) would cause uniform sharpening ($d\nu \propto k_{\text{ex}}$) of all pyridinium resonances as $k_{\text{ex}} < \pi\Delta\nu/\sqrt{2} \rightarrow k_{\text{ex}} \ll \Delta\nu$. Instead, $d\nu(\mathbf{c}')$ decreases, while $d\nu(\mathbf{c}'', \mathbf{b}'', \mathbf{b}')$ all increase. This is accompanied by an increase in $d\nu(\mathbf{d}, \mathbf{e}, \mathbf{f})$, such that the 278 K $(\text{Ni-TAPP})_2\subset\text{CB}[8]_4$ spectrum resembles the room-temperature spectra of the other $(M\text{-TAPP})_2\subset\text{CB}[8]_4$ systems. The broadening of all resonances except $(\mathbf{c}')$ likely occurs due to $\Delta\nu(\mathbf{c}') < \Delta\nu(\mathbf{c}'', \mathbf{b}'', \mathbf{b}')$ upon linear interconversion, as outlined in **Section 5.6.2**.

Quantitative temperature-dependent $d\nu$ behaviour for all $(M\text{-TAPP})_2\subset\text{CB}[8]_4$ is summarised in **Figure 5.29**. The variation of $\ln(d\nu)$ with $1/T$ appears approximately linear for thioanisyl resonances (**d, e, f**) with mostly similar gradients, corresponding to thioanisyl libration and/or linear shuttling activation energies of 49 ± 7 & 48 ± 5 kJ mol $^{-1}$ for $(\text{H}_2\text{-TAPP})_2\subset\text{CB}[8]_4$ & $(\text{Zn-TAPP})_2\subset\text{CB}[8]_4$, respectively, and a significantly lower 25 ± 8 kJ mol $^{-1}$ for $(\text{Ni-TAPP})_2\subset\text{CB}[8]_4$. The similar (**d, e, f**) gradients within each system indicate a single chemical exchange process responsible for the temperature-dependent broadening; deviations from this may represent interplay between thioanisyl libration and linear shuttling. However, more temperature data points are required before conclusions can be confidently drawn.

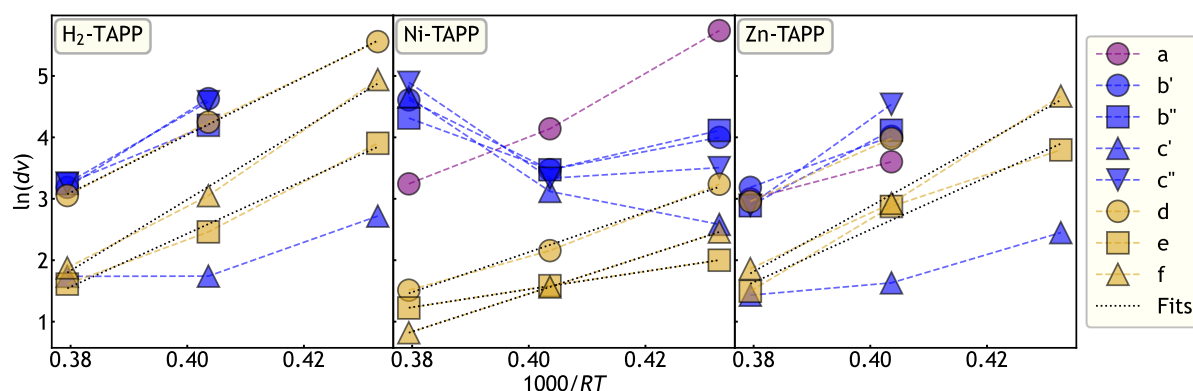


Figure 5.29. Summary of $(M\text{-TAPP})_2\subset\text{CB}[8]_4$ VT-NMR data, illustrating variation of ^1H -NMR resonance peak FWHM ($d\nu$; Hz) with temperature (T ; K), plotted as $\ln(d\nu)$ vs. $-1000/RT$. Relationship is approximately linear for thioanisyl resonances (**d, e, f**) indicating (mostly) a single chemical exchange process responsible for signal broadening. Conversely, significant and divergent deviation from linearity for pyridinium resonances (**b, c**) indicates complex interplay between multiple dynamic processes.

Even with limited data, interplay between linear and librational exchange dynamics is more obvious for pyridinium resonances (**b**, **c**), with significant deviations from linearity in all cases. For (Ni-TAPP)₂CB[8]₄, crossover of the fast and slow exchange regimes is immediately apparent from the change in sign of $\partial(\ln(d\nu))/\partial(1/T)$ across the temperature range, while a gradient change is observed for (H₂-TAPP)₂CB[8]₄ and (Zn-TAPP)₂CB[8]₄. A divergence of $\partial(\ln(d\nu))/\partial(1/T)$ is also observed between the individual pyridinium resonances, which may suggest additional, possibly interdependent, dynamic processes not considered here.

Pyrrole resonance (**a**), while relatively obscured for H₂/Zn-TAPP, is clearly visible in the (Ni-TAPP)₂CB[8]₄ spectra at all temperatures and exhibits a positive $\partial(\ln(d\nu))/\partial(1/T)$, corresponding to fast exchange with activation energy 47 ± 5 kJ mol⁻¹. The increased exchange activation energy relative to (**d**, **e**, **f**) suggests that the Ni-TAPP singlet/triplet equilibrium rate is slower than that of thioanisyl libration or linear shuttling.

Again, significantly more temperature data will be required to deconvolute the influence and activation energies of the various intracomplex motions. First, more data points within the current temperature range should reveal the shape of the existing data with greater precision. However, temperature measurements outside the current effective range are also strongly recommended and may be achieved by conducting VT-NMR experiments at higher and lower spectrometer field strengths.^{261,491}

5.6.4 Final NMR Comments

The proton environment assignments in **Figure 5.23** and the spectral interpretation discussed throughout this section were rationalised by comparison to similar EV₂CB[*n*] systems. While the relative peak integrations and temperature-dependent spectral broadening appear consistent with the current interpretation, further characterisation of the system is required.

Specifically, 2D ¹H-NMR techniques should be used to measure the through-bond and through-space proton correlations (via COSY and NOESY, respectively). Ideally, these should be performed at various temperatures/field strengths to resolve the slow and fast exchange limits of the (M-TAPP)₂CB[8]₄ intracomplex dynamics, where possible. Comparison of this data with comprehensive characterisation results of known (EV)₂CB[8]₂ complexes should provide more information regarding similarities/differences between such pseudo-1D systems and the pseudo-2D (M-TAPP)₂CB[8]₄ dimers here.

5.7 M-TAPP $\subset$ CB[n] UV-Vis & PL Analysis

Based on **Section 5.6** and previous EV $\subset$ CB[n] analyses,^{260,261} M-TAPP and CB[n] evidently form discrete M-TAPP $\subset$ CB[7]₄ and (M-TAPP)₂ $\subset$ CB[8]₄ complexes in aqueous solution, as expected. As with previous EV $\subset$ CB[n] systems, enforced monomerisation or dimerisation of M-TAPP is expected to have distinct effects on optical absorption and emission.²⁶¹

All aqueous M-TAPP $\subset$ CB[n] systems ([M-TAPP] = 1 μ M) were analysed with UV-Vis and PL spectroscopy (**Figure 5.30**, **Table 5.1**). The 2D (metallo)porphyrin structures exhibit more complex behaviour than analogous EV $\subset$ CB[n] systems containing simple aromatic fluorophore cores. Nevertheless, the existing theory base^{386,472,473} regarding the electronic structure of porphyrins aids interpretation of these results.

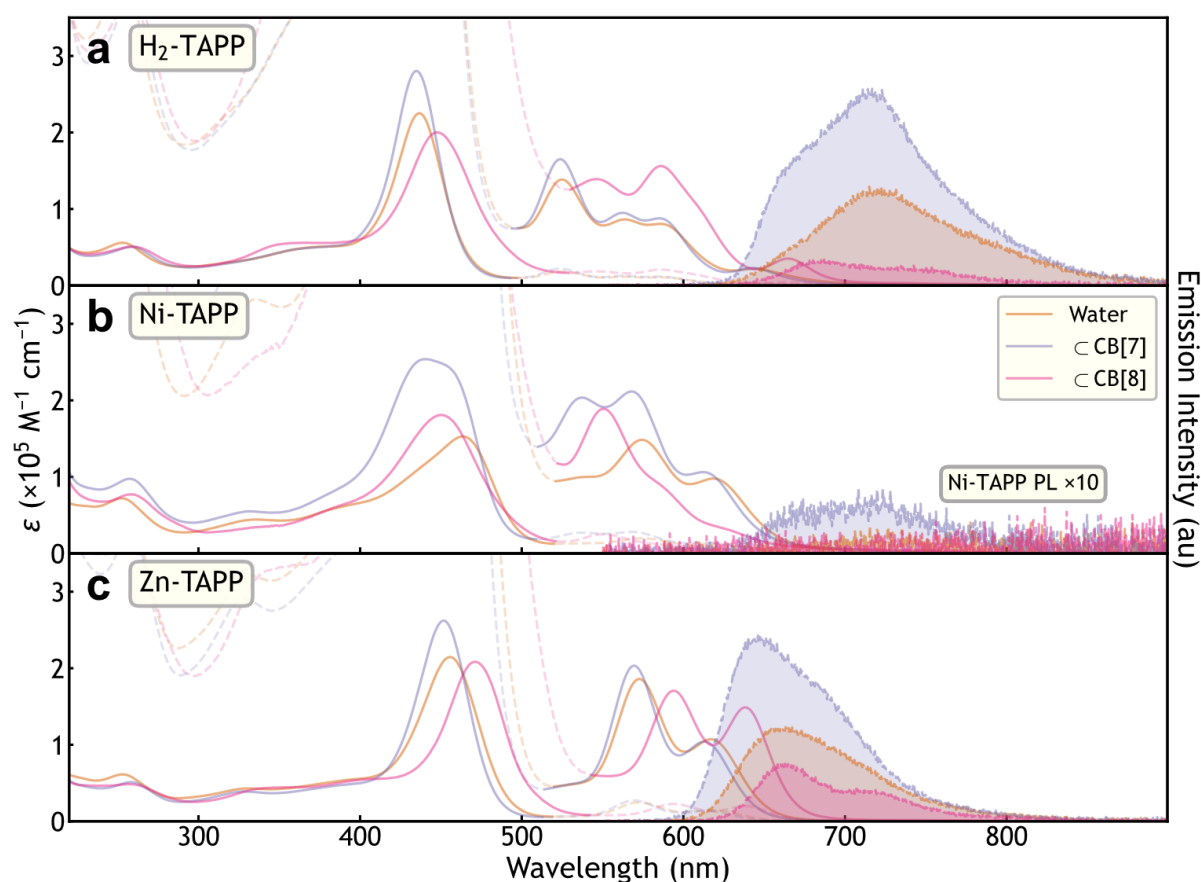


Figure 5.30. UV-Vis and PL spectra of M-TAPP and M-TAPP $\subset$ CB[n] in water. Q bands have been magnified for clarity. All spectra recorded at 1 ± 0.1 μ M M-TAPP with appropriate equivalents of CB[n] to form the 1:4 and 2:4 complexes.

M-TAPP $\subset$ CB[7]₄ encapsulation (**Section 5.7.1**) increased both the optical extinction coefficient and PL QY. Non-polar encapsulation and/or weak rotational restriction of the *N*-arylpyridinium moieties leads to some recovery of the vibronic PL structure via slight destabilisation of intramolecular CT states (**Section 5.4.2**). (M-TAPP)₂ $\subset$ CB[8]₄ dimers (**Section 5.7.2**) exhibited redshifted absorption and emission, accompanied by decreased PL intensity. This is characteristic of an offset face-to-face dimer of polarisable multipolar

fluorophores. Intramolecular CT is more significantly destabilised in (M-TAPP) $_2\subset$ CB[8] $_4$ than in M-TAPP $\subset$ CB[7] $_4$, due to significant hindrance of pyridinium rotation, evidenced by a more resolved PL vibronic structure (**Section 5.6.2**).

Table 5.1. Peak absorption wavelengths (λ_{abs}), extinction coefficients (ϵ) and Soret/Q energy splitting ($E_{\text{Soret}} - E_{\text{Q}}$) data from **Figure 5.30**.

λ_{abs} (nm); $10^{-5} \epsilon$ (M $^{-1}$ cm $^{-1}$); $E_{\text{Soret}} - E_{\text{Q}}$ (eV)										
System	Band	Free M-TAPP			M-TAPP $\subset$ CB[7] $_4$			(M-TAPP) $_2\subset$ CB[8] $_4$		
H $_2$	Soret	437	22.3		435	21.0		447	15.0	
	Q $_y$ (0-1)	525	1.84		524	1.65		546	1.39	
	Q $_y$ (0-0)	564	1.18	0.639	562	0.95	0.644	586	1.56	0.658
	Q $_x$ (0-1)	586	0.84		585	0.88		611*	0.81*	
	Q $_x$ (0-0)	644	0.29	0.912	643	0.23	0.922	665	0.35	0.909
Ni**	Soret	464	11.5		440	19.0		450	13.6	
	Q(0-2)	537*	0.99*		537	2.04		551	1.89	
	Q(0-1)	574	1.48		568	2.12		587*	0.87*	
	Q(0-0)	618	0.98	0.666	612	1.06	0.792	629*	0.29*	0.784*
Zn	Soret	456	16.1		452	19.7		471	15.6	
	Q(0-2)	529*	0.47*		529*	0.47*		549*	0.59*	
	Q(0-1)	573	1.86		569	2.03		594	1.71	
	Q(0-0)	617	1.07	0.709	613	1.04	0.720	638	1.49	0.689

*approx.

**apparent values given based on spectral maxima for illustrative purposes only, due to convolution of triplet and singlet spectra

5.7.1 M-TAPP $\subset$ CB[7] $_4$

M-TAPP $\subset$ CB[7] $_4$ encapsulation increases the extinction coefficients of the Soret and Q bands compared to free aqueous M-TAPP, accompanied by a small blueshift in each. This is similar to the effect of organic solvation observed for M-TAPP (**Section 5.4**) and H $_2$ -TMPyP.³⁸⁶ Here, a slight increase in the Q $_y$ (0-1)/Q $_y$ (0-0) intensity ratio of H $_2$ -TAPP suggests a decrease in electron-withdrawing character of the *N*-arylpyridinium groups in the electron rich-CB[7] cavity.^{357,386,472,485} Otherwise, such small differences indicate little perturbation of excited state CI strength (**Section 5.3.3**) compared to free M-TAPP. The absence of additional peaks indicates that the free M-TAPP concentration is negligible, consistent with ^1H -NMR results (**Section 5.7**).

No change in Q $_x$ /Q $_y$ energy splitting was observed upon H $_2$ -TAPP $\subset$ CB[7] $_4$ encapsulation. If the original solvochromic energy shift (**Section 5.4.2**) was due to increased porphyrin-water H-bonding, CB[7] does not appear to disrupt this. This implies that, while NH tautomerisation rate appears to increase with CB[7] encapsulation (**Section 5.6.1**), the dominant H-bonding configurations remain the same.

Once again, Ni-TAPP exhibits more complex spectral behaviour. Ni-TAPP $\subset$ CB[7] $_4$ encapsulation appears to significantly increase the Ni-TAPP singlet state population, evidenced by the double Soret peak and increase in relative intensity of the higher-energy Q band peaks.⁴⁷³ This, again, is attributed to steric hindrance of Ni-water axial ligation by CB[7].

The relative intensity of the triplet spectrum is higher than observed for free Ni-TAPP in MeOH/MeCN (**Figure 5.16**) indicating some axial water ligation. This is consistent with the observed ^1H -NMR shift of pyrrole resonance (**a**), which increases (shifts downfield) in the order $M\text{-TAPP}/d_6\text{-DMSO} < \text{Ni-TAPP} \subset \text{CB}[7]_4/\text{D}_2\text{O} < \text{Ni-TAPP}/\text{D}_2\text{O}$ (**Figures 5.10, 5.23**), together with apparent triplet state population.

$\text{CB}[7]$ complexation increases the PL intensity of both $\text{H}_2\text{-TAPP}$ and Zn-TAPP . Unlike the broad, featureless emission of free aqueous $\text{H}_2/\text{Zn-TAPP}$, slightly more vibronic structure is observed (*cf.* $\text{H}_2\text{-TAPP}$ PL in MeOH/MeCN; **Figure 5.16a**). As discussed (**Section 5.4.2**) and reported^{313,386} previously, this broadening is caused by coupling between the porphyrin S_1 excited state and intramolecular porphyrin-to-pyridinium CT states. These CT states are facilitated by porphyrin-pyridinium π -conjugation via rotational freedom of the pyridinium groups, and are stabilised by a high environmental dielectric constant. Conversely, the vibronic structure remains distinct if CT states are destabilised by lower solvent polarity and/or conformational restriction.

The modest increase in PL vibronic structure of $M\text{-TAPP} \subset \text{CB}[7]_4$ therefore indicates slight destabilisation of these intramolecular CT states by a lower environmental dielectric constant inside the non-polar $\text{CB}[7]$ cavity.^{313,386,403} CT destabilisation also reduces NRR rate, increasing PL intensity.³²⁴ The fact that significant broadening remains is consistent with the free pyridinium rotation evidenced in **Section 5.6.1**.

Interestingly, addition of $\text{CB}[7]$ yields a slight Ni-TAPP PL signal increase, not present in the unbound complex. Generally, any observed Ni porphyrin fluorescence is usually attributed to impurities;^{481,486} the peak positions here align with those of freebase $\text{H}_2\text{-TAPP}$, which may indicate a small amount of Ni de-ligation, or simply contamination. The reason for this emission signal is currently unknown and requires further investigation. Repeat experiments should be performed with extra care to prevent $\text{H}_2/\text{Zn-TAPP}$ contamination, and the PL signal monitored for changes over several days/weeks.

5.7.2 $(M\text{-TAPP})_2 \subset \text{CB}[8]_4$

$(M\text{-TAPP})_2 \subset \text{CB}[8]_4$ dimerisation significantly redshifts the visible absorption of all three systems, as observed previously for $(\text{EV})_2 \subset \text{CB}[8]_2$ dimers.^{2,260,261,275} The large spectral shift, plus general retention of spectral structure, is characteristic of well-defined geometric alignment, strong electronic coupling and substantial electron delocalisation between the two parallel π -systems.^{265,327,511}

This behaviour can be understood in the context of the Kasha/Frenkel excitation model.^{265,511} Briefly, strong electronic coupling between transition dipole moments within a fluorophore dimer leads to splitting of the monomer absorption spectrum. For parallel fluorophore alignment (expected in $(M\text{-TAPP})_2 \subset \text{CB}[8]_4$), one of the two resulting electronic transitions is allowed, the other forbidden. For a face-to-face geometry (H-type aggregation;

Figure 5.31b), the lower-energy transition is forbidden and the absorption spectrum appears blueshifted. Conversely, a head-to-tail arrangement (J-type aggregation; **Figure 5.31c**), yields a redshifted spectrum and the higher-energy transition is forbidden.

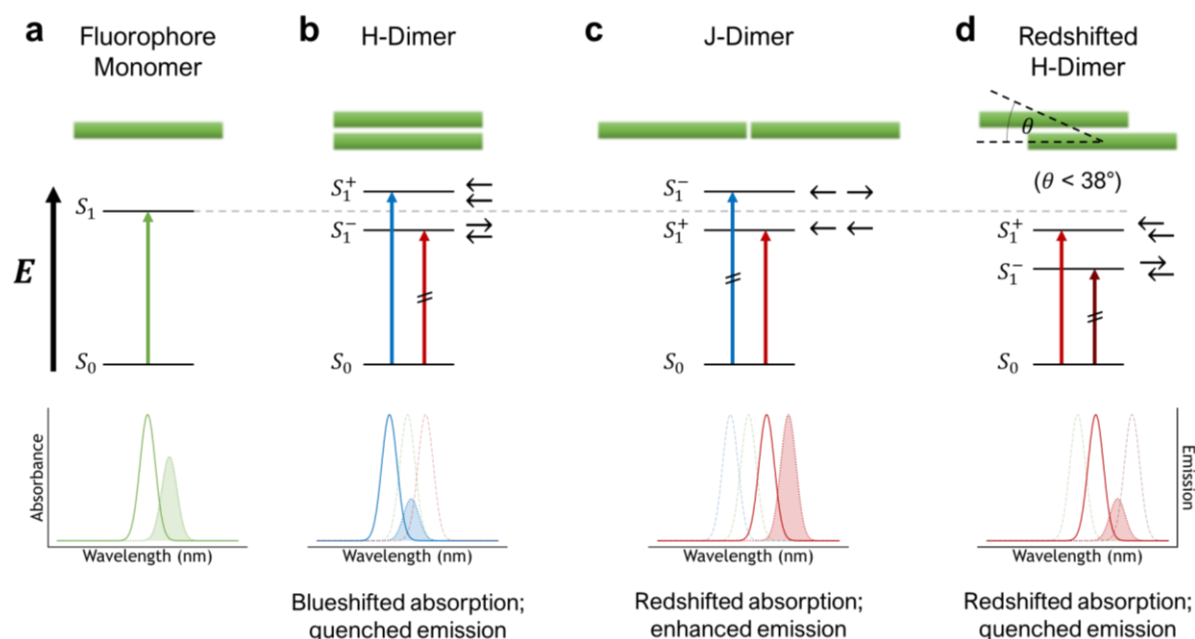


Figure 5.31. Fluorophore arrangements, energy level diagrams and simplified absorption/emission profiles for a generic fluorophore **(a)** monomer, **(b)** H-dimer, **(c)** J-dimer and **(d)** offset face-to-face dimer, aka “redshifted H-dimer”. Top: schematics illustrating monomeric and dimeric geometries of one or two generic fluorophores (green rectangles). Redshifted H-dimerisation **(d)** occurs for highly polarisable, multipolar molecules; θ range for this behaviour depends on intermolecular separation and molecular structure.^{331,512} Middle: energy level diagrams illustrating splitting of fluorophore $S_1 \leftarrow S_0$ transitions upon dimerisation. S_1^+ and S_1^- denote energy levels resulting from symmetric ($\leftarrow + \leftarrow$) and antisymmetric ($\leftarrow + \rightarrow$) coupling of $S_1 \leftarrow S_0$ transition dipoles, respectively. For parallel fluorophore alignment as in **(b-d)**, $S_1^+ \leftarrow S_0$ is allowed and $S_1^- \leftarrow S_0$ is forbidden.²⁶⁵ Bottom: simplified illustration of absorption (unshaded peaks; solid = allowed, dashed = forbidden) and emission (dotted/shaded peaks) for each of the geometries. Vibronic transitions have been omitted here for simplicity.

According to this Kasha/Frenkel exciton model,²⁶⁵ fluorescence is quenched or enhanced for H- or J-dimers, respectively. However, for highly polarisable multipolar molecules (e.g. M-TAPP), the J- and H-dimer formalism can be misleading.^{331,513} Here, for example, the bathochromic absorption shifts of both $(H_2\text{-TAPP})_2\subset\text{CB}[8]_4$ and $(Zn\text{-TAPP})_2\subset\text{CB}[8]_4$ are characteristic of offset face-to-face stacking,^{378,389,514} i.e. J-aggregation.^{265,511,515} The redshift is larger for Zn-TAPP (15 nm) than H_2 -TAPP (10 nm), consistent with higher π -delocalisation in the former. However, the PL intensity decreases upon dimerisation in both cases, which, according to the Kasha/Frenkel model, is instead characteristic of an H-aggregate.^{265,511}

Redshifted absorption with quenched fluorescence has been observed previously for certain fluorophore assemblies and has been called “non-fluorescent J-aggregation”⁵¹⁶ or “redshifted H-aggregation”.³³¹ Such non-Kasha behaviour can occur when each fluorophore within a laterally offset face-to-face dimer strongly perturbs the charge distribution of the other.⁵¹³ This perturbative coupling stabilises the pair of excited states, such that both transitions of the split exciton band are lower in energy than the monomeric excited state

(**Figure 5.31d**). In such a system (e.g., (M-TAPP) $_2\subset$ CB[8] $_4$) the higher-energy transition is allowed and PL is quenched, as in an H-aggregate, but redshifted absorption is observed, as in a J-aggregate.

The Zn-TAPP absorption bands do not significantly broaden upon CB[8] complexation. The lower energy/intensity difference between the Soret & Q bands (**Table 5.1**) indicates weaker excited state CI than in monomeric Zn-TAPP and therefore some perturbation of the $1a_{1u}(\pi)$ and/or $3a_{2u}(\pi)$ orbitals (**Figure 5.13**). This is likely due to a complex interplay between the effects of both encapsulation and dimerisation, although further investigation is beyond the scope of this work. The higher relative Q(0-0) intensity in the dimer indicates a significant offset (small θ in **Figure 5.31d**) in π - π overlap.^{331,511} Further understanding of dimerisation geometry (H-type vs J-type) may be possible in future experiments via temperature dependence of the relative vibronic band intensities.⁵¹²

The (H $_2$ -TAPP) $_2\subset$ CB[8] $_4$ absorption spectrum is more significantly broadened, and the Q_x/Q_y energy splitting is decreased. The relative Q band intensity also increases upon dimerisation, to a greater extent than Zn-TAPP. This implies stronger perturbation of the HOMO/HOMO-1 energies, although the extent is difficult to quantify due to the change in Q_x/Q_y splitting.

These differences may suggest changes in the core NH environment via intermolecular H-bonding and/or proton exchange between the two porphyrin cores, facilitated by the confined geometry and/or electronically coupled ground state. Unfortunately, the core proton dynamics were not resolved with NMR in **Section 5.6**, and more VT-NMR experiments are required to explore this further.

At first glance, the (Ni-TAPP) $_2\subset$ CB[8] $_4$ Soret absorption appears blueshifted from that of free Ni-TAPP. However, the intensity ratio change and uniform redshift of the Q band peaks reveals a change in relative singlet/triplet population accompanying the expected bathochromic shift. ^1H -NMR analysis indicates a lower triplet population in (Ni-TAPP) $_2\subset$ CB[8] $_4$ than free Ni-TAPP in d_6 -DMSO (**Figures 5.10, 5.23**). The absence of shoulders either side of the (Ni-TAPP) $_2\subset$ CB[8] $_4$ Soret band suggests the same may be true when compared to Ni-TAPP in MeOH/MeCN (**Figure 5.16b**), although the Soret peak width adds some uncertainty. The Ni-TAPP/DMSO UV-Vis absorption should be measured for more direct comparison. The broadening may be due to pentacoordinate Ni-TAPP (one axial water ligand per Ni centre) sterically prevented from forming the hexacoordinate complex by the confined dimer geometry. Addition of a strong Lewis base (e.g. pyridine or imidazole)^{351,470,473} to (Ni-TAPP) $_2\subset$ CB[8] $_4$, may reveal further insights upon UV-Vis and ^1H -NMR analysis.

The (M-TAPP) $_2\subset$ CB[8] $_4$ emission spectra (excluding Ni-TAPP) are similarly redshifted from the M-TAPP $\subset$ CB[7] $_4$ emission. Stokes shifts are not compared quantitatively here due to spectral convolution and uncertainty of the absolute 0-0 vibronic peak positions. Qualitatively, the Stokes shifts appear similar to free M-TAPP and M-TAPP $\subset$ CB[7] $_4$. In contrast to these

systems, however, is the distinct vibronic (M-TAPP) $_2\subset$ CB[8] $_4$ PL structure. This is consistent with the restricted pyridinium rotation²⁶¹ in (M-TAPP) $_2\subset$ CB[8] $_4$ (**Section 5.6**), which destabilises the intramolecular CT states responsible for PL broadening and increases the vibronic structure definition.^{386,403,517}

5.7.3 Final UV-Vis/PL Comments

Long-lived excited states (>10 ns) and variable PL QYs have been reported for similar EV $\subset$ CB[8] dimers.^{260,261} This indicates significant dependence of radiative vs non-radiative relaxation pathways on fluorophore arrangement, clamping geometry and freedom of motion in both the ground and excited states. Future experiments should therefore begin with excited state lifetime analysis (via TCSPC) and PL QY measurements of the M-TAPP $\subset$ CB[7] $_4$ and (M-TAPP) $_2\subset$ CB[8] $_4$ systems to add to the growing photophysical dataset.

The small (M-TAPP) $_2\subset$ CB[8] $_4$ PL stokes shifts imply allowed 0-0 vibronic emission, which is characteristic of a J-aggregate and forbidden for standard H-aggregates. The nonzero size of this shift indicates geometric relaxation before emission, consistent with a long-lived excited state.^{260,261} The intensity ratios of the vibronic absorption bands indicate significant lateral offset between the two M-TAPP molecules, consistent with “red-shifted H-aggregate” behaviour;³³¹ the temperature dependence of these intensities should provide further information on the H/J-aggregate character of the (M-TAPP) $_2\subset$ CB[8] $_4$ dimers.

Similar decreases in PL QY have been observed for (EV) $_2\subset$ CB[8] $_2$ dimers with non-parallel clamping moieties. This suggests that intracomplex linear shuttling motion (**Figure 5.24a**) or restriction thereof may play an important role in excited state decay pathways. This could be explored using *bis*-TAPP analogues of M-TAPP by comparing PL QY & lifetime of the *cis* (nonlinear) and *trans* (linear) isomers and CB[8]-mediated dimers thereof. This understanding may be augmented with femtosecond transient absorption (fsTA) spectroscopy to optically probe intracomplex motion and/or geometric relaxation of the (M-TAPP) $_2\subset$ CB[8] $_4$ excited states.

5.8 NPoM Experiments

M-TAPP and M-TAPP $\subset$ CB[n] NPoM samples were prepared as described in **Section 4.2** and **Methods 7.2**; both DF and PL spectra were measured (**Methods 7.4.1**). For each NPoM, immediately following the collection of the DF z-stack (**Section 1.3.2**), the nanoparticle is re-focused and irradiated at 447 nm, and the scattered light (>500 nm) is analysed. NPoM SERS measurements (**Methods 7.4.2**) were performed for M-TAPP NPoMs without CB[n].

As with ArV $\subset$ CB[n], DF NPR analysis (**Section 5.8.1**) yielded mostly reasonable values of d and n_g . The NPoM PL spectra behave as expected in some cases, but not others (**Section 5.8.2**). Low PL intensity from H₂-TAPP $\subset$ CB[7]₄ NPoMs is consistent with $\lambda_{\text{ex}} > \lambda_{\text{Soret}}$, indicative of isolated H₂-TAPP monomers; (M-TAPP)₂ $\subset$ CB[8]₂ NPoMs exhibit complex, λ_c -dependent PL behaviour, indicative of nonzero plexcitonic coupling.^{120,121} Overall, the combined DF NPR and PL results indicate that M-TAPP $\subset$ CB[n] structure is retained upon NPoM assembly.

M-TAPP NPoM SERS analysis ($\lambda_{\text{ex}} = 633$ nm) required significantly lower laser powers (5 μ W) than simpler aromatic thiol monolayers (100-300 μ W),^{25-27,50} indicating SERRS behaviour (**Section 5.8.3**). Higher laser powers led to spectral instability, indicative of facile Au surface rearrangement. The energy mismatch between the solution-phase M-TAPP absorbance (**Figures 5.14, 5.16**) and Raman excitation wavelength may indicate interaction with low-lying direct singlet-to-triplet transitions, demonstrated previously for Zn-TAPP.¹²⁰

Future NPoM characterisation experiments should include DF NPR analyses of repeat NPoM preparations and optimisation of M-TAPP $\subset$ CB[n] SAM deposition. More in-depth PL analysis with tuneable excitation wavelength is recommended to probe low lying M-TAPP($\subset$ CB[n]) excited states in the cavity.¹²⁰ TCSPC measurements should also be performed to determine the cavity-modified PL decay rates and quantify the Purcell effect for each system.¹¹⁹ SERS measurement of M-TAPP $\subset$ CB[n] NPoMs is also recommended, to explore the effects of supramolecular structure on Au surface stability^{50,99,154} and electron transport across the gap.

5.8.1 DF & NPR Analysis

As observed for ArV($\subset$ CB[n]) NPoMs (**Section 4.2**), NPR analysis¹⁷ of the M-TAPP and M-TAPP $\subset$ CB[n] NPoMs yields reasonable d and n_g values for most systems, although with significant deviations in some cases (**Figure 5.32**). This variability highlights the sensitivity of the NPR technique to small deviations in various geometric and physicochemical NPoM parameters, in addition to d and n_g . This uncertainty is visible in the deviation of CB[n] data points from the expected $n_g = 1.1$ -1.3, $d = 0.9$ nm positions. As such, the data below should be interpreted with caution and is mainly useful for qualitative comparison.

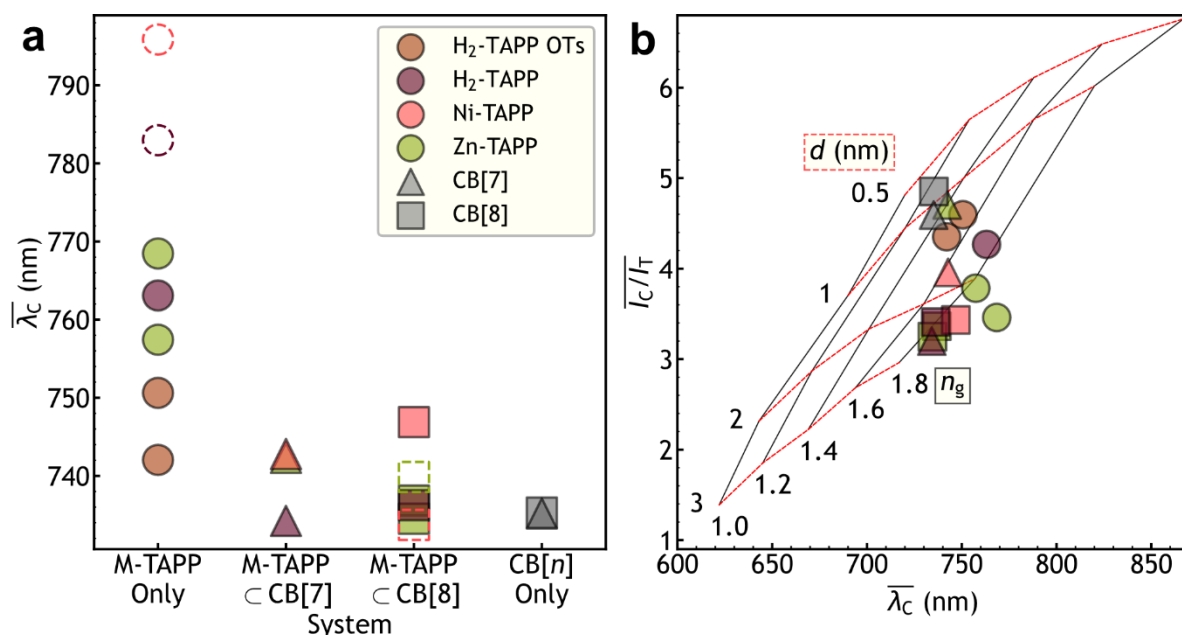


Figure 5.32. (a) λ_C values for all M-TAPP and M-TAPP $\subset$ CB[n] NPoMs (b) I_C/I_T vs λ_C of the same datasets. Slanted background grid indicates theoretical values for a range of d (red dashed lines) and n_g (grey solid lines).¹⁷ As in **Figure 4.3**, Data points with broken outlines present in (a) but not (b) are λ_C from experiments with misaligned optical collection, for which λ_C remains reliable, but I_C/I_T data does not.

Large λ_C and I_C/I_T variation is apparent between the M-TAPP-only NPoMs, indicating a strong dependence of n_g and d on metal centre and counterion. Non-negligible variability was also observed for repeat preparations of each system, indicating high sensitivity of optical response to packing and impurities within the SAM. As mentioned previously, the theoretical data grid in **Figure 5.32b** does not account for gap conductance (G), an increase in which is expected to decrease both λ_C and I_C .^{26,102}

Here, the difference in NPR data between the chloride and tosylate salts of H₂-TAPP suggests smaller n_g and d in the latter, possibly due to decreased molecular packing caused by the bulky counterion. Conversely, Zn-TAPP exhibits a significantly lower I_C/I_T and similar λ_C to H₂-TAPP chloride, indicating higher n_g and d .

M-TAPP@Au binding is hypothesised to be bidentate (**Figure 5.33a**) rather than mono- (**Figure 5.33b**) or tetradentate (*cf.* **Figure 2.15a**) to maximise both S-Au bonding and intermolecular π - π interactions. This is consistent with the high apparent n_g in **Figure 5.32b** and is briefly discussed in **Section 5.8.2**, but requires further nano- and optical characterisation to confirm.

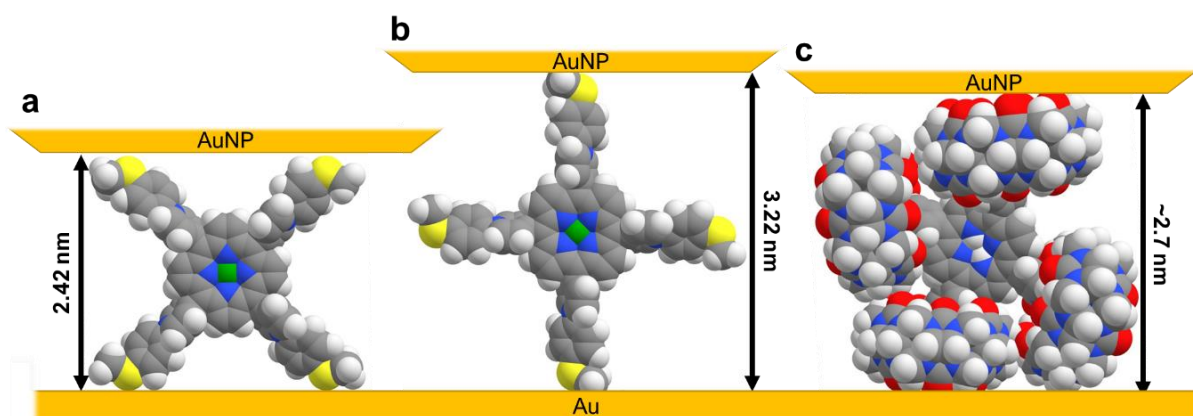


Figure 5.33. Proposed binding geometries of **(a, b)** Zn-TAPP and **(c)** H₂-TAPP₂CB[7]₄ between Au surfaces. Zn-TAPP may bind in a **(a)** bidentate or **(b)** monodentate fashion with respect to S-Au coordination. Distances quoted in **(a, b)** are based on centre-centre distance between top and bottom sulfur atoms in DFT-optimised Zn-TAPP structure (**Figure A74a**), plus $2r_{\text{S-Au}}$ from ArVSM₂-Au₂ DFT structure (**Figure A22**). Structure **(a)** is hypothesised to be more likely than **(b)** due to increased S-Au bonding interaction. Distance in **(c)** is based on approximate centre-centre distance of CB[7] carbonyl oxygens of GFN2-xTB⁵¹⁸ H₂-TAPP₂CB[7]₄ structure (**Figure A88**), plus the oxygen vdW diameter. Atom colours: C (grey), H (white), N (blue), O (red), S (yellow), Zn (green).

The large d (~2-2.5 nm) implied for Zn-TAPP in **Figure 5.32b** is therefore feasible, based on the theoretical molecule heights in **Figure 5.33**, although this implies small ϕ (near-vertical orientation) if binding is bidentate (**Figure 5.33a**). Alternatively, the lower-than-expected $\overline{I_C/I_T}$ may indicate nonzero G , consistent with the higher π -conjugation expected for Zn-TAPP, (**Sections 5.4-5.5**), accompanied by a slightly higher n_g . This agrees with previous STM measurements of alkanethiol-tethered porphyrins on Au, which revealed a higher conductance of Zn-TMPyP than H₂-TMPyP.⁵¹⁹ Similar measurements²⁵ would be useful for calibrating conductance of the M-TAPP NPoMs here.

Conversely, the Ni-TAPP $\overline{\lambda_C}$ value (**Figure 5.32a**) appears significantly redshifted from both Zn-TAPP and H₂-TAPP which, assuming similar molecular orientation and packing, could imply smaller G , consistent with the lower π -electron density hypothesised for Ni-TAPP throughout **Sections 5.3-5.7**. However, this should also yield lower n_g and therefore a blueshifting effect. The Ni spin state may have some effect, but more data points and reliable $\overline{I_C/I_T}$ values are required to explore this further.

The M-TAPP₂CB[n] NPR data, while still somewhat variable, is more predictable and consistent than the M-TAPP only data. The $\overline{I_C/I_T}$ and $\overline{\lambda_C}$ positions of H₂-TAPP₂CB[7]₄ and all (M-TAPP)₂CB[8]₄ NPoMs indicate $n_g \approx 1.8-1.9$ and $d \approx 2.5-3$ nm, approximately consistent with the proposed M-TAPP₂CB[7]₄ binding geometry in **Figure 5.33b**. The Ni/Zn-TAPP₂CB[7]₄ data, however, do not agree with the expected d values.

The similarity between the CB[n] only and Zn-TAPP₂CB[7]₄ $\overline{I_C/I_T}$ and $\overline{\lambda_C}$ positions, in particular, may indicate dissociation of the supramolecular complex. Despite this, the nonzero Zn-TAPP PL signal of the Zn-TAPP₂CB[7]₄ NPoM (**Figure 5.34f**; **Section 5.8.2**) does indicate presence of Zn-TAPP in the gap. As the PL band shape and position does not vary significantly

between Zn-TAPP and Zn-TAPP₂CB[7]₄ (either in NPoM or aqueous solution) it is currently unclear whether supramolecular structure has been retained, or the NPoM gap consists of separate, interspersed CB[7] and Zn-TAPP with $d = 0.9$ nm.

The Ni-TAPP₂CB[7]₄ NPoM results, contrastingly, indicate $d \approx 1.8$ nm and $n_g \approx 1.7$, more consistent with a Ni-TAPP monolayer. This may again indicate complex dissociation, but with d determined by Ni-TAPP, rather than CB[7]. Alternatively, the deviation in the Zn/Ni-TAPP₂CB[7] NPR results could also be due to variations in conductance or impurities within the spacer layer or substrate material. As with NPoM DF measurements in general, more exploration and refinement is required to identify the source of and minimise the experimental and theoretical errors involved in this technique.

5.8.2 DF + PL

The M-TAPP and M-TAPP₂CB[n] NPR results were augmented with NPoM PL measurements. Here, the NPoMs were excited with focused 447 nm laser light (**Methods 7.4.1**); each photoluminescence spectrum ($\lambda > 500$ nm) was background subtracted (to remove laser leak and Au background emission) and divided by the square root of the DF spectrum at the same focal height to correct for outcoupling efficiency.¹²¹ The NPoM PL results are summarised, together with the corresponding λ_c frequency distributions, in **Figure 5.34**.

As with the DF spectra in previous λ_c histograms, each coloured PL spectral trace is the average of PL spectra from all NPoMs in the λ_c histogram bin of corresponding colour. For all Zn-TAPP systems, the NPoM PL spectra loosely correspond to their solution-phase counterparts. The H₂-TAPP spectra exhibit slightly more variation, while the Ni-TAPP spectra exhibit unexpected PL intensity.

The PL maximum of the H₂-TAPP NPoM (without CB[n]) occurs at a longer wavelength (~673 nm) than the higher-energy S₁(ν_0)→S₀(ν_0) vibronic peak of the organic-phase H₂-TAPP emission (661 nm; **Figure 5.14a**), indicating some intermolecular excitonic coupling within the monolayer.^{265,512} This redshift from free H₂-TAPP is smaller than that observed upon aqueous (H₂-TAPP)₂CB[8]₄ complexation (**Figure 5.30a**), indicating weaker excitonic coupling and/or a different offset between the porphyrin π -systems in the tilted H₂-TAPP monolayer than in (H₂-TAPP)₂CB[8]₄. Whether this translates to a larger or smaller θ (**Figure 5.31d**) is currently unclear and would require deeper theoretical treatment of the system.^{331,512} A shoulder is visible at longer wavelengths, similarly redshifted from its analogous solution-phase position. This may correspond to the S₁(ν_0)→S₀(ν_1) transition.

