Photophysics of small molecule organo-metallic complexes for OLED applications



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How many light bulbs does it take to change a man...?

Declaration

I hereby declare that except where specific reference is made to the work of others, the contents of this dissertation are original and have not been submitted in whole or in part for consideration for any other degree or qualification in this, or any other University. This dissertation is the result of my own work and includes nothing which is the outcome of work done in collaboration, except where specifically indicated in the text. This dissertation contains less than 65,000 words including appendices, bibliography, footnotes, tables and equations and has less than 150 figures.

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Abstract

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Over the last 3 decades, advances in chemistry have produced new semiconducting materials with very different properties, transitioning from inorganic to organic semiconductors, allowing previous material constraints to be worked around.

Organic semiconductors can be transparent, flexible, and soluble and are able to be tuned to absorb or emit across a wide range of wavelengths. This has revolutionised device technology, already competing in global lighting and display industries. Whilst organic semiconductors avoid some of the problems inherent in inorganic technologies, they have their own limitations. The electronic transitions in organic materials are highly spin sensitive, as excitons form due to lower dipole moments. Triplet excitons cannot directly couple radiatively to the ground state, so unless additional processes to alter spin angular momentum exist 75% of excitations formed cannot emit light.

I have studied a new class of small molecules, Carbene Metal Amides (CMAs) which display efficient emission, and have been used in OLEDs, breaking the efficiency records for both solution processed devices (27.5%), and evaporated host free emissive layers (23%).

Herein I present my work using a variety of time resolved spectroscopic techniques to study the photophysical properties this new class of emitters, explaining the rapid and efficient excited state spin conversion, and the effects of molecular modification. I show that this class of emitter sits between two existing technologies for emission from triplet states, namely heavy metal phosphorescence and organic Thermally Activated Delayed Fluorescence (TADF).

The incorporation of both sets of physical processes which have previously allowed emission from triplet states has resulted in a class of materials with near 100% photoluminescence and internal device efficiencies, and I show the nature of the states involved in the emission process, how they respond to a number of modifications to the molecular structure, and discuss how this class of materials may be further developed for device applications.

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Nomenclature

When introducing terms, for the sake of consistency I have used the definitions from the IUPAC compendium of chemical terminology.

Where my usage of terms differs from the definitions provided herein, or where the usage in the literature deviates from these definitions I have clarified for the purposes of discussion within this thesis.

Chapter 1 Introduction

Fiat Lux

In this first chapter, I introduce lighting and display as one of the single most important technological resources on the planet, and frame this body of research in the context of the wider field and the global problems that these technologies aim to help solve which have been the motivation for my work.

1.1 Lighting and display technology in the 21st century

The interplay between energy usage and materials technology is one of the defining scientific topics of this century.

Regardless of nationality, religion, political alignment or profession, we all need light. It has become such a defining feature of modern life that lack of access to artificial light is classed as "light poverty" and is linked to poor economic productivity, health and safety. Currently \sim 20% of the world's population do not have access to electricity or modern lighting.¹

In a world of increasing population, and rapid uptake of technology in developing regions, the global demand for lighting is increasing dramatically. In 2006, it was estimated that ~19% of all global power use goes on lighting.

Incandescent bulbs are only ~5% efficient. Current LEDs are able to achieve 40-50% efficiency, ²³ so if all commercially available lighting solutions could be brought to approach 40-50% efficiency, this could reduce global energy usage by ~15-17%.

In addition to lighting, the area of electronic display screens is also on the increase. In 2019 there were 278 million square meters of flat panel display produced and by 2022 this is projected to increase to 327 million square meters.⁴

As well as considering the efficiency of these products during operation, the manufacturing process itself is an industry on a global scale and the scarcity of resources used, energy required to process, and production cost all also limit the ability of the market to uptake newer, improved technologies for both lighting and display application.

Within this context the global demand for new materials for lighting and display applications is clear.



Figure 1.1 global lighting overview

Figure 1.1 shows a comparison of global population density(persons per square km) (top)⁵ a map of global poverty by percentage of population (middle)⁶ with a NASA composite of global night time light pollution in October 2012 (bottom). ⁷ Regions like sub-Saharan Africa and India show clear disparity between population density and availably lighting, and correlate to the regions with most severe poverty.