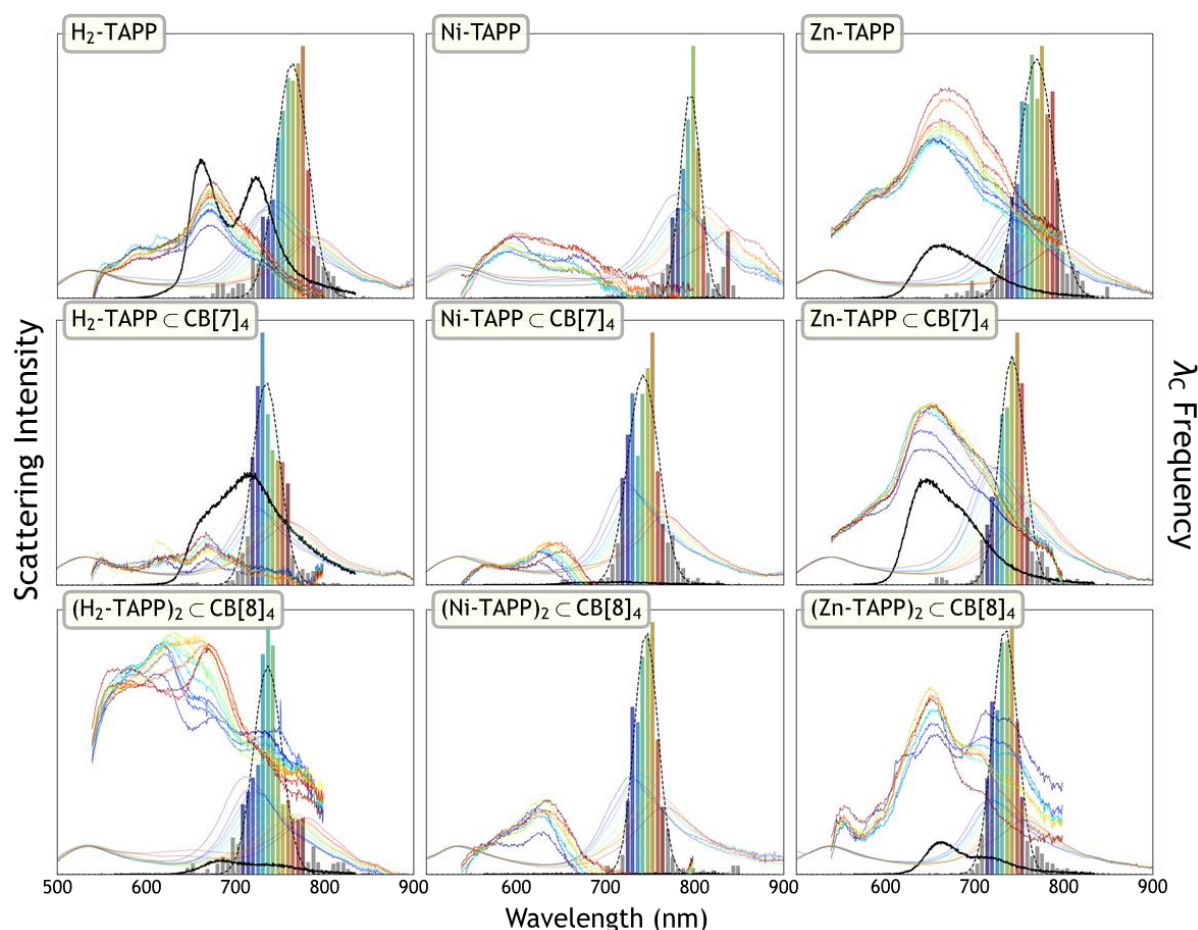


Figure 5.34. M-TAPP and M-TAPP $\subset$ CB[n] NPoM DF λ_c frequency distributions (coloured bars) with DF and PL spectra corresponding to averages of each coloured histogram bin. Smooth, semi-transparent background traces are average DF spectra of each λ_c bin, colour-coded as before. Thicker, noisy traces (blue-shifted from DF spectra) correspond to the average NPoM PL spectrum (ex. 447 nm) of each λ_c bin of the same colour. Black traces are solution-phase M-TAPP($\subset$ CB[n]) PL spectra from **Figure 5.30**. Each individual PL spectrum has been background subtracted to remove laser leak and corrected for outcoupling efficiency using the NPoM DF scattering intensity at the same focal height. PL scattering intensities have been uniformly scaled here to allow direct comparison between systems.

The corresponding PL maximum of the H₂-TAPP $\subset$ CB[7]₄ NPoM appears at shorter wavelength (665 nm), indicative of the monomeric species with no intermolecular coupling. This is consistent with the significantly decreased PL intensity relative to the H₂-TAPP-only NPoM; the Soret band of monomeric H₂-TAPP $\subset$ CB[7]₄ lies at higher energy (435 nm; **Figure 5.30a**) than the incident laser wavelength (447 nm), and excitation is therefore inefficient. Because of this, the significant PL intensity of the H₂-TAPP-only NPoM further supports excitonic coupling within the CB[n]-free H₂-TAPP monolayer. Additionally, the dominant H₂-TAPP $\subset$ CB[7]₄ NPoM PL peak corresponds to the higher-energy shoulder of the aqueous spectrum, while the dominant solution-phase vibronic band is markedly decreased in NPoM, indicating significant modification of radiative efficiency from the different vibronic states.

Conversely, the (H₂-TAPP)₂ $\subset$ CB[8]₄ NPoM exhibits higher PL intensity due to near-perfect alignment of the Soret position (447 nm; **Figure 5.30a**) with the excitation laser, providing strong evidence for retention of supramolecular structure. The PL maxima for NPoMs with

large λ_C (orange, red traces) occur around 671 nm, blueshifted from the aqueous system by ~ 13 nm. This blueshift may indicate smaller θ between the two porphyrin π -systems^{331,511,512} due to confinement of the dimer within the cavity. This should also yield a blueshift in Soret position and may be explored in future by probing the excitation spectrum of the NPoM system.^{119,120}

Alternatively, the blueshift may indicate enhanced radiative emission via plasmonic outcoupling.³ Many aqueous $(\text{EV})_2 \subset \text{CB}[8]_2$ complexes undergo fast geometric relaxation in the excited state before radiative emission, resulting in large Stokes shifts.^{260,261} Here, fast emission before such relaxation occurs may reduce the observed Stokes shift and manifest as a blueshift relative to the aqueous emission. The magnitude of this effect would depend strongly upon the optical response of the nanostructure and the wavelength-dependent plasmonic outcoupling efficiency.^{48,121}

Several emission peaks are observed for this $(\text{H}_2\text{-TAPP})_2 \subset \text{CB}[8]_4$ NPoM, with relative intensities that do change steadily with λ_C . Specifically, the higher energy peak (~ 619 nm) increases in intensity as λ_C decreases, and dominates when λ_C is most closely aligned with the aqueous emission curve. This is accompanied by an increase in the lower-energy emission band around 740 nm. Similar higher-wavelength emission bands are also observed for the other $\text{H}_2\text{-TAPP}$ NPoMs and vary in peak position between the systems. While nonzero broadband emission may be a background subtraction artefact (**Appendix 8.1**), the consistency of PL peak positions within (and variation between) each system, may indicate PL from higher vibronic states. This is again consistent with enhancement of radiative emission rate by weak plexcitonic coupling.

The differences in emission enhancement for the various higher excited states are very likely related to the $\text{CB}[n]$ -mediated isolation, dimerisation and re-orientation of the fluorophores within the cavity, together with the associated changes in G , d and n_g . This behaviour should be explored further with time-resolved optical analyses (e.g. fsTA and TCSPC) and variable excitation wavelength to probe the excited state dynamics.^{48,111,119–121} The degree of Purcell emission enhancement may also be inferred via simulation of the field strength in the gap.^{48,101,111}

The Zn-TAPP and $\text{Zn-TAPP} \subset \text{CB}[7]_4$ NPoMs exhibit higher PL intensities than the analogous $\text{H}_2\text{-TAPP}$ systems, while the $(\text{Zn-TAPP})_2 \subset \text{CB}[8]_4$ NPoM PL intensity is lower than for $(\text{H}_2\text{-TAPP})_2 \subset \text{CB}[8]_4$. This is consistent with the Soret band positions of aqueous $\text{Zn-TAPP}(\subset \text{CB}[n])$ systems relative to those of $\text{H}_2\text{-TAPP}(\subset \text{CB}[n])$ and the different excitation efficiencies at 447 nm (**Figure 5.30a,c**).

The Zn-TAPP NPoM emission is stronger than, and redshifted from, that of the $\text{Zn-TAPP} \subset \text{CB}[7]_4$ NPoM, despite the similar aqueous Soret band positions. The redshift again suggests excitonic coupling within the Zn-TAPP monolayer; the redshift here is larger than for $\text{H}_2\text{-TAPP}$, indicating stronger intermolecular interactions, consistent with increased Zn-TAPP

π -conjugation (**Section 5.5.1**). The Soret redshift expected from such coupling is expected to decrease the excitation efficiency at 447 nm and therefore the PL intensity. The opposite is instead observed, with increased Zn-TAPP NPoM PL intensity indicating significantly higher molecular density in the hotspot.

The (Zn-TAPP) $_2\subset$ CB[8] $_4$ NPoM PL exhibits qualitatively similar λ_C dependence to the (H₂-TAPP) $_2\subset$ CB[8] $_4$ system. In this case, however, the higher-energy emission peak is not present and the spectrum is instead dominated by the longer-wavelength band(s) for smaller λ_C . The nature of the electronic states and transitions responsible for the various emission bands are currently unknown, and require more investigation before more in-depth conclusions can be drawn.

All Ni-TAPP($\subset$ CB[n]) NPoMs have nonzero PL signal below 700 nm. Again, this may be an artefact of the background subtraction process, but could also be due to plasmonically enhanced emission that outweighs the fast nonradiative relaxation expected for Ni(II) porphyrins.^{481,486} The presence of Au may also affect the Ni-TAPP electronic structure via S-Au bond formation⁹⁷ and/or facilitate emission from low-lying Ni triplet states via the external heavy atom effect.¹²⁰ The former may be tested using Ni-APP analogues without terminal SME groups, while the latter can again be explored through time- and wavelength-resolved PL measurements.^{119–121}

Overall, NPoM PL analysis provides strong evidence for retention of M-TAPP $\subset$ CB[n] supramolecular structure within the plasmonic hotspot and reinforces the conclusions drawn from the NPR results (**Section 5.8.1**). At the very least, supramolecular control over intermolecular coupling, molecular density and geometric alignment of M-TAPP within the nanocavity field has been demonstrated, consistent with the ArV $\subset$ CB[n] results of **Chapter 4**.

This validates the potential for increased control over light-matter interactions between plasmonic nanostructures and large, complex fluorophores with metal ligating capabilities. Extrapolation to other chemical scaffolds of arbitrary core and/or peripheral functionality should therefore be relatively straightforward, given the modular nature of *N*-arylpyridinium $\subset$ CB[n] supramolecular assembly.^{260,261}

5.8.3 SERS

M-TAPP NPoM SERS spectra (without CB[n]) were measured with $\lambda_{\text{ex}} = 633$ nm (**Methods 7.4.2**). Preliminary analyses revealed significant spectral instability when using the 100-300 μW laser powers commonly employed for aromatic thiol NPoMs.^{25,26,50} Power series measurements were therefore performed for H₂-TAPP to identify the laser power range required for stable SERS lines (**Figure 5.35**). However, laser powers as low as 10 μW still caused significant spectral splitting and wandering over time, and the frequency of picocavity^{50,51} and flare⁵² events increased consistently with laser power. This behaviour indicates a significantly reduced activation barrier for Au surface reconstruction¹⁵⁴ when M-TAPP is present.

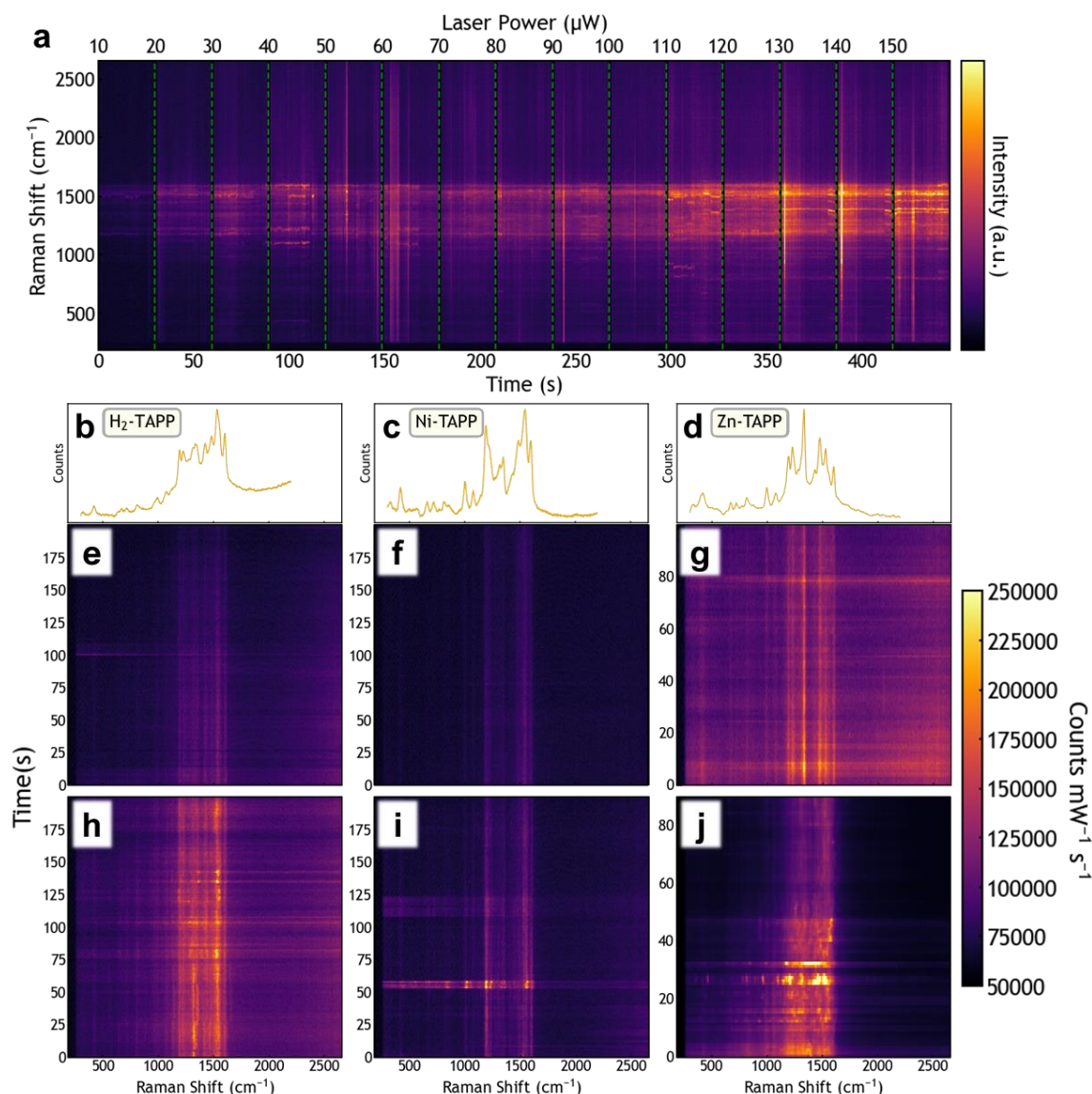


Figure 5.35. (a) H₂-TAPP only NPoM SERS timescan & power series. Laser power ($\lambda_{\text{ex}} = 633$ nm) was increased from 10 to 150 μW in 10 μW steps (power changes indicated by green dashed lines). Increasing laser power increases Raman signal intensity and probability of picocavity^{50,51} and flare⁵² events. (b-j) M-TAPP NPoM SERS measurements (5 μW excitation). (b-d) Time-averaged single-cavity SERS spectra and (e-g) stable SERS timescans of individual M-TAPP NPoMs. (h-j) SERS timescans of different individual NPoMs, illustrating persistence of spectral instability in some cases.

Subsequent measurements were performed for the three M-TAPP NPoM systems using 5 μ W excitation, which mostly yielded stable SERS signals (**Figure 5.35e-g**). However, spectral wandering and flare emission were still occasionally observed, even at these low powers (**Figure 5.35h-j**).

Despite the poor resonance between the excitation laser and plasmonic nanostructure at 633 nm, extraordinarily high signals (10^5 - 10^6 counts $^{-1}$ mW $^{-1}$ s $^{-1}$; **Figure 5.35e-j**) were observed in many cases. Assuming a lateral gap field intensity FWHM¹¹² (**Section 1.3.4**) of $\Delta x \approx \sqrt{Dd}/n_g \approx 7$ nm (using $n_g \approx 1.8$, $d \approx 2$ nm; **Figure 5.32b**) and a molecular vdW area of ~ 1.74 nm 2 (from DFT; **Figure A73a**) with near-perfect packing, the observed signals originate from 20-25 M-TAPP molecules. This implies signals of 2000-10000 counts $^{-1}$ mW $^{-1}$ s $^{-1}$ per molecule, higher even than observed for BPC¹ (**Section 3.3.2**).

While these values are approximate and possibly overestimated, the data indicates a significant SERRS effect. The 633 nm excitation is approximately electronically resonant with the Q $_x$ (0-0) transition of H $_2$ -TAPP in aqueous solution, but 18 nm redshifted from the analogous Q(0-0) transition of Ni/Zn-TAPP. Nevertheless, the Zn-TAPP NPoMs exhibited the highest average SERRS signals at this excitation wavelength, indicating, again, redshifted Zn-TAPP absorption due to excitonic coupling within the monolayer (**Section 5.8.2**).

Despite the similar aqueous Q(0-0) positions, the average Ni-TAPP NPoM SERRS intensity appeared lower than for Zn-TAPP, although more data is required to confirm this. If true, this may indicate a less redshifted Q(0-0) band due to lower excitonic coupling in the SAM, consistent with lower π -density in Ni-TAPP. A high singlet state population in the gap may also be responsible for decreased SERRS, via reduced Q(0-0) strength (**Section 5.4.2**). This would indicate steric restriction of Ni ligation in the close-packed SAM. This highlights the possibility of exploring chemical accessibility of the metal centre in Ni-TAPP NPoM cavities with and without CB[n], via analysis of the PL or SERRS excitation spectra upon exposure to various ligands.

Subsequent M-TAPP NPoM SERS experiments should include M-TAPP $\subset$ CB[n] NPoMs. Investigation of the power dependence of picocavity and flare events (*cf.* **Figure 5.35a**) for these systems may yield insights into the effects of CB[n] complexation upon Au surface stability. Moving further forward, the next recommended step is to investigate the ability of various M-APP($\subset$ CB[n]) systems to trap and transport photogenerated hot electrons, as studied for smaller spacer molecules by de Nijs *et al.*,²⁷ and characterise the effects of supramolecular structure, terminal functionality and metal centre upon the process. Spectroelectrochemical analysis can then be used to explore the possibility of charge transfer to external chemical substrates via the exposed metal centre.⁹⁷ Further investigation of these systems as low-energy molecular switches is also recommended. This can be achieved by monitoring SERS signatures of changes in ring torsion, oxidation state and/or spin state upon application of bias across the nanojunction.²⁵

5.9 M-TAPP $\subset$ CB[n] Conclusion

This chapter was inspired by the results of the BPc (**Chapter 3**) and ArV $\subset$ CB[n] (**Chapter 4**) plasmonic systems. The initial goal was to design, synthesise and explore the nano self-assembly properties of a water-soluble molecular spacer with a chemically accessible metal centre, strong optical absorption/emission and CB[n] complexation ability via modular guest moieties.

Porphyrins were chosen for their diverse chemical tailorability, broad academic attention and diverse functionality. The vast library of existing porphyrin (and viologen) research provided a solid knowledge base to aid synthesis and characterisation of these compounds and facilitate understanding of their supramolecular and plasmonic behaviour. *N*-arylpyridinium functionality was incorporated, inspired by the modular CB[n]-mediated isolation and dimerisation of ArVs/EVs and the successful plasmonic self-assembly using ArV $\subset$ CB[n] spacers.

5.9.1 Summary

M-TAPP synthesis proved more complex than for simpler viologen systems, requiring harsh conditions to convert TPyP into the *N*-(2,4-dinitrophenyl)pyridinium Zincke intermediate. Significant modifications to the existing literature report were required, but the intermediate was eventually synthesised with good purity and yield. The second step was novel and required milder reaction conditions than expected; once the method was established, synthesis and workup were relatively simple. Metallation and ion exchange were straightforward and achieved using slightly modified literature methods.

Solvochromism and oxidative instability were observed during aqueous M-TAPP analysis. Solvent choice influenced the Ni-TAPP spin state (via axial ligation), as well as intramolecular CT processes. The terminal thioether groups oxidised slowly in aqueous solution (and rapidly in D₂O) due to photosensitising behaviour of the porphyrin fluorophores in aerobic environments.

Successful discrete M-TAPP $\subset$ CB[7]₄ and (M-TAPP)₂ $\subset$ CB[8]₄ complexation was confirmed with ¹H-NMR spectroscopy. VT-NMR analysis revealed multiple hindered chemical exchange processes in (M-TAPP)₂ $\subset$ CB[8]₄. This was rationalised by two-dimensional restriction of motion (*cf.* one dimension for (ArV/EV)₂ $\subset$ CB[8]₂) by the bulky porphyrin core and perpendicular CB[n]-clamped *N*-arylpyridinium groups. CB[n] complexation also perturbed intramolecular CT, axial ligation and/or metal spin state, and (M-TAPP)₂ $\subset$ CB[8]₄ dimerisation was evidenced by a significant redshift in both absorption and emission.

Finally, M-TAPP($\subset$ CB[n]) NPoMs were self-assembled and characterised with DF, PL and SERS. Like ArV $\subset$ CB[n], NPR characterisation was ambiguous in some cases, but yielded more predictable *d* and *n_g* overall. This indicates higher stability of M-TAPP $\subset$ CB[n] structures than

previous ArV/EV systems, consistent with more *N*-arylpyridinium $\subset$ CB[n] clappings per M-TAPP molecule. NPoM PL analysis was consistent with structural retention of M-TAPP $\subset$ CB[n] within the nanocavity. Additional, higher-energy emission peaks were observed for all systems, and significant λ_c dependence of relative PL band intensities was observed for (M-TAPP) $_2\subset$ CB[8] $_4$. Both observations indicate some plexcitonic coupling, but deeper investigation is required to confirm this. Extremely large NPoM SER(R)S intensities were observed and unexpectedly low laser powers were required for spectral stability.

5.9.2 Outlook

Overall, *tetrakis*-(*N*-arylpyridinium)porphyrin molecular spacers show great promise in nanophotonics and chemistry. The goal of this chapter was to develop a plasmonic spacer to introduce catalytic functionality into the hotspot, together with tuneable plexcitonic coupling capability mediated by supramolecular chemistry. So far, the initial synthesis, supramolecular assembly and nano self-assembly objectives proved successful, accompanied by some characterisation of the optoelectronic and chemical behaviour of these multicomponent systems in nanojunctions and solution. Future experiments should begin with AuNP aggregation and nano-characterisation (*cf.* **Sections 4.3 & 4.5**) and M-TAPP $\subset$ CB[n] NPoM SERS characterisation. Next, the wider utility of these molecular spacers should be explored in the context of the nanophotonic applications in **Section 1.4.1** and beyond.

The demonstration of supramolecular control over intermolecular interactions between porphyrins, particularly the formation of discrete, long-lived, electronically coupled dimers, illustrates the potential for tuneable photophysical and chemical behaviour. The modular nature of the *N*-arylpyridinium structure creates an extended toolbox for porphyrin-based optoelectronic, nanophotonic and photocatalytic devices. One exciting possibility is quantitative heterodimerisation via complementary terminal functionality,²⁷⁵ which should allow assembly of hetero-bimetallic porphyrin dimers for advanced modification of optical and catalytic behaviour. This could be explored by comparing aqueous PDT, water splitting or CO $_2$ electroreduction behaviour of (M-APP, M-APP') $\subset$ CB[8] $_4$ heterodimers across a range of M-APP functionality and binary metal centre combinations.

While the M-TAPP($\subset$ CB[n]) NPoM PL spectra facilitated general SAM characterisation, more in-depth analysis is required to probe the various excited state dynamics of the system. Initially, scanning the excitation spectra of the various NPoMs would aid comparison with the solution-phase systems and help characterise any changes in supramolecular structure and intermolecular coupling upon SAM formation and nanoconfinement. This may also elucidate the Ni-TAPP spin state via Soret band position, and/or reveal the energy of low-lying triplet states for all M-TAPP if external heavy atom spin-orbit coupling is significant. TCSPC measurements would help determine whether plasmonically-decreased excited state lifetime

is responsible for the higher-energy NPoM emission peaks, while fsTA analysis could provide insights into the higher vibronic states revealed by this enhanced emission.

While NPoM analysis yields insights into the single-junction behaviour of M-TAPP $\subset$ CB[n]@AuNP nanostructures, AuNP aggregates offer greater scalability for macro-scale application of the advanced nanophotonic phenomena in **Section 1.4.1**. Therefore, aqueous M-TAPP($\subset$ CB[n])AuNP aggregate extinction and SERS characterisation (as in **Chapter 4**) should be performed next to understand the extended self-assembly properties of these spacers.

Moving further forward, the vision for these compounds is advanced optical control over chemistry. More specifically, the goal is to influence transition metal (electro)catalytic reactions (e.g. CO₂ reduction) with enhanced light-matter interactions. This will first require deeper understanding of the redox behaviour and electrochromism of the M-TAPP $\subset$ CB[n] systems, both in solution and molecular junctions. This may be achieved via spectroelectrochemical measurements of solution phase UV-Vis/PL and NPoM SERS/PL behaviour of M-TAPP($\subset$ CB[n]) (+CO₂) at different applied potentials. Plasmonic manipulation of the electrocatalytic reaction can then be explored via strong or weak plexcitonic coupling of M-TAPP($\subset$ CB[n]) to the nanocavity across a range of oxidation states.

Such exploration should not be limited to the M-TAPP compounds explored in this thesis. The Zincke reaction allows addition of an enormous range of terminal functionality to the porphyrin scaffold, many of which can be obtained using DNPP as a starting material. The porphyrin core also facilitates inclusion of most metals in the periodic table. Therefore, in parallel to the experiments described above, the effects of terminal functionality and metal centre on the CB[n] complexation dynamics, optical properties, redox activity and catalytic behaviour may be readily explored, together with the perturbation of these effects by confinement within a plasmonic hotspot.

5.10 M-TAPP $\subset$ CB[n] Methods

5.10.1 Synthetic Details

2,4-dinitrophenyl tosylate (DNTB)

2,4-dinitrophenol (23.258 g, ≤ 107.4 mmol; $\geq 15\%$ water) and tosyl chloride (28.420 g, 149 mmol) were dissolved in DCM (350 mL). Triethylamine (50 mL) was added and the solution was stirred at room temperature for 21 h. Deionised water (350 mL) was added and the mixture transferred to a separating funnel with an additional 50 mL DCM. The aqueous phase was separated and extracted with more DCM (3 x 85 mL). The combined DCM extracts were washed with saturated NaHCO₃ (3 x 100 mL) and NaCl brine (3 x 100 mL). The washed organic solution was concentrated under reduced pressure, triturated with hot MeOH and filtered. The

crude product was recrystallised from ethyl acetate to yield 22.389 g of DNTB as chunky golden crystals (66.2 mmol, $\geq 61.6\%$). The recrystallisation supernatant was filtered through silica gel and the solvent removed under reduced pressure to yield a further 3.450 g of DNTB as off-white crystalline powder (11.1 mmol, $\geq 10.3\%$). Total yield = 25.839 g ($\geq 72.0\%$). Anal. Calc.: C, 46.16; H, 2.98; N, 8.28. Found: C, 46.13; H, 2.99; N, 8.26. The product was also characterised with single-crystal XRD (**Figure 5.36**) and NMR (**Figure 5.37**).

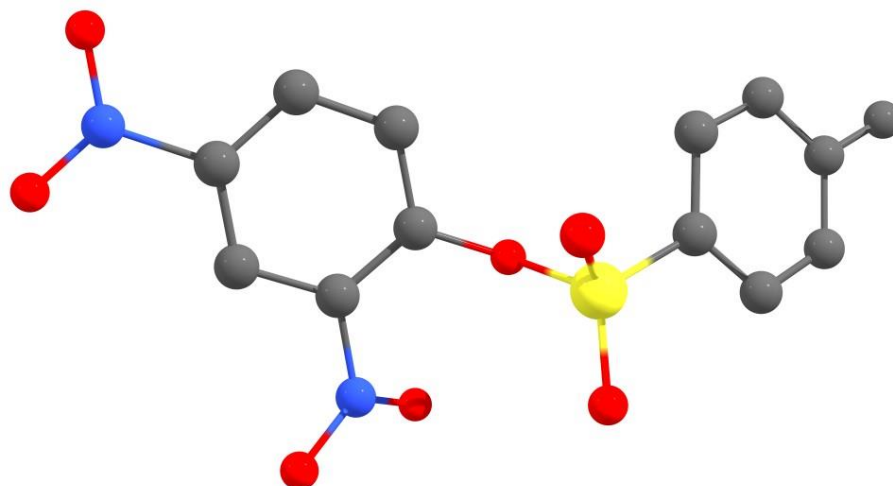


Figure 5.36. DNTB X-Ray crystal structure. Hydrogen atoms omitted for clarity. Atom colours: C (grey), N (blue), O (red), S (yellow).

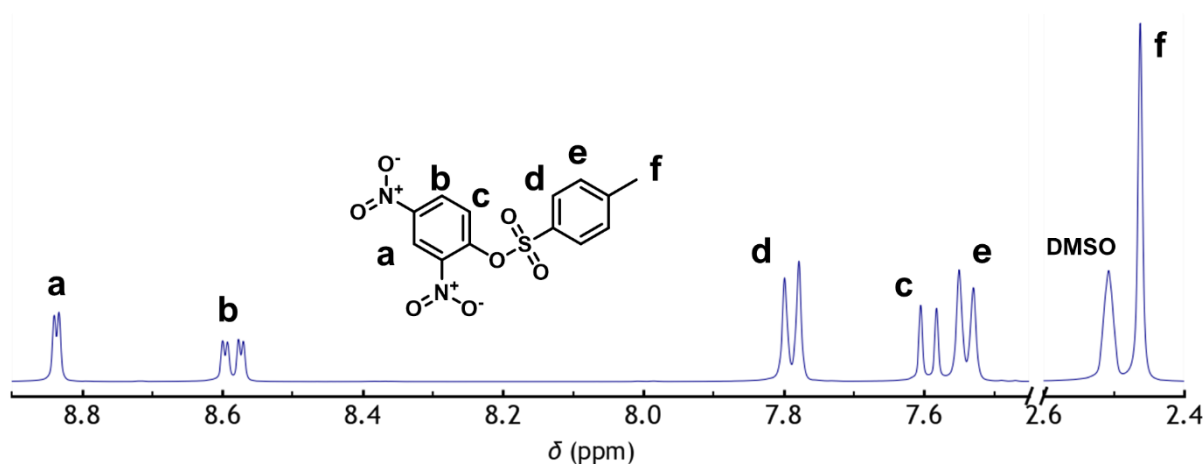


Figure 5.37. DNTB ^1H -NMR spectrum and assignment. Identical NMR spectra were measured for both crystals and powder.

DNPP Tosylate

2,4-dinitrophenyl tosylate (DNTB) (12.9 g, 38.1 mmol) and TPyP (378 mg, 611 μmol) were finely crushed together and dried under vacuum for 24 h. 10.4 g of the mixture was added to a 10 mL Schlenk flask and purged with N_2 (vac/refill) while stirring. The mixture was heated to 132 $^\circ\text{C}$ and the melt was stirred for 18 h under N_2 . The mixture was cooled to room temperature, dissolved in DMAc (180 mL) and filtered. The filtrate was precipitated with Et_2O /acetone (40:60 v/v; 300 mL) and centrifuged. The precipitates were washed/centrifuged twice each with acetone, then Et_2O and dried under vacuum for 14 h to yield 861.0 mg shiny

deep-red solid (71.5%). The product was characterised with LCMS (**Figure 5.6**), UV-Vis (**Figure 5.38**), FTIR (**Figure 5.39**) and NMR (**Figure 5.40**, **Figure 5.41**)

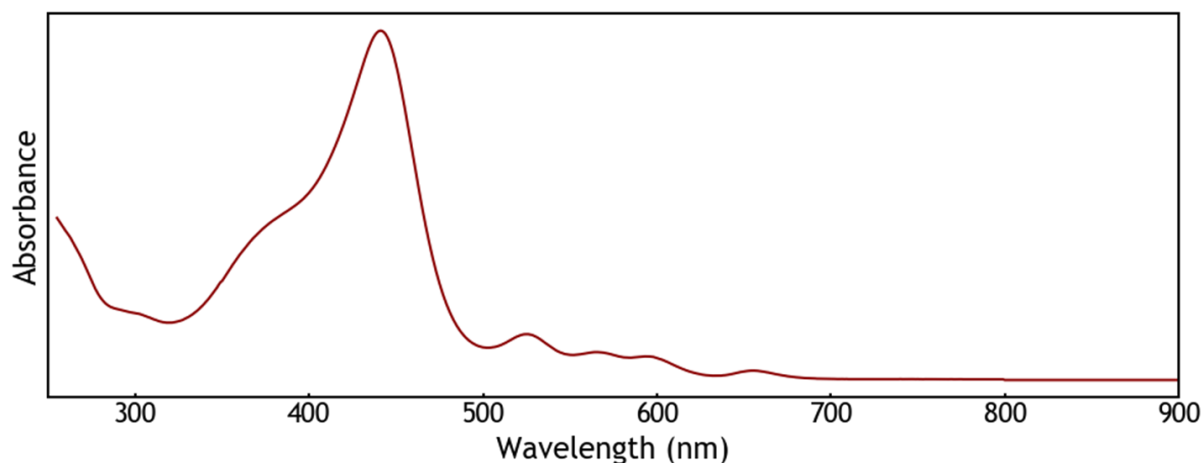


Figure 5.38. *tetrakis*-DNPP UV-Vis spectrum (normalised) in DMSO.

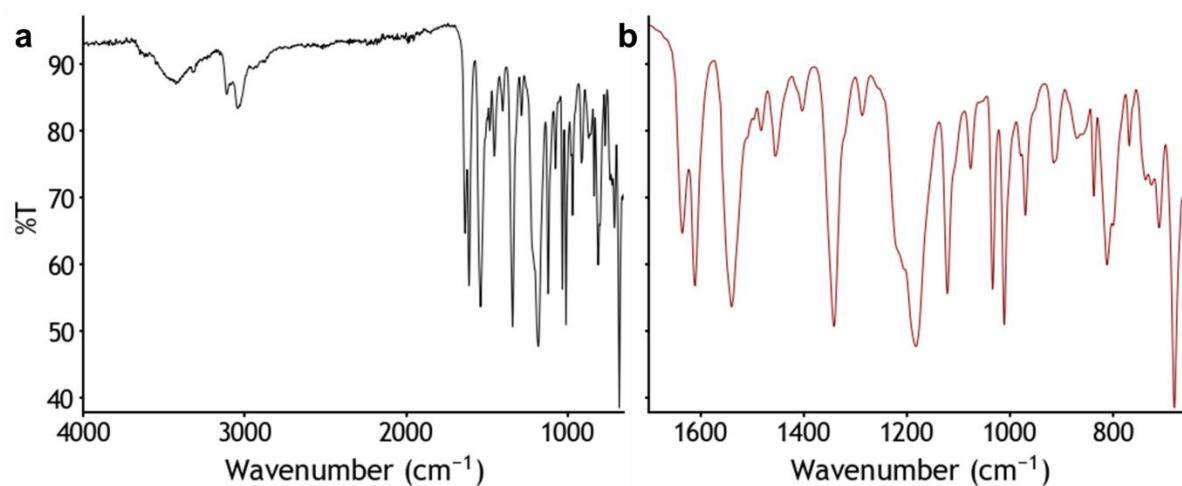


Figure 5.39. (a) DNPP FTIR spectrum; (b) low-wavenumber region of (a) with NO₂ peaks at 1535, 1340 cm⁻¹.

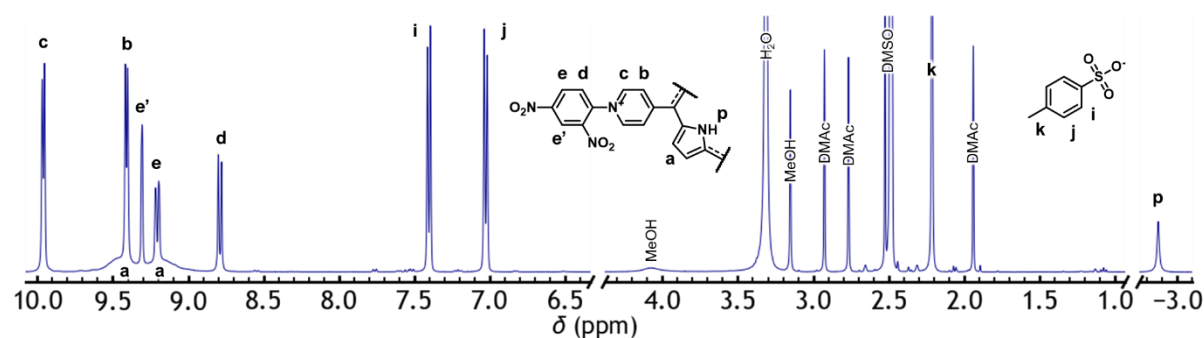


Figure 5.40. *tetrakis*-DNPP tosylate ¹H-NMR spectrum in d₆-DMSO; solvent/aliphatic region included.

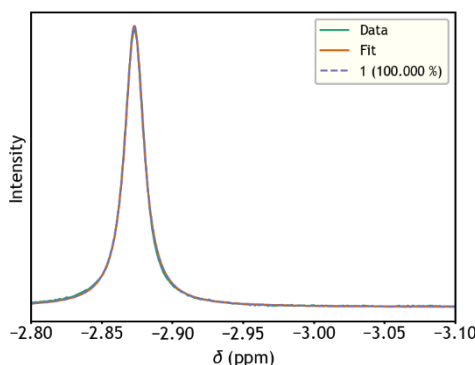


Figure 5.41. *tetrakis*-DNPP tosylate ^1H -NMR spectrum (core NH region) in d_6 -DMSO. Single peak in this region indicates single porphyrin product.

H₂-TAPP Tosylate

In a 10 mL Schlenk flask, finely powdered ***tetrakis*-DNPP Tosylate** (506 mg, 257 μmol) was purged with N_2 (vac/refill). Enough 4-MTA to cover the material (3 mL) was added via syringe and the mixture stirred under N_2 for 1.5 h. DMAc (8 mL) was added and the mixture was stirred under N_2 for another 15 min. The viscous mixture was transferred to a sintered glass filter with another 30 mL DMAc and washed through with MeOH (10 mL). Et_2O (120 mL) was added dropwise to the filtrate with rapid stirring. The mixture was centrifuged and the precipitates washed/centrifuged three times with Et_2O . The combined solids were redissolved in minimum DMAc and triturated/centrifuged/washed with Et_2O again. The solids were dried under vacuum for 6 h to yield 344.5 mg shiny red/green solid (191.8 μmol ; 74.8%). The product was analysed with NMR (**Figure 5.42**, **Figure 5.43**) and used without further purification.

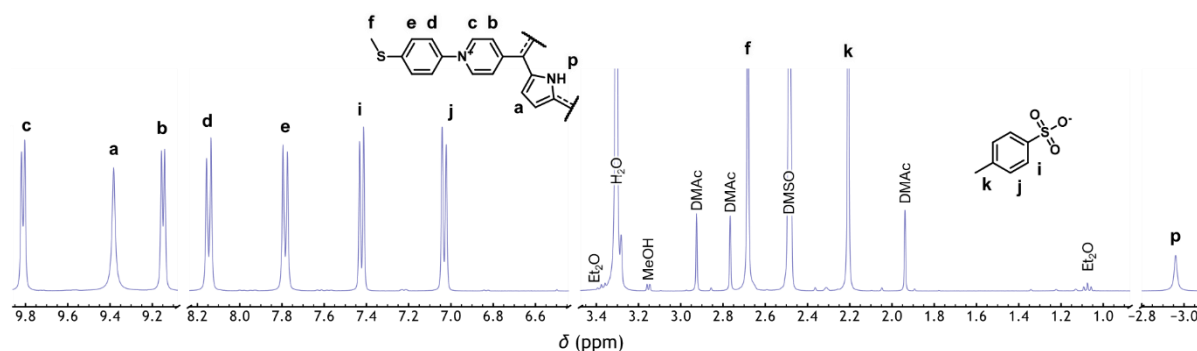


Figure 5.42. H₂-TAPP tosylate ^1H -NMR spectrum in d_6 -DMSO; solvent/aliphatic region included.

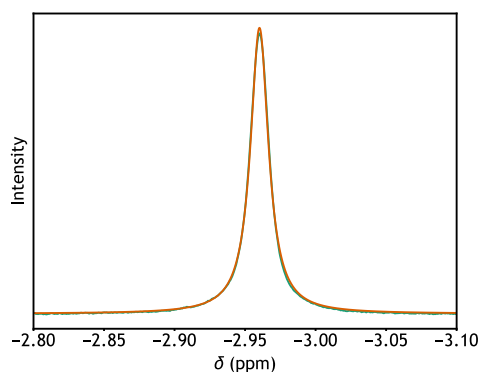


Figure 5.43. H₂-TAPP tosylate ¹H-NMR spectrum (core NH region) in d₆-DMSO. Single peak in this region indicates single porphyrin product.

H₂-TAPP Chloride

H₂-TAPP Tosylate (95 mg, 53 μmol) was dissolved in DMAc (17 mL) at 45 °C. Saturated Bu₄NCl/MeCN solution (2 mL) was added dropwise to the warm stirred solution over 5 min, followed by MeCN (20 mL, dropwise). The slurry was centrifuged and the precipitate washed/centrifuged again with MeCN. The precipitate was redissolved in DMAc (12 mL, 45 °C), and Bu₄NCl/MeCN (4 mL) was added as before, followed by MeCN (40 mL). The slurry was centrifuged again, then washed/centrifuged with MeCN (x2) and Et₂O (x1). The crude product was redissolved in DMAc (17 mL) and triturated/centrifuged as above with MeCN/Et₂O (8:3 v/v). Finally, the resulting solids were dissolved in MeOH/MeCN (1:1 v/v, 45 °C) and triturated/centrifuged with Et₂O. The solids were dried under vacuum for 3 h to yield 65.0 mg shiny red solid (51.9 μmol; 98.1%). The product was characterised with LCMS (**Figure 5.9a**), UV-Vis (**Figure 5.14a**, **Figure 5.16a**), and NMR (**Figure 5.44**).

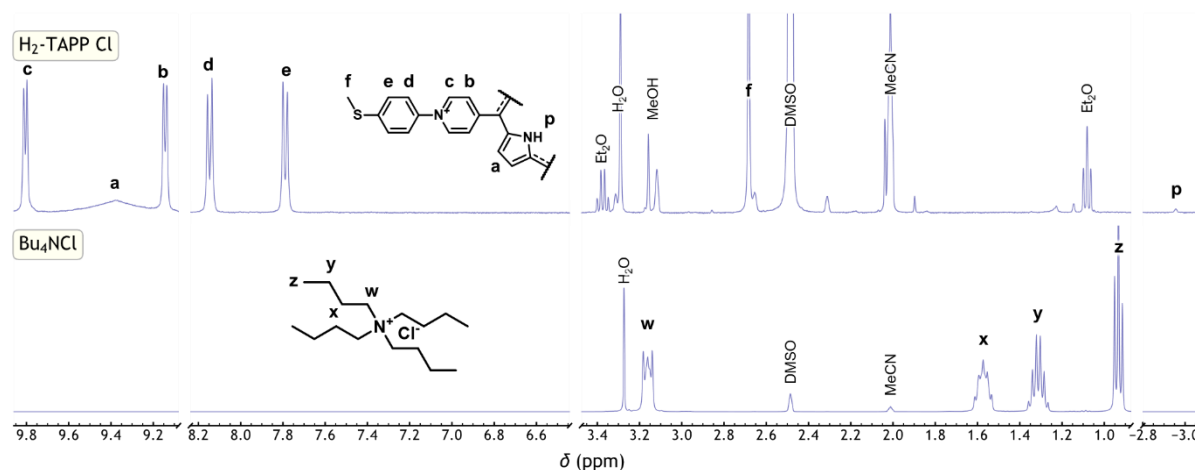


Figure 5.44. ¹H-NMR spectra (in d₆-DMSO) of H₂-TAPP chloride and Bu₄NCl. Secondary peaks in MeOH, MeCN and (f) regions attributed to solvent caging effects, although further analysis is required to confirm this.

Ni-TAPP Chloride

H₂-TAPP Tosylate (101 mg, 56.2 μmol) in DMAc (5 mL) was mixed with nickel(II) acetate tetrahydrate (141 mg, 567 μmol) in deionised water (5 mL). The mixture was purged with N₂ (bubbled/stirred, 15 min), after which 2,6-lutidine (4 mL, 34.5 mmol) was added. The mixture

was stirred at 100 °C under N₂ for 15 h, then cooled to 45 °C. Saturated NH₄PF₆ solution (5 mL, aq) was added dropwise, and the mixture was stirred at 45 °C for a further 10 min. Deionised water (25 mL) was added dropwise to the stirred solution, forming a dark grey suspension. The mixture was centrifuged, then washed/centrifuged again with deionised water (x2). The precipitate was redissolved in DMAc (10 mL, 45 °C) and triturated/centrifuged with water a second time. Further ion exchange (Bu₄NCl/MeCN) and purification was performed as above (**H₂-TAPP Chloride**), yielding 157.2 mg brown solid (120 μmol; 214%). The solid was redissolved in MeOH/MeCN (1:1 v/v) and filtered. The filtrate was triturated/centrifuged with Et₂O and the combined precipitate dried to yield 67.0 mg shiny red solid (51.1 μmol; 90.9%). The product was characterised with LCMS (**Figure 5.9b**), UV-Vis (**Figure 5.14b**, **Figure 5.16b**), and NMR (**Figure 5.45**).

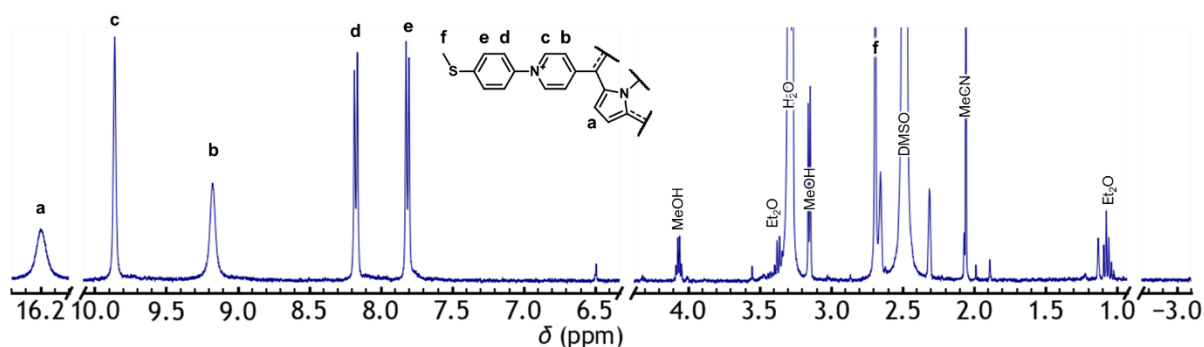


Figure 5.45. Ni-TAPP chloride ¹H-NMR spectrum in d₆-DMSO. Secondary peaks in DMSO, MeCN and (f) regions attributed to solvent caging effects, although further analysis is required to confirm this.