1.2 Organic materials for lighting application

Over the last ~30 years, the field of organic electronics has emerged, where instead of making devices out of naturally occurring materials and highly purified crystalline solids, new electronically active classes of materials have been synthesised.

Being based around carbon, hydrogen, oxygen etc. these materials exhibit many of the material characteristics found in plastics and other organic systems. They can be flexible, transparent, soluble and highly chemically versatile, ranging from small molecules to polymers.

One of the main differences to inorganic materials is that electronic transitions in organic systems are spin dependent.

For the majority of materials, this means that only 25% of electrically generated excitations are able to produce light, which is clearly a non-ideal upper limit on the efficiency of devices utilising these new materials.

This limit is due to the ratio of formation of spin singlet (25%) and spin triplet (75%) excitations, as emission of a photon cannot change the spin angular momentum of a system, and most materials have singlet ground states.

To try to overcome this limit there has been a large amount of work has gone into developing systems where additional effects are present which allow the spin orbit angular momentum to be influenced in the excited state, allowing radiative transitions from triplet excitations.

One of the classes of materials which is being explored for this purpose are Carbene Metal Amides (CMAs).

1.3 Carbene Metal Amides

Carbene Metal Amides (CMAs) are a recently developed class of emissive small molecules which have been the primary focus of my research during my PhD. Developed by Alexander Romanov at the University of East Anglia, this class of molecules was first reported in 2015.⁸ These demonstrate high efficiency emission from excited triplet states which occurs faster than many other material systems designed for emission from triplet states which is desirable for device applications.

Since their first report, there has been a large amount of work to understand the photophysics of this system in parallel with developing chemistry of new, improved versions of these emitters. In this thesis I will discuss 3 of the main projects which I have worked on to this end during my PhD.

In chapter 4, I introduce one of the first, and most comprehensively studied molecules in the CMA family, which is referred to in literature as "CMA1". The aim of this chapter is to characterise what we take as "normal" behaviour for CMA materials as a standard to compare modifications to. In this chapter the photophysics of CMA1 is investigated using time resolved emission and absorption techniques, and high efficiency devices are demonstrated from both solution and thermal vapour deposition. I show that CMA1 displays rapid, sub-microsecond, from excited triplet populations, with near 100% quantum efficiency, and that they are can be processed via both solution and TVD, with and without host material, offering a competitive alternative to existing chromophores.

In chapter 5, I explore the effects of changing the metal atom in the CMA molecule and how this effects the spin transitions in the system. As mentioned above, without some additional process to influence the spin angular momentum in the excited state, triplet excitons are not able to emit light. One of the ways such a process can be introduced is by incorporating a heavy atom within the molecule. I show that by substituting the bridge metal atom in the CMA architecture, that the rate of emission from triplet states can be changed considerably.

In chapter 6, I explore the effect of a number of donor group modifications to the CMA architecture for gold and copper bridged versions of the CMA archetype. The aim of this investigation was to explore how far chemical modification of the motif can go without disrupting the desirable photophysical properties of the system. Two groups of modifications are considered; one with large steric bulk intended to be incorporated into polymer hosted devices, the other with smaller modifications such that thermal vapour deposition is still possible. I show that from both classes of modification, candidates exist which retain the desirable photophysical characteristics, and establish that donor group modification can also be used to achieve chromatic shifting of the emission without sacrificing high device performance. Solution and vapour deposited devices are demonstrated for the two groups of modifications respectively.

Chapter 2 Theory and Literature review

"The more you know, the more you know you don't know"

-Aristotle

In this chapter I set out the theoretical description of the processes which are necessary to understand the data presented in this thesis, and the measurements which have been used to characterise the material systems reported.

I also provide a summary of the current state of the field of organic electronics for lighting purposes, and the physical processes defining/ limiting the technology.

The effects governing the optical and electronic properties of these materials also vary, from quantum confinement within nanoscale objects, to conjugation of carbon bonds, to relativistic heavy atom interactions within a single molecule. The processing methods for these materials, interfaces and cavity effects, morphology and host interaction also exponentiates the parameter space for discussion.

For the purposes of this thesis, I will consider some of these advances in discrete categories, defined by the physical processes allowing emission of a photon from within an OLED device, and focus on the subset of material systems which have led to the development of the small molecule organo-metallic TADF emitters which I study.