Zn-TAPP Chloride

H₂-TAPP Tosylate (101 mg, 56.2 μmol) in DMAc (5 mL) was mixed with zinc(II) acetate dihydrate (44.4 mg, 202 μmol) in deionised water (5 mL) and stirred at 45 °C for 90 min. Ion exchange (NH₄PF₆/H₂O then Bu₄NCl/MeCN) and trituration was performed as above (**Ni-TAPP Chloride**), yielding 44.8 mg shiny green solid (34.0 μmol; 60.5%). The product was characterised with LCMS (**Figure 5.9c**), UV-Vis (**Figure 5.14c**, **Figure 5.16c**), and NMR (**Figure 5.46**).

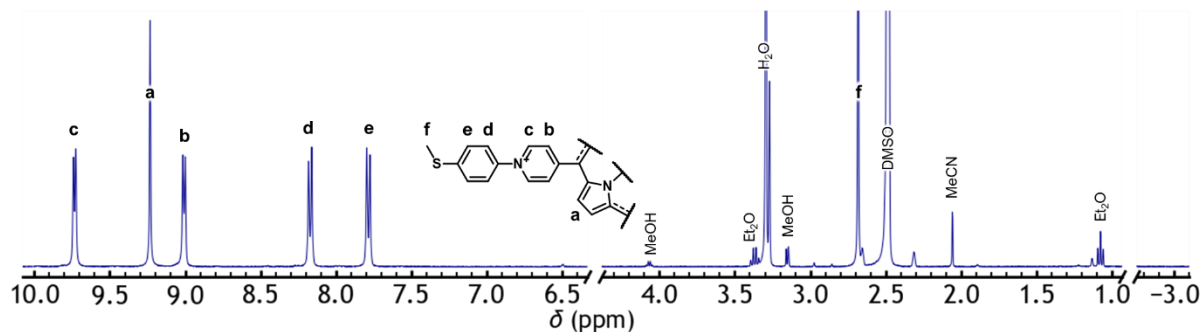


Figure 5.46. Zn-TAPP chloride ¹H-NMR spectrum in d₆-DMSO. Secondary peaks in DMSO and (f) regions attributed to solvent caging effects, although further analysis is required to confirm this.

5.10.2 Aqueous [M-TAPP] Calibration

For each M-TAPP chloride (M = 2H, Ni, Zn), approx. 2 mg was dissolved in d₆-DMSO (1.5 mL). 100 μ L of this was combined with 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) sodium salt (114.5 ± 0.7 mM in d₆-DMSO; 3 ± 0.005 μ L) and more d₆-DMSO (600 μ L). The M-TAPP concentration was accurately measured ($\pm 3\%$) using relative ¹H-NMR peak integrals (e.g. **Figure 5.47**) of the two species over three repeat readings. Several accurate dilutions ($\pm 0.5\%$) of the analyte solution in MeOH/MeCN (1:1 v/v) were then used to prepare UV-Vis calibration curves based on the Soret intensity (**Figures 5.48-5.49**). Subsequent M-TAPP concentration measurements were then performed as needed, via the Soret intensity of an accurately diluted aliquot.

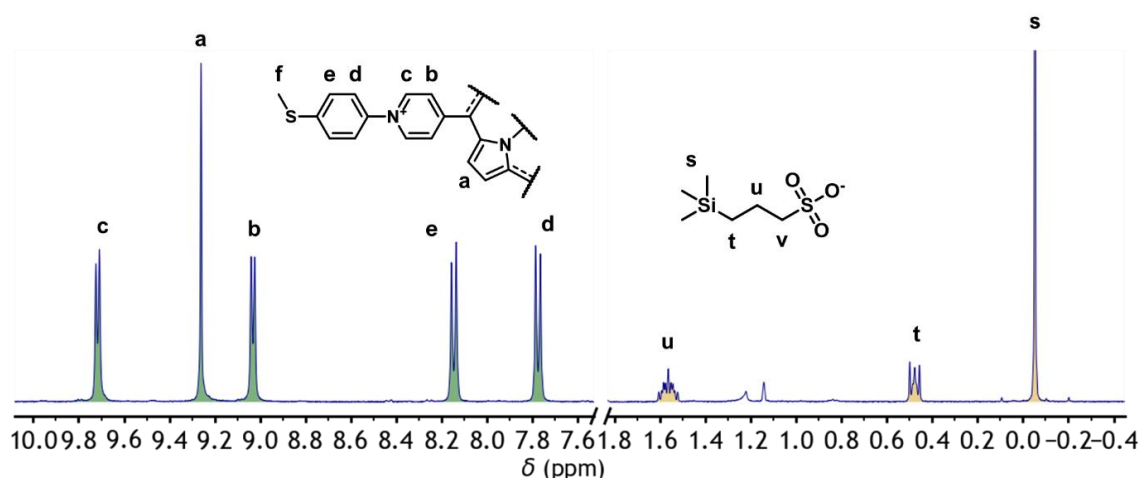


Figure 5.47. Example ¹H-NMR measurement of Zn-TAPP (green resonances (a-e)) concentration in d₆-DMSO using DSS internal standard (yellow resonances (s-u)) via comparison of peak integrals. Resonances (f) and (v) not used due to overlap with solvent peaks.

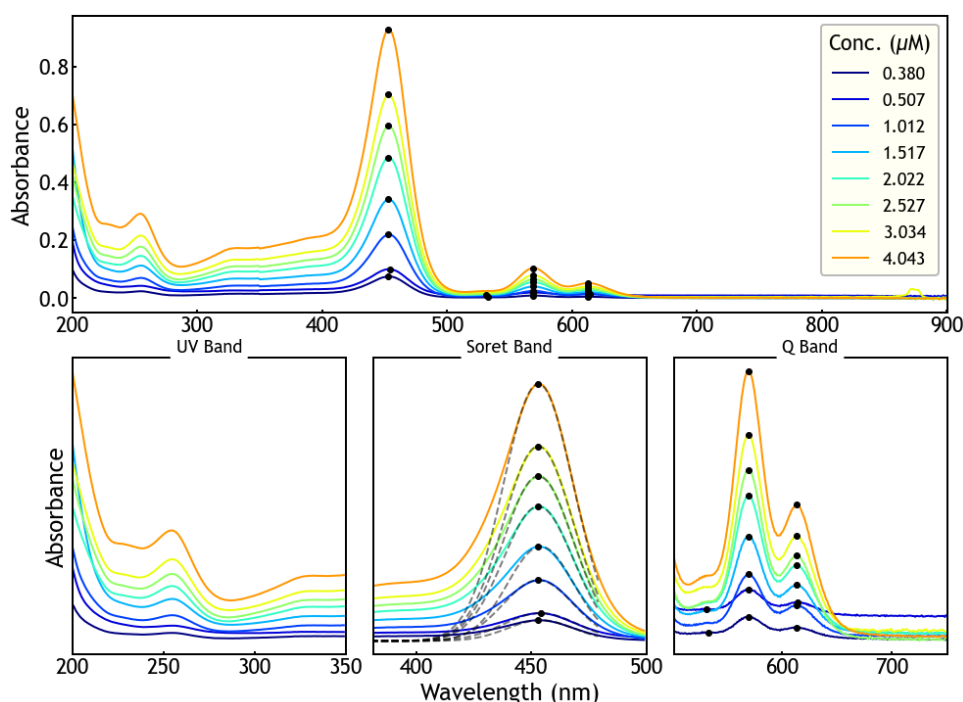


Figure 5.48. Example UV-Vis calibration measurement using Zn-TAPP solution from **Figure 5.47** diluted in MeOH/MeCN (1:1 v/v).

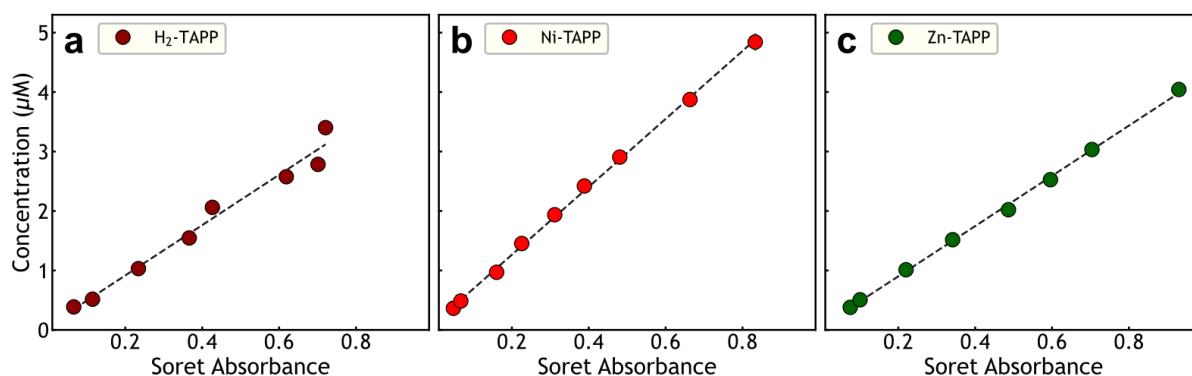


Figure 5.49. UV-Vis calibration curves for (a) $\text{H}_2\text{-TAPP}$, (b) Ni-TAPP and (c) Zn-TAPP in MeOH/MeCN (1:1 v/v).

5.10.3 Computational Details

M-TAPP DFT calculations were performed using B3LYP^{446,447} with GD3BJ⁴⁴⁸ dispersion and Def2SVP⁵²⁰ basis set. Implicit aqueous effects were included using a polarisable-continuum model. All DFT calculations were implemented (by myself) using an ultrafine integration grid in Gaussian 09 Rev. E.⁴⁵⁶ $\text{H}_2\text{-APP} \subset \text{CB}[n]$ geometry optimisation was performed by Denes Berta* using the semiempirical quantum chemical GFN2-xTB⁵⁰⁹ method (v5.9) with self-consistent D4 dispersion and implicit water.

* Department of Physics, University College London

6. Summary & Outlook

The core theme of this thesis was synthesis, characterisation & utilisation of novel molecular spacers for the self-assembly of plasmonic nanojunctions based on AuNPs. The principles behind the nanostructure designs used in this work were introduced, beginning with a brief history of SERS, plasmonics and nano self-assembly techniques (**Sections 1.1-1.2**). The theory and recent literature required to understand the optical response of these nanostructures was then introduced (**Section 1.3**).

This was followed by an overview of nanoscale light-matter interactions for enhanced sensing, reaction monitoring, quantum electrodynamics, plasmonic catalysis, molecular electronics, and nanometrology (**Section 1.4.1**). Several chemical criteria were outlined for the design of bespoke molecular spacers to advance these nanophotonic applications (**Section 1.4.3**). Three novel classes of molecular spacer were then designed/chosen and introduced (**Chapter 2**), based on these functional criteria.

6.1 BPc

BPcs were initially explored for their potential applications in sensing and catalysis, and served as a prototype spacer for introducing metal centres and advanced optoelectronic functionality into plasmonic nanojunctions. The potential for nanometrology was also revealed, based on the fine control over SAM thickness afforded by the BPc metal centre. Also noted, although not explored here, was a future possibility of molecular magnetic devices with plasmonically-enhanced optical readout via exchange interactions between the Pc_2 π -system and the lanthanide $4f$ J -states.

A set of functionalised BPc* derivatives with improved solubility and surface assembly behaviour were designed, synthesised and characterised, together with two unsubstituted BPc compounds. BPc NPoM assembly procedures were formulated for the two spacer types, with BPc* performing best, as expected. These BPc NPoMs exhibited extremely high SERRS signals due to a combination of electronic resonance and ultrasmall NPoM cavities. Unfortunately, evaluation of NPoMs as single-cavity gas sensors was precluded by the existing device geometry.

BPc@AuNP aggregates were then investigated as sensing substrates. Several aggregation methods were attempted, but were complicated by the hydrophobic spacer. Aggregation was achieved at the interface of a two-phase liquid system using unsubstituted BPc, and the resulting structures analysed with TEM and SERS. While high BPc SERS signals could be measured from within the enclosed gas sensing apparatus, no changes in BPc vibrational signature were observed upon exposure to the chemical vapours tested.

NPoM DF characterisation revealed an anomalously large $\overline{\lambda_C}$ shift as BPc SAM thickness (via metal centre size) was varied, challenging the current nanometrological understanding of sub-nm plasmonic gaps. To explain the result, the influence of metal centre on various BPc properties was explored, including magnetic moment, SAM conductance, Au electron density redistribution and molecular polarisability. DFT was used to investigate the fine variation in molecule height and anisotropic polarisability with metal centre, and explored the effects of oxidation state, peripheral substitution, Pc-Au ligation and Pc-Pc skew angle. n_g values were estimated using the calculated molecular heights and polarisabilities, although the validity of such treatment is questionable at the sub-nanoscale dimensions of this system. Similarly, estimation of λ_C using this data was further compounded by the presence of non-classical plasmonic behaviour not accounted for by the available analytical models.

All of the above analysis failed to explain the observed λ_C shift. However, DFT calculation of $\alpha_{zz}(\lambda)$ yielded more a promising result. The $\alpha_{zz}(\lambda)$ curves of neutral [BPc*]⁰ exhibited several resonances in the λ_C region of interest, whose arrangement appeared uncorrelated with metal centre. Conversely, a single resonance in the same region was calculated for each reduced [BPc*]⁻, the position of which smoothly redshifted with decreasing lanthanide size by an amount directly comparable to the observed λ_C shift.

Comparison of two BPc* NPoM λ_C datasets measured three years apart, yielded two distinct λ_C vs Ln curves for the same systems. Based on the extensive analysis of BPc* properties, the two datasets are consistent with reduced (2017 data) and neutral (2020 data) BPc* monolayers. The difference is attributed to systematic contamination of the older NPoM substrates with chromium during the Au evaporation/deposition process. This hypothesis has not yet been tested, and requires repeat BPc* NPoM DF measurements to verify, either using chromium-doped Au substrates or monolayer electroreduction.

If confirmed, this behaviour may be exploited in future for optical detection of impurities/dopants in Au and other metals. Regardless, the unexpected λ_C behaviour emphasises the extraordinary sensitivity of coupled plasmonic systems to their environment. For accurate, and convenient, theoretical treatment of BPc* NPoMs and other systems with complex electronic structures and sub-nm gap sizes, improved analytical models are needed. Existing DF NPR d and n_g calibration data (using theoretical λ_C and I_C/I_T) should be augmented to include gap conductance and nonlocal/quantum corrections to the predicted λ_C and I_C/I_T data. The results of **Chapter 3** also call for more accurate models to derive n_g from α for molecular SAMs.

6.2 ArV $\subset$ CB[n]

ArV $\subset$ CB[n] supramolecular complexes were chosen as plasmonic spacers for their water solubility and vast modular design potential. The multiple CB[n] molecules in each ArV $\subset$ CB[n] unit facilitate binding to and self-assembly of AuNPs, while modification of the ArV terminal moieties and/or extension of the core structure allows incorporation of arbitrary chemical functionality into plasmonic hotspots. CB[7] protects some parts of the guest molecule while allowing chemical access to others, while CB[8]-mediated dimerisation offers additional supramolecular control over chemical and optoelectronic properties, increasing the possibilities for advanced nanophotonic utility.

ArVs were used as simple prototypes to determine the correct experimental conditions for structural retention of (ArV/EV) $\subset$ CB[n] complexes during AuNP self-assembly, serving as a starting point for incorporation of more complex chemical functionality into the spacer layer. Two terminal aromatic functionalities (phenyl and 4-thioanisyl) were tested to evaluate the nano self-assembly behaviour with and without explicit Au binding functionality.

ArV($\subset$ CB[n]) SAM deposition parameters were explored for NPoM formation, and the resulting nanostructures characterised with DF spectroscopy with NPR analysis. Variable $\overline{\lambda_C}$ and $\overline{I_C/I_T}$ behaviour was observed, with d and n_g consistent with retention of ArV $\subset$ CB[n] in some cases, but not all. This indicates partial stability of the supramolecular structure during NPoM preparation; further optimisation is required to ensure reproducibility, but the NPR results imply overall that ArV $\subset$ CB[n] NPoM assembly is possible. Any future experiments should include PL and SERS measurements to aid characterisation.

AuNP aggregation was performed with the various ArV($\subset$ CB[n]) combinations at a range of concentrations and analysed with extinction spectroscopy and SERS. λ_{dim} was found to blueshift steadily with increasing aggregant concentration in all cases. Several hypotheses for this were discussed, including differences in molecular packing, Au surface electron density, variable gap spacing and local & extended aggregation geometry. The current hypothesis is that average AuNP facet overlap decreases with increasing aggregant concentration, and the resulting drop in gap capacitance causes a blueshift. Overall, the λ_{dim} vs concentration curves appeared distinct for the various combinations of ArV and CB[n], demonstrating presence of both species in the gap.

SERS analysis of the same ArV $\subset$ CB[n]@AuNP aggregates provided strong evidence for retention of ArVSM $\subset$ CB[n] supramolecular structure in the interparticle gaps. This was achieved via comparison of vibrational peak intensity ratios with polarised DFT SERS spectra, as well as the relative population of SMe and S-Au vibrations. The vibrational intensities of the latter varied in a manner consistent with the variable facet overlap hypothesis above. ArVH $\subset$ CB[n] structure appears to have been retained in some cases, but insufficient evidence was observed due to weak ArVH SERS intensities.

While more analysis is required to reveal exact conditions for reliable retention of ArV $\subset$ CB[n] supramolecular structure during AuNP self-assembly, the current data shows that it is possible. Greater evidence of successful assembly was observed for AuNP aggregates than NPoM. Naturally, the presence of an Au-anchoring group (SMe) appeared to improve the stability of the complexes in the nanocavity, as did the stronger supramolecular binding afforded by CB[8].

6.3 M-TAPP $\subset$ CB[n]

M-TAPP compounds were designed based on the results of **Chapters 3-4**. The metalloporphyrin core was chosen for its complex, but well-understood, optical properties and ability to ligate transition metals in a chemically accessible geometry. Addition of *N*-thioanisylpyridinium moieties was performed to impart water solubility, CB[n] complexation ability and the ability to self-assemble AuNPs (*cf.* ArV $\subset$ CB[n] in **Chapter 4**) while retaining M-TAPP $\subset$ CB[n] supramolecular structure.

Synthesis and characterisation of the new M-TAPP compounds was achieved using both novel and modified literature procedures. The M-TAPP aqueous concentrations were calibrated against an internal standard with NMR, followed by UV-Vis, allowing rapid concentration measurements of subsequent preparations via optical absorbance. Solvchromism was observed, with spectral variation caused by metal-water ligation and subsequent spin state changes, hydrogen bonding between solvent and core NH protons, and/or (de)stabilisation of intramolecular CT states based on solvent polarity.

Oxidation of SMe groups of H₂/Zn-TAPP was also observed, consistent with photosensitisation via generation of singlet oxygen in solution. The kinetics and chemical shifts indicated higher photoactivity and higher π -conjugation of Zn-TAPP than H₂-TAPP. Little photosensitisation was observed for Ni-TAPP due to fast NRR, concurrent with its quenched PL intensity.

M-TAPP $\subset$ CB[n] assembly was explored with NMR, and formation of discrete M-TAPP $\subset$ CB[7]₄ and (M-TAPP)₂ $\subset$ CB[8]₄ complexes was confirmed. Multiple intracomplex chemical exchange processes were observed for (M-TAPP)₂ $\subset$ CB[8]₄ around the NMR timescale. This was attributed to restricted motion in two directions by the multiple perpendicular *N*-arylpyridinium $\subset$ CB[n] clampings. The chemical exchange kinetics were explored using VT-NMR, suggesting different activation energies for the two (or more) intracomplex interconversion processes. Intracomplex motion was less hindered for Ni-TAPP, either due to lower π -electron density or a non-planar singlet state geometry; further experiments are required to explore this. Future experiments involving larger temperature ranges and different field strengths are recommended, and should include NOESY and COSY measurements.

Aqueous M-TAPP $\subset$ CB[7]₄ and (M-TAPP)₂ $\subset$ CB[8]₄ solutions were analysed with UV-Vis and PL spectroscopy. H₂/Zn-TAPP $\subset$ CB[7]₄ complexes had similar UV-Vis spectra for free H₂/Zn-TAPP, indicating minimal stacking of uncomplexed aqueous M-TAPP. The PL spectra indicated slight restriction of pyridinium rotation and intramolecular CT destabilisation. Ni-TAPP spin state was affected by complexation with both CB[n] homologues, consistent with perturbation of axial water ligation energetics. (M-TAPP)₂ $\subset$ CB[8]₄ complexes exhibited redshifted absorption and emission with decreased PL intensity, consistent with an offset face-to-face dimer geometry. (H₂/Zn-TAPP)₂ $\subset$ CB[8]₄ PL had more vibronic structure than the aqueous M-TAPP($\subset$ CB[7]₄) systems, indicating significant destabilisation of intramolecular CT processes via restriction of molecular motion.

Finally, M-TAPP($\subset$ CB[n]) NPoMs were assembled and analysed with SERS, DF (+ NPR) and PL spectroscopy. DF NPR analysis revealed reasonable d and n_g values in most cases, indicating greater supramolecular stability of M-TAPP $\subset$ CB[n] than ArV $\subset$ CB[n] during NPoM assembly; this is correlated with the number of *N*-arylpseudopyridinium $\subset$ CB[n] clamping units. NPoM SERS spectra were measured for M-TAPP without CB[n]. Significant spectral instability was observed, indicating lowering of Au surface tension by M-TAPP. This was accompanied by extremely large scattering intensities, indicating SERRS.

The NPoM PL spectra provided good evidence for M-TAPP $\subset$ CB[n] structural retention in the cavity. Slight differences in PL band position and significant intensity variation observed between the M-TAPP $\subset$ CB[n] systems were consistent with excitonic coupling within the SAM, CB[7]-mediated M-TAPP isolation and CB[8]-mediated dimerisation. The shape of the (H₂/Zn-TAPP)₂ $\subset$ CB[8]₄ NPoM PL spectra varied significantly with λ_c , indicating some plexcitonic coupling. Additional PL peaks were observed at higher wavelengths than in solution, indicating plasmonically-enhanced emission rates from higher vibronic states. The nature of this emission is currently unknown and further analysis of the excited state dynamics is required.

6.4 Future Possibilities

Several recommendations for future experiments to reinforce and advance the work of this thesis have already been outlined in the conclusions of each chapter. However, the possibilities for these molecular spacers and plasmonic nanostructures thereof extend far beyond this.

BPC@AuNP nanostructures offer the potential for plasmonically-enhanced optical manipulation of Ln 4*f* states (**Section 2.1.1**); single-molecule switching behaviour may also be possible via NPoM junction bias. These two properties hint at molecular information storage and spintronic applications. The redox-dependent λ_c , if confirmed, should yield plasmonic electrochromism, useful for NPoM-based displays. These applications may also be explored

with multiple-decker $\text{Ln}_x\text{Pc}_{x+1}$ compounds and or actinide-based BPcs, which should offer greater chemical accessibility in the hotspot for catalytic and/or sensing applications.

The ArV and M-TAPP results have similar implications, respectively representing a proof-of-concept and a demonstration of more advanced hotspot functionality. The advanced redox possibilities of the viologen/transition metal combination in M-TAPP may improve functionality of flow batteries, electrochromic displays, sensors, smart windows and other organic redox-based devices. Recently reported $\text{CB}[n]/\text{AuNP}/\text{quantum dot}$ light-harvesting materials⁵²¹ may also be augmented with M-TAPP for improved utilisation of photogenerated radical species.

Another open-ended possibility combines the concepts of M-TAPP with BPc in the form of $\text{Ln}(\text{TAPP})_2$ complexes. The properties of such compounds should resemble existing bis-porphyrins, but with added water solubility, modified redox activity and possible $\text{CB}[n]$ -mediation of optoelectronic properties. The electronic resonance between M-TAPP and the plasmonic cavity may also be improved by introducing fused benzene rings to yield *tetrakis*-(*N*-arylpyridinium)tetrabenzporphyrin compounds, the intense, redshifted Q-band of which would greatly encourage strong plexcitonic coupling.⁵²²

6.5 Final Summary

Three novel families of molecular spacer were successfully incorporated into AuNP-based nanostructures. This widens the available repertoire of chemical and optoelectronic functionality of plasmonic hotspots for improvement of nanophotonic devices. The anomalous λ_{C} shift of **Chapter 3** is now more understood than originally reported;¹ additional experiments are required to confirm the current hypothesis (**Sections 3.5.6-3.5.7**). Notwithstanding, the current models used for rapid NPoM DF analysis and understanding of sub-nanoscale n_{g} require refinement.

The **Chapter 4** results mostly agree with existing nano self-assembly reports using similar systems. Regarding the specific $\text{ArV} \subset \text{CB}[n]$ systems used here, further refinement of nano self-assembly conditions is possible. However, the available evidence serves as a proof-of-concept for multicomponent functional molecular spacers. Explanations were hypothesised for the concentration-dependent λ_{dim} shift observed during AuNP aggregation, also requiring further experiments to confirm (**Section 4.4.2**).

Finally, the results of **Chapter 5** demonstrate a marriage of the concepts of the preceding chapters, demonstrating advanced supramolecular control over optical properties of the molecular spacer both in and outside the cavity. The ability to incorporate chemically accessible transition metals into plasmonic hotspots was also demonstrated. Given the strong optical absorption of metalloporphyrins, this sets the stage for improved manipulation of chemistry with plasmonically-enhanced light-matter interactions. The modular nature of the system and the associated supramolecular control now facilitate rapid exploration of the

chemical parameter space for optimisation of the chemo-nanophotonic properties of the system.

While more invasive nano-characterisation technologies offer precise, complementary characterisation information, the various optical responses of plasmonic nanojunctions serve as efficient, increasingly reliable self-characterisation methods. Nevertheless, room for improvement exists, highlighted by several results throughout this work. Overall, the molecular spacers designed and introduced here demonstrate just a few novel ways to incorporate chemical functionality into plasmonic nanojunctions, illustrating the wealth of advanced nanophotonic applications still waiting to be explored.

7. Materials & General Methods

7.1 Materials

All materials were used without further purification unless explicitly stated. 1,2-dicyanobenzene, lanthanide acetate hydrates (Ln = Lu, Er, Tb, Sm), DBU, DMSO, silica gel (230-400 mesh, 60 Å pore size), 4,5-dichlorophthalonitrile, 1-dodecanethiol, pentane, TPyP, tosyl chloride, 2,4-dinitrophenol, NaHCO₃, NaCl, DMAc, Ni(OAc)₃·4H₂O, Zn(OAc)₃·2H₂O, NH₄PF₆, Bu₄NCl and all deuterated NMR solvents were purchased from Sigma-Aldrich. All ArV and CB[*n*] compounds (and aqueous solutions thereof) were previously synthesised and calibrated by Guanglu Wu^{2,261} and Zehuan Huang.^{275,286}

Acetic anhydride was purchased from Breckland Scientific. 1-Hexanol, triethylamine and DNCB were purchased from Alfa Aesar. Acetone, CHCl₃, MeOH, DCM, K₂CO₃, 40-60 petroleum ether, EtOAc, MgSO₄, propan-2-ol, EtOH, *n*-hexane, *n*-heptane, THF, Et₂O, MeOH, MeCN and Decon90 came from Fisher Scientific. Colloidal AuNPs in sodium citrate buffer solution were purchased from BBI solutions.¹³ Bio-Beads S-X1 SEC beads were from Bio-Rad. Polished (roughness <3 Å) 100 mm Si(100) wafers were purchased from Si-Mat. Au pellets for evaporation were purchased from Kurt J. Lesker company. Epoxy resin used for TSG preparation was Epo-Tek 377.

7.2 Chemical Characterisation

¹H-NMR measurements in **Section 5.6** were performed* using a Bruker Avance 500 MHz spectrometer with an Avance 500 TCI liquid helium cryoprobe. All other NMR spectra were recorded using a Bruker Avance 400 MHz Spectrometer with a Prodigy liquid nitrogen cryoprobe and Avance Neo console. Both spectrometers were controlled by TopSpin.

BPC MALDI-TOF analysis was performed by the EPSRC UK National Mass Spectrometry Facility, Swansea. M-TAPP LCMS analysis was performed using a Waters Acquity UPLC with a Premier Glycan BEH C18 AX, 95Å, 1.7 µm, VanGuard FIT 2.1 x 50 mm column and Waters Xevo G2-S benchtop ESI QTOF mass spectrometer. CHN microanalysis was performed† on an Exeter Analytical Inc. CE 440 Elemental Analyzer. HAADF-STEM images were collected‡ at 200 keV using an FEI Tecnai Osiris TEM with FEI XFEG electron gun. Single-crystal X-Ray analysis was performed§ using a Bruker D8-Quest diffractometer with CuK(α) radiation and a Photon-100 detector.

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†by Dr Nigel Howard, Department of Chemistry, University of Cambridge

‡by Dr Giorgio Divitini, Department of Materials Science and Metallurgy, University of Cambridge

§by Dr Andrew Bond, Department of Chemistry, University of Cambridge

UV-Vis absorption spectra were measured using a Varian Cary 400 UV-Vis spectrophotometer. PL spectra were measured with a Horiba Duetta fluorescence/absorbance spectrometer. Both UV-Vis and PL analyses were performed using a quartz cuvette with 1 cm path length (at 298 K). FTIR spectra were measured using a PerkinElmer Spectrum 100 FTIR spectrometer with 4 cm⁻¹ resolution and averaged over 4 scans.

7.3 Template-Stripped Gold & NPoM Preparation

Flat Au films were prepared using an existing template-stripping procedure.⁹² 10 cm diameter silicon wafers were cleaned sequentially with Decon90, deionised water, EtOH and 2-propanol. Au was deposited onto the freshly cleaned wafer using a Moorfield thermal evaporator (nanoPVD-T15A). Under UHV, Au was thermally evaporated from a crucible heated using constant current of ~10 A, and condensed onto the Si wafer at 0.1 Å s⁻¹ until 100 nm Au thickness was achieved. Small (~1 cm²) silicon wafer segments were then attached to the Au layer using <1 µL Epo-Tek 377 thermal epoxy glue. The system was cured at 150 °C for 12 h, then cooled to room temperature at a rate of 1-2 °C min⁻¹. Once cooled, the adhered wafer segments were lifted off individually, as needed, to reveal flat Au substrates prior to use.

To form each molecular spacer SAM, a fresh Au substrate was immersed in a solution of molecular spacer for a predetermined period of time. Deposition time and concentration varied for each spacer system, and optimised values are quoted in the corresponding chapters. The SAM-functionalised Au substrate was then washed with clean deposition solvent and dried with a compressed air stream. AuNP colloidal solution¹³ (~80 µL; $D = 80$ nm; 1.1×10^{10} AuNPs cm⁻³) was drop-cast onto the freshly prepared SAM and incubated for 5-120 s (again dependent on the spacer), optimised to ensure sparse formation of isolated, optically-resolvable NPoMs.

7.4 Nanostructure Characterisation

7.4.1 NPoM DF & PL

DF imaging and spectroscopic measurements were performed using a customised Olympus BX51 microscope in reflection mode (**Figure 7.1**). Samples are illuminated at high angles (60.5-69°) with collimated white light (Phillips 7023 halogen bulb) using a circular beam block and an Olympus PlanFL N-BC 100x, 0.85 NA objective. The scattered light from the sample is collected at low angles (0-58°) and passes through a 50:50 beamsplitter to a Lumenera Infinity 2 camera (with IR filter removed) for real-time DF imaging. The reflected light from the beamsplitter is spectroscopically analysed using a cooled (-20 °C) OceanOptics QEPro spectrometer. PL measurements are similarly performed by illuminating the sample with a focused (spot diameter 1 µm) 447 nm laser (125 µW) instead of white light. In this case, the scattered light passes through a pair of LP500 filters before reaching the spectrometer.

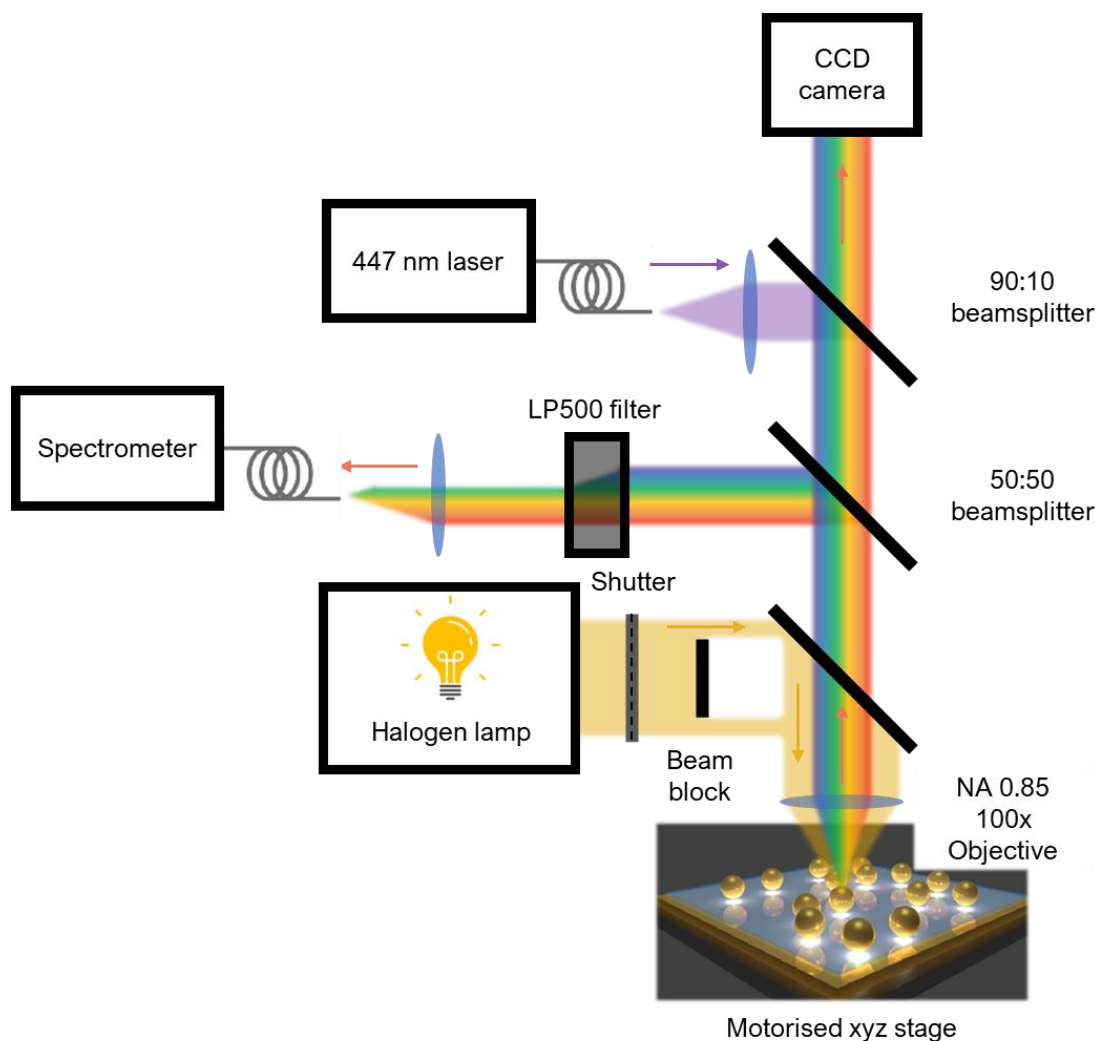


Figure 7.1. Schematic of optical setup used for NPoM DF + PL analysis.

The raw intensity data $I_{\text{raw}}(\lambda)$ is processed using a background spectrum $I_{\text{bg}}(\lambda)$, recorded in the absence of sample illumination, and a reference spectrum $I_{\text{ref}}(\lambda)$, obtained via white light illumination of a white light diffuser. The referenced scattering spectrum is obtained via:

$$I(\lambda) = \frac{I_{\text{raw}}(\lambda) - I_{\text{bg}}(\lambda)}{I_{\text{ref}}(\lambda) - I_{\text{bg}}(\lambda)} \quad (6)$$

To account for the different emission angles of various NPoM modes and resulting chromatic aberration of DF spectra, depth scans are performed as described in **Section 1.3.2**. Sample positioning (100 nm step size) is achieved using a motorised xyz translation stage (Prior Scientific). Particles are automatically located and analysed sequentially using particle identification software developed by Dr William Deacon and Dr Richard Bowman.* Raw data was processed using custom Python code (**Appendix 8.1**).

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7.4.2 NPoM SERS

NPoM SERS measurements were performed using a customised Olympus BX51 microscope in reflective DF geometry (*cf.* **Section 7.4.1**), augmented with two CW diode lasers (633 & 785 nm; Integrated Optics Matchbox series), an Andor Shamrock i303 spectrograph and a Newton EMCCD (**Figure 7.2**). Both lasers are spectrally filtered using 3 nm bandpass filters. The 785 nm optical power is mediated with a continuously-variable neutral density (ND) filter; the 633 nm power is regulated using an acousto-optic modulator (AOM) driven at 1 kHz. Raman scattered light is collected with a Zeiss 100x, 0.9 NA objective and passed through a dichroic mirror and two notch filters (Laserlines, 20 nm) to remove Rayleigh scattered laser light. The Raman signal is dispersed with a 600 lines/mm grating and recorded in kinetic acquisition mode (cycle time <50 ms).

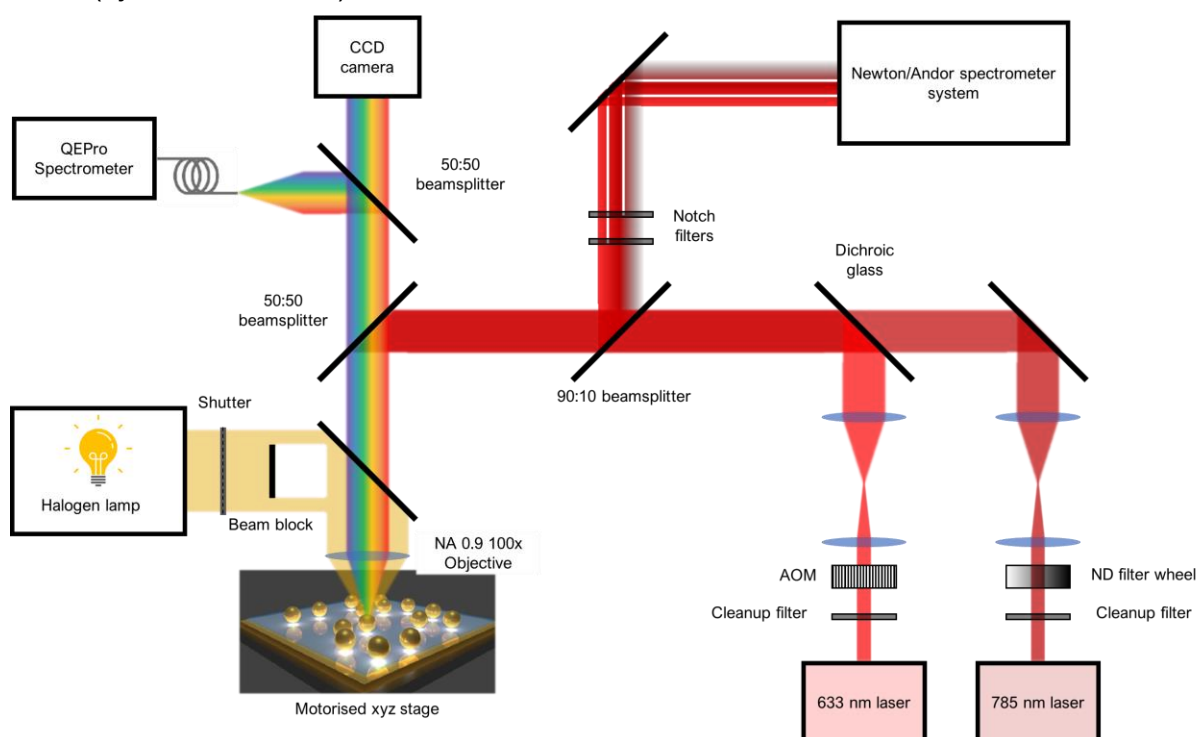


Figure 7.2. Schematic of optical setup used for NPoM SERS analysis.

7.4.3 Aggregate Extinction

Broadband light (LS-1-LL OceanOptics tungsten halogen lamp, 100 W) is guided through a multi-mode optical fibre (50 μm , NA 0.22), collimated, and passed through a quartz (**Section 3.4.2**) or polystyrene (**Section 4.3**) cuvette (path length 1 cm) containing the analyte solution (**Figure 7.3**). The transmitted light is collected with a lens into another multi-mode fibre and analysed with an OceanOptics QE65000 spectrometer. Absorbance is calculated as $A(\lambda) = -\log_{10}(I/I_0)$, where I_0 and I are the incident and transmitted light intensity, respectively. Before measurement, a reference spectrum is taken using deionised water, and a background spectrum recorded without illumination. Spectra are recorded sequentially with 300 ms integration (~ 0.5 -1 s cycle time).

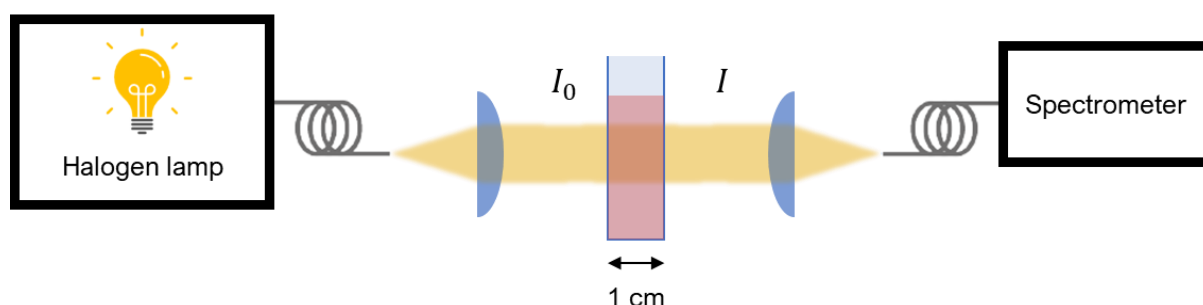


Figure 7.3. Schematic of optical setup used for AuNP aggregate extinction analysis.

7.4.4 Raman & Aggregate SERS

Bulk Raman and Aggregate SERS measurements were performed using a commercial Renishaw inVia Raman microscope equipped with a 785 nm diode laser and a 633 nm HeNe laser. Optical power was tuned using a set of discrete neutral density filters and light was collected with one of several objectives (5x, 0.12 NA; 20x, 0.45 NA; 50x, 0.75 NA). Liquid samples were analysed using a polypropylene 96 multi-well plate (340 μL /well), with focal height optimised for maximum Raman intensity via a pre-measurement depth scan. Dry samples were analysed at the optical focal height. Scattered light was dispersed with a 1200 lines/mm grating before spectroscopic analysis.

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8. Appendix

8.1 NPoM Analysis

8.1.1 DF & PL Data Processing

Raw NPoM DF & PL data was collected as described in **Methods 7.4.1** and analysed as in **Section 1.3.2** using custom Python code written specifically for this project. Each NPoM z-scan is truncated to the range $450 < \lambda < 900$ nm ($500 < \lambda < 900$ nm if PL measurements were performed) to remove high- and low-end noise, then transformed into a 1D spectrum by calculating the intensity vs focal height centroid at each wavelength.¹⁷

The spectrum is smoothed using a Butterworth lowpass filter (in both directions to prevent shifting along the x axis) and the position of the central spectral minimum is located (**Figure A1a**). The wavelength position and intensity of the largest maximum on the long wavelength side of this minimum are then taken to be λ_C and I_C , respectively. Spectra with two distinct maxima in this spectral region (**Figure A1b**) are flagged and optionally discarded later. I_T is approximated as the intensity of the smoothed spectrum at $\lambda_T = 533$ nm. This method of $(\lambda_C, I_C, \lambda_T, I_T)$ analysis is favoured over a multiple Gaussian or Lorentzian fit due to overfitting issues and lower reliability of I_T, I_C data when using the latter.

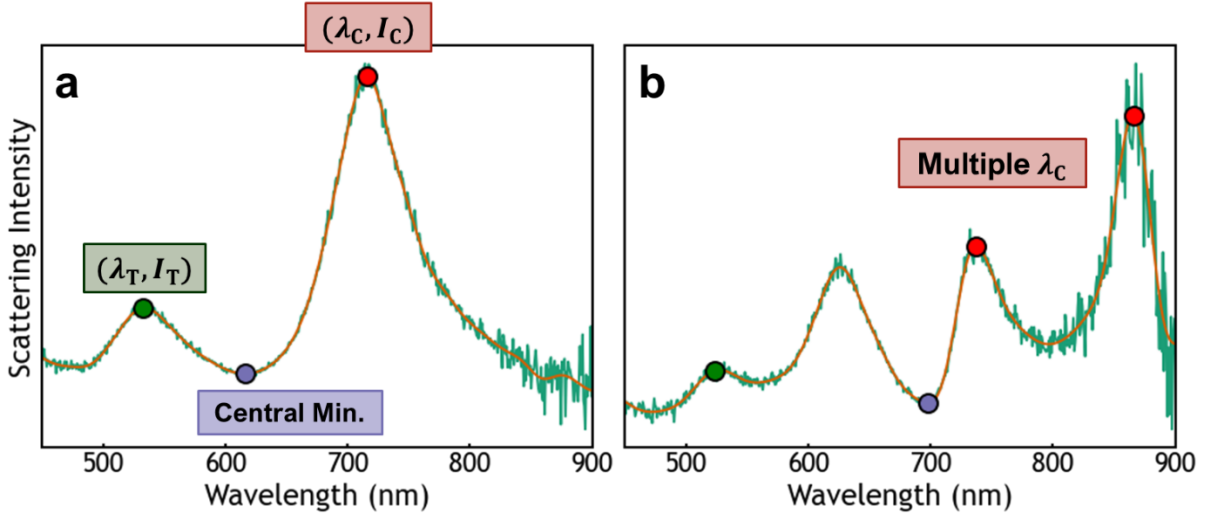


Figure A1. Illustration of automated detection of $(\lambda_C, I_C, \lambda_T, I_T)$.