This is not intended to detract from the broad scope of the field, or to imply a common developmental aim, logic, or chronology to the progress discussed, but only to place my research in the context in which I have approached it.

2.1 Overview of lighting technologies

The development of materials for use within the field of organic electronic applications over the last 3 decades has been incredibly rapid, with progress being led by synthetic advances in parallel with the improved understanding of the physics.

The variety of material systems and physical processes now being incorporated into "organic electronics" is vast. There are conductive polymers, small molecules, quasi crystalline systems like perovskites, quantum dots, nanocrystals and self-assembling frameworks like COFs and MOFs.

Materials which have conventionally been used for electronic applications have been metals and crystalline semiconductors. These sorts of materials have electronically conducting or semiconducting properties as they occur naturally, or can be purified into a state where they do, and arise from either having highly mobile delocalised electrons in a partially filled valence band in metals, or from the emergent property of band structure emerging in a highly regular lattice from the superposition of allowed solutions to the wavefunction from subsequent sites.

Historically the class of electronically active materials did not tend to include organic materials which are predominantly carbon based. The structure of the bonds in most organic materials also determines their physical properties like flexibility, solubility, and whether they can be transparent in the visible range of wavelengths.

There is at least one example of a naturally occurring, carbon based material with conductive properties, which is graphite (like carbon motor brushes). This is however the exception, and generally speaking, most naturally occurring organic materials, or those which have been synthetically produced do not display conductive or semiconducting properties and are usually insulators. Even today, the primary purpose of organic material in the field of electronics is as an insulator, and everyone knows that you find plastic around the *outside* of a wire.

A notable historic counter-example to this, which could be viewed as portentous if you are so inclined, would be that the first light bulb demonstrated by Humphry Davy to the Royal Institute in 1803 used 2 charcoal rods as filaments, and the filament in the first light bulbs commercially available was made from carbonised bamboo between 1882 and 1904 when they were superseded with tungsten filaments. ⁹

Roughly a century later, carbon based materials returned to the scene of lighting applications with the birth of OLEDs, though now functionalised for their electroluminescence rather than thermal incandescent radiation.

To understand what makes this possible, we must consider the behaviour of an electron in an atomic context, how this translates into allowed orbitals, how these behave in molecular systems of different bonding configurations, and finally how this determines the allowed intrinsic semiconducting properties of certain types of organic compounds via a distinctly different origin to the Bloch description of crystalline inorganic semiconductors.

2.2 Electronic properties of organic materials

In the context of inorganic materials, there is a somewhat blurred transition between what constitutes an "insulator" versus a "semiconductor". For the case of crystalline inorganic materials, the electronic transitions which are allowed depend on the size of the bandgap, and how large the bandgap is relative to the potential difference across the material determines whether it is behaving as an insulator or semiconductor.

This behaviour of how semiconducting properties emerge for highly regular systems is described by the Bloch theory of extrinsic semiconductors, and could of course be applied to a regular arrangement of carbon atoms just as well as silicon for example.

If we were to describe an infinite 1D chain of carbon atoms, a similar description would be reached.

This is precisely the approach which resulted in the Nobel Prize in Chemistry in 2000 "for the discovery and development of conductive polymers".

In the field of semiconducting molecules and polymers however we do not have a quasiinfinite arrangement of regularly spaced atoms. A given molecule with some degree of conjugation could be thought of as a truncated version of the series described above, where the strong covalent interaction between atoms will have begun to establish some band-like structure to the allowed electronic transitions.
2.2.1 Electrons on an isolated carbon atom

If we start by considering an isolated carbon atom, there are 4 electrons in the outer, unfilled shell. The electronic configuration in the ground state is $(1s)^2 (2s)^2 (2p)^2$.



Figure 2.1 electrons on a carbon atom

Figure 2.1 shows the configuration of the outer electrons in an isolated carbon atom¹⁰

2.2.2 Sigma and pi bonding

The different types of atomic bond are described by their symmetry. These are called sigma and pi bonding.

2.2.2.1 Sigma bonding

Sigma bonding has cylindrical symmetry on the axis of the two bonded atoms. This can be S to S, P to P, or P to S or S to P if bonded end on.



Figure 2.2 sigma bonding

Figure 2.2 shows the configurations possible for sigma bonding between p and s orbitals.