NPoM PL spectra are first divided by the square root of the DF spectrum of the same NPoM at the same focal height to correct for plasmonic outcoupling efficiency (**Figure A2a,b**). A bi-exponential fit is then performed using only the high- and low-wavelength regions of the spectrum to model the broad laser background (**Figure A2b**); subtracting this reveals the final, processed spectrum (**Figure A2c**). Significant variability in PL spectral shape between individual NPoMs is observed due to imperfect outcoupling correction and background

subtraction. However, averaging PL spectra across many NPoMs with similar λ_c reveals persistent spectral features of the nanocavity contents (**Figure 5.34**).

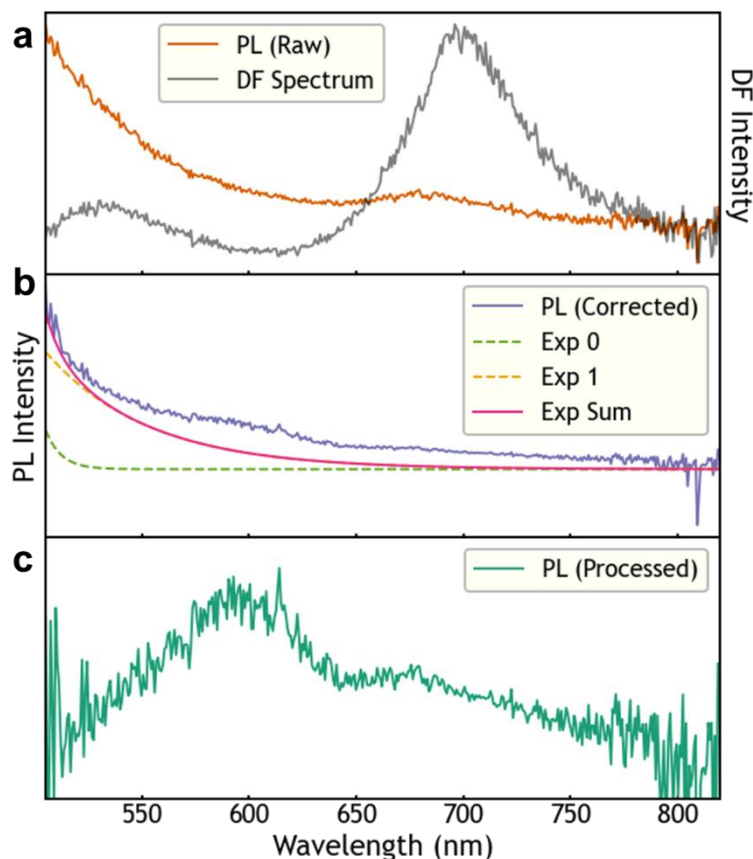


Figure A2. Example PL spectrum processing and background subtraction from a single NPoM. **(a)** Raw PL and DF data. **(b)** Outcoupling-corrected PL spectrum bi-exponential fit thereof (fit to spectral regions $505 \leq \lambda \leq 540$ and $820 \leq \lambda \leq 900$). **(c)** Final processed, background-subtracted PL spectrum.

8.1.2 λ_c Distribution Inspection

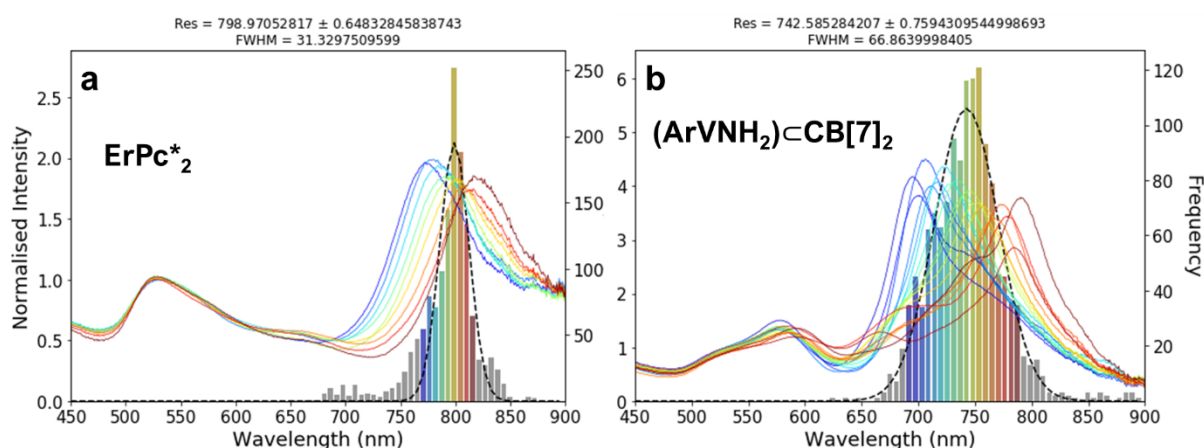


Figure A3. Example of **(a)** narrow λ_c distribution with uniform spectral averages, indicating a uniform monolayer and **(b)** broad λ_c distribution with high spectral variability, indicating significant monolayer variability between individual NPoMs.

8.2 BPc

8.2.1 Synthesis

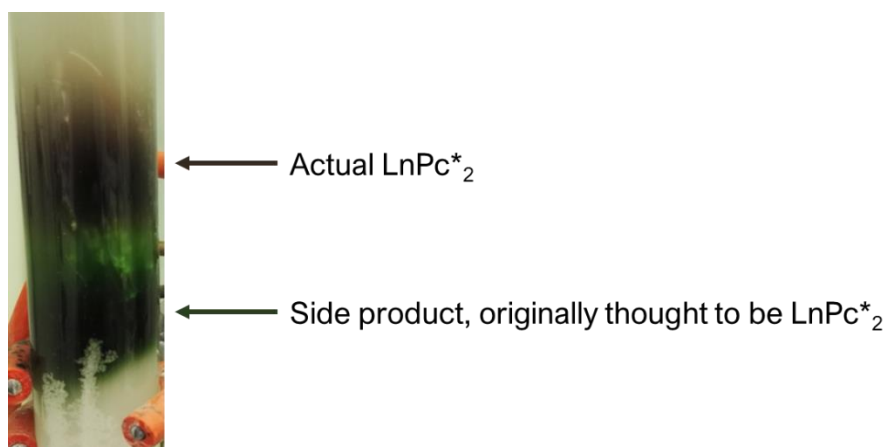


Figure A4. BPc* column chromatography fractions.

8.2.2 BPc NPoM Characterisation

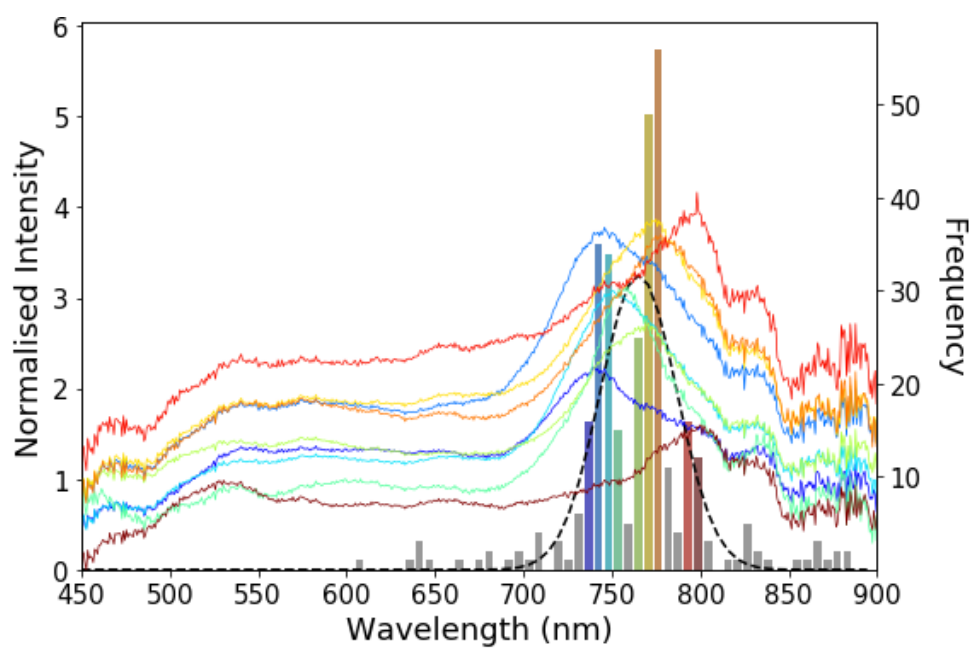


Figure A5. λ_c distribution of NPoM with LuPc₂ spacer deposited for 30 min from CHCl₃.

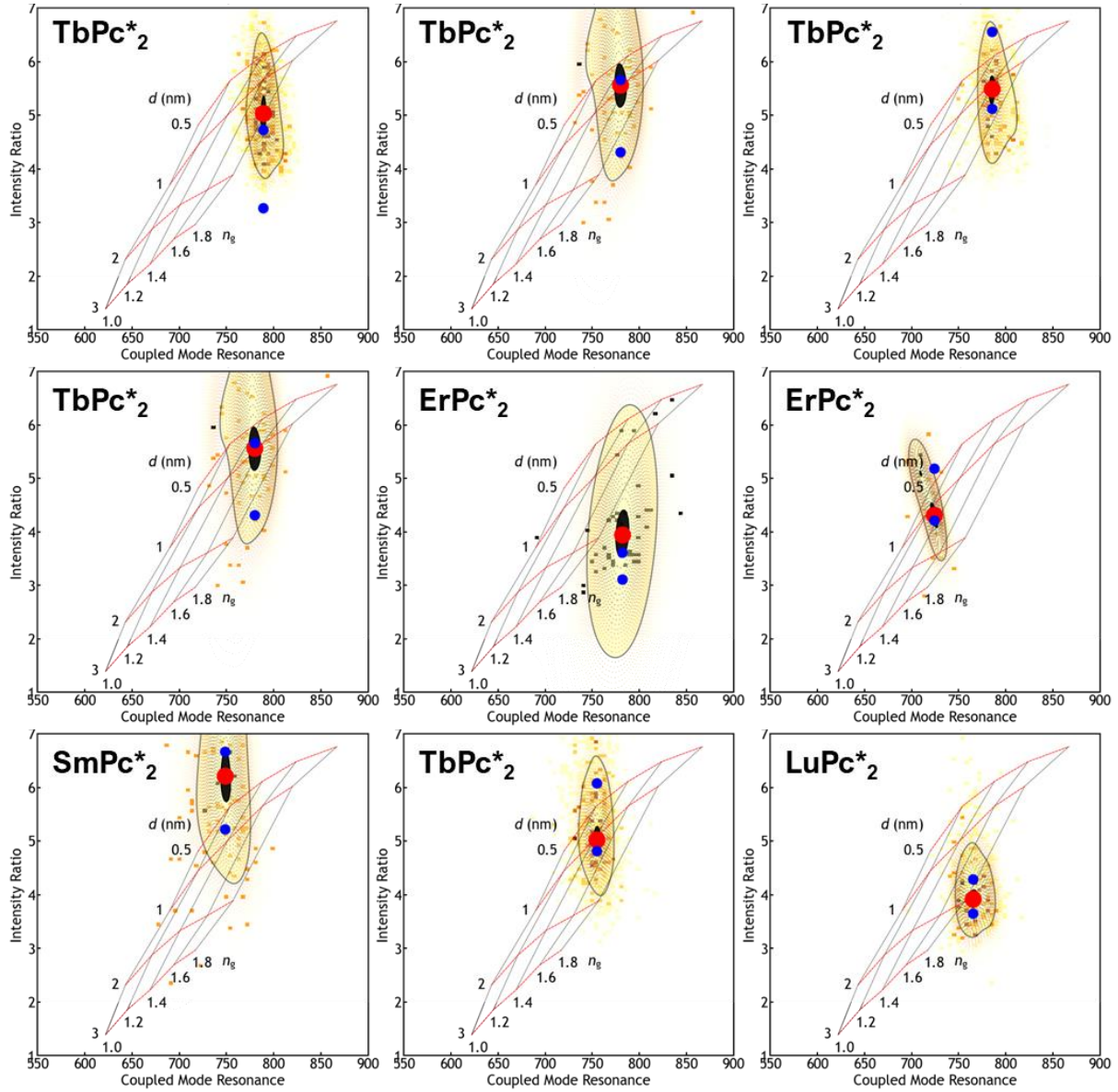


Figure A6. Some BPC* NPoM I_C/I_T vs λ_C density plots. Illustrating high variability and unsuitability of the NPR method for characterisation of these systems. Curved black/grey lines are density contours of I_C/I_T vs λ_C scatter plot (yellow points). Filled black ovoid is 90% contour, red marker is I_C/I_T vs λ_C centroid, blue markers are peak centres of bimodal gaussian fits of I_C/I_T frequency distribution.

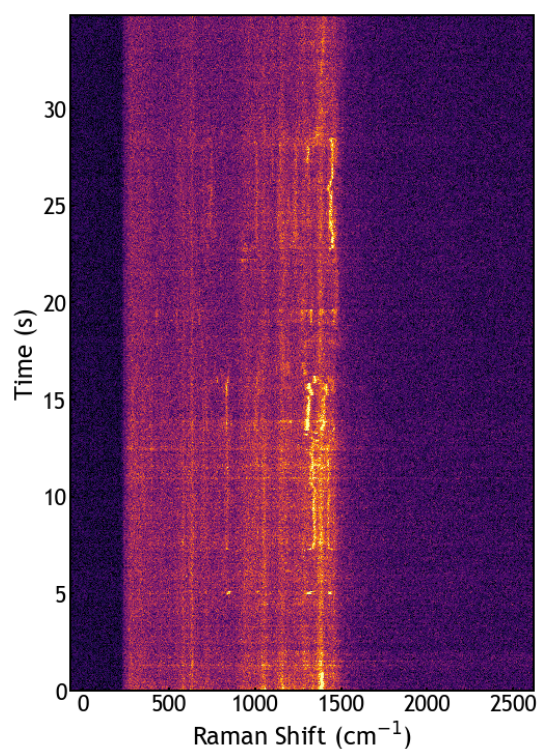


Figure A7. BPc* NPoM SERS timescan with significant spectral wandering and picocavity formation.

8.2.3 BPc Raman & Aggregate SERS

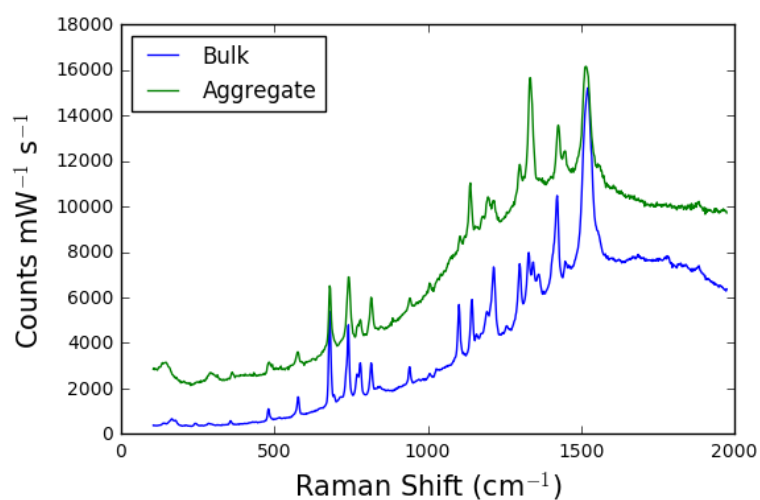


Figure A8. Bulk LuPc₂ Raman spectrum and LuPc₂@AuNPs ($D = 16$ nm) SERS spectrum. $\lambda_{\text{ex}} = 633$ nm.

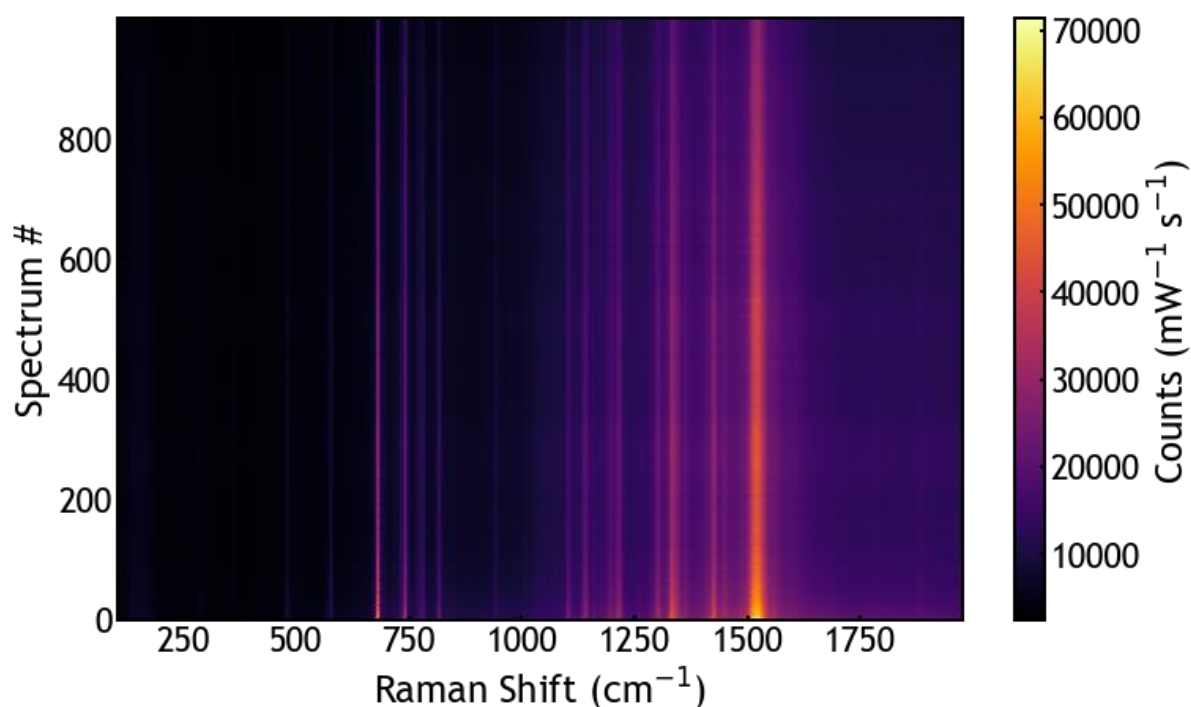


Figure A9. LuPc₂@AuNP aggregate ($D = 16$ nm) SERS timescan in air + THF vapour atmosphere. Scan was started immediately after addition of THF liquid to gas cell. Evaporation occurred after 2-3 min. Total measurement time = 60 min.

8.2.4 Pillow Effect

λ_C may be affected by local electron density redistribution at the Au surface, caused by electrostatic interaction with BPc*. This can disrupt the effective vacuum level and decrease the local Au work function upon physisorption, affecting electron spillout length.^{152,432} This so-called “pillow effect” may also lower the BPc* MO energies relative to the Au Fermi level, increasing favourability of electron transfer from Au to BPc*.¹⁵²

Slight differences in BPc* electron affinity (EA) may affect the average charge state of the molecular layer and strength of this pillow effect. The electrostatic interactions may then affect the local ω_p around the hotspot, inducing a λ_C shift (**Section 1.3.1**). While accurate determination of absolute EA values is non-trivial using DFT - and further complicated by perturbation of BPc* energy levels upon adsorption - qualitative trends can be extracted via comparison of SUMO eigenvalues. For methylthio-substituted BPc' (LnPc'₂; Ln = Sm, Tb, Er, Lu; **Section 3.5.2**) the eigenvalues indicate a slight EA decrease from Sm to Lu (**Figure A10**), consistent with literature redox potentials,²²⁰ indicating a higher probability of BPc* reduction with increasing r_{Ln} .

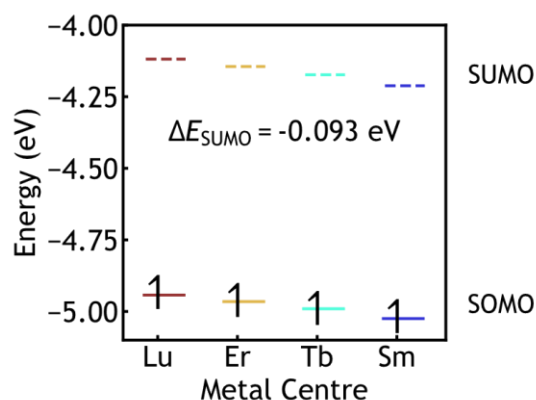


Figure A10. Frontier spin orbital eigenvalues calculated for neutral BPc'. Solid lines = occupied states, dashed lines = unoccupied. Here, $\Delta E_{\text{SUMO}} = E_{\text{SUMO}}(\text{Sm}) - E_{\text{SUMO}}(\text{Lu})$.

An increase in anionic character of the BPc* monolayer should electrostatically decrease the local Au electron density and therefore ω_p . If ΔE_{SUMO} were to significantly affect λ_c in this way, a redshifting effect would be observed from Lu to Sm. A decrease in surface electron density may also decrease the extent of electron spillout from the surface, lowering the tunnelling conductance and redshifting λ_c further as r_{Ln} increases. Again, this should lead to a smaller $-\partial \overline{\lambda_c} / \partial d$ than predicted by classical models, the opposite of what is observed experimentally here. Other unknown factors include the redox-independent variation of λ_p with Ln, degree of BPc*-Au covalency and compressibility of the electron gas. Again, theoretical treatment of these factors requires a deeper quantum mechanical description of the BPc*-Au interface and is beyond the scope of this work

8.2.5 BPc DFT

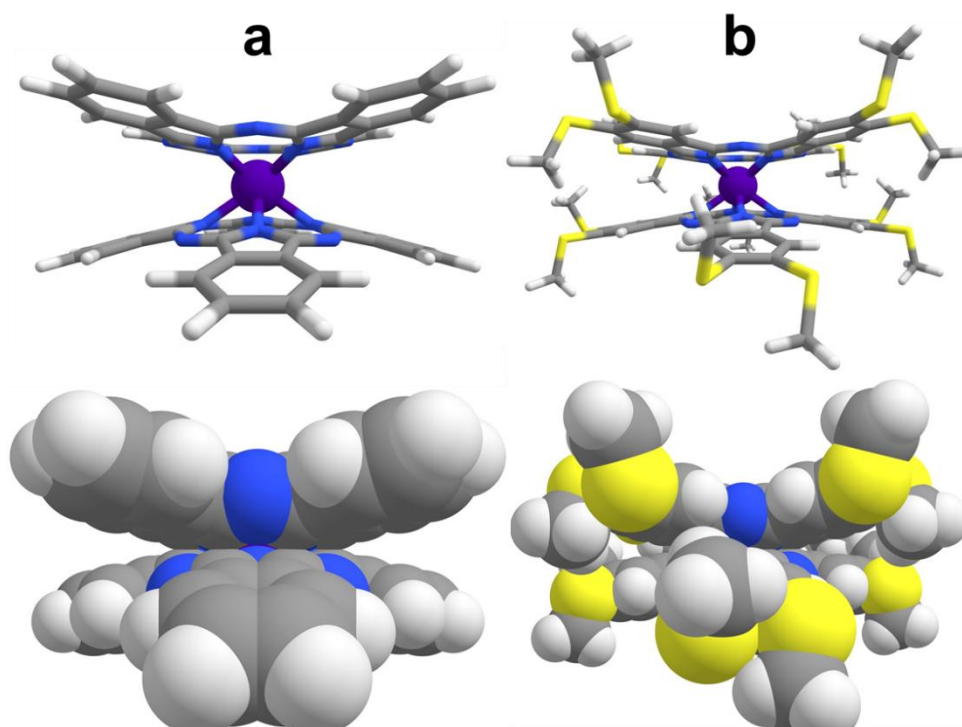


Figure A11. DFT optimised geometries of **(a)** ErPc₂ and **(b)** ErPc'₂ without dispersion corrections. Atom colours: C (grey), H (white), N (blue), S (yellow), Er (purple).

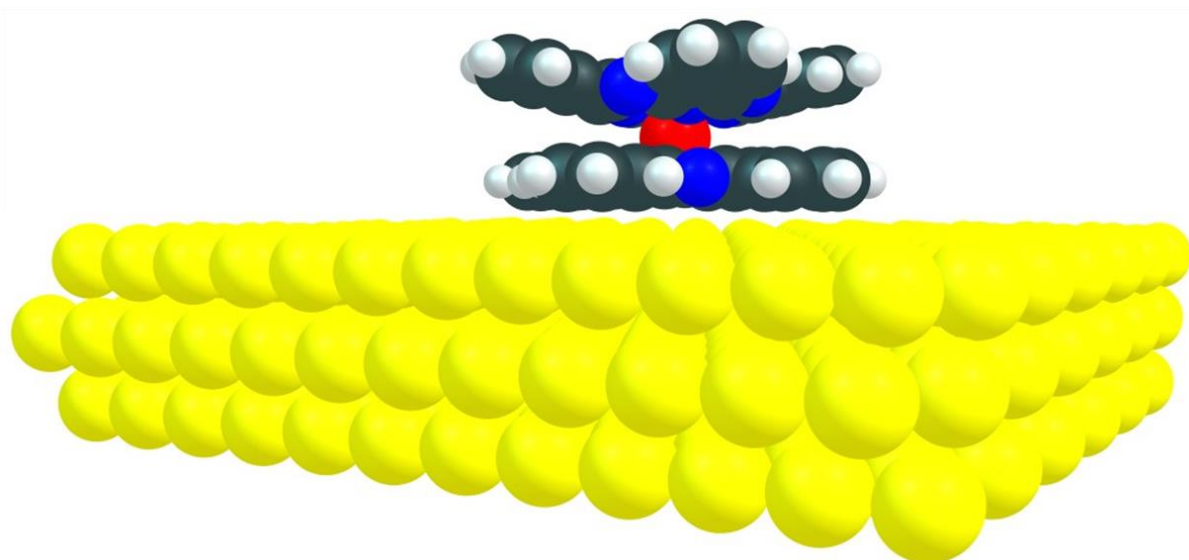


Figure A12. Partially-optimised structure of LuPc₂ on an Au slab, illustrating induced planarity of Pc ring upon Au contact. Calculated by Istvan Szabo (Department of Physics, University College London); see **Methods 3.7.3** for computational details. Atom colours: C (black), H (white), N (blue), Lu (red), Au (yellow).

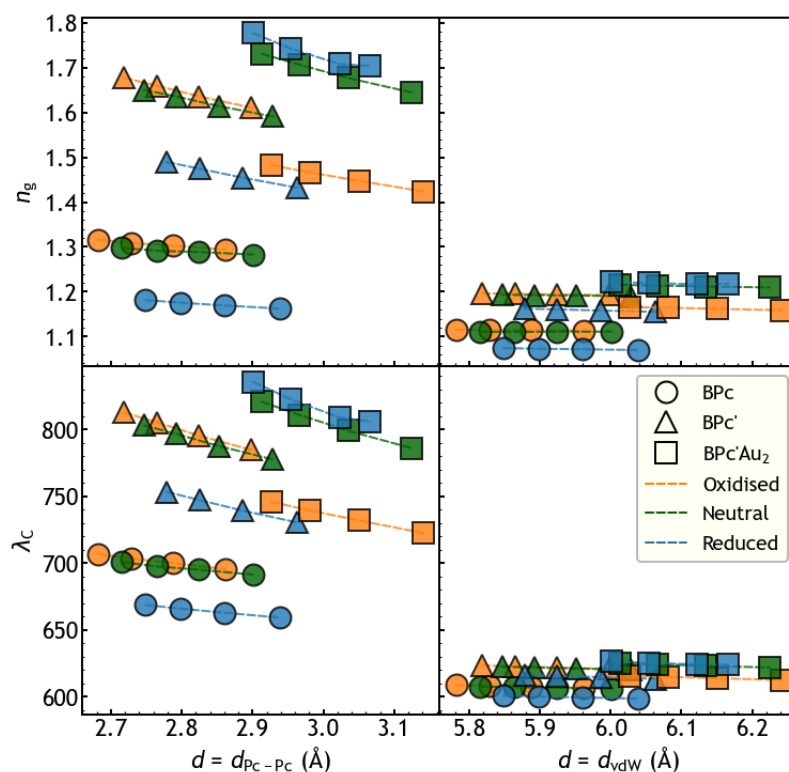


Figure A13. Comparison of calculated variation of n_g (top) and λ_c (bottom) with $d = d_{PC-PC}$ (left) and $d = d_{vdW}$ (right) for BPc, BPc' and BPc'Au₂. When $d = d_{PC-PC}$, largest predicted $|\Delta\lambda_c| = 34$ nm compared to $|\Delta\lambda_c| = 3.3$ nm when $d = d_{vdW}$ is used. Note that the large n_g and λ_c shifts for $d = d_{PC-PC}$ are most likely an artefact of **Equation (5)** when $\Delta d \rightarrow d$.

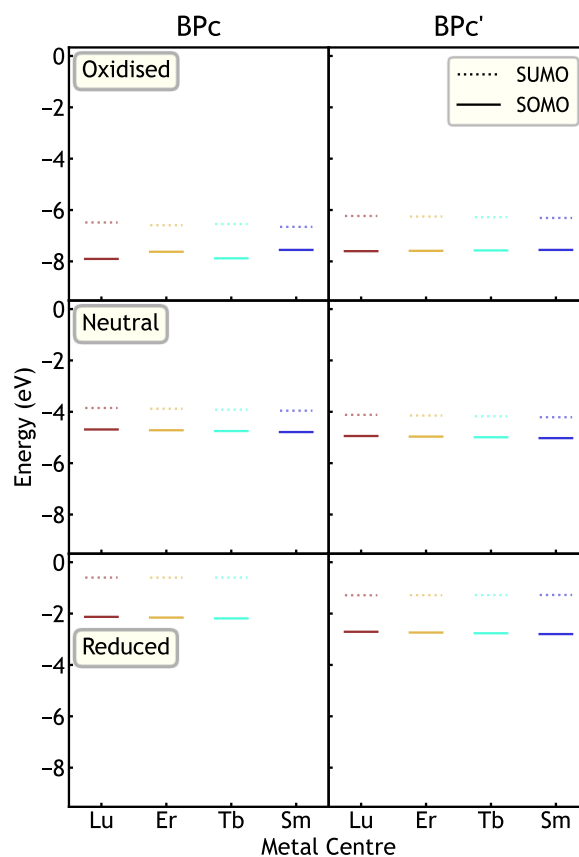


Figure A14. Comparison of SOMO and SUMO eigenvalues calculated for BPc and BPc'.

8.2.6 Calculating BPc NPOM $\Delta\bar{\lambda}_C$ via $n_g(\lambda)$

Experimental $n_g(\lambda)$ measured for TbPc₂ films by Robaschik *et al.*^{198,430} was incorporated into the LCR model via modification of **Equation (2)** (**Section 1.3.1**):

$$\lambda_C = \lambda_1^l = \lambda_p \sqrt{\varepsilon_\infty + 2\varepsilon_d + 4\varepsilon_d \frac{C_g}{C_{NP}}}$$

Recalling from earlier that $C_g/C_{NP} = \varepsilon_g^\chi \ln[1 + \zeta D/2d]$ and $\varepsilon_g^\chi \approx n_g$ for $\chi \approx 0.5$, **Equation (2)** can be rewritten as

$$\left(\frac{\lambda_C}{\lambda_p}\right)^2 = \varepsilon_\infty + 2\varepsilon_d + 4\varepsilon_d n_g(\lambda_C) \ln\left[1 + \frac{\zeta R}{d}\right] \quad (7)$$

In the λ_C region of interest ($750\text{nm} < \lambda < 900\text{ nm}$), the experimental $n_g(\lambda)$ data for TbPc₂^{198,430} can be approximated as a quadratic function of λ (**Figure A15**):

$$\left(\frac{\lambda_C}{\lambda_p}\right)^2 = \varepsilon_\infty + 2\varepsilon_d + 4\varepsilon_d (a\lambda_C^2 + b\lambda_C + c) \ln\left[1 + \frac{\zeta R}{d}\right] \quad (8)$$

This can be rewritten $a'\lambda_C^2 + b'\lambda_C + c' = 0$, where $a' = ka - 1$, $b' = kb$, $c' = kc + \lambda_p^2(\varepsilon_\infty + 2\varepsilon_d)$ and $k = 4\varepsilon_d \lambda_p^2 \ln[1 + \zeta R/d]$; evaluation of the roots then allows calculation of λ_C .

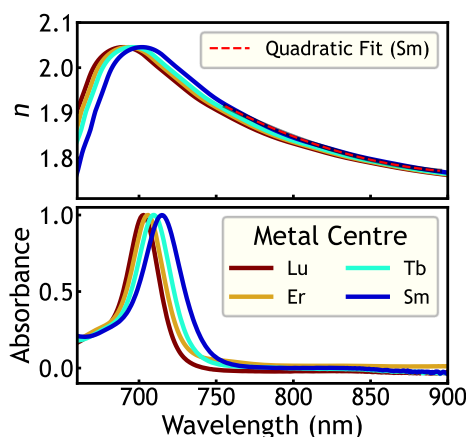


Figure A15. Predicted $n(\lambda)$ for unsubstituted LnPc₂ (Ln = Sm, Tb, Er, Lu) based on experimental data for TbPc₂ multilayer^{198,430} shifted by appropriate $\Delta\lambda_Q$ taken from UV-Vis spectra (bottom) of BPc*

Assuming that $n_g(\lambda)$ can be approximated for each Ln by shifting TbPc₂ $n(\lambda)$ according to $\lambda_Q(\text{Ln}) - \lambda_Q(\text{Tb})$, this treatment allows approximate prediction of $\Delta\lambda_C$. Although the literature $n(\lambda)$ was measured for unsubstituted TbPc₂, the λ_Q shift from Sm to Lu is approximately the same for BPc and BPc* and qualitative determination of the sign of Δn_g is still possible. Additionally, λ_C values calculated using this method are overestimates due to the absence of nonlocal corrections. However, the method remains useful for qualitative exploration of the perturbative effects of different $n(\lambda)$ on $\Delta\lambda_C$ within the bounds of the LCR model.^{76,102} Once again, $n_g(\text{Lu}) < n_g(\text{Sm})$ in all cases (see supplementary information of Readman *et al.*¹ for more details) yielding a smaller $\Delta\lambda_C$ than the static n_g scenario.

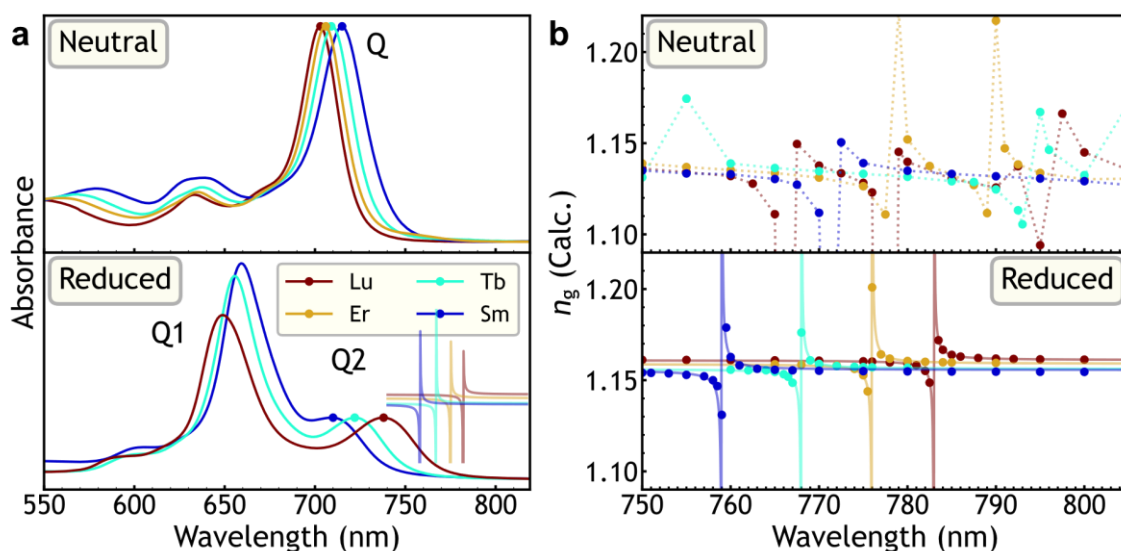


Figure A16. (a) UV-Vis absorption spectra (Q-band only; normalised) for neutral (top) and reduced (bottom) BPc* in CHCl₃ and NaBH₄/THF, respectively. Semi-transparent inset illustrates relative position of $n_g(\lambda)$ resonances. (b) Approximate $n_g(\lambda)$ calculated for BPc' using $\alpha_{zz}(\lambda)$ and d_{vdW} via **Equation (5)** (**Section 3.5.3**).

$\alpha_{zz}(\lambda)$ was then calculated for [BPc']⁰ and [BPc']⁻ with DFT (**Methods 3.7.3**), from which $n_g(\lambda)$ was approximated using **Equation (5)**⁴³⁶ (**Figure A16b**). The resulting Fano-like resonances can each be approximated by fitting to a Breit-Wigner-Fano function:⁴⁴²

$$n(\lambda) = \frac{A(q\Gamma/2 + \lambda - \mu)^2}{(\Gamma/2)^2 + (\lambda - \mu)^2} \quad (9)$$

With amplitude A , centre μ , linewidth σ and Fano parameter q . This can be incorporated into **Equation (7)**, as before, yielding:

$$\left(\frac{\lambda}{\lambda_p}\right)^2 = \varepsilon_\infty + 2\varepsilon_d + 4\varepsilon_d \left(\frac{A(q\Gamma/2 + \lambda - \mu)^2}{(\Gamma/2)^2 + (\lambda - \mu)^2} \right) \ln \left[1 + \frac{\zeta R}{d} \right] \quad (10)$$

Which can be rearranged to give a quartic function in λ :

$$a\lambda^4 + b\lambda^3 + c\lambda^2 + d\lambda + e \quad (11)$$

with

$$\begin{aligned} a &= 1 \\ b &= -2\mu \\ c &= (\Gamma/2)^2 - \mu - \lambda_p^2[\varepsilon_\infty + \varepsilon_d(1 + 4kA)] \\ d &= 2\lambda_p^2\{\varepsilon_\infty\mu + \varepsilon_d[\mu + 2kA(2\mu - \Gamma q)]\} \\ e &= \lambda_p^2 \left[\varepsilon_d \left(kAq^2\Gamma^2 + 4kAq\Gamma\mu - \frac{1}{2}\Gamma^2 - \mu^2 - 4kA\mu^2 \right) - \varepsilon_\infty((\Gamma/2)^2 + \mu^2) \right] \end{aligned}$$

and

$$k = \ln[1 + \zeta R/d]$$

Solving for λ using SymPy⁵²³ yields real roots of $1725 < \lambda_c < 1755$ nm from Sm to Lu. While these λ_c values are large overestimates due to the classical nature of the LCR model and the

approximate nature of **Equation (5)**, the value of $\Delta\lambda_C$ matches well with the experimental $\Delta\bar{\lambda}_C$ (**Figure A17**).

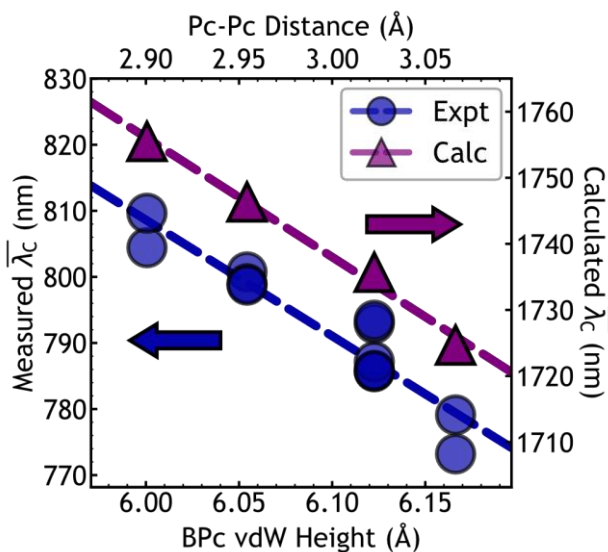


Figure A17. Comparison of experimental BPC* NPoM $\bar{\lambda}_C$ and theoretical λ_C values for $[\text{BPC}']^-$, calculated using Breit-Wigner-Fano fit of theoretical $n_g(\lambda)$ (via DFT $\alpha_{zz}(\lambda)$ and **Equation (5)**) combined with the LCR model via **Equation (7)**. The two datasets are plotted on separate y-axes with different offsets, but identical scales for direct comparison of $\Delta\lambda_C$.

8.3 ArV

8.3.1 NPoM

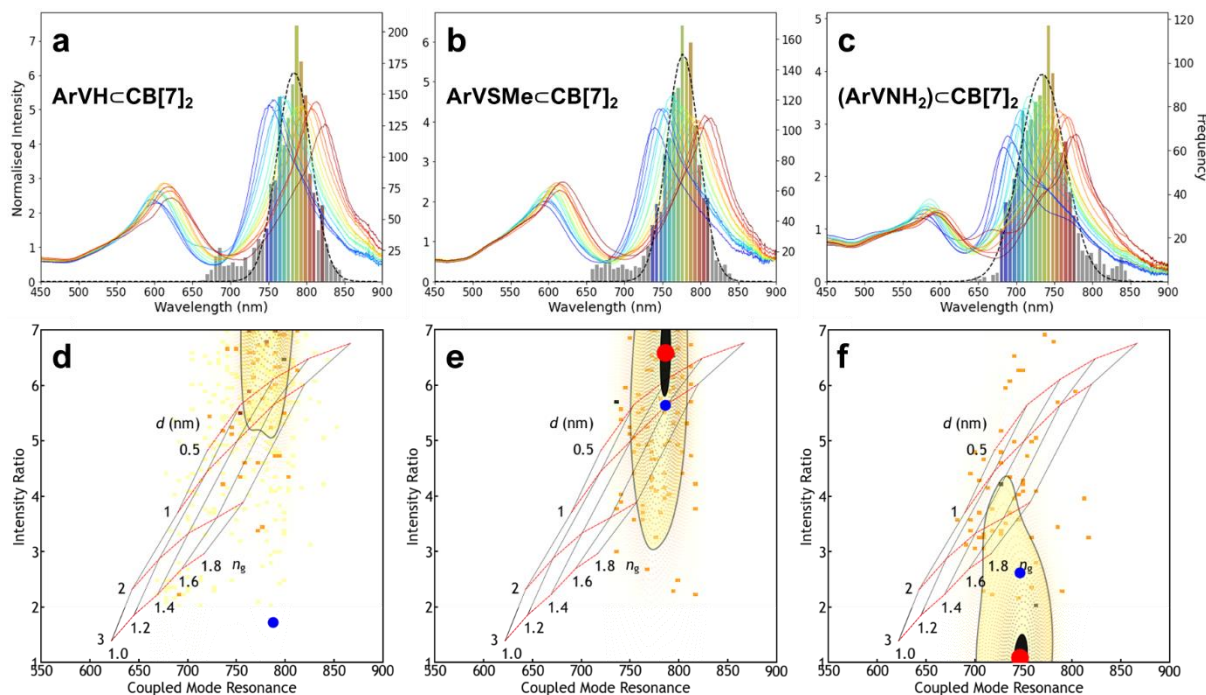


Figure A18. (a-c) λ_C distributions and (d-f) NPR data for (a,d) $\text{ArVH}\equiv\text{CB}[7]_2$, (b,e) $\text{ArVSM}\equiv\text{CB}[7]_2$ and (c,f) $\text{ArVNH}_2\equiv\text{CB}[7]_2$. SAM deposition time = 6 h. $D = 80$ nm. Different coloured traces/points in (d-f) are as labelled in **Figure A6**.

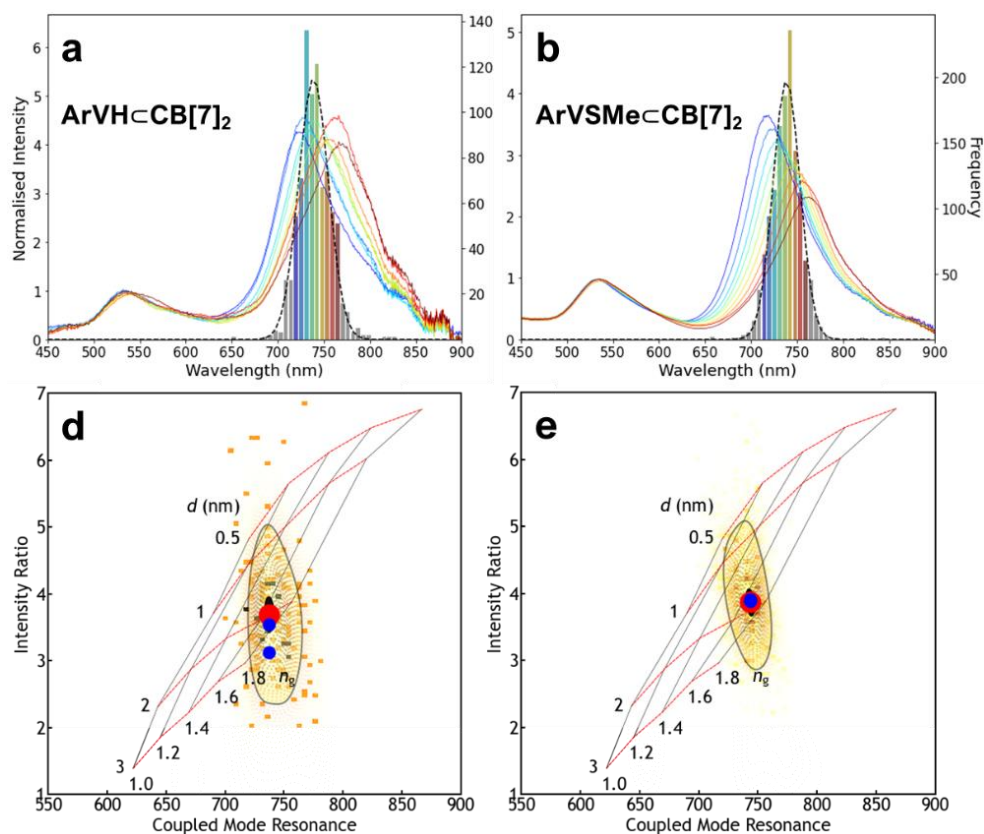


Figure A19. (a-b) λ_C distributions and (d-e) NPR data for (a,d) ArVH≡CB[7]₂ and (b,e) ArVSM≡CB[7]₂. SAM deposition time = 24 h. $D = 80$ nm. Data in (d-f) as labelled in **Figure A6**.

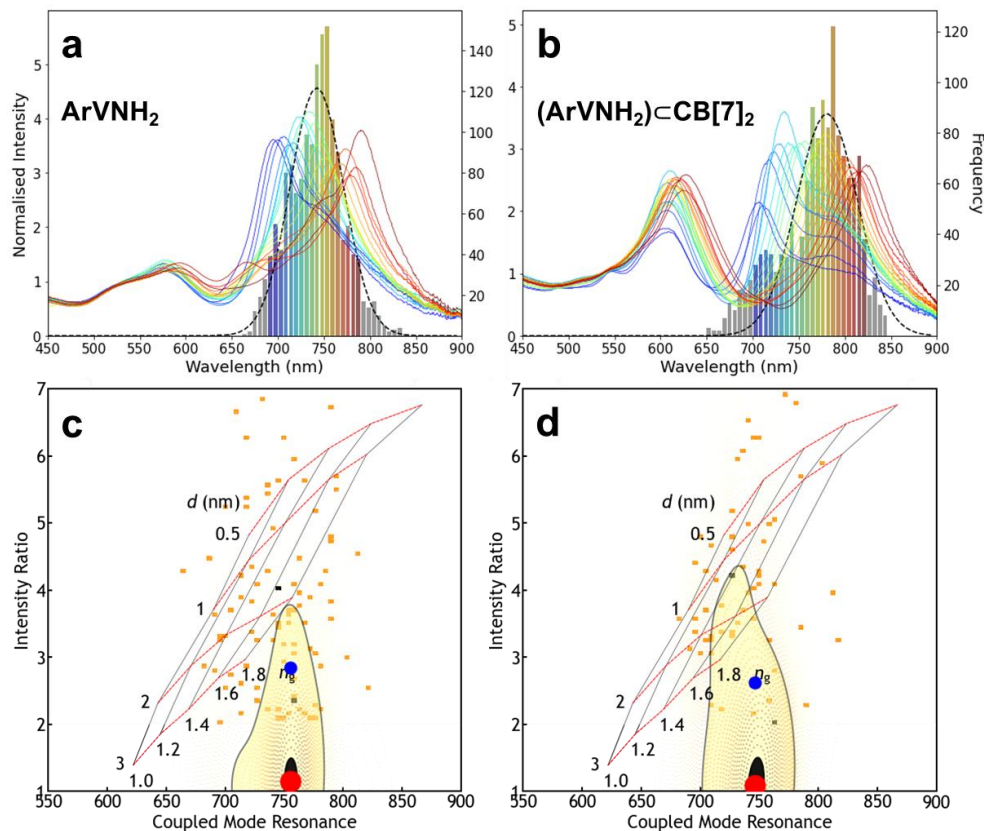


Figure A20. (a-b) λ_C distributions and (c-d) NPR data for (a,c) ArVNH₂ and (b,d) ArVNH₂≡CB[7]₂. (c-d) Illustrated as in **Figure A6**. Deposition time = 22 h

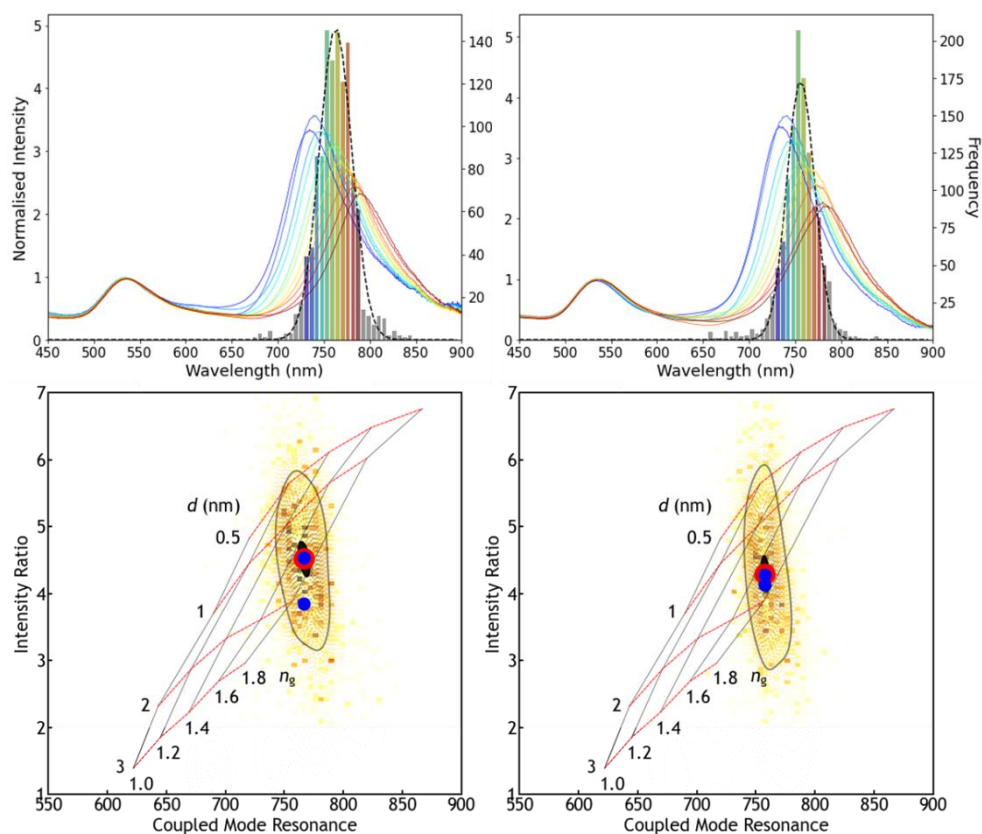


Figure A21. (a) λ_c distribution and (b) NPR data for ArVSMc NPoMs without CB[n].

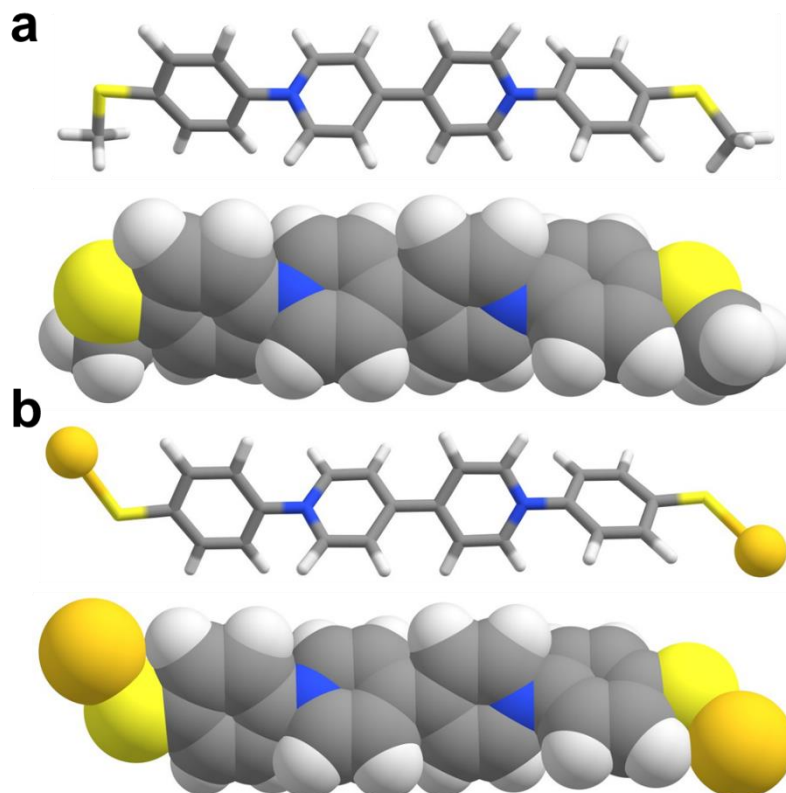


Figure A22. DFT-optimised (a) ArVSMc and (b) ArVSAu geometry; see **Methods 4.7.1** for computational details. Atom colours: C (grey), H (white), N (blue), S (yellow), Au (gold).

8.3.2 AuNP Aggregate Extinction

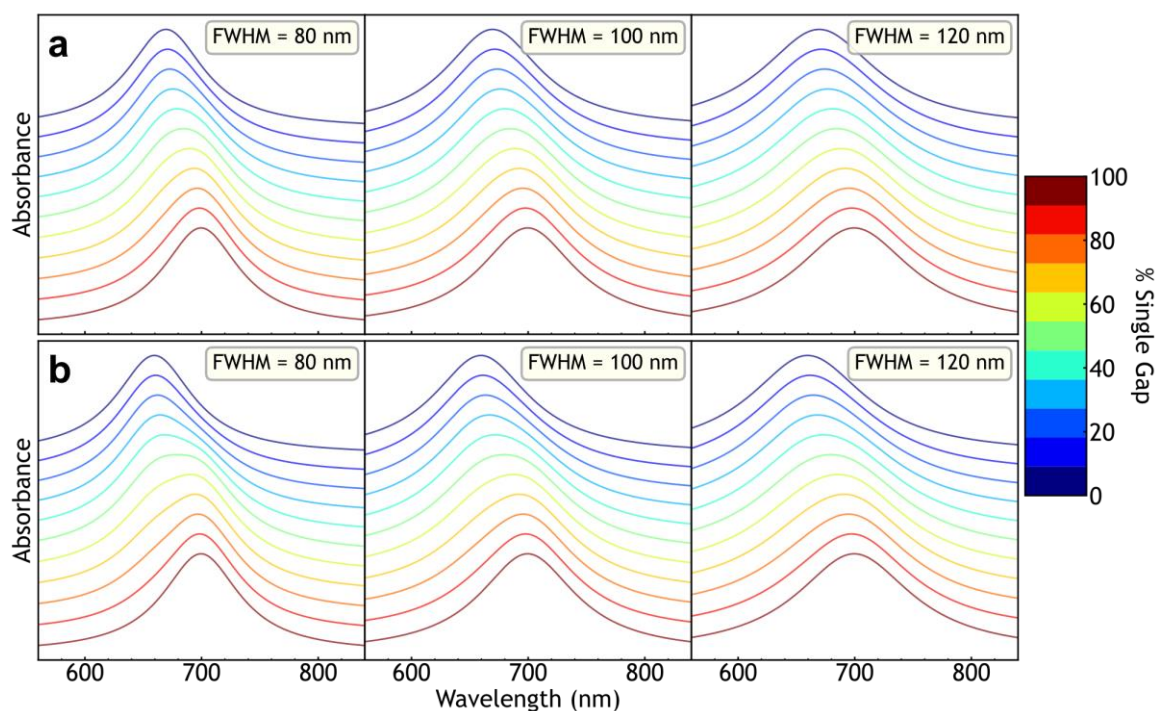


Figure A23. Calculated peak appearances for weighted sums (see colour bar) of two λ_{dim} resonances with $\Delta\lambda_{\text{dim}} =$ (a) 30 or (b) 40 nm. (a) Two resonances with $\Delta\lambda_{\text{dim}} = 30$ nm may manifest as a single peak if individual peak FWHM > 80 nm. (b) A larger separation of $\Delta\lambda_{\text{dim}} = 40$ nm is noticeable even for FWHM = 100 nm.

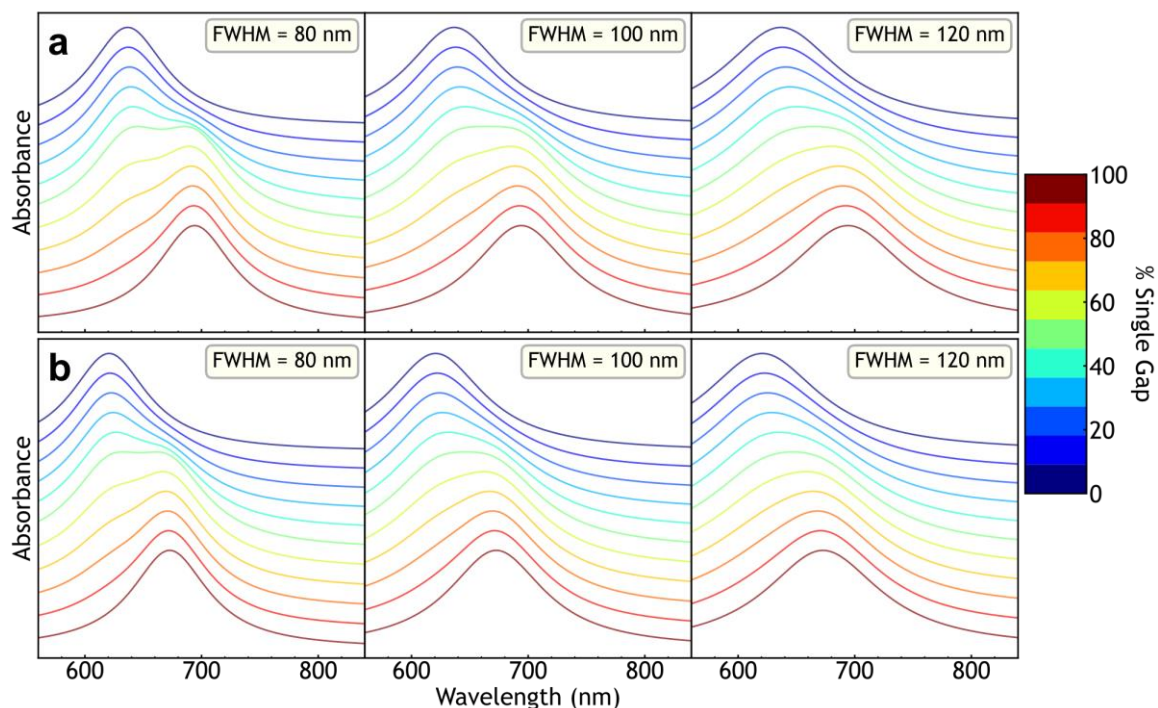


Figure A24. Calculated peak appearances for weighted sum (see colour bar) of two Lorentzian λ_{dim} resonances (FWHM = 80, 100 or 120 nm) for single/double-thickness gaps of (a) ArVSMc ($d = 1.7$ nm, $2d = 3.4$ nm; $n_g = 1.6$) or (b) ArVSMcCB[7]₂ ($d = 1.7$ nm, $2d = 3.4$ nm; $n_g = 1.66$). $D = 60$ nm, $w = 15$ nm, $n_m = 1.333$.

8.3.3 DLVO Model

This appendix section explores the possibility of a D threshold in CB[7]@AuNP aggregation. DLVO theory^{58,465} models the distance-dependent interaction potential between two spherical nanoparticles in solution as

$$V_{\text{DLVO}} = V_{\text{vdW}} + V_{\text{dl}} \quad (12)$$

where:

$$\frac{V_{\text{vdW}}(d)}{k_{\text{B}}T} = -\left(\frac{H}{6k_{\text{B}}T}\right) \left[\frac{2R^2}{d(4R+d)} + \frac{2R^2}{(2R+d)^2} + \ln\left(\frac{d(4R+d)}{(2R+d)^2}\right) \right] \quad (13)$$

is the attractive dispersion potential between the two Au spheres of radius R , with Au Hamaker constant $H = 3.0 \times 10^{-19} \text{ J}$,⁵⁸ and:

$$\frac{V_{\text{dl}}(d)}{k_{\text{B}}T} = \frac{2\pi\epsilon_0\epsilon_r\psi_0^2R}{k_{\text{B}}T} \ln(1 + e^{-\kappa d}) \quad (14)$$

is the repulsive electrostatic potential between the electrical double layers of the AuNPs, where:

$$\psi_0 = \zeta \left(1 + \frac{1}{\kappa R}\right) e^{+1} \quad (15)$$

is the effective AuNP surface potential for experimental zeta potential $\zeta \approx -40 \text{ mV}$, and:

$$\kappa = \frac{2q_e^2I}{\epsilon_0\epsilon_r k_{\text{B}}T} \quad (16)$$

is the inverse Debye length $\epsilon_r = 80.2$ is the relative permittivity of water, q_e is the fundamental electric charge, ϵ_0 is the vacuum permittivity and I is the ionic strength of the solution. ζ , and therefore V_{dl} , is related to the surface coverage of the negatively charged citrate capping ligands and is perturbed by displacement of citrate by spacer molecules. This theoretical treatment allows estimation of the activation barrier for AuNP aggregation and the effects of citrate coverage, AuNP size and ionic strength of solution. **Figure A25a** illustrates the distance-dependent interaction potential between two AuNPs ($D = 60 \text{ nm}$) in aqueous solution ($I = 5 \text{ mM}$) and the relative contributions of the attractive V_{vdW} and repulsive V_{dl} potentials. The activation barrier to aggregation in this case is around $180 k_{\text{B}}T$ and colloidal stability is predicted.

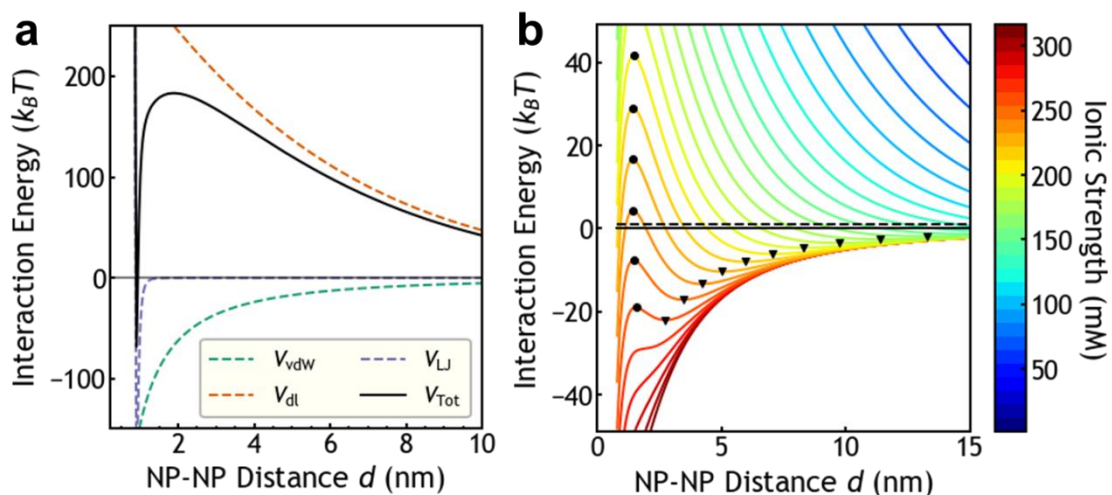


Figure A25. Interaction energy vs interparticle separation for 60 nm AuNPs at **(a)** $I = 5$ mM, illustrating the relative decay of V_{dl} and V_{vdW} and **(b)** a range of ionic strengths. Energy maxima are highlighted with black circles, and flocculation minima with triangles.

Figure A25b illustrates interaction potentials for the same system at a range of ionic strengths, predicting reversible AuNP flocculation for $I \geq 20$ mM, but stability towards irreversible aggregation for $I \leq 200 - 250$ mM. It should be noted that the ionic strength of this system lies just outside the I/R ratio for which the model is strictly valid (according to Wijenayaka *et al.*⁵⁸), so this threshold value of I is likely to vary.

The CB[7]-AuNP aggregation mechanism is more complex and less well understood.^{57,60,96} Displacement of citrate ligands upon CB[7] adsorption lowers ψ_0 , which decreases the magnitude of the repulsive V_{dl} and destabilises the colloid. However, the bridging of AuNPs with CB[7] implies an additional adhesive effect, with an attractive interaction between surface-bound CB[7] molecules and the neighbouring AuNP. To model this, a Lennard-Jones interaction potential (V_{LJ}) is added to **Equation (12)**, to give:

$$V = V_{vdW} + V_{dl} + N_{CB[7]} V_{LJ} \quad (17)$$

where $N_{CB[7]}$ is the number of CB[7] molecules per facet, assuming linear additive scaling, and:

$$V_{LJ} = 4nV_{C=O \rightarrow Au} \left[\left(\frac{\sigma}{d} \right)^{12} - \left(\frac{\sigma}{d} \right)^6 \right] \quad (18)$$

with carbonyl-Au bond strength $V_{C=O \rightarrow Au}$ (assumed to be 100 kJ mol^{-1})*, $n = 7$ for CB[7] and $\sigma = 2^{-1/6} r_{C=O \rightarrow Au}$ is the carbonyl-Au distance at which $V_{LJ} = 0$. This model assumes additive behaviour of independent $C=O \rightarrow Au$ bonds. The curve is then shifted along d by 0.9 nm to reflect the size of the CB[7]-bridged gap. The lowering of ψ_0 by citrate displacement is modelled using the CB[7] surface coverage, Θ , such that $\psi'_0 = \psi_0(1 - \Theta)$ replaces ψ_0 in **Equation (15)**.

*Arbitrarily based on $\sim 2/3$ the thiol-gold bond strength.^{524,525} Likely a significant overestimate but used here for model illustration purposes.

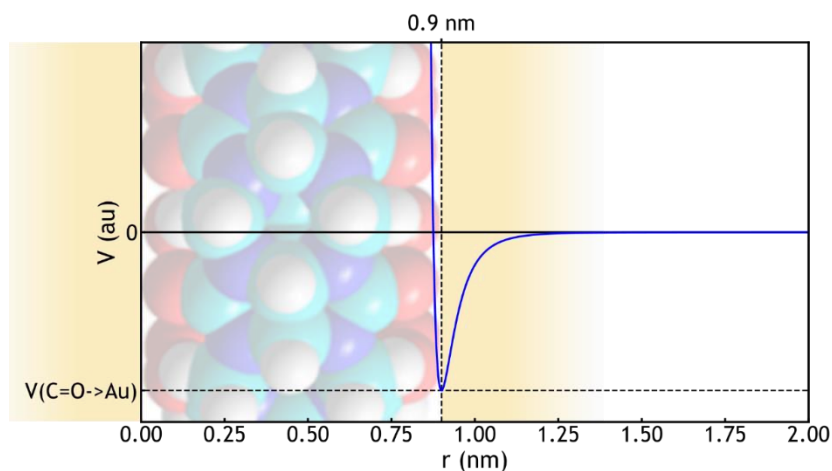


Figure A26. Lennard-Jones potential for carbonyl-gold interaction, shifted along d to reflect the 0.9 nm gap spacing created by CB[7]. Atom colours: C (cyan), H (white), N (blue), O (red).

While CB[7] molecules only extend outwards 0.9 nm from the surface (a far shorter distance than the V_{DLVO} maximum), the Lennard-Jones potential well at short distances may become deep and broad enough to affect the height of the DLVO stability peak once the contribution of multiple CB[7] molecules is summed. Considering only the V_{LJ} contribution of CB[7] (i.e. ignoring citrate displacement) leads to **Figure A27a**, which leads to a new potential minimum at $d = 0.9$ nm and moves the activation barrier to larger d as θ increases and the total V_{LJ} curve widens and deepens, but does not appreciably decrease its height. **Figure A27b** shows the same system with effects of citrate displacement included, demonstrating a significant decrease in V_{dl} and therefore activation barrier as θ increases. Contribution of displaced citrate to ionic strength of solution was calculated to be negligible (<10 ppm).

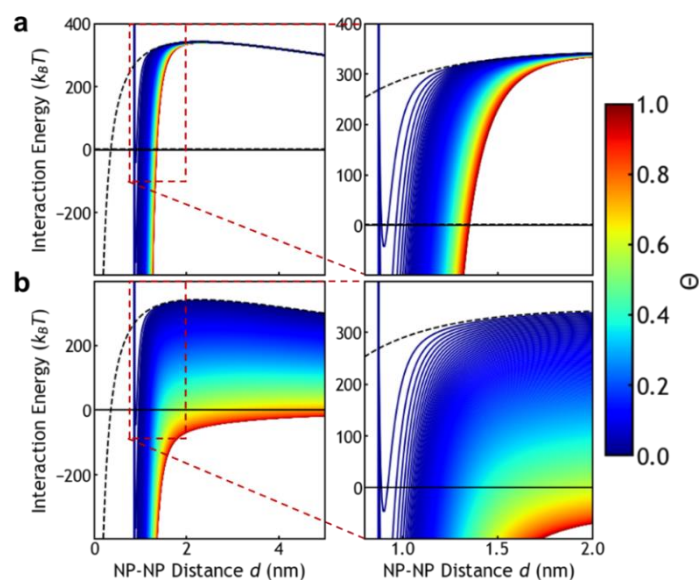


Figure A27. Potential energy vs distance curves for 60 nm AuNPs with varying CB[7] surface coverage θ assuming (a) no citrate displacement and (b) citrate displacement proportional to θ . Dashed line indicates V_{DLVO} for $\theta = 0$. Right-hand plots are zoomed in views of the same data as the left plots.

For aggregation to occur only above a threshold D , the V_{DLVO} peak (i.e. activation energy) should increase with decreasing D , and, above a certain D , this peak should be less than $1 k_{\text{B}}T$. (**Figure A28**) shows how V_{DLVO} varies with D for a range of θ at $I = 1, 10$. While the potential vs distance curves are affected by the AuNP size distribution in both cases, the corresponding distribution of E_{Act} only appears to straddle $1 k_{\text{B}}T$ at higher ionic strength (**Figure A28b**) and then only over a small range of θ and in the wrong direction.

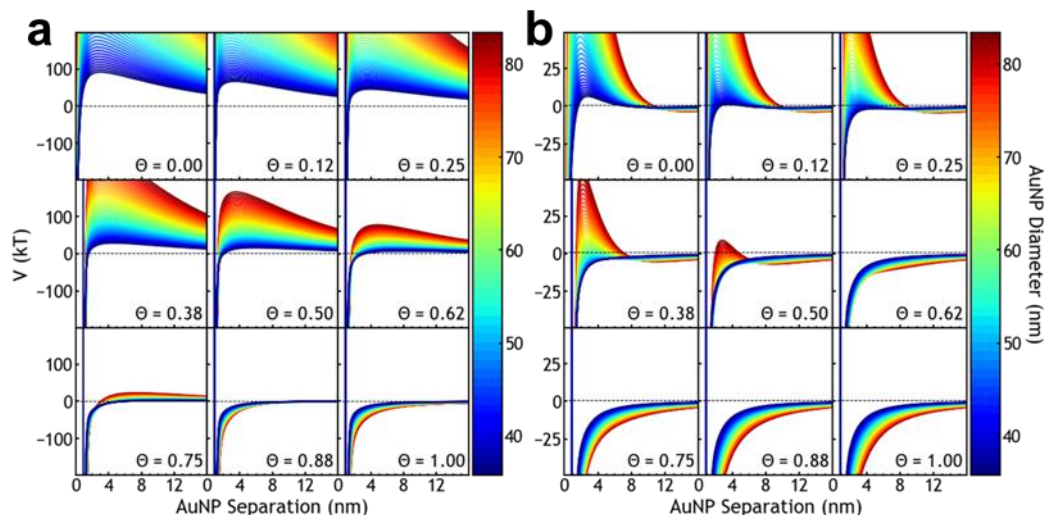


Figure A28. DLVO + Lennard-Jones potential curves for aqueous AuNPs ($35 < D < 85$ nm) at a range of CB surface coverages. **(a)** $I = 1$ mM; **(b)** $I = 10$ mM.

The current model, therefore, does not support AuNP polydispersity as the cause of $\Delta\lambda_{\text{dim}}$. However, this model is very simple and clearly fails to correctly model the true interaction between CB[7] and the electrical double layer around the AuNP; this is especially true if smaller (more reasonable) values for the C=O--Au bond energy are used. The V_{LJ} model (**Equation (18)**) also treats the C=O--Au coordination bond as a purely dispersive interaction, which is unlikely to be the case. Further improvements are under discussion but beyond scope of this work.

8.3.4 AuNP Aggregate SERS

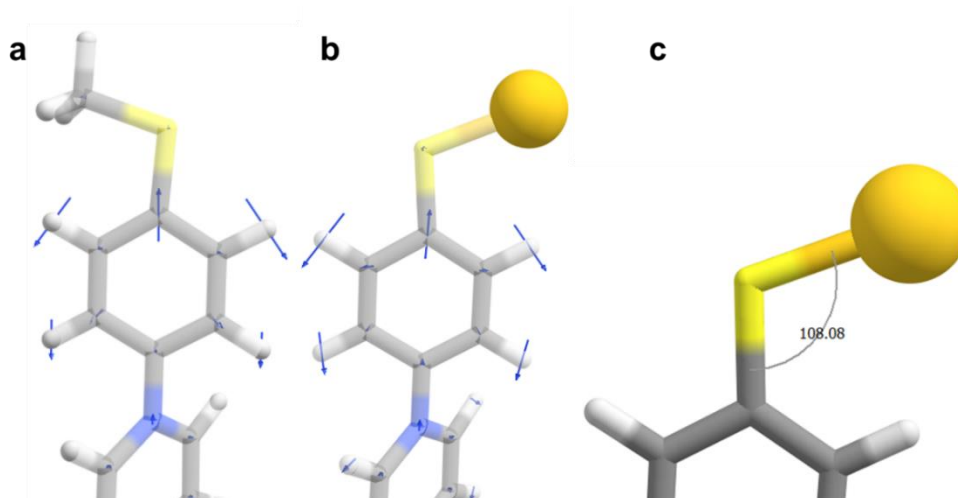
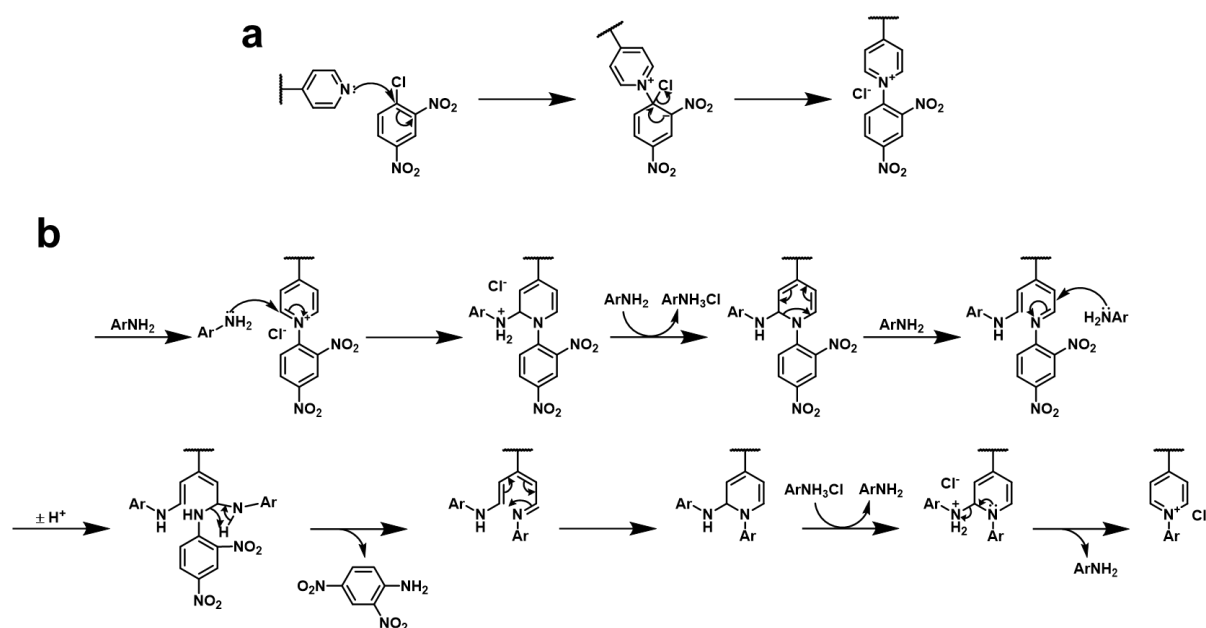


Figure A29. (a, b) Truncated structures of (a) ArVSMc and (b) ArVSAu with relative atomic displacement vectors for the terminal C-S stretch in each case. Raman frequencies: (a) 1078.5 cm^{-1} (b) 1068.5 cm^{-1} . (c) Optimised C-S-Au bond angle (108.08°). All structures and vibrations calculated with DFT (Methods 4.7.1). Atom colours: C (grey), H (white), N (blue), S (yellow), Au (gold).

8.4 M-TAPP Synthesis

8.4.1 Zincke Reaction Mechanism



Scheme A30. Full Zincke reaction mechanism.⁴⁷⁷ (a) Addition of 2,4-dinitrochlorobenzene to pyridyl compound to form activated *N*-(2,4-dinitrophenyl)pyridinium intermediate (b) Replacement of 2,4-dinitrophenyl group with arbitrary aryl group via nucleophilic attack on pyridinium α -carbons, and sigmatropic rearrangement.

8.4.2 Full Synthetic Details

DNPP #1

In a glovebox (N_2), TPyP (149 mg, 0.241 mmol) and DNCB (1.80 g, 8.89 mmol) were added to a heavy-walled glass pressure tube (35 cm³, 150 psi limit @ 120 °C). The tube was tightly sealed with a threaded PTFE stopper, removed from the glovebox and heated to 130 °C in an oil bath, with stirring, in a blast-containment fume hood. The mixture was stirred for 7.5 days. A temperature of 130 °C was not consistently maintained due to heat loss issues (average 120–125 °C) and the reaction mixture fully cooled to room temperature twice (4–6 hours each time) due to thermocouple malfunction.

After 7.5 days, the mixture was cooled fully to room temperature and dispersed in cold acetone (6.8 mL). The suspension was filtered, and the collected solid was washed with acetone (2 x 22.5 mL), dried on the filter under N_2 stream, then dried under vacuum, yielding 110.7 mg of dark red/brown solid (32%). FTIR result (**Figure A31**) shown below. See main text for ¹H-NMR (**Figure 5.2**, **Figure 5.4**) and LCMS data (**Figure 5.3**).

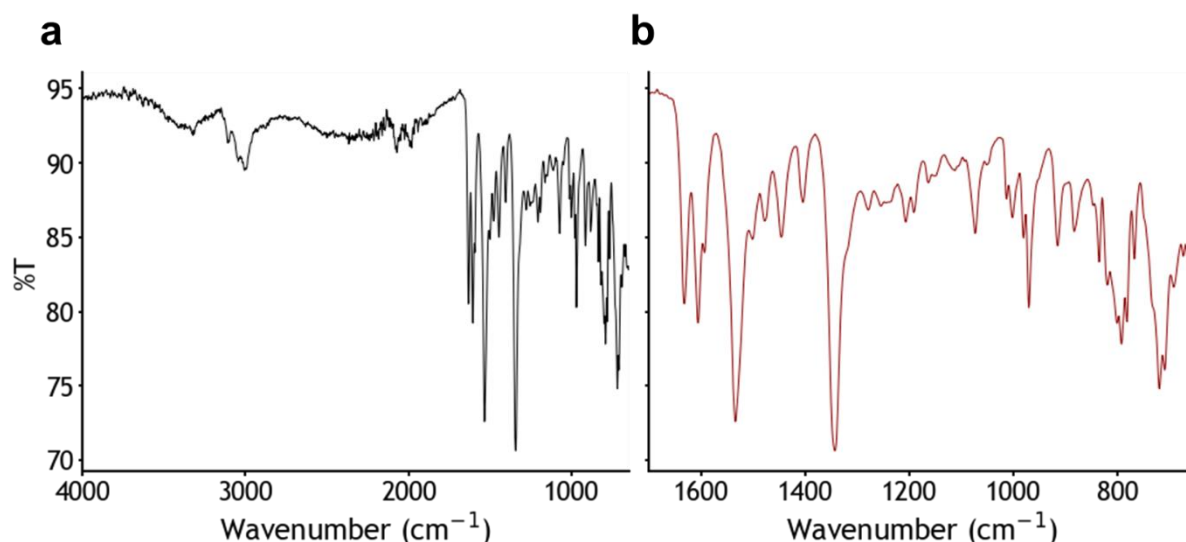


Figure A31. (a) DNPP #1 FTIR spectrum. (b) Closeup of low-wavenumber region, with aromatic NO₂ resonances at 1535, 1340 cm⁻¹.

DNPP #2

TPyP (213 mg, 0.344 mmol) and DNCB (2.58 g, 12.7 mmol) were gently heated until molten and poured carefully into the same glass pressure tube as before. Under N_2 flow, the melt was stirred at 60 °C for 10 min, then cooled to room temperature. The reaction vessel containing the solid reaction mixture was sealed under N_2 , then heated to 130 °C using an oil-filled steel jacket and stirred for 7 days.

The mixture was removed from the oil bath and cooled to room temperature. Acetone (10 mL) was added and the mixture was stirred until fully dispersed. The dispersion was transferred to 12 x 2 mL Eppendorf tubes, centrifuged (14300 rpm, 5 min) and the yellow

supernatant removed. Precipitates were vortexed with fresh acetone (12 x 1.5 mL) and centrifuged again. This centrifuge-trituration process was repeated until TLC analysis indicated removal of all DNCB (50:50 ethyl acetate : 40-60 petroleum ether) and TPyP (90:10 CHCl₃:MeOH). The resulting precipitates were dried under vacuum overnight, yielding 312.0 mg dark red/brown solid (61%). See below and in main text for characterisation data.

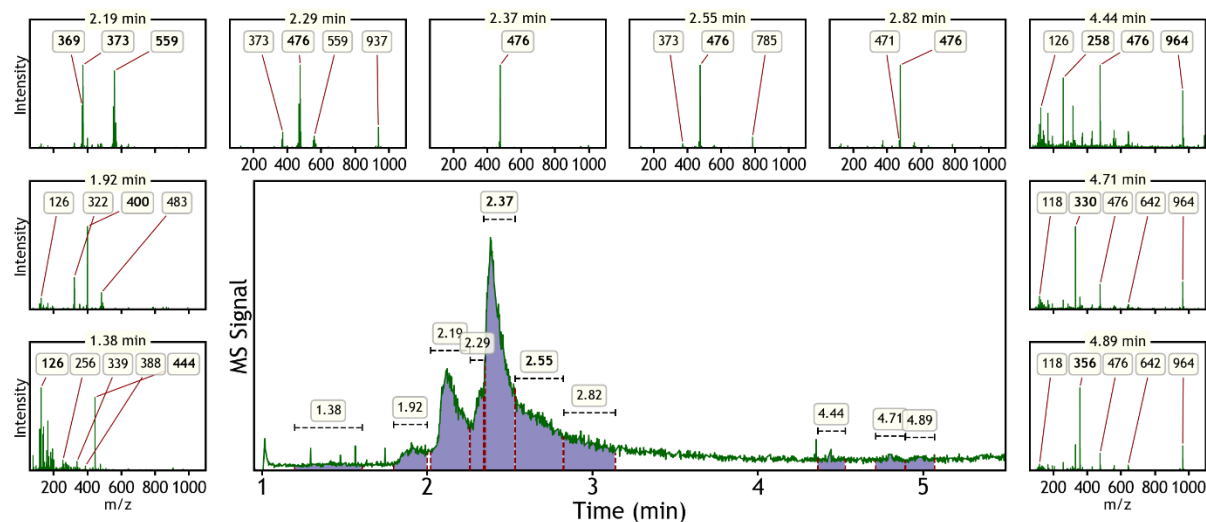


Figure A32. DNPP #2 LCMS data. *m/z* @ 2.19 min: 373 (*tris*-DNPP³⁺), 559 (*tris*-DNPP²⁺); @ 2.37 min: 476 (*bis*-DNPP²⁺).

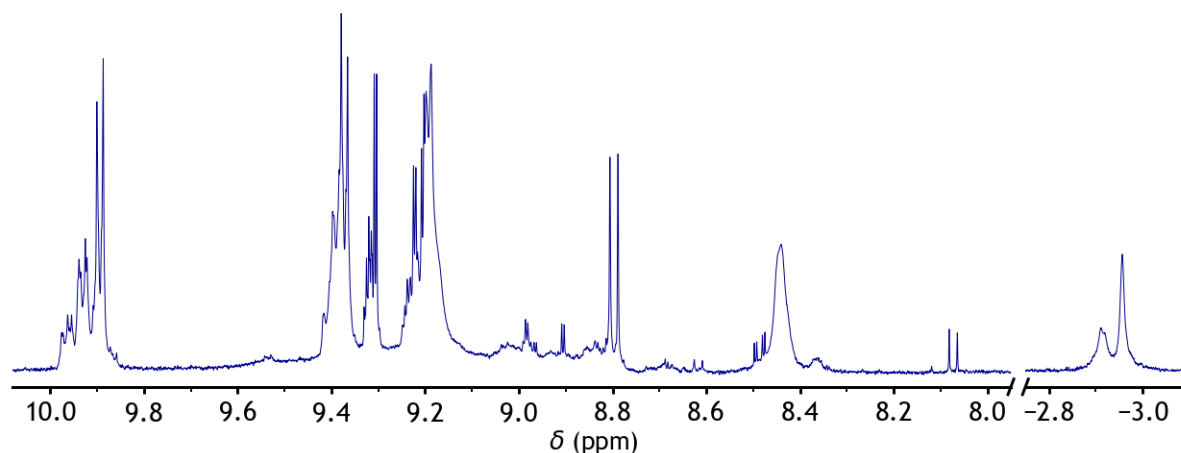


Figure A33. DNPP #2 ¹H-NMR spectrum in d₆-DMSO (solvent region omitted for clarity).

DNPP #3

Pre-dried (2 h in vacuum desiccator) powdered DNCB (3578 mg, 17.6 mmol) was heated gently until molten with TPyP (265 mg, 428 μmol) and poured carefully into the glass pressure tube. The remaining residue was transferred using another 330 mg molten DNCB. The reaction was stirred at room temperature under N₂ flow until solid and the tube sealed under N₂ atmosphere as before. Using the apparatus described in DNPP #2, the reaction mixture was heated to 135 °C and stirred for 10 days.

The mixture was cooled to room temperature, stirred with acetone (15 mL) until suspended, then centrifuge triturated (6 x 2 mL Eppendorf tubes, 13400 rpm, 5 min, cooled

using additional ice-filled tubes) with acetone (6 x 1.5 mL/tube), until DNCB no longer present in TLC. The resulting precipitate was dried under vacuum overnight, yielding 454.7 mg dark red/brown solid (74%). A small portion was recrystallised from hot MeCN for analysis.

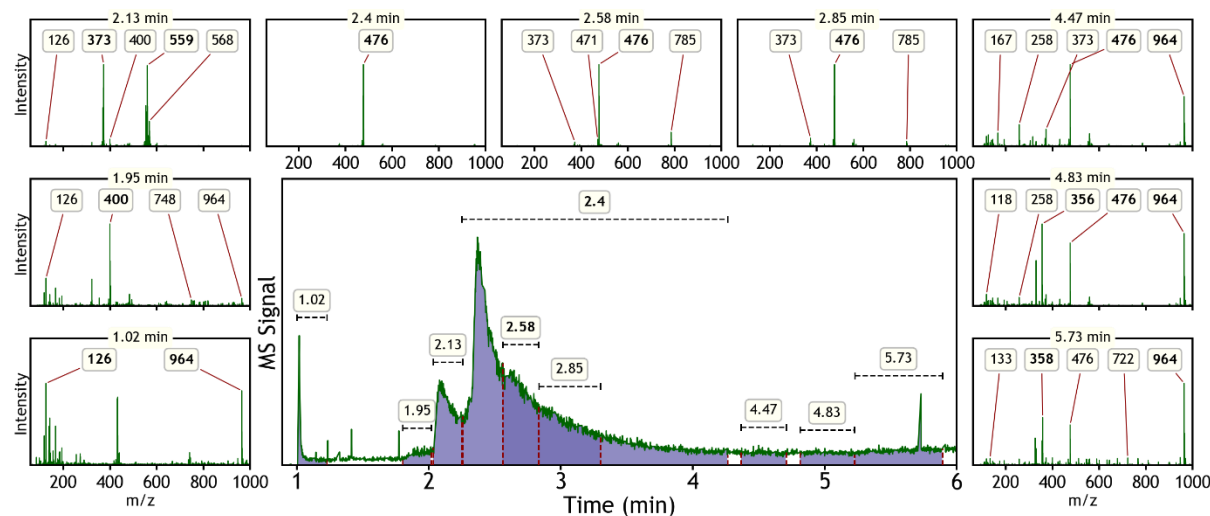


Figure A34. DNPP #3 LCMS data. *m/z* @ 2.13 min: 373 (*tris*-DNPP³⁺), 559 (*tris*-DNPP²⁺); @ 2.4 min: 476 (*bis*-DNPP²⁺); @ 2.58 min: 785 (*mono*-DNPP⁺).