Sigma bonds: "Sigma bonds are relatively stronger when compared with pi bonds. Hence, pi bonds are easily broken while sigma bonds aren't. There can be only one sigma bond between two particular atoms in a molecule. But there can be a maximum of two pi bonds between two atoms in a molecule." ¹¹

2.2.2.2 Pi bonding

Pi orbital as antisymmetric, and named as they share the antisymmetric distribution of the P orbital.

These can only form from P to P side on, or D to D side on.



Figure 2.3 pi bonding

Figure 2.3 shows the bonding configuration for pi bonding of p orbitals.

Pi bonds: "A Pi bond is a covalent bond which is formed by the side-to-side overlap of two atomic orbitals. The atomic orbital combinations can be p_x-p_x or p_y-p_y . Similar to the sigma bonding," ¹¹

How close the electron density is to the nuclei determines how large the energy splitting is. Since in the sigma bond, the electron density is averaged around the axis directly between the two bonded atoms, there is more interaction with the nuclear potential.

This results in Sigma orbitals having larger energy splitting that Pi, as they are out of plane, and the average electron density interacts less with the nucleus.

2.2.3 Hybrid orbitals in molecules

The carbon atom can then form bonds with different involvement of 2S and 2P orbitals in different hybridised orbitals with different geometries.



Figure 2.4 bonding in ethane

Figure 2.4 shows the case of the molecule ethane, where a carbon double bond is formed and two additional hydrogens are bonded to each carbon. ¹² The carbon double bond consists of a sigma bond directly between the two carbons and a pi bond out of plane with this.

For the purposes of organic electronics, it is the SP2 hybridisation which is of interest. This is formed by mixing of 2s, 2px and 2py orbitals, resulting in a sigma bond with the next atom. The electron in the 2pz is then free to form a pi bond with the adjacent carbon atom.

In the case of the sigma bond in SP3 carbon, the electron is being shared in the covalent bond which holds the material together. This means that excitation of this electron results in the carbon-carbon bond being broken, and irreversible material degradation.

The energy of this transition typically lies in the region of ~2-3 eV, or the energy of UV light, and is the mechanism by which plastics bleach in sunlight. The σ to σ^* transition then does not bring any desirable transitions into this system, and the semiconducting properties in a stable system must result from the π to π^* transitions.



Figure 2.5 carbon bond hybridisation

Figure 2.5 shows the hybridisation of the bonds between the carbon atoms. The remaining sp2 orbitals are bonded to the hydrogens not shown here.

For my purposes, the key point here is that because of the difference in energy, this means excitation of electrons in carbon based systems is usually π to π^* , and σ is involved in bonding only.

This means that electronic properties and excitation in organic system occurs from the π to π^* transitions.

2.2.4 Conjugation; alternating single-double bonds

Between carbon atoms, single (σ only) and double (σ and π) bonds are possible.

If there is a system where over some extended system of carbon atoms, there are alternating single and double bonds, the overlap of subsequent π orbitals allows long range delocalisation of an electron along the carbon atoms. This is fundamentally what allows conductive or semiconductive properties in organic systems.

Conjugated aromatic systems of alternating π and σ bonds could be thought of as simply ensuring that there are enough π bonded electrons present in the system to give rise to the intrinsic semiconducting properties within the sub band of π to π^* transitions.

Structures made from aromatic rings, and conjugated backbones are the main building blocks of all molecules of organic electronic applications, and other groups may be added to tune the energy levels.

For my purposes, this means that all materials used need to contain these alternating singledouble bonds.

2.2.5 Modification via chemical alteration rather than doping

Since the "band gap" in organic molecules is a result of the molecular orbitals rather than any long range order as is the case for crystalline materials, molecular systems can be thought of as an intrinsic, rather than extrinsic semiconductor, as the constituent elements already have some degree of semiconducting behaviour present.

This introduces a number of appreciable differences in the ways we are able to process and tune the behaviour of organic semiconducting materials. One way in which they differ from their inorganic counterparts is that they are much less sensitive to long range disorder, and can be processed via methods which result in varied morphologies without losing their intrinsic semiconducting behaviour. In conventional inorganic semiconductors, this kind of disruption in the periodicity which the Bloch treatment relies on results in drastic changes in the energy levels in the system, hence highly regular single crystal domains are required.

This also means that organic semiconductors are less sensitive to defects than crystalline semiconductors, which is positive in that they can be processed from solution or thermal evaporation with a large degree of flexibility of interface quality and deposition conditions.

The converse of this is that this renders organic semiconductors less sensitive to doping in a desirable capacity, and so some of the synthetic handles for tuning properties used in inorganic systems cannot be utilised, and the properties of the material depend on molecular design and the dipole of the environment. Doping on the part per million regime, or even parts per billion regime is suitable for controlling conductivity in Silicon, but this degree of dilution would not be sufficient to meaningfully impact the behaviour of organic systems, as the vast majority of molecules would have no interaction with a dopant atom.

To achieve modification in the properties of organic systems, chemical modification of the molecule or variation in its local environment is required. In this thesis I introduce a new molecular motif, and explore the effect of a number of modifications to it.

2.3 Excited states in organic materials

Now that we have established the idea of Molecular Orbitals, we can discuss the system in terms of their ground state occupancy and excited state occupancy.

The ground state configuration is referred to as the Highest Occupied Molecular Orbital (HOMO) and the next available energy level the Lowest Unoccupied Molecular Orbital (LUMO).

In addition to considering these levels as occupied by an electron, it is useful to treat the absence of an electron in a position which would have been occupied in the ground state as a positively charged quasi particle, or a "hole".

There are then three ways in which an "excited state" can exist on a given molecule.

- An electron can be added into the LUMO of the molecules. This excited state is net negative.
- A hole can be added into the HOMO (analogous to an electron being stripped from the HOMO). This excited state is net positive.
- Both of the above can occur, such that an additional electron is in the LUMO and an additional hole is in the HOMO. This results in a bound net neutral excitation

This then can be grouped into 2 categories which correspond to net charged and net neutral excited states, known as polarons or excitons respectively.

2.3.1 The polaron

Polarons are net charged, which occurs by gaining or losing an electron from the ground state configuration. From a chemistry perspective this is oxidation (loss of an electron) and reduction (gain of an electron).

If this can happen reversibly, the materials should remain chemically stable in the excited state. If these oxidation and reduction processes are not reversible, then the molecule is prone to undergo chemical change in the excited state. This information is accessed by cyclic voltammetry.

For electrical excitation, electrons and holes are separately injected from the anode and cathode, and if they meet on a given molecule, then an exciton is formed. This represents the regime in which excitations form in OLEDs when a bias it applied. Polarons are the charge carriers in both OLED and OPV.

2.3.2 The exciton

Excitons are net neutral quasi particles consisting of an additional hole and an electron which are bound by Coulombic attraction. This can occur on an individual or across adjacent molecules.

These are relevant in organic materials as the magnitude of the electric field induced is smaller than for inorganic materials.

Due to the considerably lower dielectric in organic materials, the coulombic attraction between the electron which has been excited to the π^* orbital and the 'hole' left in the π orbital is strong enough to form a bound state, or 'exciton'.

Crystalline silicon for example has a relative dielectric constant (ɛr) of 12, whereas for a typical organic semiconductor this is in the range of 2-4.¹³

The length scale over which this quasi particle is bound is governed by the strength of charge screening in the material.

In materials of high dielectric constant, excitons form with very low binding energy of the order of 0.01eV. This results in the radius being larger than the lattice spacing of the crystal. These were described in 1937 by G. Wannier and are referred to as Wannier-Mott excitons ¹⁴. These and are not considered in any of the material systems explored in this thesis.

For organic materials with a much lower dielectric constant, we have a quasi-particle localised on the order of several nm. This class of bound excitation was described by J. Frenkel in 1931, and are referred to as Frenkel exciton ¹⁵. In this thesis, wherever the word "exciton" is used, it refers to a Frenkel exciton.

One of the key differences between organic and inorganic electronics is a direct consequence of this. Since this excited state is a quasi-particle made up of a bound electron and hole, there are 4 possible spin configurations on which an exciton can form.

A quantum mechanical description of the spin quantum number has the allowed values of either $\frac{1}{2}$ or $\frac{-1}{2}$ assigned as "spin-down" or "spin-up". When an electron is excited, this results in 2 unpaired electrons for which there are then 4 possible arrangements for if the electron in the HOMO and LUMO are parallel, or anti-parallel.