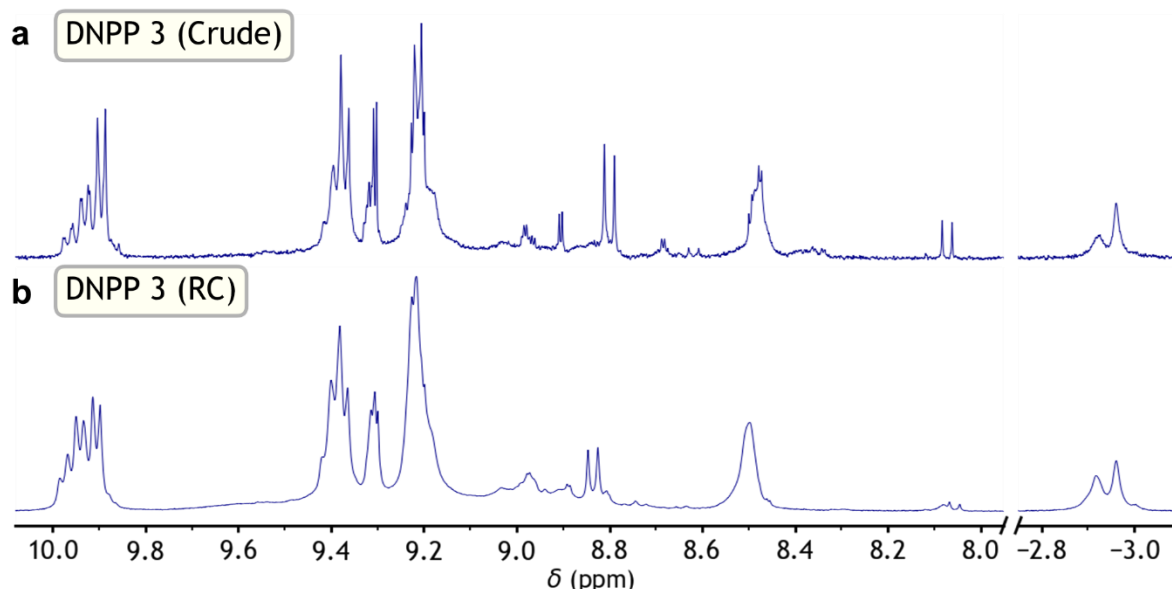


Figure A35. ¹H-NMR spectra (in d₆-DMSO) of (a) crude DNPP #3 and (b) DNPP #3 after recrystallisation from hot MeCN. Solvent region omitted for clarity.

DNPP #6

DNPP #3 (20.4 mg, 18.5 μmol) and **2,4-dinitrophenyl** tosylate (DNTB (368.1 mg, 1.088 mmol) were mixed in a 5 mL round-bottomed flask, heated under N₂ until molten and stirred under N₂ at 135 °C for 17 h. The reaction mixture was triturated/centrifuged (2 x 2 mL Eppendorf tubes, 13400 rpm, 5 min, cooled using additional ice-filled tubes) with acetone (6 x 1.5 mL/tube) and the resulting precipitates were dried in a desiccator for 3 h, yielding 18.4 mg dark solid (50.5-57.9%).

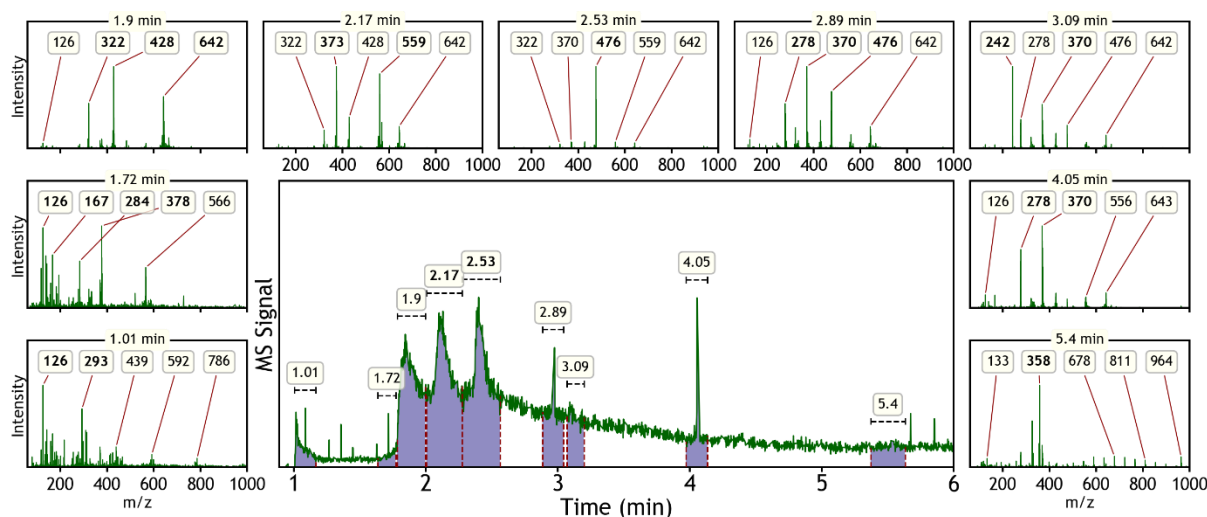


Figure A36. DNPP #6 LCMS result. m/z @ 1.90 min: 322 (*tetrakis*-DNPP⁴⁺), 428 (*tetrakis*-DNPP³⁺), 642 (*tetrakis*-DNPP²⁺); @ 2.17 min: 373 (*tris*-DNPP³⁺), 559 (*tris*-DNPP²⁺); @ 2.53 min: 476 (*bis*-DNPP²⁺).

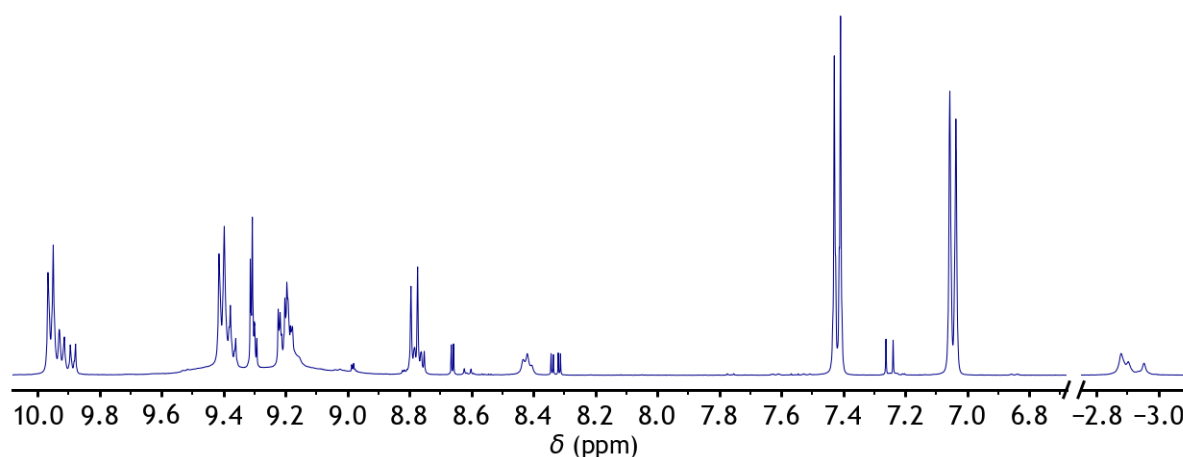


Figure A37. DNPP #6 ¹H-NMR spectrum in d₆-DMSO (solvent region omitted for clarity).

DNPP #8

DNPP #3 (100.8 mg, 91.27 μ mol) and **2,4-dinitrophenyl** tosylate (DNTB (1660 mg, 4.91 mmol) were crushed together in the previously used glass pressure tube and dried under vacuum for 90 min. The tube was sealed under N₂ atmosphere as with **DNPP #3**, heated to 130 °C and stirred for 6 days. The mixture was cooled to room temperature and dispersed in acetone (3 mL). The precipitate was filtered, washed with acetone (20 mL) and dried in a desiccator overnight, yielding 146.7 mg of dark solid (81.5-87.6%).

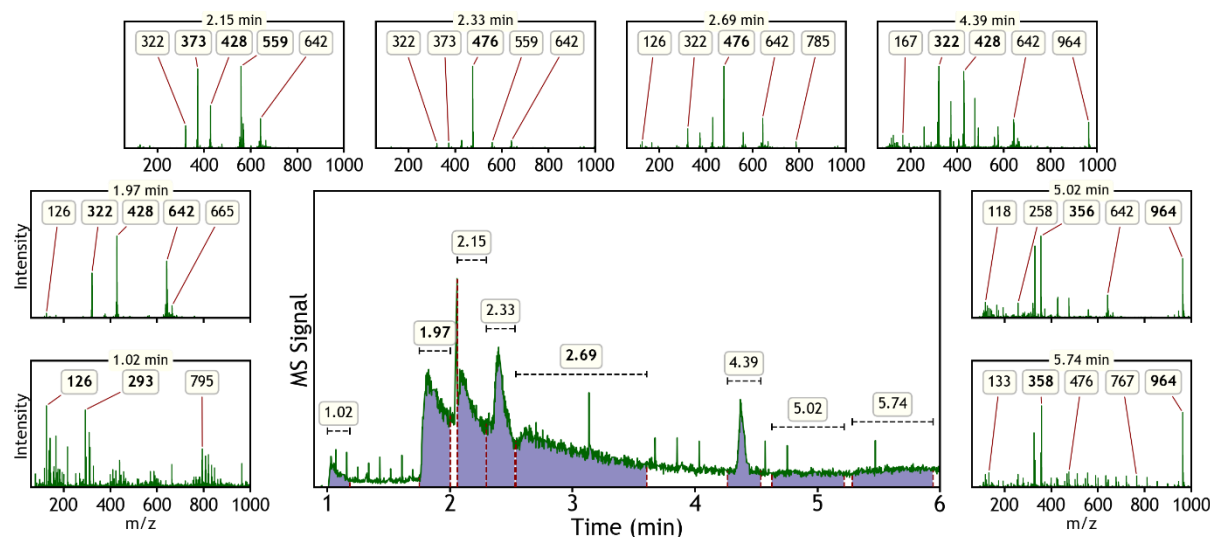


Figure A38. DNPP #8 LCMS data. m/z @ 1.97 min: 322 (*tetrakis*-DNPP⁴⁺), 428 (*tetrakis*-DNPP³⁺), 642 (*tetrakis*-DNPP²⁺); @ 2.15 min: 373 (*tris*-DNPP³⁺), 559 (*tris*-DNPP²⁺); @ 2.33 min: 476 (*bis*-DNPP²⁺); @ 2.69 min: 785 (*mono*-DNPP⁺).

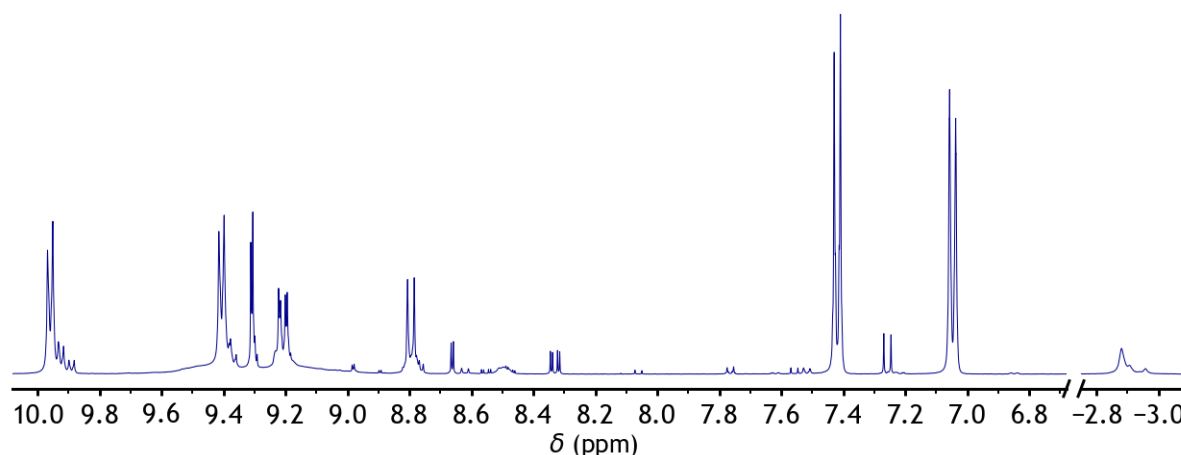


Figure A39. DNPP #8 ¹H-NMR spectrum in d₆-DMSO (solvent region omitted for clarity).

DNPP #9

DNPP #3 (28.3 mg, 25.6 μ mol) and **2,4-dinitrophenyl** tosylate (DNTB) (361.9 mg, 1.070 mmol) were added to a 5 mL round-bottomed flask and dried under vacuum for 2 h. The mixture was heated to 135 °C under N₂. DBU (30 μ L, 0.2 mmol) was added to the stirred melt via syringe, liberating grey mist/vapour that settled quickly. The mixture was stirred under N₂ at 135 °C for 12.5 h. After cooling the mixture (now dark green in colour) to room temperature, Et₂O (2 mL) was added, and the mixture took on a gummy consistency. Acetone (2 mL) was then added and the now-dispersed mixture was centrifuge-trituated (3 x 2 mL Eppendorf tube, 13400 rpm, 5 min) with acetone (5 x 1.5 mL/tube). The combined precipitates were dried under vacuum for 4 h, yielding 44.8 mg of dark solid (88.7-95.3%).

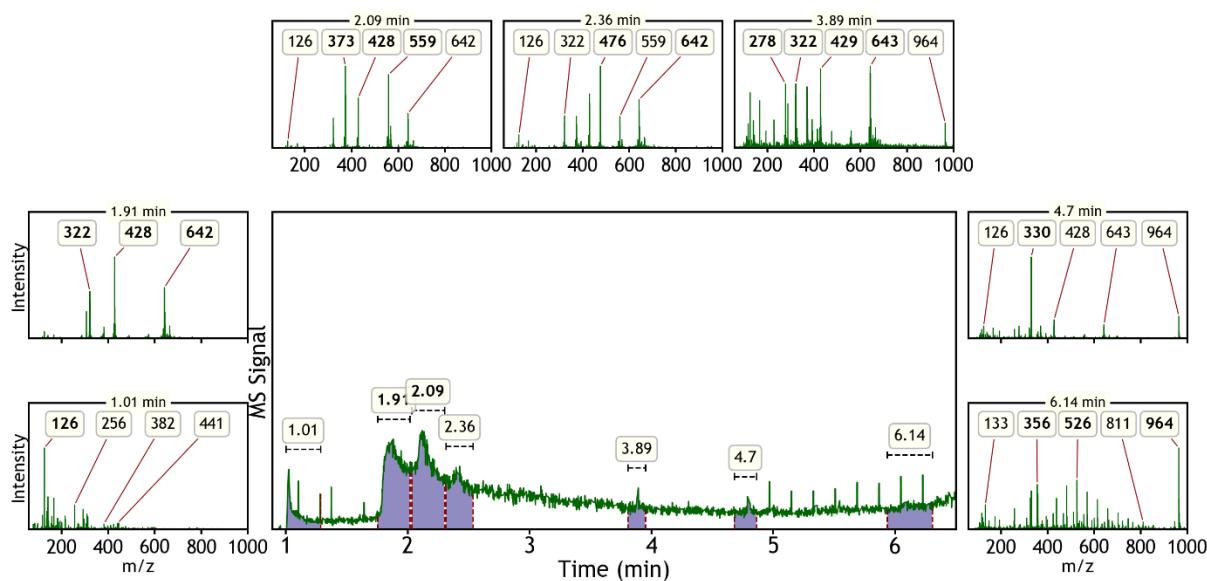


Figure A40. DNPP #9 LCMS data. m/z @ 1.91 min: 322 (*tetrakis*-DNPP⁴⁺), 428 (*tetrakis*-DNPP³⁺), 642 (*tetrakis*-DNPP²⁺); @ 2.09 min: 373 (*tris*-DNPP³⁺), 428 (*tetrakis*-DNPP³⁺), 559 (*tris*-DNPP²⁺), 642 (*tetrakis*-DNPP²⁺); @ 2.36 min: 476 (*bis*-DNPP²⁺).

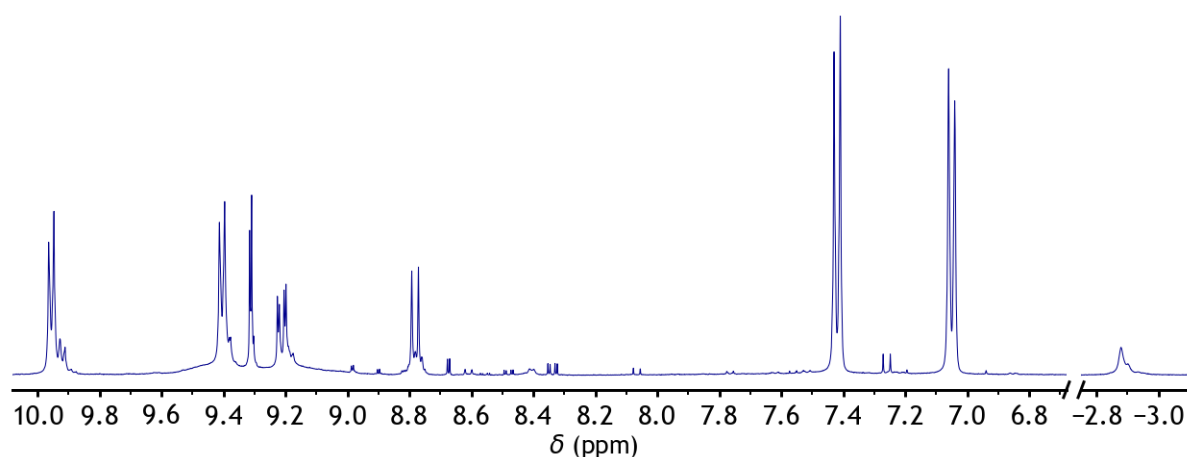


Figure A41. DNPP #9 ¹H-NMR spectrum in d₆-DMSO (solvent region omitted for clarity).

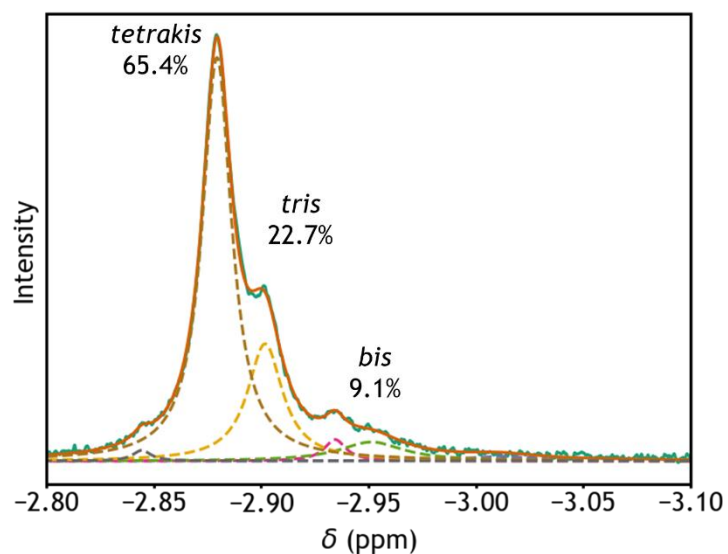


Figure A42. DNPP #9 ¹H-NMR spectrum (core NH region) in d₆-DMSO.

DNPP #10

DNPP #3 (60 mg, 54 μmol) and **2,4-dinitrophenyl** tosylate (DNTB (675 mg, 2.00 mmol)) were crushed together in the bottom of the previously used glass pressure tube and dried in a desiccator for 2 h. The mixture was transferred to a N_2 glovebox and DBU (previously dried over molecular sieves, 3 $\text{\AA}$; 60 μL , 0.40 mmol) was added; a green colour was immediately observed. The pressure tube was sealed, removed from the glovebox and stirred at 135 $^\circ\text{C}$ for 68 h.

The mixture was cooled to room temperature and dispersed in acetone (5 mL). The precipitate was filtered, washed with acetone until the filtrate ran clear (~ 25 mL) and dried on the filter under N_2 flow. The crude product was recrystallised 4 times from MeCN, yielding 108 mg dark solid (101%).

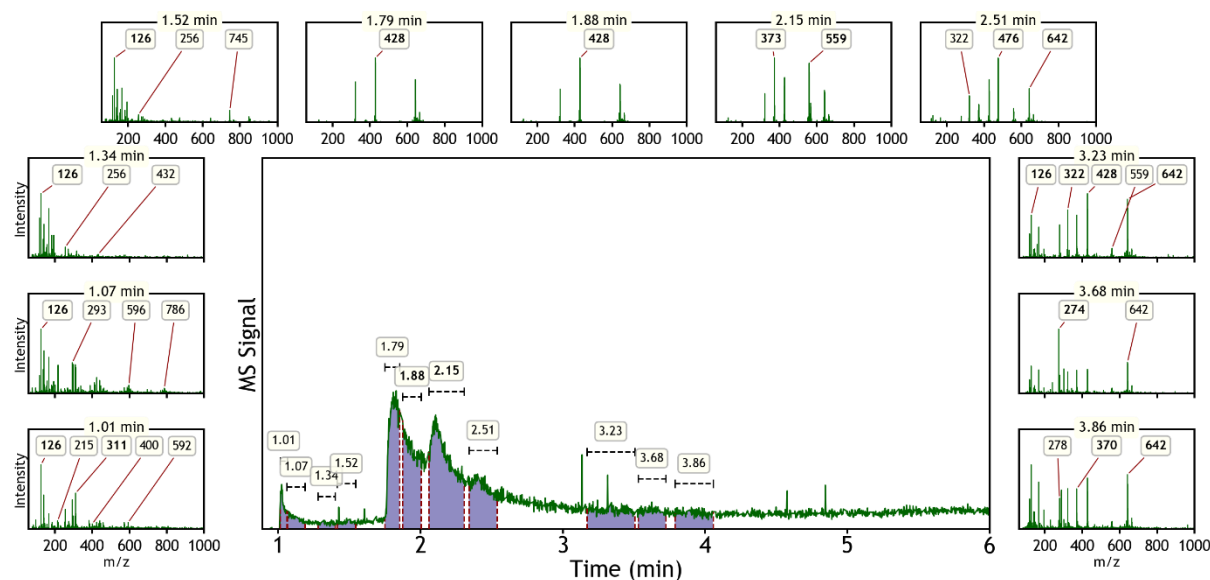


Figure A43. DNPP #10 LCMS data. m/z @ 1.79 min: 322 (*tetrakis*-DNPP $^{4+}$), 428 (*tetrakis*-DNPP $^{3+}$), 642 (*tetrakis*-DNPP $^{2+}$); @ 2.15 min: 373 (*tris*-DNPP $^{3+}$), 559 (*tris*-DNPP $^{2+}$); @ 2.51 min: 476 (*bis*-DNPP $^{2+}$).

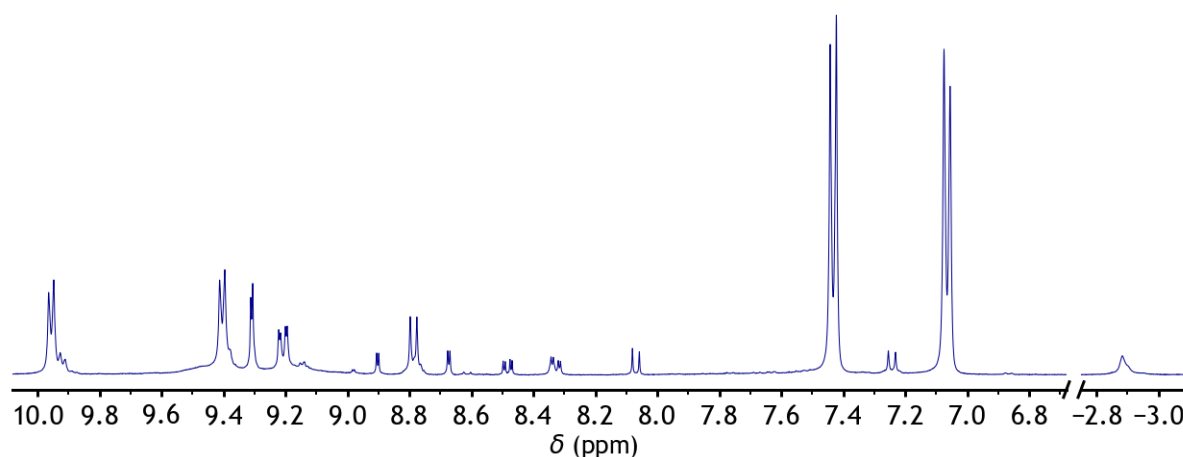


Figure A44. DNPP #10 ^1H -NMR spectrum in d_6 -DMSO (solvent region omitted for clarity).

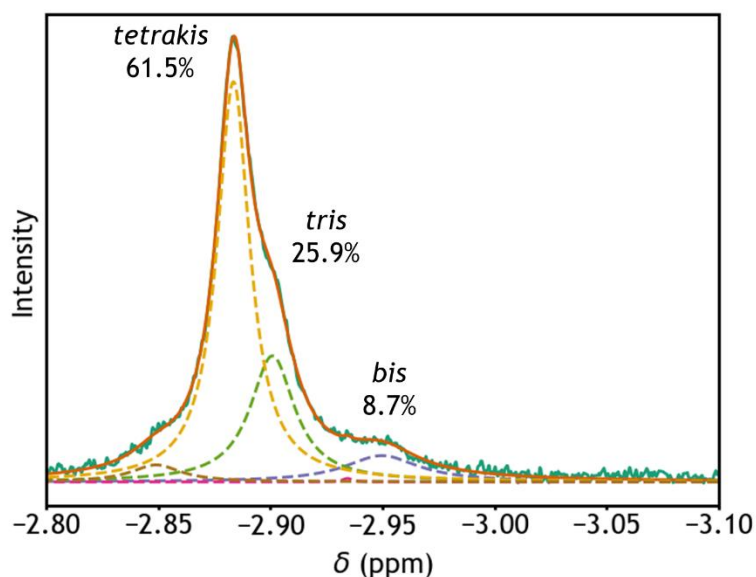


Figure A45. DNPP #10 ^1H -NMR spectrum (core NH region) in d_6 -DMSO.

TAPP #1

DNPP #2 (47 mg, 43 μmol) and 4-MTA (60 μL , 480 μmol) were dissolved in degassed MeOH (10 mL) in a 2-necked round-bottomed flask (50 mL) and refluxed under N_2 for 20 h. A 2 mL aliquot was taken and concentrated to 0.5 mL under reduced pressure. The aliquot was centrifuge-triturated (2 mL Eppendorf tube, 13400 rpm, 5 min) with THF (4 x 1.5 mL) then DCM (3 x 1.5 mL). The supernatant was analysed with TLC (30:70 EtOAc : 40-60 pet ether) and the precipitate was analysed with FTIR. No reaction was evidenced (**Figure A47b**).

The solvent was removed from the main reaction mixture under reduced pressure, and EtOH (20 mL) was added, followed by a further 17.5 mg (15.9 μmol) DNPP #2 and 100 μL (804 μmol) 4-MTA. The new mixture was refluxed under N_2 for 21 h. An aliquot was taken and analysed with TLC; no evidence for reaction was observed.

Anhydrous DMAc (10 mL; freeze-pump-thaw degassed) was added via syringe, the temperature was raised to 135 $^\circ\text{C}$ and the mixture refluxed under N_2 for a further 29 h. Again, no reaction was observed by TLC.

The reaction mixture was concentrated under reduced pressure to remove EtOH and stirred under N_2 at 180 $^\circ\text{C}$ for another 20 h. TLC analysis showed formation of 2,4-dinitroaniline side product. The reaction mixture was heated to 190 $^\circ\text{C}$ and refluxed under N_2 for a further 20 h. TLC analysis showed increased [2,4-dinitroaniline]/[4-MTA] ratio. Another 50 μL (400 μmol) 4-MTA was added and the mixture was refluxed under N_2 for a further 20 h.

The solution was cooled to room temperature and centrifuge-triturated (50 mL Corning tube, 10000 rpm, 5 $^\circ\text{C}$, 20 min) with THF (1 x 35 mL) and DCM (4 x 35 mL). The precipitate was re-suspended in DCM (35 mL), filtered and extracted with MeOH (50 mL). After filtration, the solvent was removed under reduced pressure, yielding 16.5 mg dark green/brown solid.

The solvent was removed from the combined supernatants by rotary evaporation followed by vacuum distillation. The solid residue was re-dispersed in DCM and filtered and the precipitate extracted with MeOH. After filtration, the solvent was removed under reduced pressure, yielding 20.1 mg dark green/brown solid (34.4%).

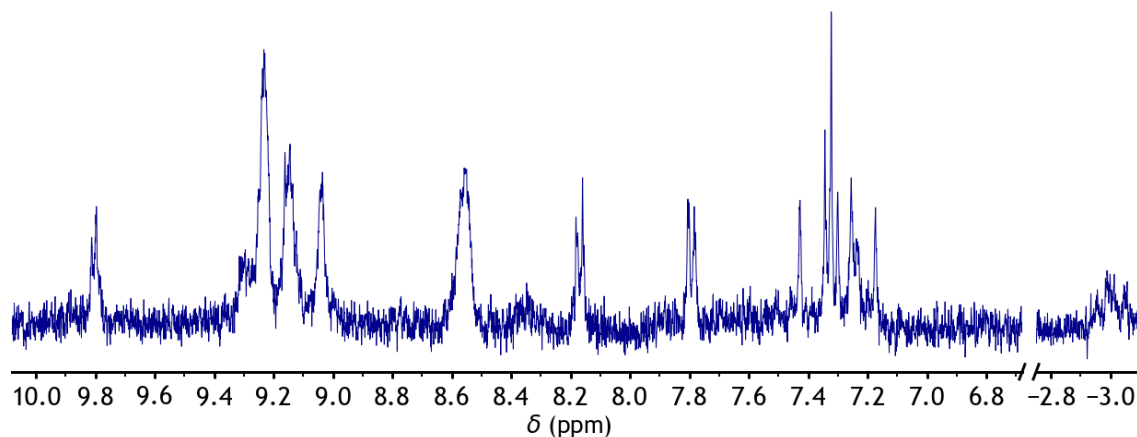


Figure A46. TAPP #1 ^1H -NMR spectrum in d_6 -DMSO (solvent region omitted for clarity).

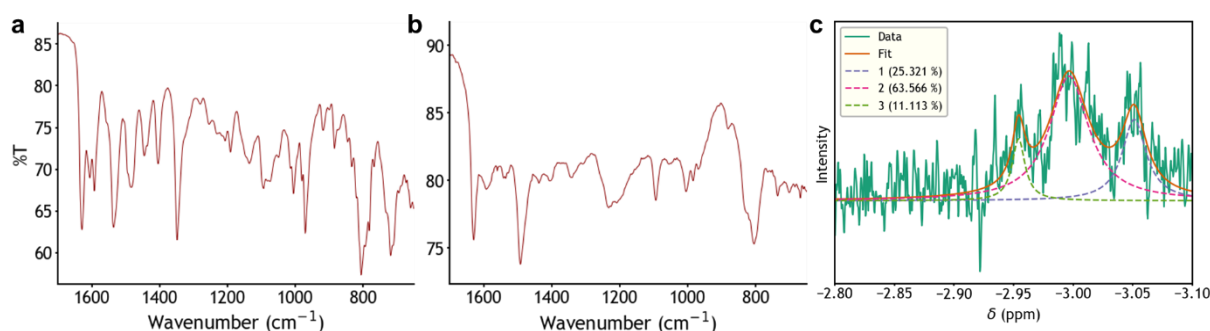


Figure A47. (a) FTIR spectrum (low-wavenumber region) of TAPP #1 after reaction in MeOH; NO_2 resonances (1535 , 1340 cm^{-1}) are still present, indicating unsuccessful reaction. (b) Final FTIR spectrum after reaction in DMAc at higher temperature; NO_2 resonances no longer present (c) Final ^1H -NMR spectrum (NH porphyrin region) of TAPP #1 in d_6 -DMSO.

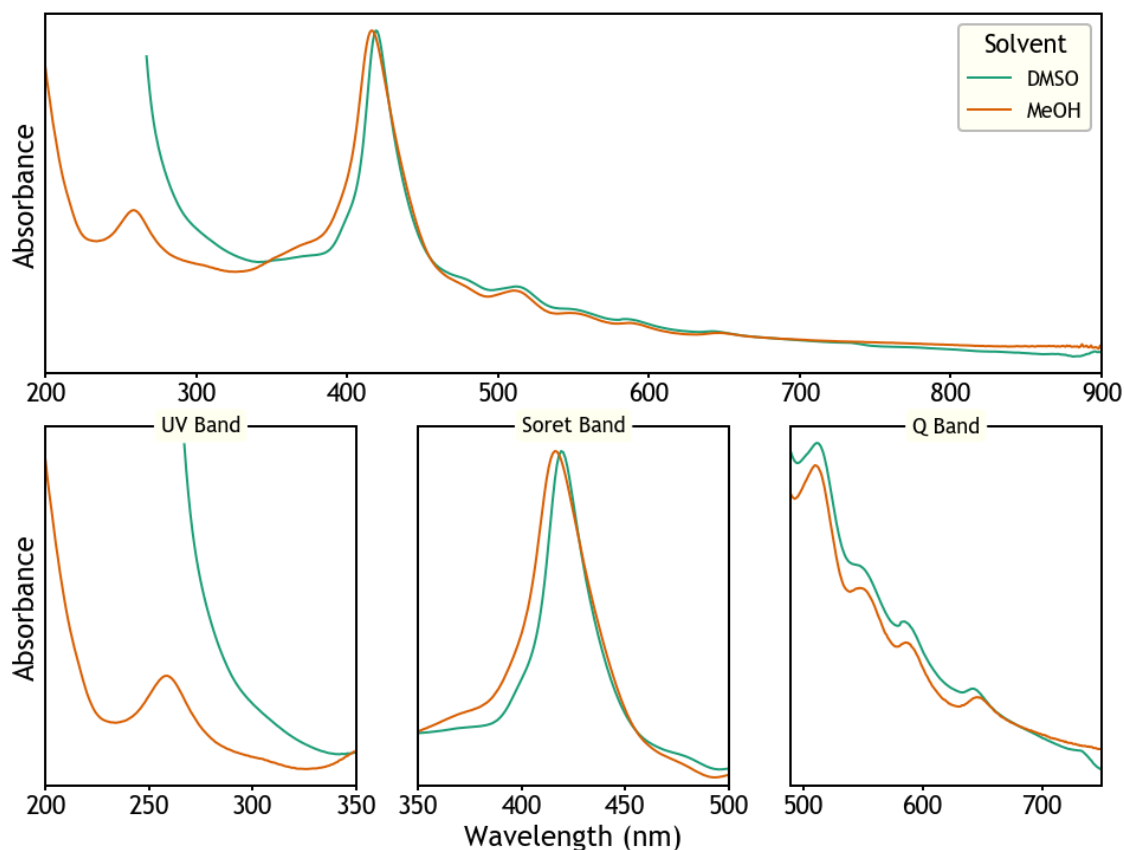


Figure A48. UV-Vis spectra of TAPP #1 in DMSO and MeOH. Peak around 250 nm in MeOH solution indicates presence of 4-thioanisyl moiety.

TAPP #2

The reaction setup (see **TAPP #1**) was dried with a heat gun under high vacuum before use. **DNPP #2** (60 mg, 54 μmol) was added under positive N_2 flow and 4-MTA (0.25 mL, 2.01 mmol) was added via syringe. Dry DMAc (16 mL) was added via syringe and the mixture was refluxed (195 $^\circ\text{C}$) under N_2 in the dark for 70 h. Aliquots were taken regularly (via syringe) for UV-Vis analysis. The mixture was cooled to room temperature and precipitated with cold Et_2O (100 mL). The precipitate was filtered, washed with cold DCM (100 mL) and extracted with MeOH (100 mL). The extract was very weakly coloured, indicating minimal product formation.

TAPP #3

The reaction setup (see **TAPP #1**) was dried with a heat gun under high vacuum before use. **DNPP #2** (64.3 mg, 58.2 μmol) and 4-MTA (0.25 mL, 2.01 mmol) were dissolved in dry DMAc (20 mL) under N_2 and stirred at 120 $^\circ\text{C}$ in the dark for 39 h. Aliquots were taken regularly (via syringe) for UV-Vis analysis. The mixture was cooled to room temperature and cold THF (100 mL) was added. No precipitate was collected upon filtration or centrifugation; the THF was removed from the mixture under reduced pressure and cold Et_2O (50 cm^3) was added. The precipitate was isolated by filtration, washed with cold DCM (150 mL), dried on the filter, extracted with MeOH (100 mL) and filtered again. The solvent was removed under reduced pressure, yielding 11.9 mg dark green solid (20.5%).

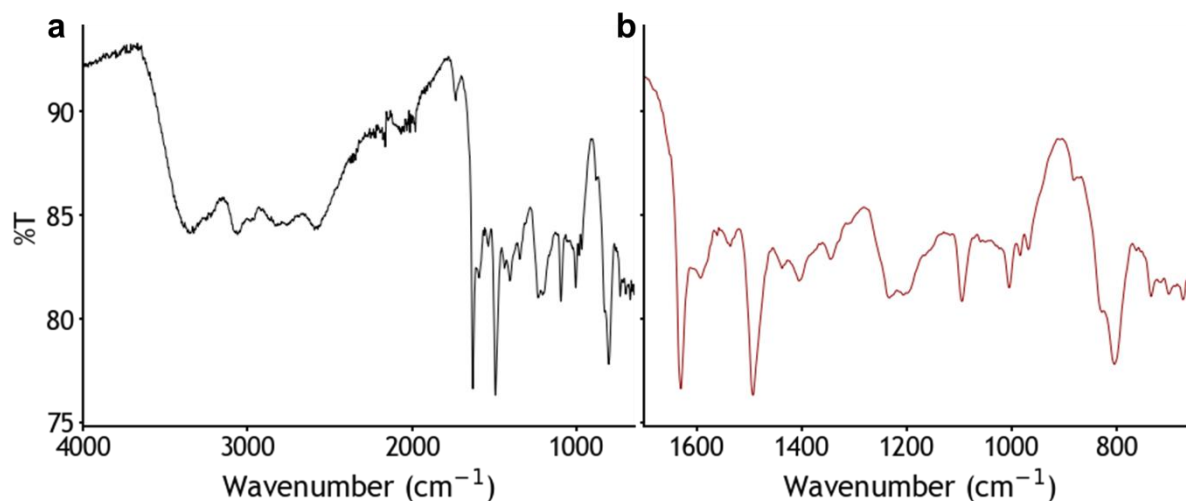


Figure A49. FTIR spectrum of TAPP #3. (a) Full range; (b) low-wavenumber region. No NO_2 peaks (1535, 1340 cm^{-1}) observed.

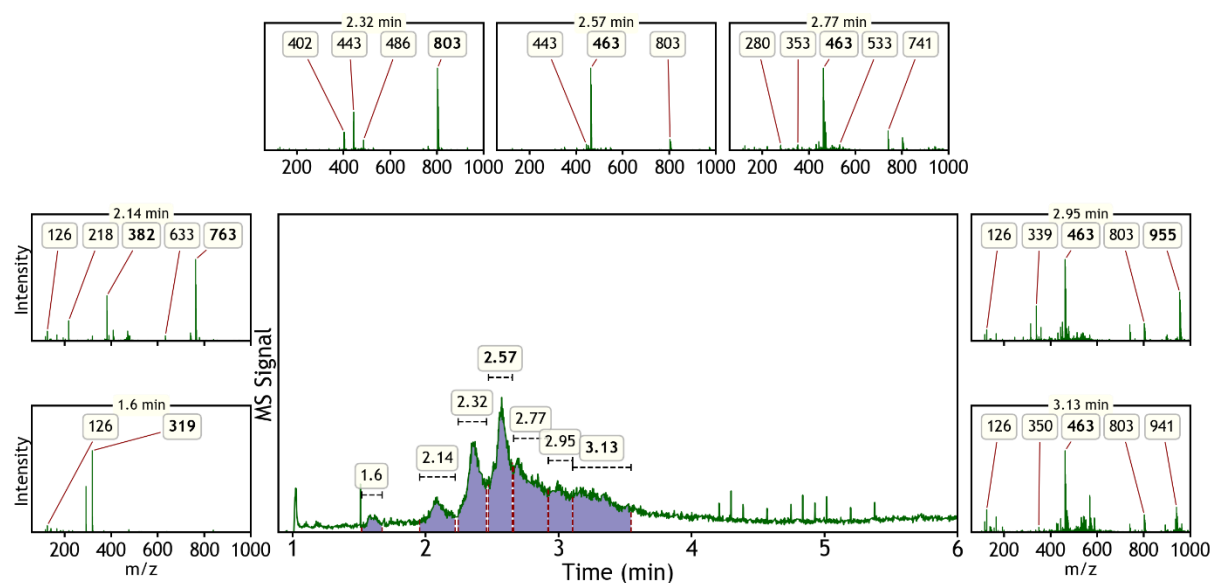


Figure A50. LCMS data for TAPP #3. No m/z peaks corresponding to any TAPP or DNPP products were observed.

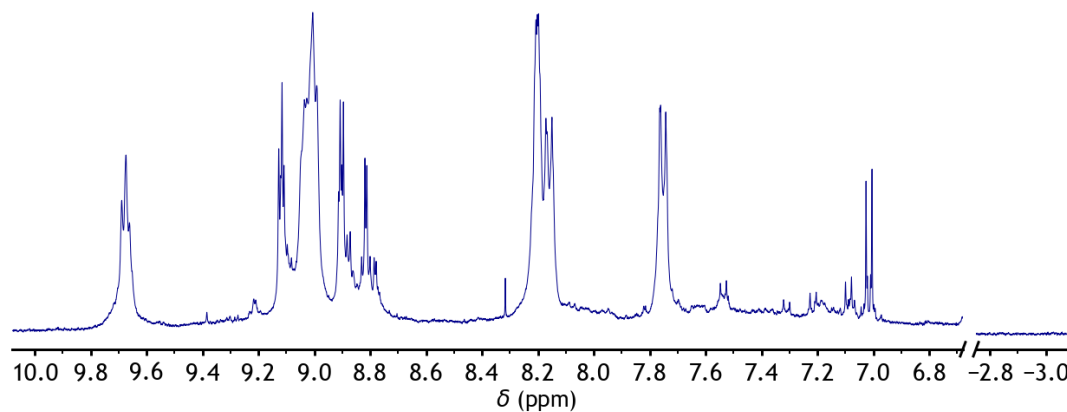


Figure A51. TAPP #3 ^1H -NMR spectrum in d_6 -DMSO (solvent region omitted for clarity). No core NH porphyrin peaks ($\delta < 0$) observed.

TAPP #4

The reaction setup (see **TAPP #1**) was dried with a heat gun under high vacuum before use. Activated molecular sieves, **DNPP #2** (25 mg, 23 μmol) and 4-MTA (130 μL , 1.05 mmol) were added under positive N_2 pressure. The system was purged (vac/refill x 5) with more N_2 , dry DMAc (10 mL) was added via syringe and the mixture was stirred at 120 $^\circ\text{C}$ under N_2 in the dark for 32.5 h. Aliquots were taken regularly via syringe for UV-Vis analysis.

The mixture was cooled to room temperature and cold Et_2O (40 mL) added. The precipitate was filtered, washed with cold DCM (15 x 10 mL) and extracted with MeOH (100 mL). Removal of the solvent yielded 5.7 mg dark green solid (25%).

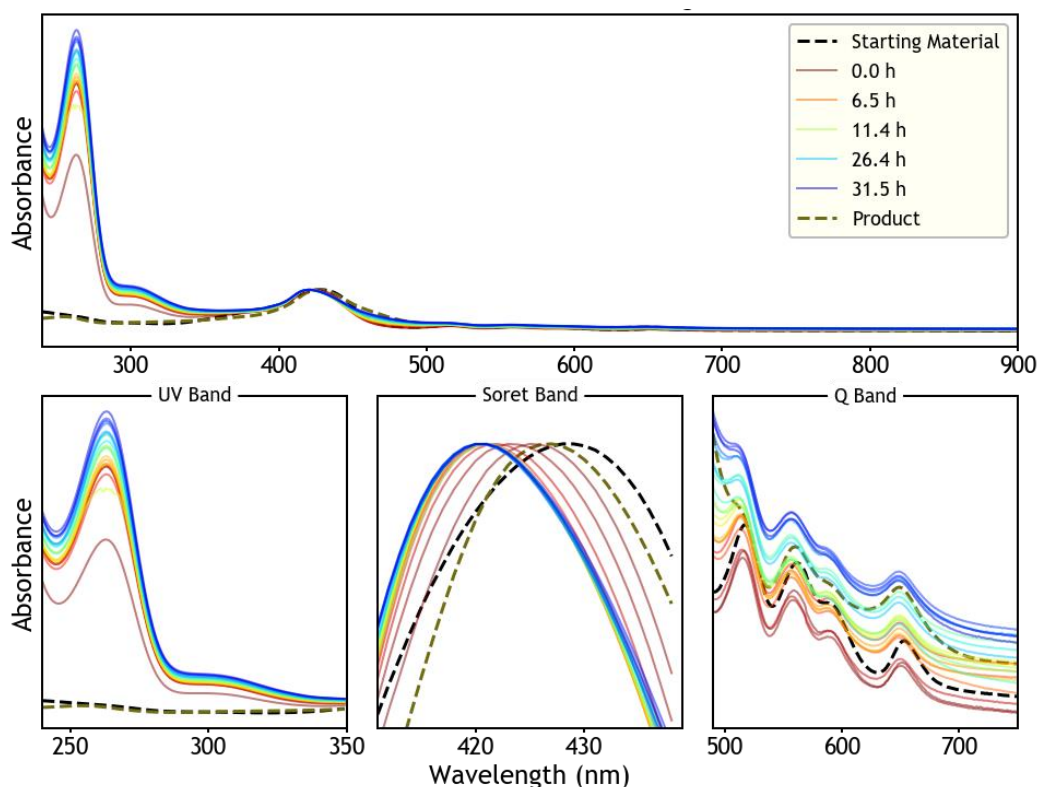


Figure A52. Temporal UV-Vis spectrum evolution of TAPP #4 reaction mixture (diluted with MeOH).