Figure 2.6 singlet and triplet spin configuration

Figure 2.6 shows the arrangements of the spin orbital angular momentum which result in singlet and triplet excitons. ¹⁶

Three of the possible states formed have a spin angular momentum quantum number of S=1. These are referred to as triplet excitons.

The remaining configuration with antiparallel spins results in an angular momentum quantum number of S=0. This state is labelled as the singlet exciton.

Since there are 3 times more ways for a triplet to form than a singlet, this results in singlets and triplets forming in a ratio of 1:3 if spins are injected randomly.

Since angular momentum is a quantity which is conserved, this becomes one of the factors governing which transitions between which states are allowed. Most materials have a ground state which is singlet in character, and so unless there is a mechanism by which angular momentum can be changed; the ground state can only couple radiatively to excited states which are also of singlet character.

When the spin angular momentum of a state changes due to external influences, this results in excited states no longer of pure singlet or triplet character, and some mixing of the wavefunction becomes allowable. The first order singlet-triplet mixing coefficient (λ).

$$\lambda = \frac{<\hat{H}_{SOC}>}{\Delta E_{ST}}$$

The numerator represents the spin orbit coupling strength, and the denominator represents the exchange energy. These two contributions separately represent the existing mechanisms for excited state spin conversion from triplet to singlet states either by utilising large spin orbit coupling by introducing a heavy atom (phosphorescence) or by minimising the exchange energy by spatial separation of the excited state wavefunction (TADF).

These two existing methods aimed to increase λ by tuning these parameters separately, however the CMA class of molecules incorporates both the influence of a heavy metal atom with spatial separation of the HOMO-LUMO wavefunctions, and so must be considered as the intersection of both phosphorescent and organic TADF principles.

2.3.3 Charge Transfer excitation

The spatial distribution of the excitation also plays an important role in the behaviour of the excited state. This can either occur between different parts of a given molecule (intramolecular charge transfer), where electron density transferred from one region known as the "electron donor" to another region known as the "electron acceptor", or between adjacent molecules of different electron withdrawing/donating strength (intermolecular charge transfer). ¹⁷

This principle is highly relevant to the materials discussed in this thesis, as intramolecular charge transfer states are utilised to control the energy levels of the singlet and triplet excited states, and play a key role in excited state spin control.

2.3.4 Optical excitation

Under optical excitation, both a hole in the HOMO and an electron in the LUMO are created together when an electron is promoted to a higher lying level when a photon is absorbed.

Whilst a photon is a spin 1 particle, the electric dipole operator does not change spin in LS coupling, so the selection rules for absorption set the conditions that:

$$\Delta S = 0$$

This means that a photon can only be absorbed or emitted between states of the same angular momentum, as it cannot impart or change angular momentum. This means that all optical transitions to/from the ground state involve higher lying singlet states for the vast majority of materials, including all described in this thesis.

There are rare exceptions to this rule, like molecular oxygen, where the ground state is triplet in character. ¹⁸ This means that the presence of molecular oxygen can act as a quencher for triplet excitations.



Figure 2.7 absorption of atomic and molecular oxygen

Figure 2.7 shows the absorption spectra of atomic versus molecular oxygen. Molecular oxygen has a triplet ground state, which is significant as it is able to quench triplet excited states on molecules. ¹⁹

A large portion of the experimental work presented in this thesis deals with optical spectroscopic characterisation of the states and transitions available in materials.

These rules provide the context for meaningfully interpreting spectroscopic data, and which states and transitions we are able to probe with absorption and photoluminescence techniques.

For optical excitation, initially 100% of excitons form in a singlet configuration. Any subsequent population of triplet states must occur via intersystem crossing from the S1 state.

2.3.5 Electrical injection

When charges are injected electrically rather than being formed from photoexcitation, we see a different picture. Since the electron and hole injected from the anode and cathode have not been formed together, their spin states are independent.

This means that when they meet and form an excitation on a given molecule/interface, that there is a random distribution of spin orientation, and so singlet excitons and triplet excitons form in the ratio of 1:3, or 25% singlet and 75% triplet.

This is the origin of one of the largest single hurdles to be overcome in the field of organic electronics. A photon can only be absorbed or emitted by a transition between two states with the same angular momentum, which is almost always of singlet character. The implication is then that three quarters of excitations generated electrically are forbidden from releasing their energy via emission of a photon, and would be lost as heat.

In the absence of additional processes facilitating change in angular momentum, this imposes an upper limit of 25% on the theoretical maximum IQE of an OLED.

2.3.6 Excitation in devices

The two main groups of devices based on light-charge interactions of OLEDs and OPVs could then be thought of in terms of the nature of the excited states, and how effectively they interconvert.

In an OPV, initially an exciton is formed by the absorption of a photon, and for the device to function; the electron and hole must separate, and be extracted by the anode and the cathode as polarons. This is achieved by designing a system where intermolecular excitation occurs as a bulk interface, and the electron and hole are then mobile enough to be extracted before recombining.

For an OLED, the reverse occurs. Polarons are injected from the anode and cathode and flow through the device, which can be thought of as an electron and a hole current. For an OLED to function, these must meet on a molecule and form an exciton, which is then able to recombine, releasing a photon. These considerations determine the energy levels, interfaces and layer thicknesses required to either inject charges, or ensure recombination occurs in the emissive layer.

2.3.7 Exchange energy

From the Pauli Exclusion Principle we can say that electrons with opposite spins are more likely to be found in the same region of space. This results from the wave functions of indistinguishable particles following the law of exchange symmetry. In the case of electrons, which are Fermions, this results in Pauli repulsion, which increases the expectation value of the distance between identical particles. In the context of singlet and triplet excitons, this means that on average, the electron which is excited has a different probability distribution relative to the other electron in the pair not excited so a different degree of coulombic repulsion occurs on average, which raises the energy of the state. This energy will be larger if the electron has a higher probability of being found near the other electron and thus experiences a greater repulsion.

For pure triplet configurations, they CAN'T be found in the same region of space, meaning the average occupancy near the unpaired electron is less than for the singlet, and thus a lesser amount of Coulomb repulsion.

The singlet is then more likely to be found in same place as the unpaired electron, so the repulsion is larger, resulting in a higher energy than the triplet exciton.

The electron exchange energy (J) is the difference between the singlet and triplet as a result of this.

This depends on the spatial overlap of the HOMO and LUMO wavefunctions (ϕ HOMO and ϕ LUMO), at positions r1 and r2, and is defined by the exchange integral ²⁰ given by equation {1}:

$$J = \iint \varphi HOMO(\bar{r}1)\varphi LUMO(\bar{r}2) \frac{1}{|\bar{r}2 - \bar{r}1|} \varphi HOMO(\bar{r}2)\varphi LUMO(\bar{r}1)d\bar{r}1d\bar{r}2$$

{1}

J is then sensitive to the separation of the charges, as the $\frac{1}{|\bar{r}2-\bar{r}1|}$ term tends to zero for distant electrons, as distant charges exert negligible Coulombic repulsion on each other.

In the context of excitations, this then means that the way to reduce the exchange energy is spatial separation of the HOMO and LUMO wavefunctions, as is achieved in either intra- or intermolecular charger transfer excitations.

This is the key concept to bear in mind for the purposes of this thesis, as for reverse intersystem crossing to occur, the singlet state must be close enough to the triplet state for it to be explored with the distribution of thermal energy at room temperature.

In the case of the CMA molecules, the HOMO and LUMO wavefunctions are spatially separated on the donor and acceptor moieties separated by the metal bridge, where wavefunction overlaps in the presence of the metal atom.

2.4 Mechanisms of changing spin angular momentum

For the orbital angular momentum to change, something must act to disrupt it.

This can result from the electron interacting with external fields. In the case of Spin Orbit Coupling, the electron experiences the effect of the electric field from the nucleus.

In the case of hyperfine interactions, the electron experience effect of the magnetic field from the nucleus.

2.4.1 Spin orbit coupling

Spin orbit coupling is an interaction which results from the motion of the electron in the electric field around the nucleus of an atom.

Given that the electron is in motion in a static electric field, it will experience an effective magnetic field effect due to the relativistic shift of the electric field.

This magnetic field acts do disrupt the orbital angular momentum, and thus can cause the spin of an excited state to process

This change in angular momentum can be thought of as the spin angular momentum coupling with the orbital angular momentum. Such that a state initially with singlet character could then have some element of triplet character.