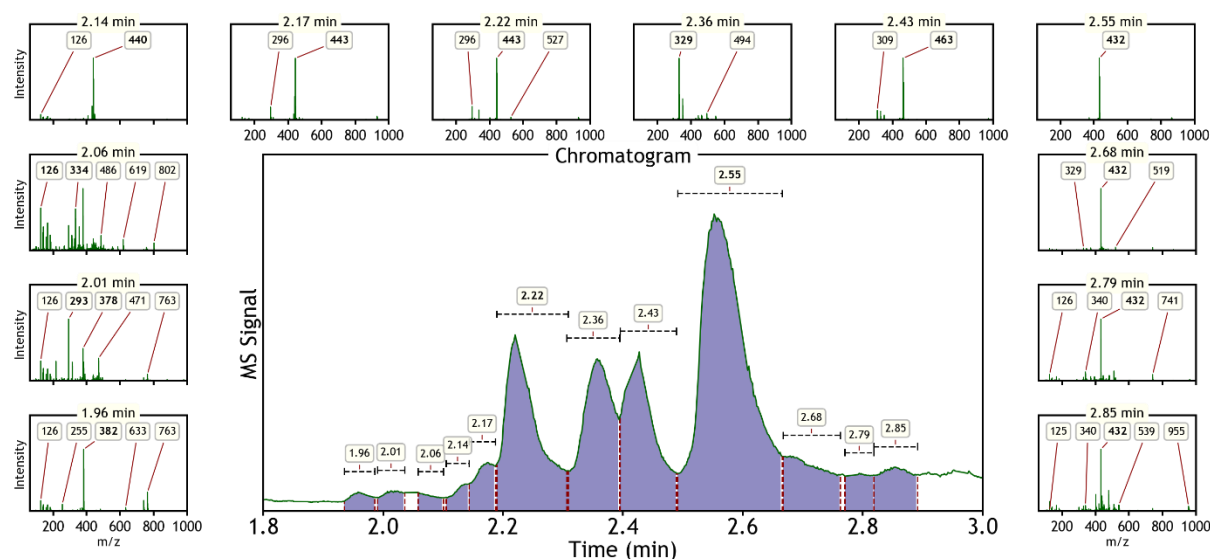


Figure A53. LCMS data for TAPP #4 product. m/z @ 2.22 min: 443 (unknown); @ 2.36 min 329 (*tris*-TAPP³⁺), 494 (*tris*-TAPP²⁺); @ 2.43 min: 463 (unknown); @ 2.55 min: 432 (*bis*-TAPP²⁺).

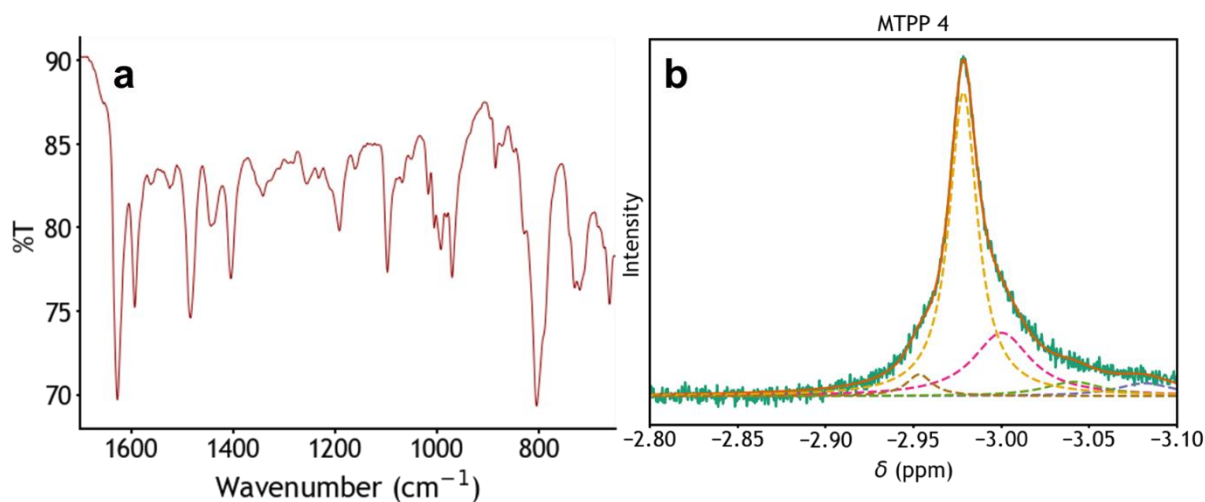


Figure A54. (a) TAPP #4 FTIR spectrum (low wavenumber region); no NO₂ peaks present. (b) TAPP #4 ¹H-NMR spectrum (core NH region); solvent: d₆-DMSO.

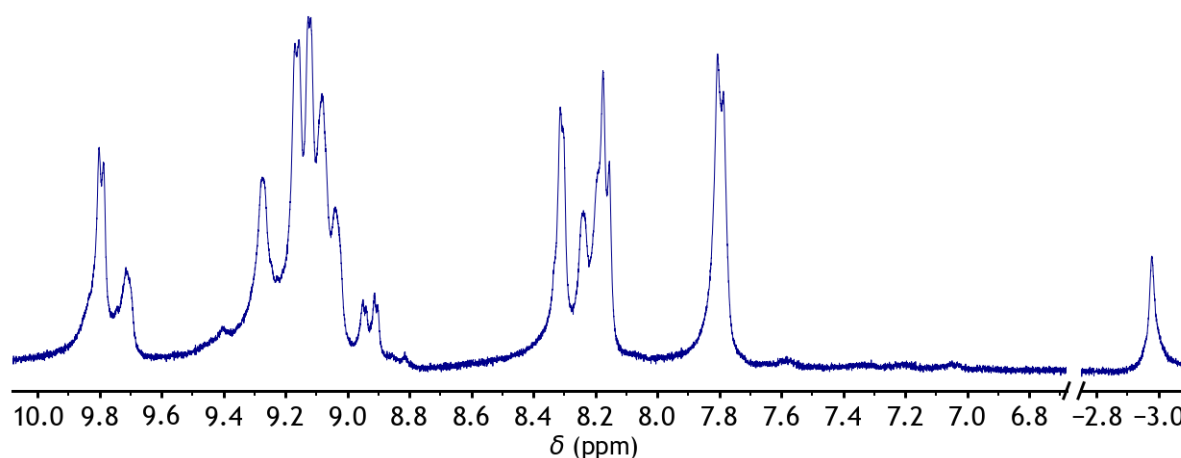


Figure A55. TAPP #4 ¹H-NMR spectrum in d₆-DMSO (solvent region omitted for clarity).

TAPP #5

The reaction setup (see **TAPP #1**) was dried with a heat gun under high vacuum before use. Activated molecular sieves, **DNPP #8** (22.2 mg, 12.1 μmol) and 4-MTA (130 μL , 1.05 mmol) were added under positive N_2 pressure, followed by dry DMAc (10 mL). The mixture was stirred at 120 $^\circ\text{C}$ under N_2 in the dark for 5.5 h. Aliquots were taken regularly via syringe for UV-Vis analysis.

The mixture was cooled to room temperature and Et_2O (15 mL) was added. The precipitate was filtered and washed with ether until the filtrate ran clear (~ 40 mL). Washing with DCM (20 mL) led to precipitate dissolution. The resulting filtrate was precipitated again with Et_2O (30 mL) and filtered. The crude reaction mixture was extracted with MeOH (25 mL) and the solvent removed under reduced pressure, yielding 9.1 mg dark solid (45%).

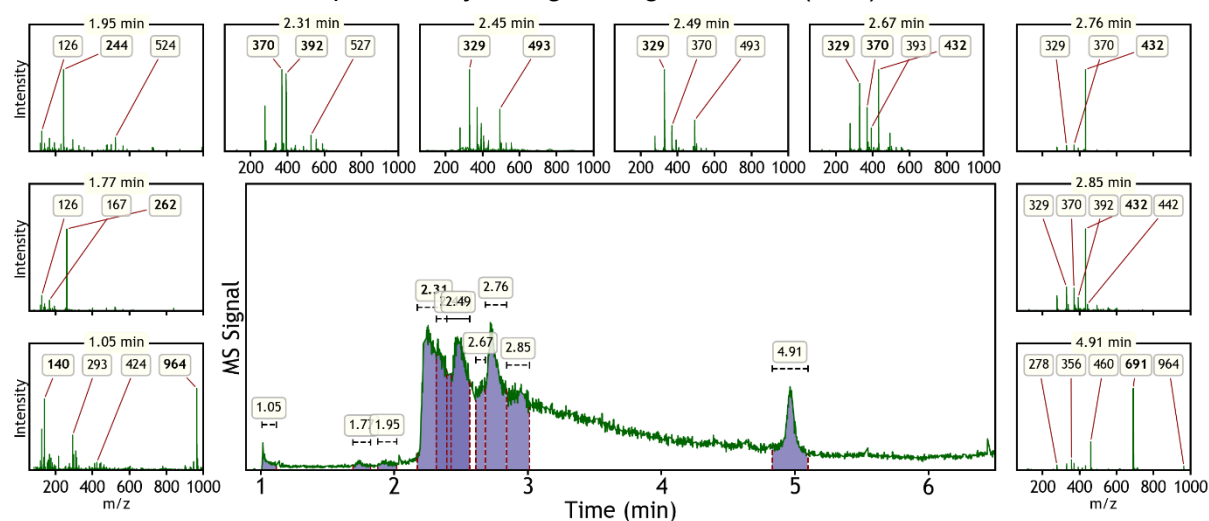


Figure A56. LCMS data for TAPP #5. m/z @ 2.31 min: 278 (*tetrakis*-TAPP $^{4+}$), 370 (*tetrakis*-TAPP $^{3+}$), 392 (unknown), 527 (unknown); @ 2.49 min: 329 (*tris*-TAPP $^{3+}$), 493 (*tris*-TAPP $^{2+}$); 2.76 min 432 (*bis*-TAPP $^{2+}$).

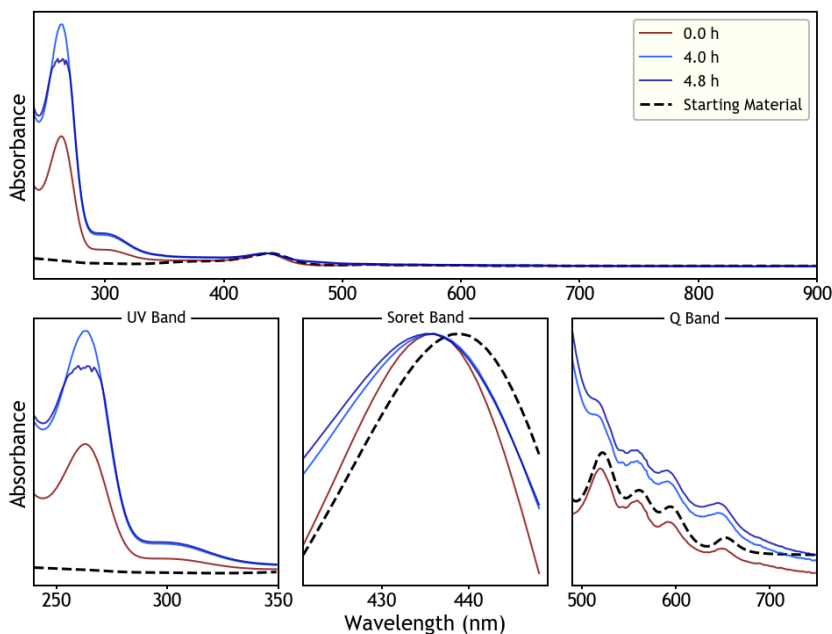


Figure A57. Temporal UV-Vis spectrum evolution of TAPP #5 reaction mixture (diluted with MeOH).

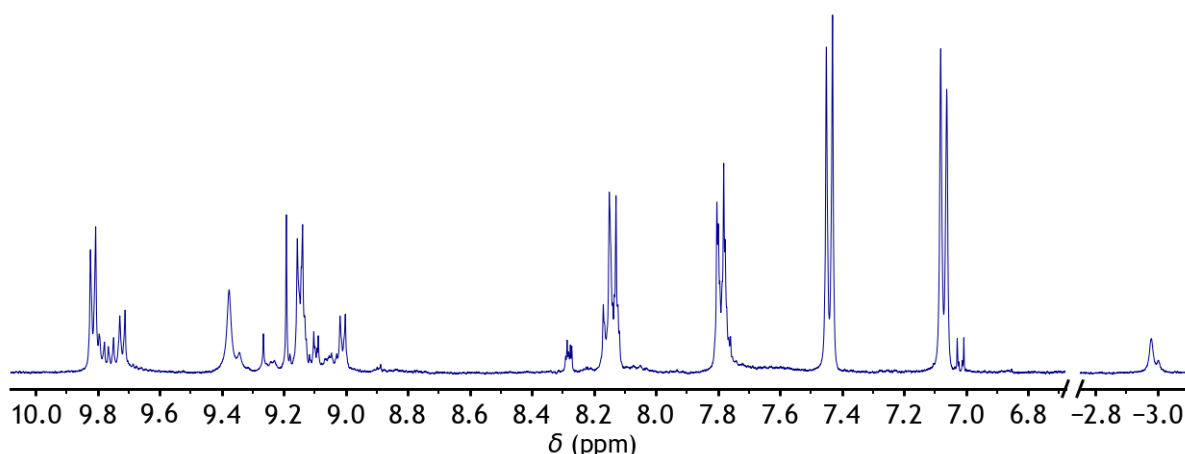


Figure A58. TAPP #5 ^1H -NMR spectrum in d_6 -DMSO (solvent region omitted for clarity).

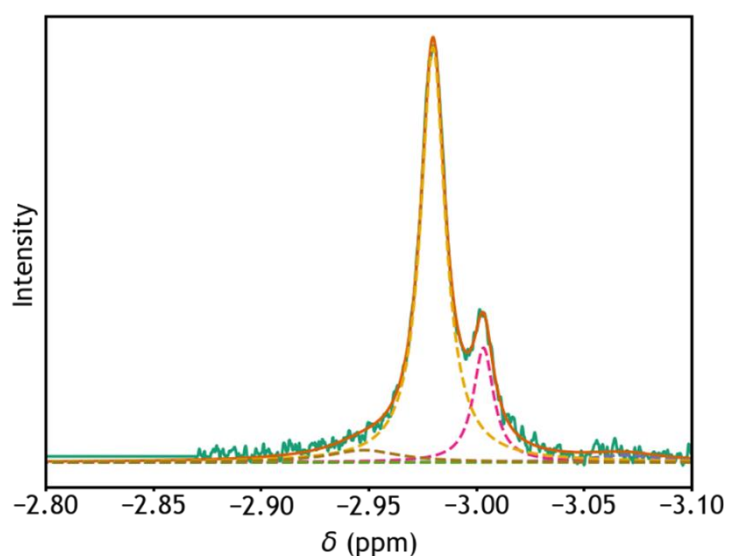


Figure A59. TAPP #4 ^1H -NMR spectrum (core NH region) in d_6 -DMSO.

TAPP #6

DNPP #10 (37.9 mg, 19.2 μmol) and 4-MTA (0.15 mL, 1.2 mmol) were dissolved in dry DMAc (10 mL) over activated molecular sieves (3 Å pore size) and stirred at 120 °C under N_2 in the dark for 5.5 h. Aliquots were taken regularly via syringe for UV-Vis analysis.

The mixture was cooled to room temperature, then in ice. Cold Et_2O (30 mL) was added and the precipitate was filtered and washed with Et_2O until the filtrate ran clear (50 mL). The crude product was extracted with MeOH (50 mL) and filtered. The solvent was removed under reduced pressure, yielding 10.2 mg dark solid (29.5%).

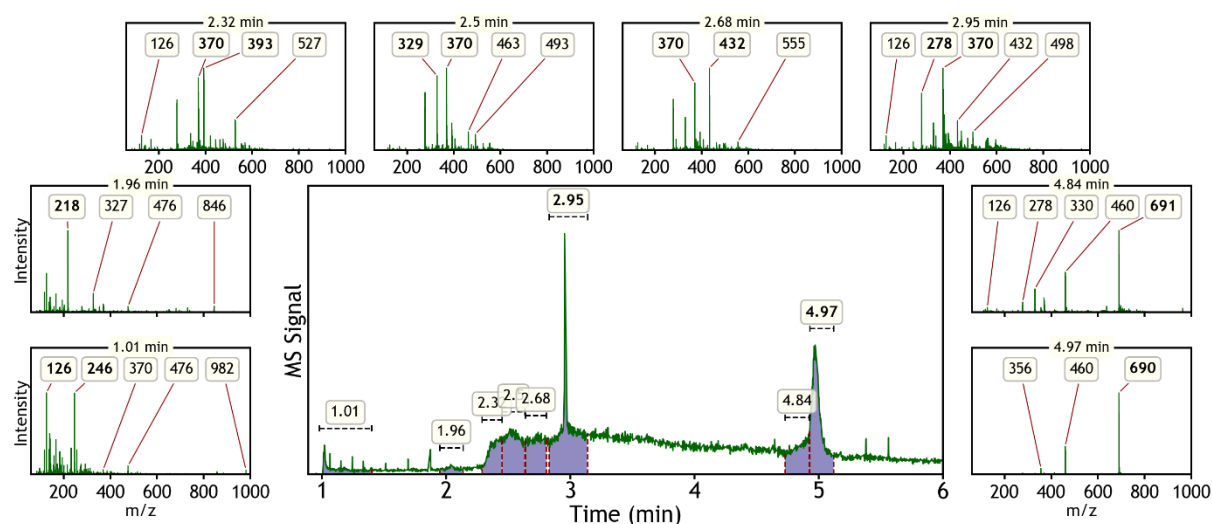


Figure A60. LCMS data for TAPP #6. m/z @ 2.32 min: 278 (*tetrakis*-TAPP⁴⁺), 370 (*tetrakis*-TAPP³⁺), 393 (unknown), 527 (unknown); @ 2.5 min: 329 (*tris*-TAPP³⁺), 370 (*tetrakis*-TAPP³⁺), 463 (unknown), 493 (*tris*-TAPP²⁺); @ 2.68 min: 370 (*tetrakis*-TAPP³⁺), 432 (*bis*-TAPP²⁺).

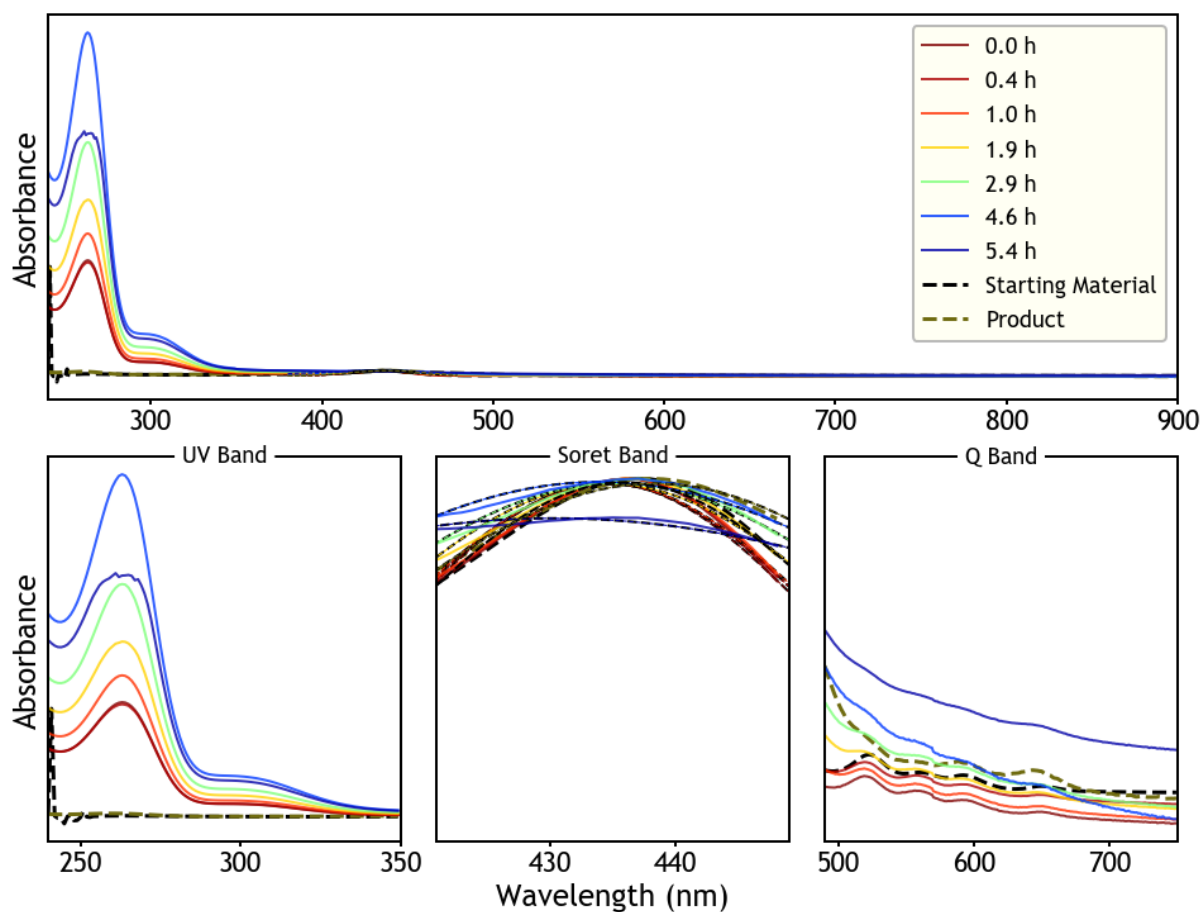


Figure A61. Temporal UV-Vis spectrum evolution of TAPP #6 reaction mixture (diluted with MeOH).

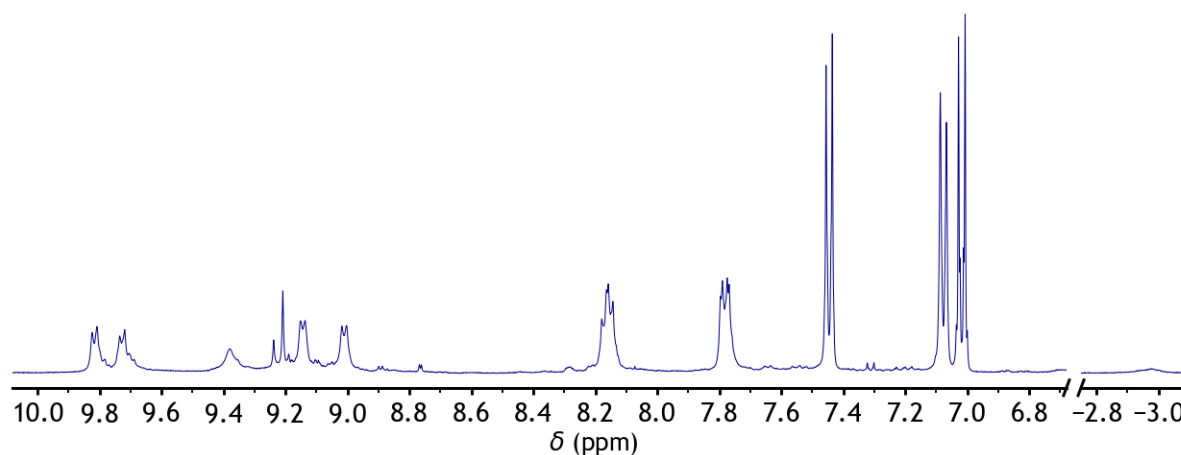


Figure A62. TAPP #5 ^1H -NMR spectrum in d_6 -DMSO (solvent region omitted for clarity).

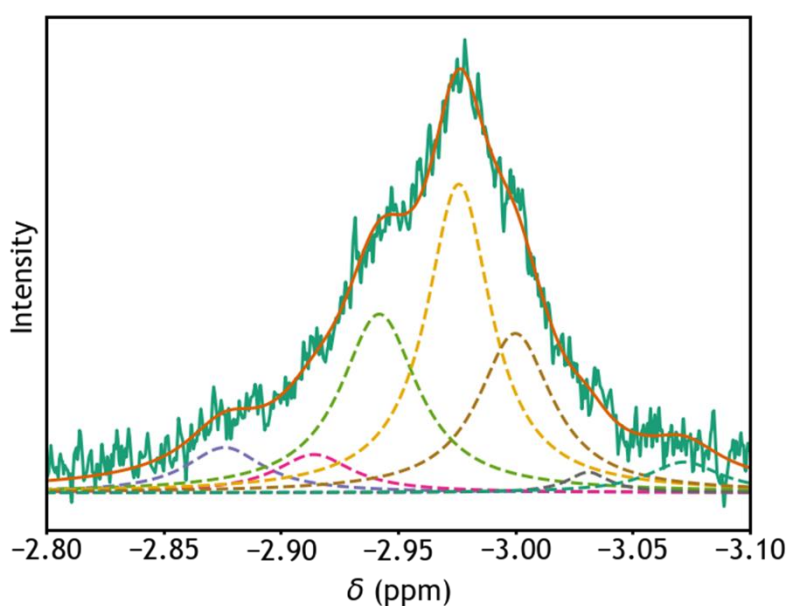


Figure A63. TAPP #6 ^1H -NMR spectrum (core NH region) in d_6 -DMSO.

TAPP #8

DNPP #9 (18.1 mg, 9.87 μmol) and 4-MTA (200 μL , 1.61 mmol) were dissolved in dry MeCN (10 mL) and refluxed under N_2 for 21.5 h. Aliquots were taken regularly via syringe for UV-Vis analysis only; no subsequent workup or characterisation was performed.

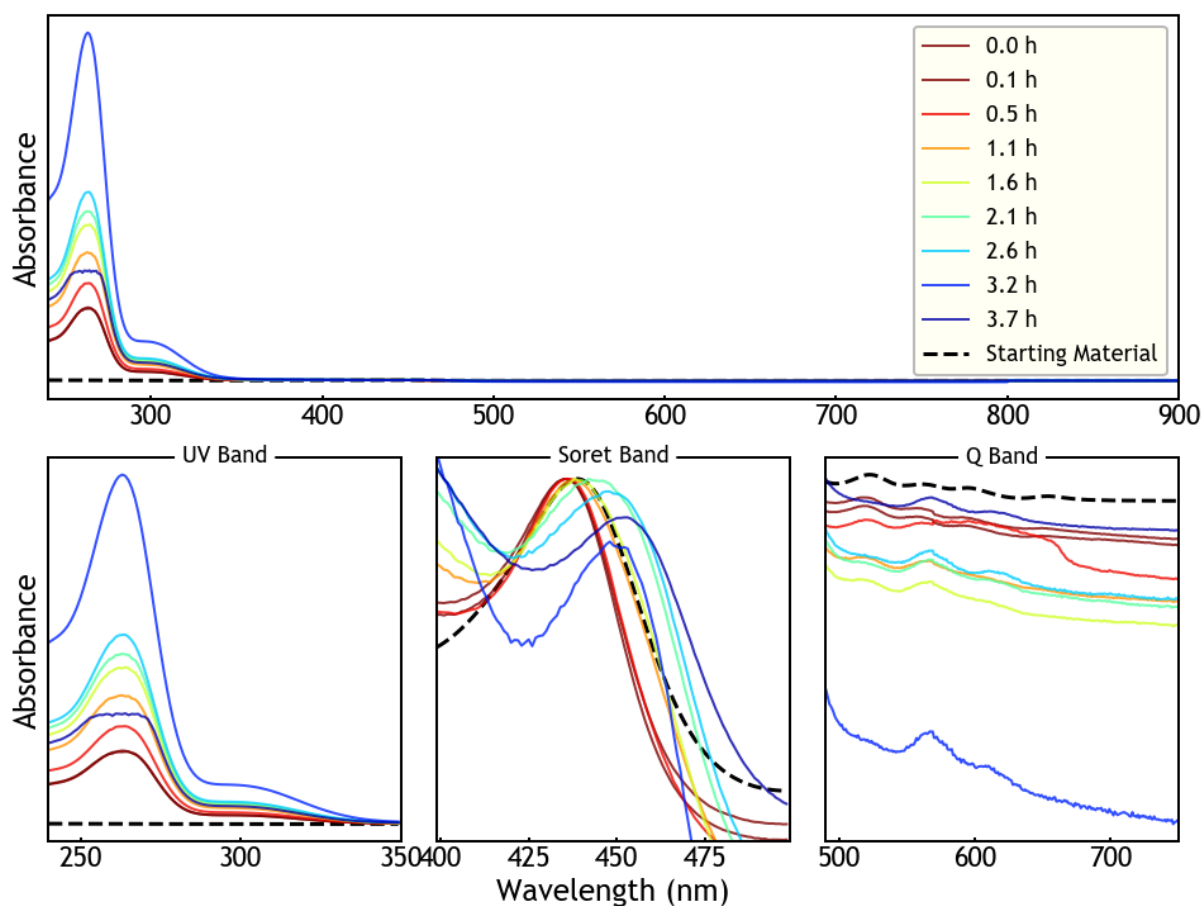


Figure A64. Temporal UV-Vis spectrum evolution of TAPP #8 reaction mixture (diluted with MeOH).

TAPP #9

4-MTA (400 μ L, 3.22 mmol) was added to **DNPP #8** (11 mg, 6.0 μ mol) under N_2 and the mixture was stirred at room temperature for 1.5 h. Et_2O (2 mL) was added and the precipitate was centrifuge triturated (2 x 2 mL Eppendorf, 13400 rpm, 5 min) with Et_2O (3 x 1.5 mL/tube) and MeCN (2 x 1.5 mL). Precipitates were dried under vacuum, yielding 4.2 mg of dark solid (42%),

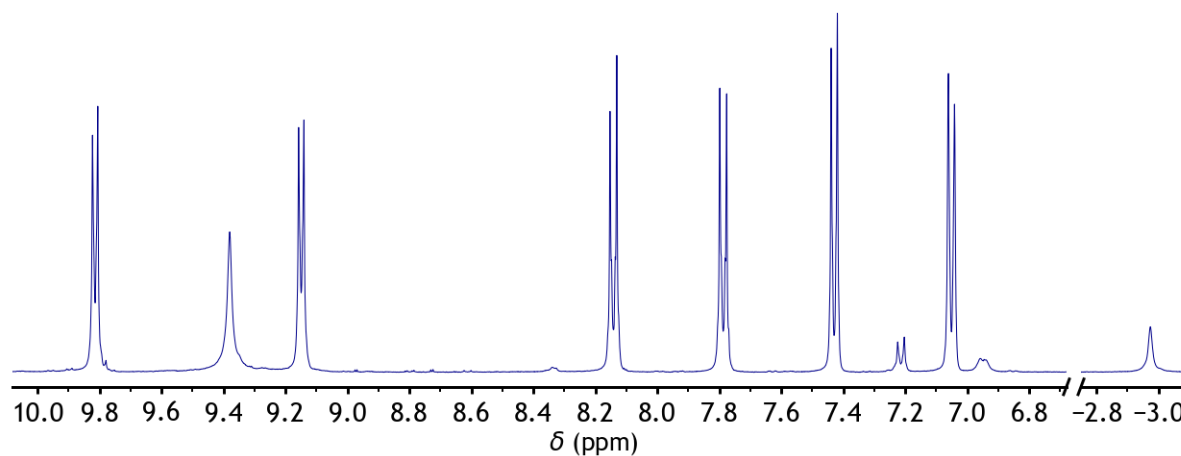


Figure A65. TAPP #9 1H -NMR spectrum in d_6 -DMSO (solvent region omitted for clarity).

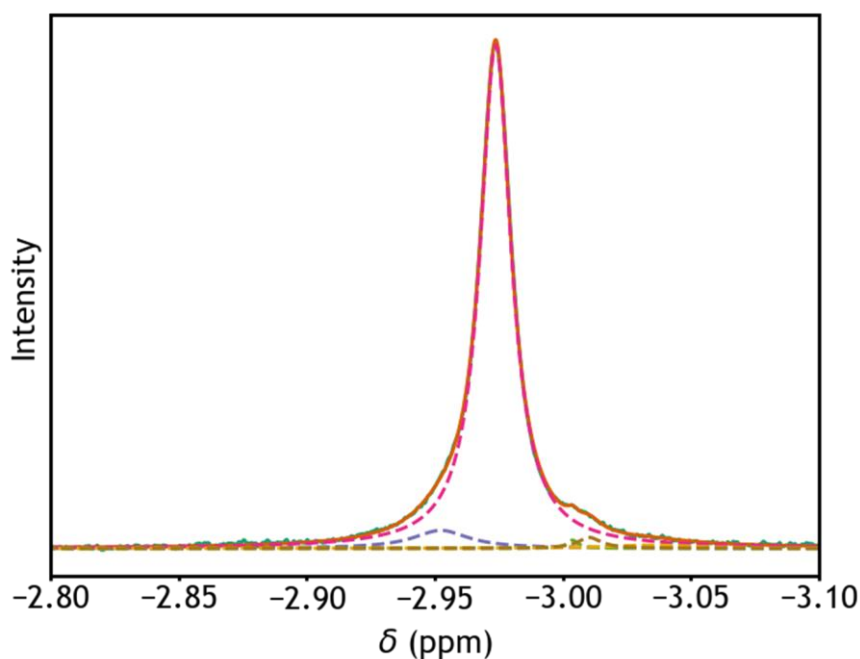


Figure A66. TAPP #9 ^1H -NMR spectrum (core NH region) in d_6 -DMSO.

TAPP #10

4-MTA (1 mL, 8 mmol) was added to **DNPP #8** (47.0 mg, 23.8 μmol) under N_2 and stirred at room temperature for 2 h. Et_2O (3 mL) was added and the resulting dispersion was centrifuge-triturated (3 x 2 mL Eppendorf tubes, 13400 rpm, 5 min) with Et_2O (5 x 1.5 mL/tube). Precipitates were dried under vacuum for 14 h, yielding 40.8 mg dark solid (95.3 %). The product was analysed by mass spectrometry, ^1H -NMR and UV-Vis spectroscopy.

A small amount of product (6 mg, 3 μmol) was centrifuge triturated (1 x 2 mL Eppendorf tube, 13400 rpm, 5 min) with 2:1:1 Et_2O /IPA/MeCN (3 x 1.5 mL/tube). The precipitate was dried under vacuum for 1 h and the solvent removed from the combined supernatants under reduced pressure.

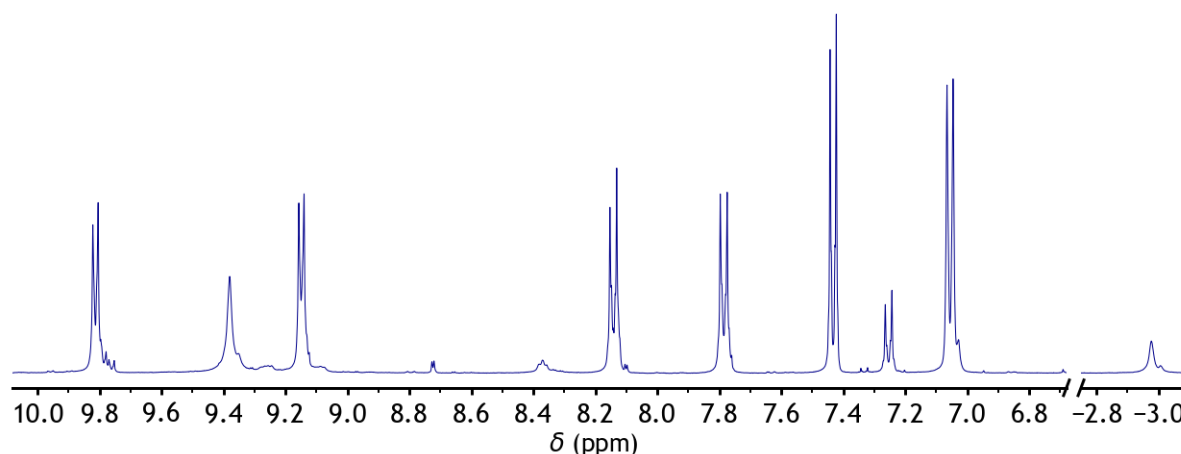


Figure A67. TAPP #10 ^1H -NMR spectrum in d_6 -DMSO (solvent region omitted for clarity).

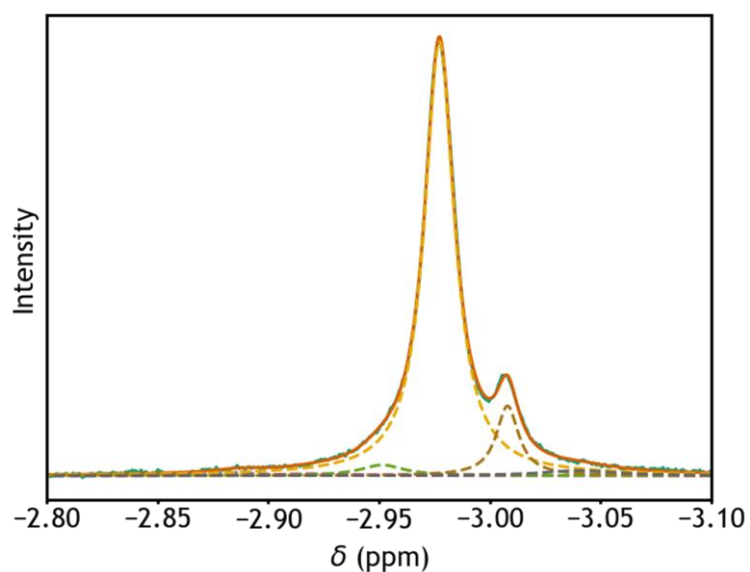


Figure A68. TAPP #10 ^1H -NMR spectrum (core NH region) in d_6 -DMSO.

8.4.3 Additional M-TAPP Characterisation Data

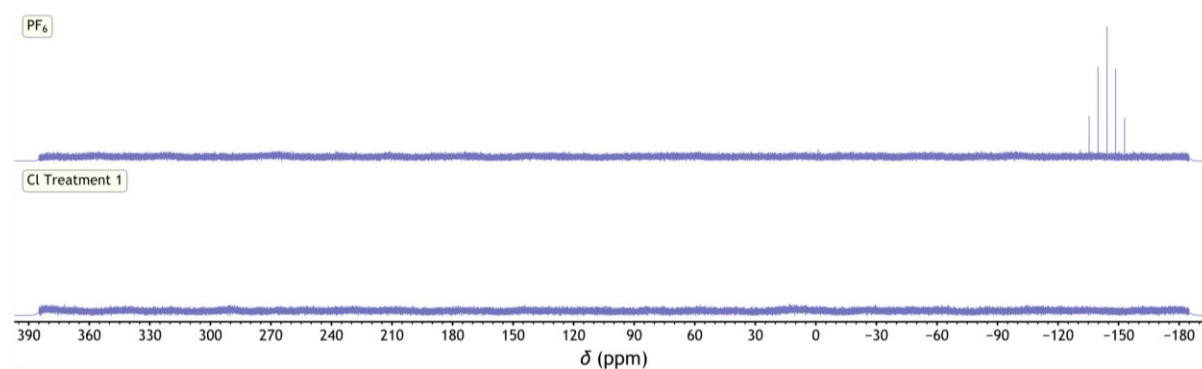


Figure A69. ^{31}P -NMR spectra (in d_6 -DMSO) of Zn-TAPP PF_6 salt before (top) and after (bottom) treatment with $\text{Bu}_4\text{NCl}/\text{MeCN}$.

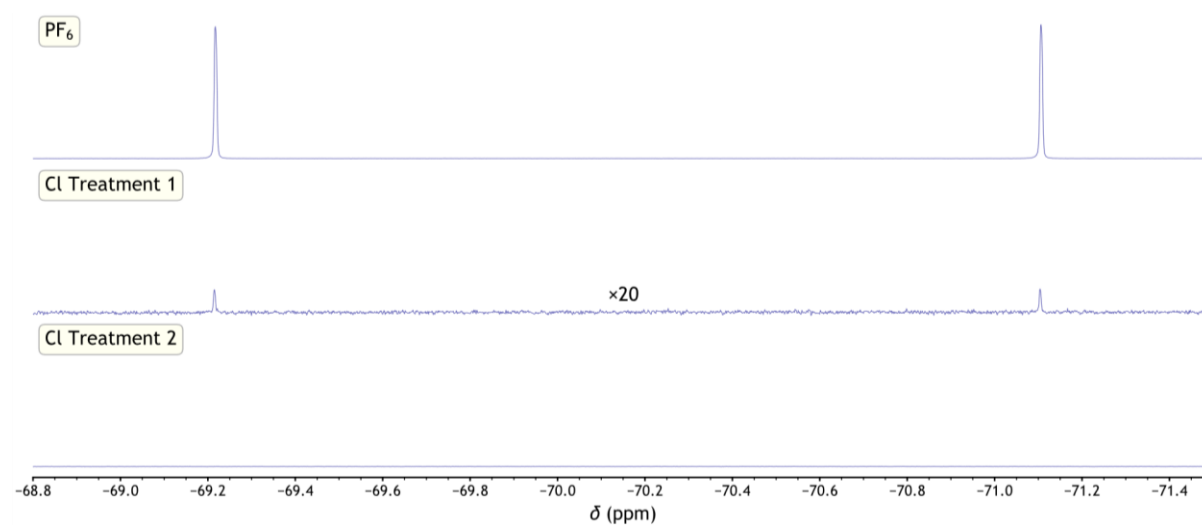


Figure A70. ^{19}F -NMR spectra (in d_6 -DMSO) of Zn-TAPP PF_6 salt before (top) and after one (middle) and two (bottom) $\text{Bu}_4\text{NCl}/\text{MeCN}$ treatments.

8.5 M-TAPP Analysis

8.5.1 Simulated NMR Lineshape

For chemical exchange between two degenerate states (without coupling), splitting and/or broadening of NMR resonances can be described by the lineshape:⁴⁹²

$$g(\nu) = \frac{K\tau(\nu_A - \nu_B)^2}{\left(\frac{1}{2}(\nu_A + \nu_B) - \nu\right)^2 + 4\pi^2\tau^2(\nu_A - \nu)^2(\nu_B - \nu)^2}$$

where $g(\nu)$ is the intensity at frequency ν , $\nu_{A,B}$ are the chemical shifts of the two nuclear environments between which the exchange occurs, $\tau = 1/k_{\text{ex}}$ for exchange rate constant k_{ex} and K is a normalisation constant.

8.5.2 D₂O Stability

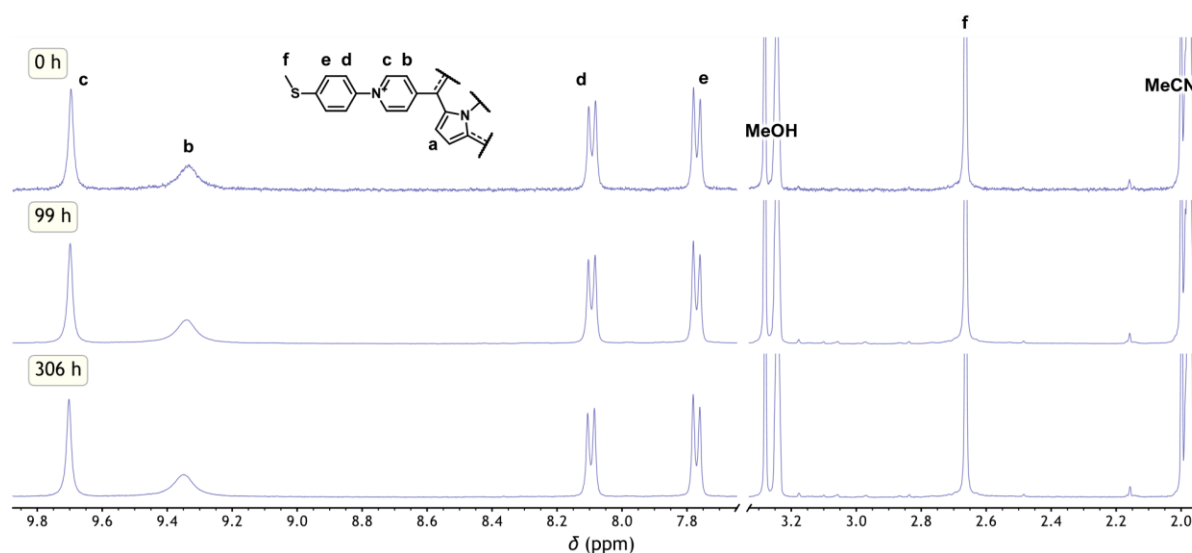


Figure A71. Temporal evolution of Ni-TAPP ¹H-NMR spectrum in D₂O under ambient conditions.

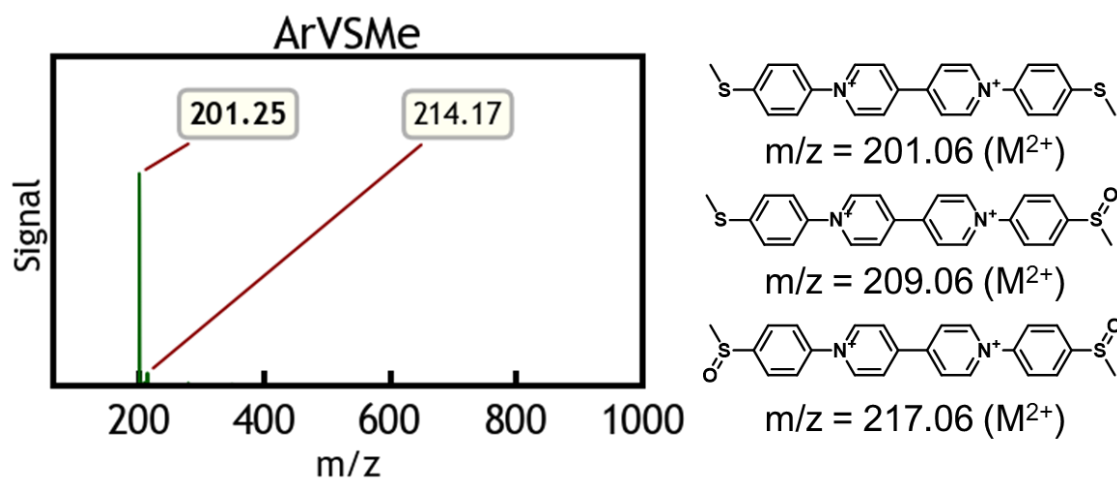


Figure A72. ArVSMe ESI-MS spectrum after >2 years' aqueous storage, indicating no appreciable concentration of oxidised compounds. Recorded by Katie King, Department of Chemistry, University of Cambridge.

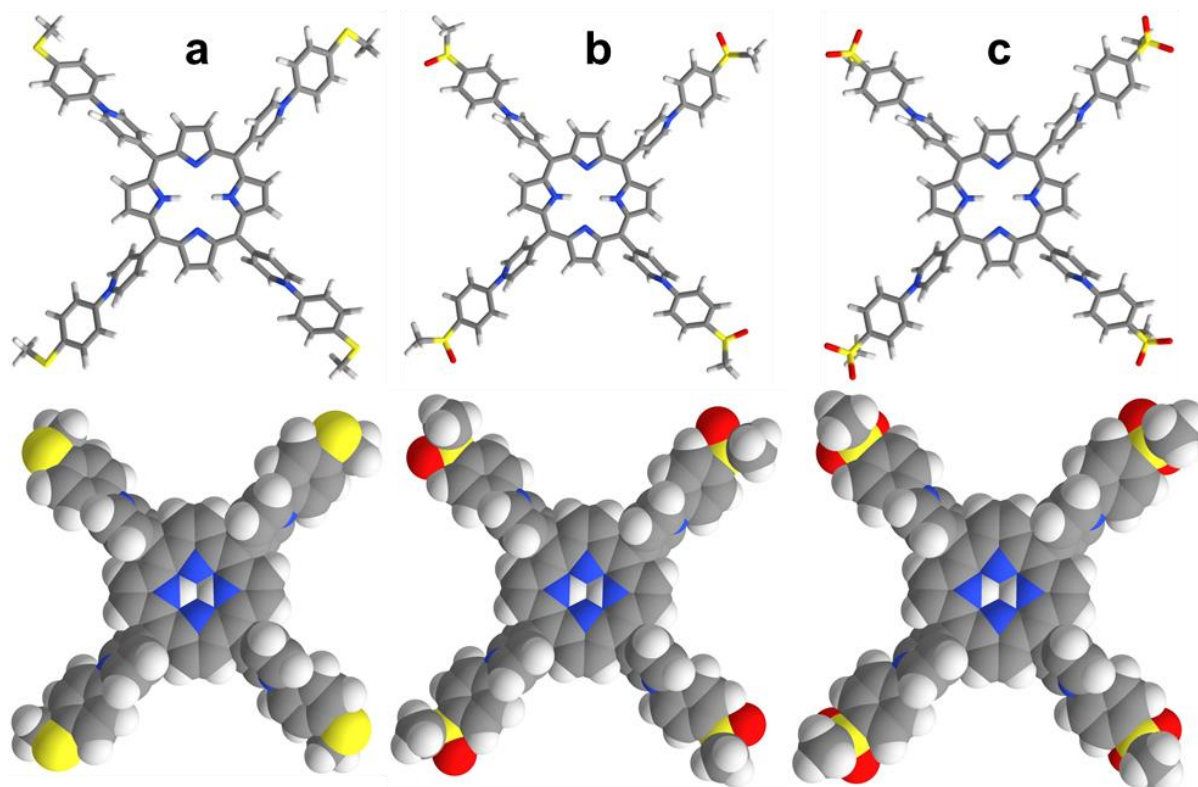


Figure A73. Stick (top) and space filling (bottom) DFT-optimised geometries of (a) H₂-TAPP, (b), H₂-TAPP(Ox1) and (c) H₂-TAPP(Ox2). All compounds are tetracationic; anions were not included. Atom colours: C (grey), H (white), N (blue), O (red), S (yellow).

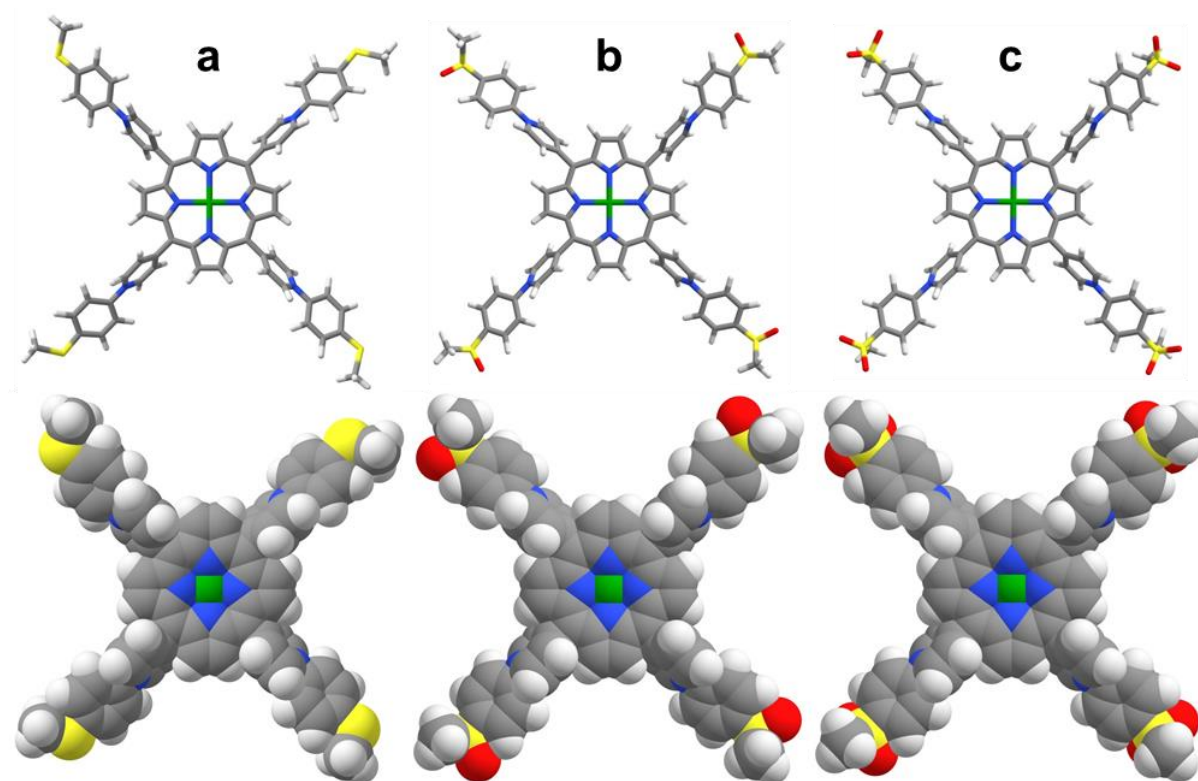


Figure A74. Stick (top) and space filling (bottom) DFT-optimised geometries of (a) Zn-TAPP, (b), Zn-TAPP(Ox1) and (c) Zn-TAPP(Ox2). All compounds are tetracationic; anions were not included. Atom colours: C (grey), H (white), N (blue), O (red), S (yellow), Zn (green).

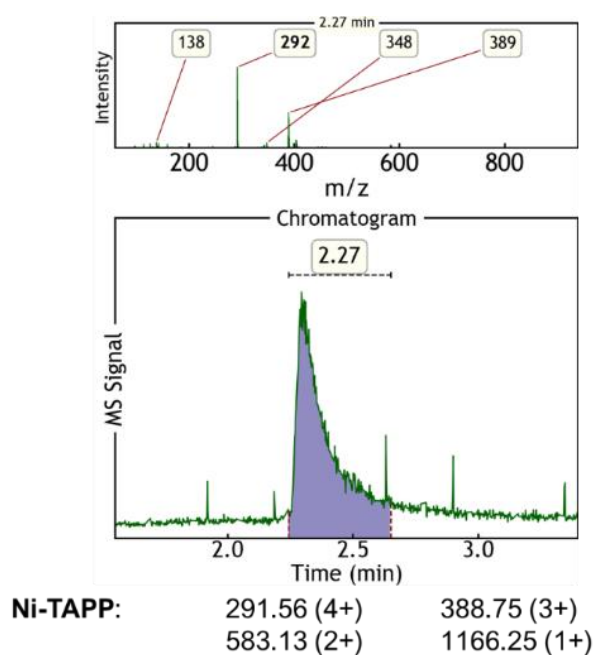


Figure A75. LCMS data for Ni-TAPP after 6 months in aqueous solution. No evidence for SMe oxidation detected.

8.5.3 Ni-TAPP Geometry

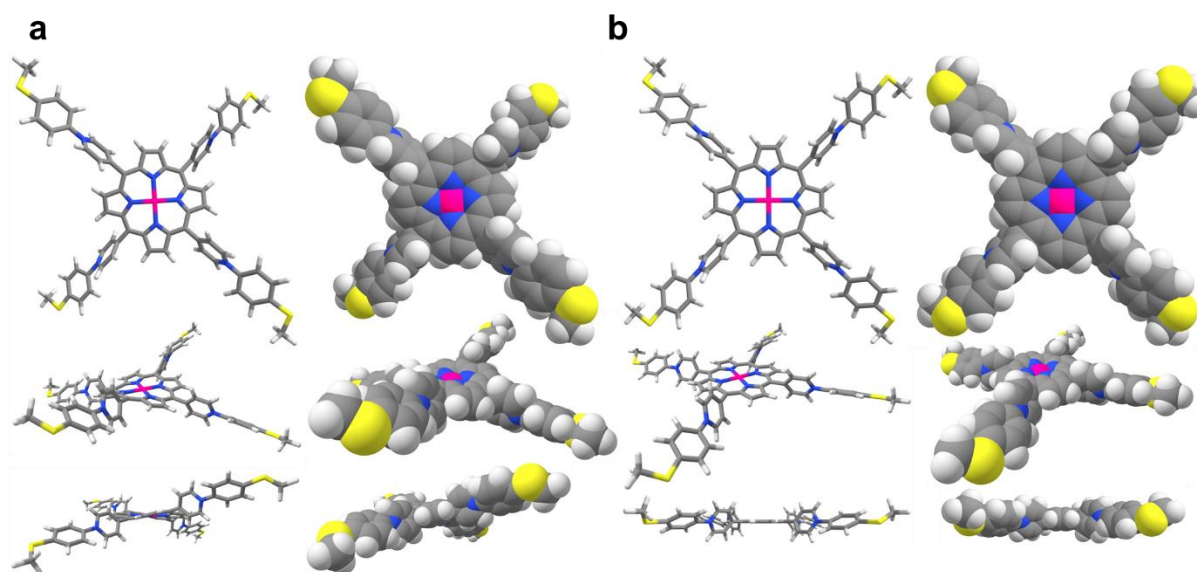
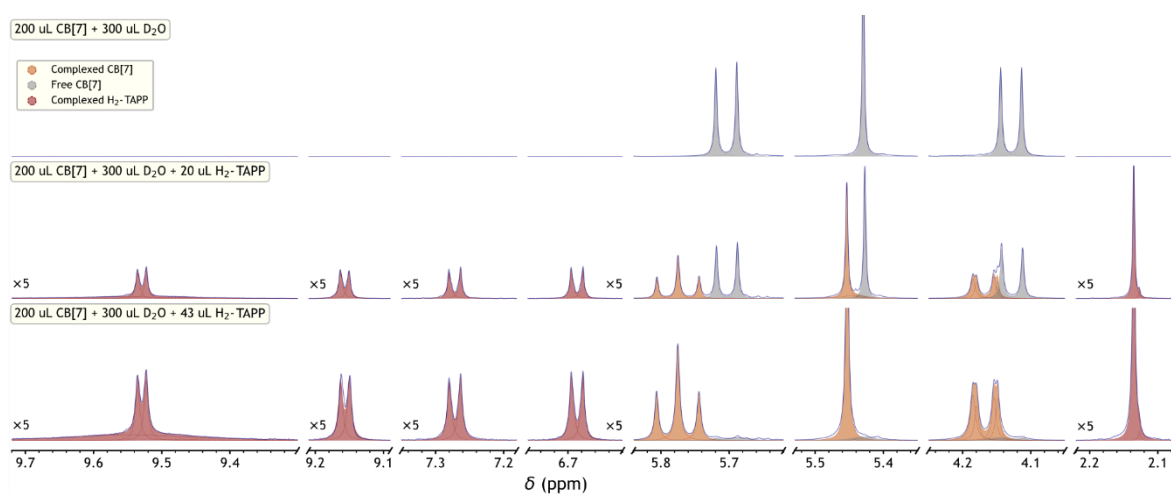
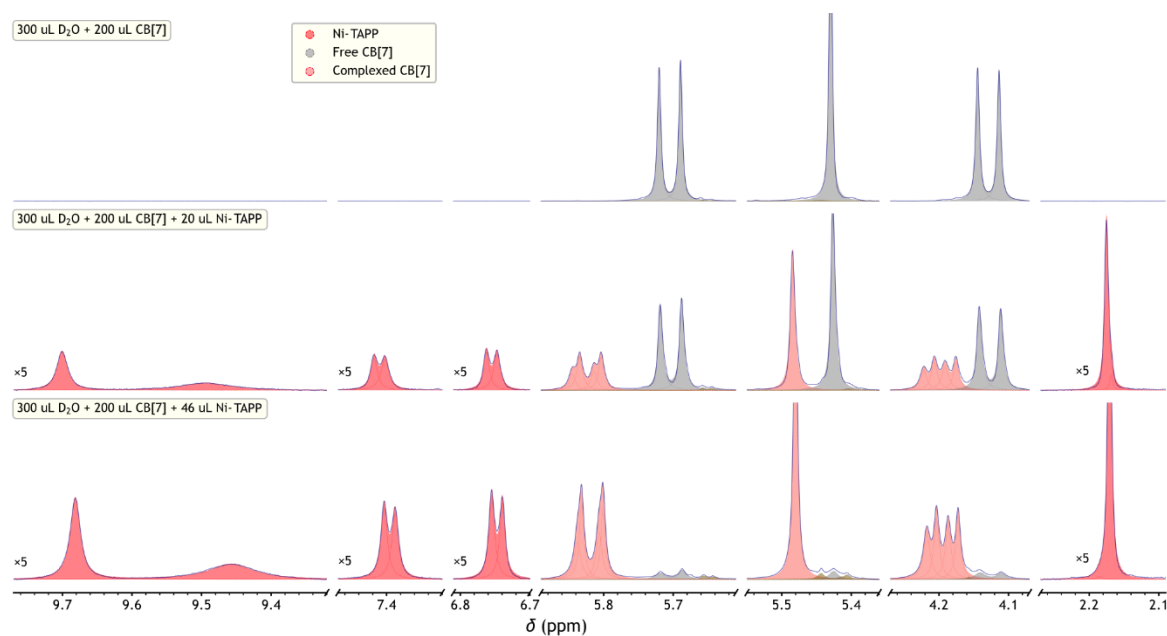


Figure A76. DFT-optimised geometry of (a) Singlet and (b) Triplet Ni-TAPP with saddled and planar geometries, respectively. Both stick and vdW models are displayed, as before. Atom colours: C (grey), H (white), N (blue), S (yellow), Ni (pink).

8.5.4 M-TAPP $\subset$ CB[7] NMRFigure A77. Titration of H₂-TAPP into CB[7] (both in D₂O), monitored with ¹H NMR.Figure A78. Titration of Ni-TAPP into CB[7] (both in D₂O), monitored with ¹H NMR.

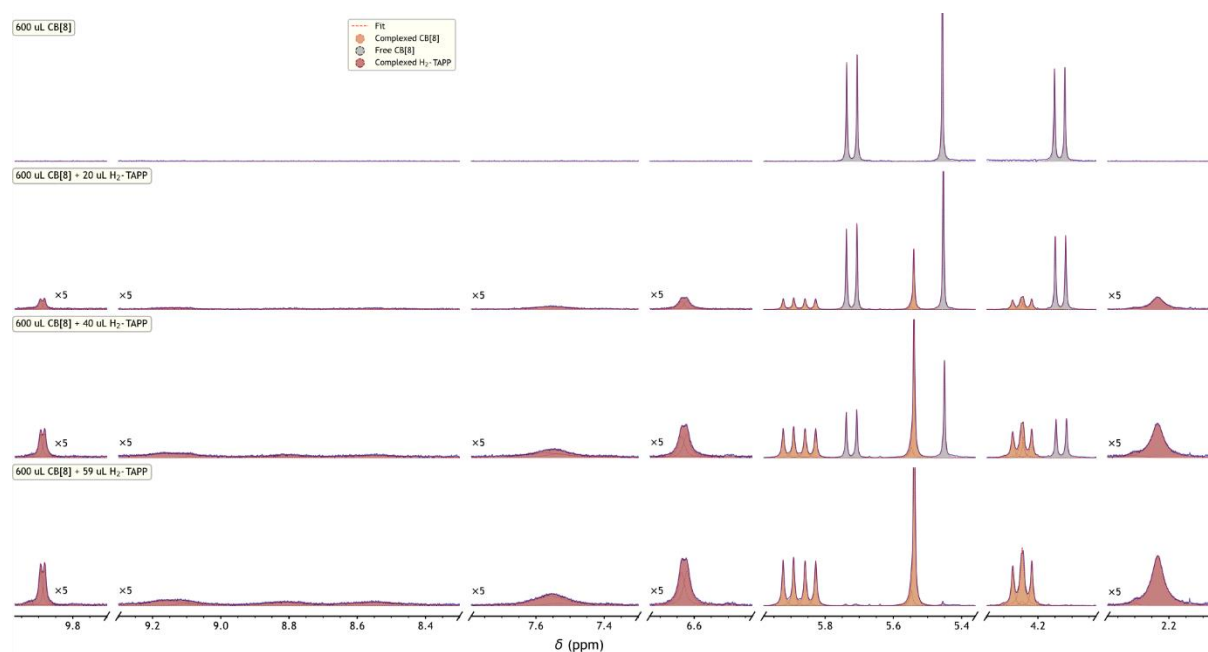


Figure A79. Titration of H₂-TAPP (in D₂O) into CB[8] (165 μM in DCl/D₂O), monitored with ¹H NMR.

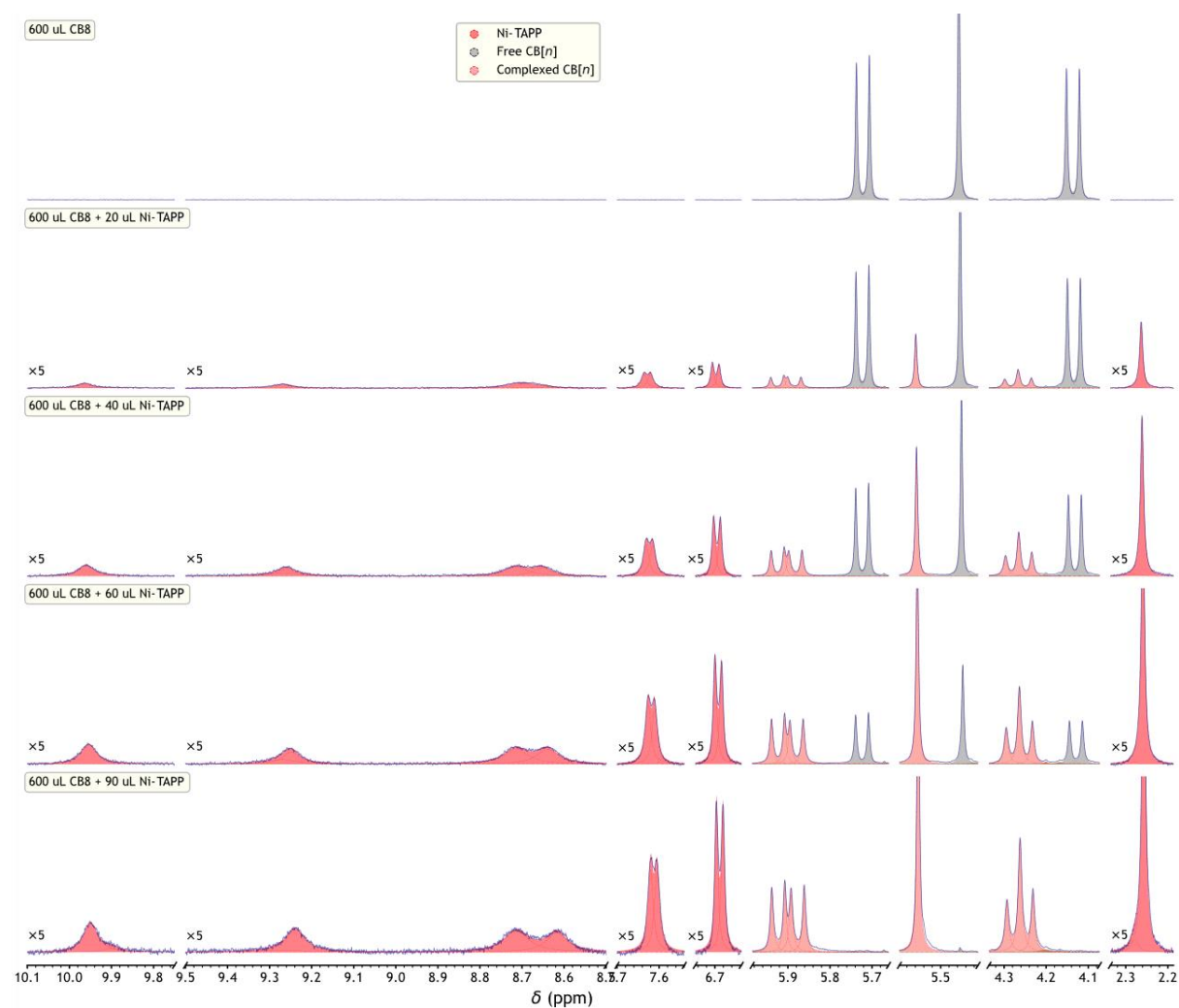


Figure A80. Titration of Ni-TAPP (in D₂O) into CB[8] (165 μM in DCl/D₂O), monitored with ¹H NMR.

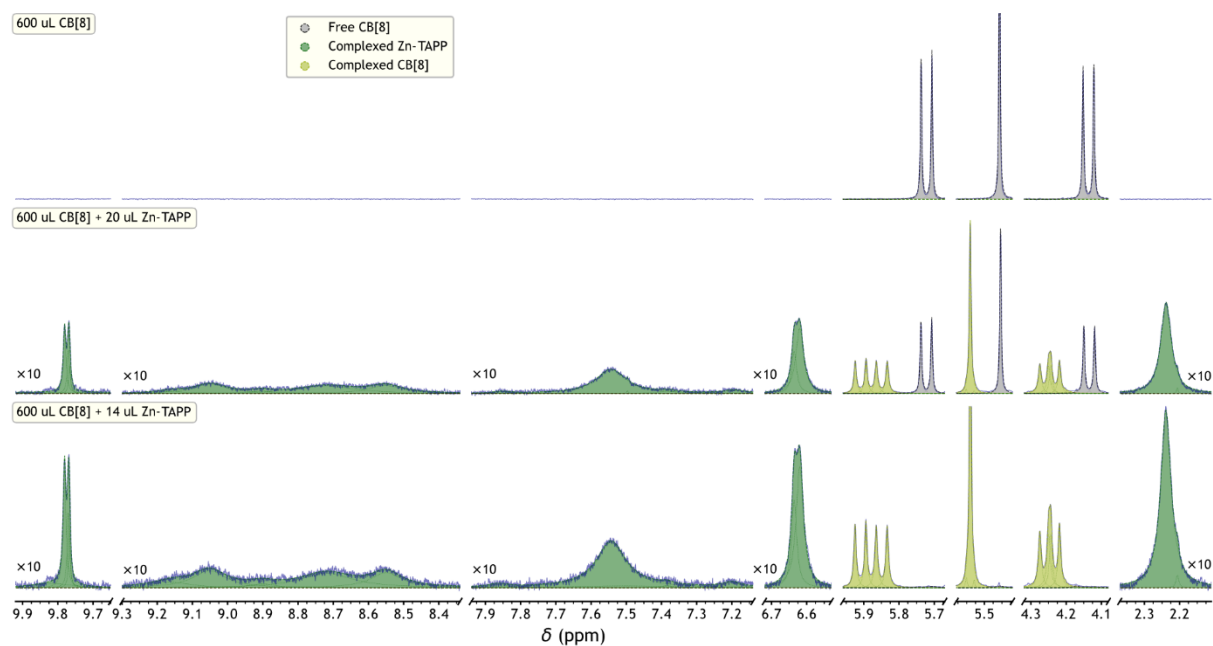


Figure A81. Titration of Zn-TAPP (in D₂O) into CB[8] (165 μM in DCl/D₂O), monitored with ¹H NMR.

a

Table S1. Diffusion coefficient of different CB[7] and CB[8] complexes obtained from DOSY measurements in D₂O at 298 K.

Species	Diffusion Coefficient ($10^{-10} \cdot \text{m}^2/\text{s}$)					
	G	G ₁ -CB[7] ₂	G ₂ -CB[8] ₂	G ₁ -CB[7] ₃	G ₂ -CB[8] ₃	G ₁ -CB[8] ₁
Ant910Me	3.56 ± 0.04	2.20 ± 0.01	2.04 ± 0.01	-	-	-
Ant15Me	3.59 ± 0.02	2.15 ± 0.01	1.98 ± 0.01	-	-	-
Ant14Me	3.49 ± 0.03	2.16 ± 0.01	1.95 ± 0.01	N.D.	1.85 ± 0.01	-
Np27Me	3.89 ± 0.01	2.18 ± 0.01	2.00 ± 0.01	-	-	-
Np14Me	3.85 ± 0.01	2.20 ± 0.01	1.98 ± 0.01	-	-	-
Np15Me	3.86 ± 0.02	2.18 ± 0.01	2.00 ± 0.01	-	-	-
Ph14Me	4.38 ± 0.02	2.20 ± 0.01	2.06 ± 0.01	-	-	-
Ph13Me	4.10 ± 0.02	2.25 ± 0.01	2.07 ± 0.01	-	-	-
Ph135Me	3.18 ± 0.02	N.D.	N.D.	1.89 ± 0.01	1.79 ± 0.01	-
VNMe ₂	-	-	2.01 ± 0.01	-	-	-
dzpy	-	-	-	-	-	3.04 ± 0.01
CB[8]	-	-	-	-	-	3.11 ± 0.01
Np14H	4.05 ± 0.02	2.24 ± 0.01	2.06 ± 0.01	-	-	-
Np14NH ₂	3.91 ± 0.03	2.26 ± 0.01	2.02 ± 0.01	-	-	-
Np14Me	3.85 ± 0.01	2.20 ± 0.01	1.98 ± 0.01	-	-	-
Np14OMe	3.83 ± 0.01	2.18 ± 0.03	1.97 ± 0.01	-	-	-
Np14SMe	3.73 ± 0.02	2.17 ± 0.01	1.99 ± 0.01	-	-	-
Np14NMe ₂	3.53 ± 0.01	2.15 ± 0.01	2.00 ± 0.01	-	-	-

b

Diffusion Coefficient / ($10^{-10} \text{ m}^2/\text{s}$)

G	G ₁ -CB[7] ₄	G ₂ -CB[8] ₄
H ₂ -TAPP	1.62 ± 0.01	1.49 ± 0.01
Zn-TAPP	1.59 ± 0.01	1.50 ± 0.01
Ni-TAPP	1.60 ± 0.01	1.50 ± 0.01

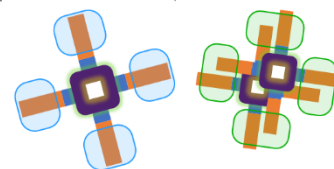


Table A82. DOSY data for (a) a range of EV-CB[n] complexes (table reproduced from Wu *et al.*²⁶¹) and (b) M-TAPP-CB[n] complexes in this work. DOSY measurements in (b) were performed and analysed by Guanglu Wu, Department of Chemistry, University of Cambridge.

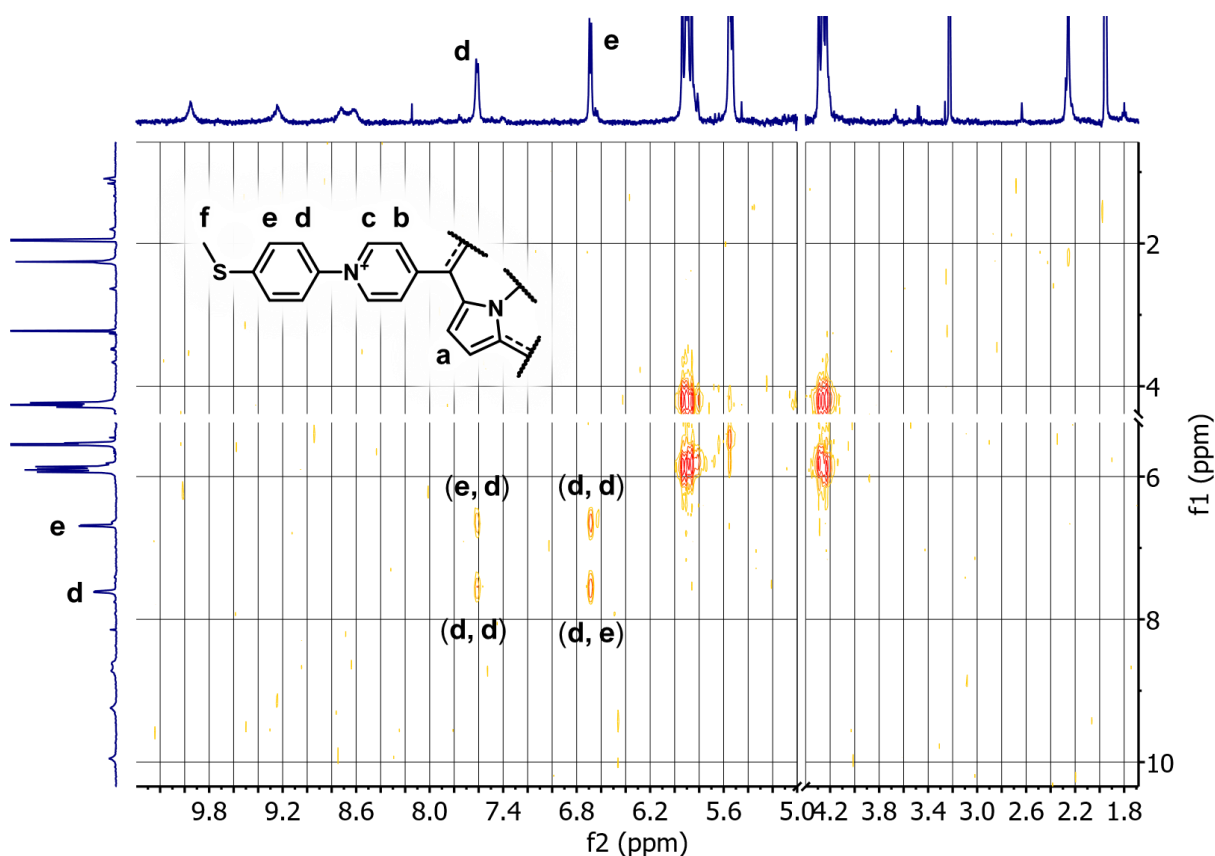


Figure A83. $(\text{Ni-TAPP})_2\text{CB}[8]_4$ ^1H -NMR COSY analysis, indicating through-bond correlation between proton environments **(d)** and **(e)**.

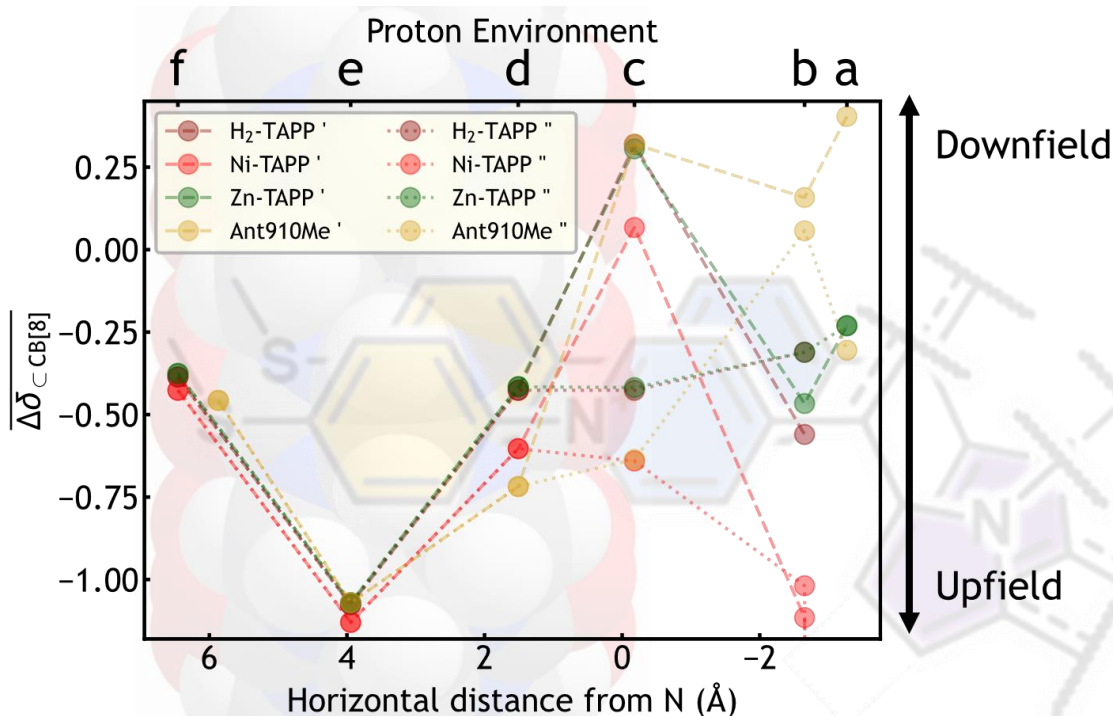


Figure A84. $\Delta\delta_{\text{CB}[8]}$ (not averaged) for different proton environments of Ant910Me^{261} and H_2 -, Zn - and Ni -TAPP, plotted against horizontal distance from pyridinium nitrogen (calculated for H_2 -TAPP using DFT). See **Figure 5.25** for more details. $\text{CB}[8]$ atom colours: C (grey), H (white), N (blue), O (red).

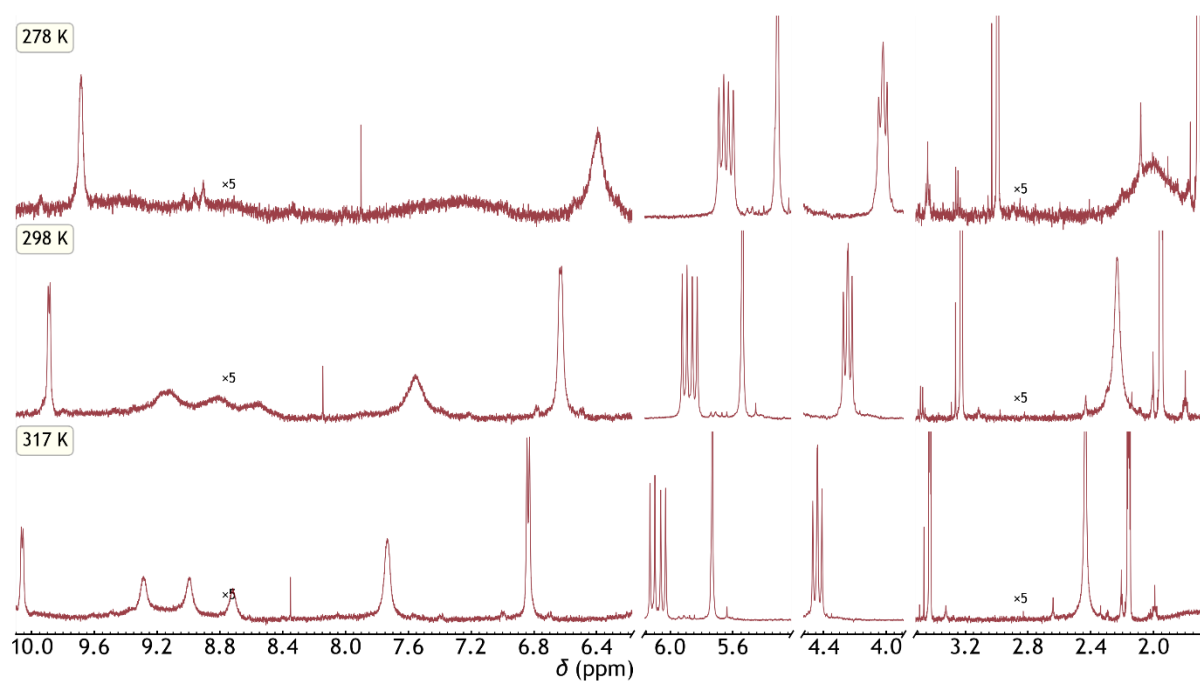


Figure A85. ^1H VT-NMR spectra of $(\text{H}_2\text{-TAPP})_2\text{CB}[8]_4$ in D_2O with CB[8] spectral regions ($6.2 < \delta < 3.8$ ppm) included.

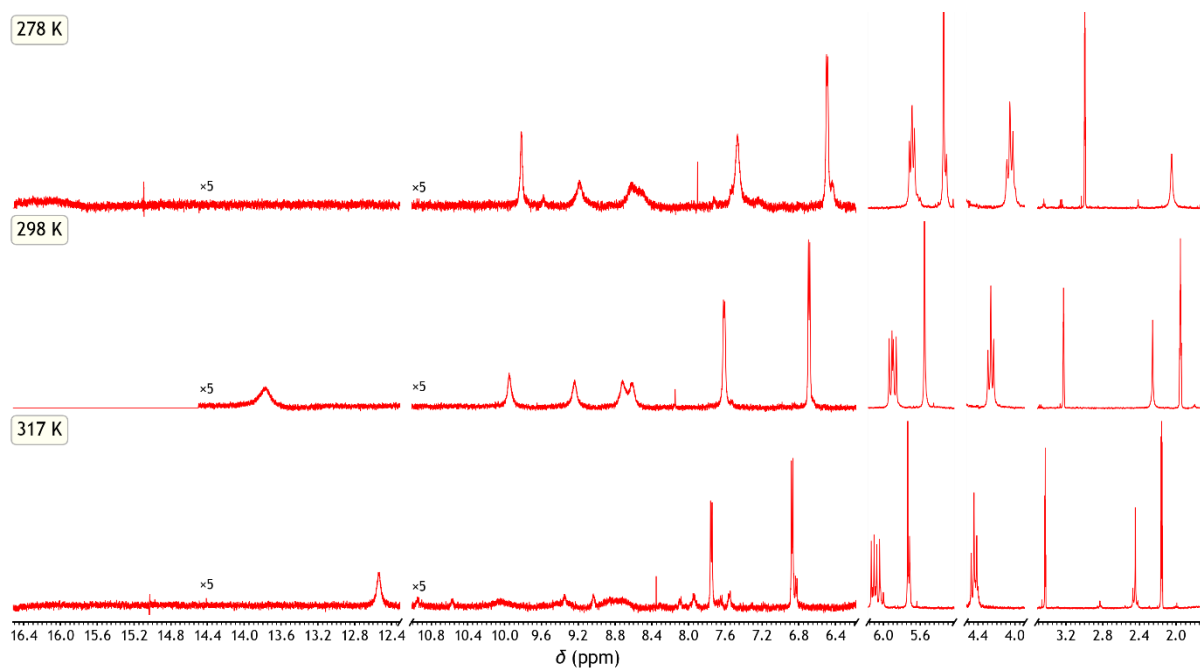


Figure A86. ^1H VT-NMR spectra of $(\text{Ni-TAPP})_2\text{CB}[8]_4$ in D_2O with CB[8] ($6.2 < \delta < 3.8$ ppm) and pyrrole ($16.5 < \delta < 12.3$ ppm) spectral regions included.

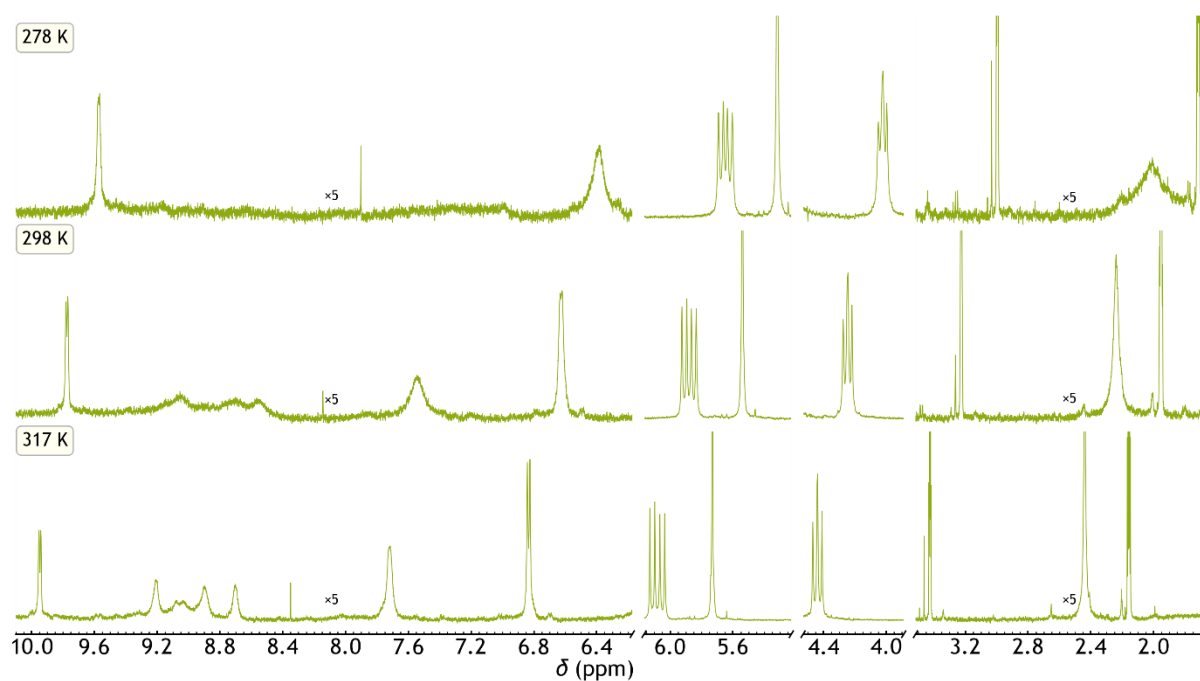


Figure A87. ^1H VT-NMR spectra of $(\text{Ni-TAPP})_2\text{@CB[8]}_4$ in D_2O with CB[8] spectral regions ($6.2 < \delta < 3.8$ ppm) included.

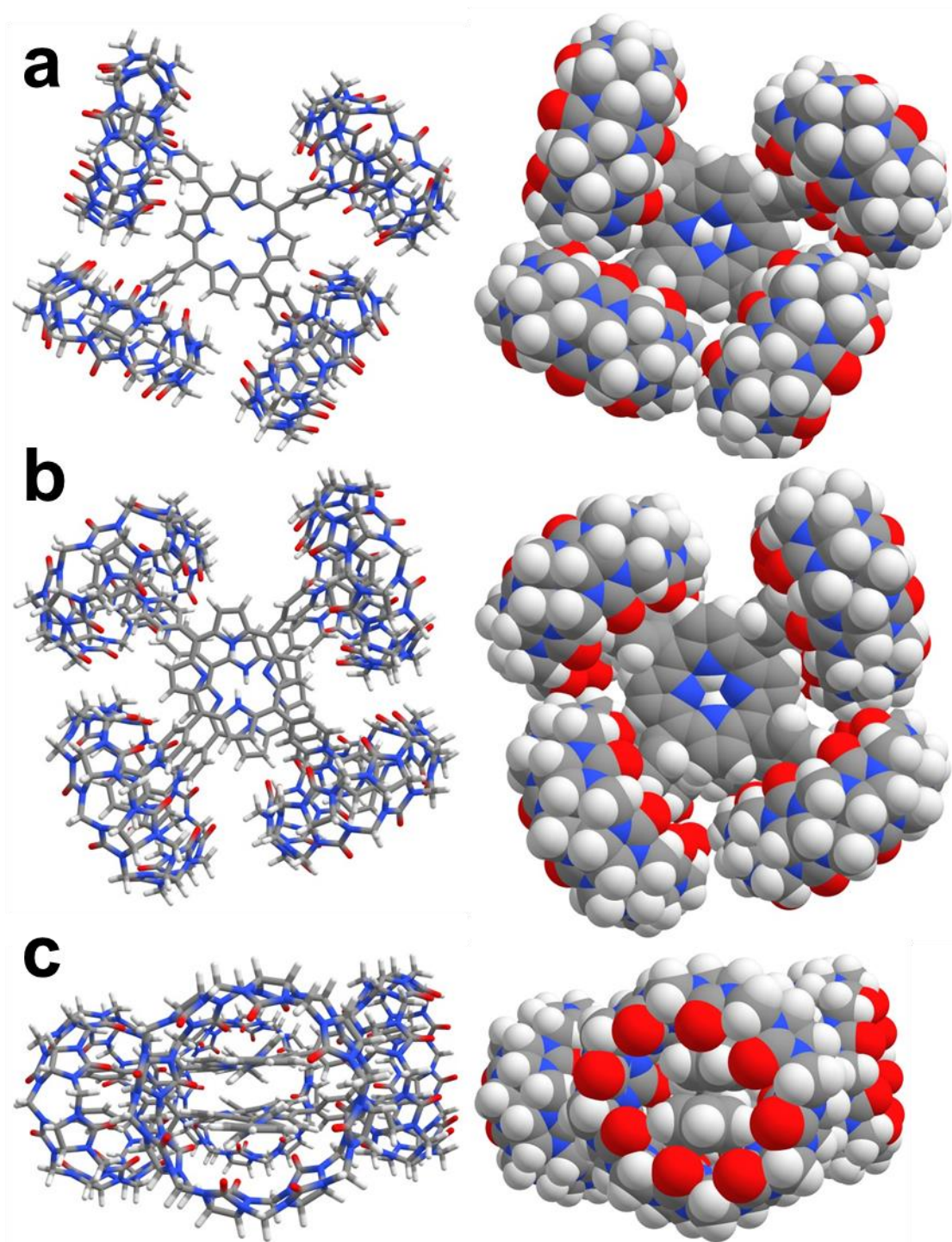
8.5.5 $\text{H}_2\text{-APP}\subset\text{CB}[n]$ Geometry Calculations

Figure A88. Optimised geometries of (a) $\text{H}_2\text{-APP}\subset\text{CB}[7]_4$ and (b, c) $(\text{H}_2\text{-APP})_2\subset\text{CB}[8]_4$. Optimisation performed by Denes Berta (Department of Physics, University College London) using GFN2-xTB.⁵⁰⁹ atom colours: C (grey), H (white), N (blue), O (red).