This can be more concisely defined as:

"The interaction of the electron spin magnetic moment with the magnetic moment due to the orbital motion of the electron. One consequence of spin-orbit coupling is the mixing of zero-order states of different multiplicity."²¹ If this is calculated for the case of the Hydrogen atom, then the spin-orbit coupling Hamiltonian, \hat{H}_{SOC} is given by equation {2}:

$$\widehat{H}_{SOC} = \frac{Zq^2}{2m^2c^2r^3}\widehat{L}.\widehat{S}$$

{2}

Where Z is the atomic number, q is the electronic charge, m is electron mass, c is the speed of light in vacuum, \hat{L} is the orbital angular momentum operator and \hat{S} is the spin operator.

In this simplest case of the hydrogen atom where this can be solved analytically, the relationship that Z^3 is proportional to r^{-3} drops out fairly intuitively, as the size of the nucleus is proportional to the radius of the orbit is a spherical case.

This yields the result that \widehat{H}_{SOC} is expected to scale with Z⁴ in hydrogenic systems.

This approximation does not hold for larger atoms where the electronic orbitals cease to be spherical, and the nucleus itself also is not so well defined.

Further complexity arises for multi electron systems as outer electrons experience some screening of the nuclear potential by other electrons in lower shells.

Computational models of spin orbit coupling strength as a function of atomic number show that this is far more complex than a Z^4 dependence, however it should be noted that within a given column of the periodic table, that there is a dependence on Z, somewhere between Z^2 and Z^4 .



Figure 2.8 spin orbit coupling strength

Figure 2.8 shows calculations of the spin orbit coupling as a function of atomic number Z. For elements in a given row of the periodic table SOC scales with Z suggesting that only core electrons contribute to screening the nucleus and the valence electron experiences minimal screening from other electrons in its shell. ^{22 23}

For the purposes of the materials studied in this thesis, the key result is that for a given atom, the spin orbit coupling strength in a given group of the periodic table should be expected to increase with atomic number. This will be discussed more in chapter 5.

2.4.2 Hyperfine interaction

The effect of the hyperfine interaction can be thought of as electrons in different positions around the nucleus being caused to precess at different rates due to differences in the local magnetic field they experience from the nucleus. Like SOC, this is a highly material dependent effect.

Current calculations suggest that in the case of singlet and triplet excited states in organic materials, that the effect of the hyperfine interaction on mixing of spin singlet and triplet states much weaker than SOC, and so cannot alone explain the behaviours observed.

"However, the hyperfine coupling constants are very small, usually in the range of 10^{-4} meV, and it therefore also appears highly unlikely that such coupling accounts for these recent observations."²⁴

This effect is included for the sake of completeness, and is not considered in the materials systems described in this thesis.

2.5 Excited states: absorption, emission and non-radiative decay

Before discussing individual spectroscopic techniques, it is important to establish what states, processes and transitions we set out to probe in spectroscopic measurements. No individual technique is sensitive to all possible radiative and non-radiative transitions within a material, and even for an "ideal" measurement, there will be intrinsic limits on the conclusions which can be drawn directly from any given data set.

2.5.1 States and transitions of isolated systems

If we take a simple energy diagram of an isolated system shown below in figure 2.9, we can make the generalisation that there are two main classes of transition. There are excitation events (dashed lines) and there are relaxation events (solid lines).

A further subdivision which is convenient for the materials discussed in this thesis is to divide these into processes which are allowed in a system without a mechanism to change spin angular momentum (green lines) and transitions which can only occur when spin can be changed by additional processes (red lines).

Radiationless relaxation through vibrational modes are displayed in blue, with transitions between higher excited states which could still result in emission as single lines, and terminal transitions to the ground state as shaded arrows.



Figure 2.9 transitions of an isolated molecule

Figure 2.9 shows the transitions available to an isolated molecular system during and after photoexcitation: 1) Photoexcitation from the singlet ground state (S0) to lowest lying singlet excited state (S1). 2) Photoexcitation from S0 to higher lying singlet excited states (S2...N). 3) Fluorescence from the S1 to the S0 ground state. 4) Photoexcitation fromS1 to S2...N. 5) Inter System Crossing (ISC) from S1 to the lowest lying triplet excited state (T1).
6) Photoexcitation from T1 to higher lying triplet excited states (T2...N).7) Direct phosphorescence from Locally Excited T1 (3LE) to S0. 8) Direct phosphorescence from the lowest lying Charge Transfer triplet state (3CT) to S0 if 3CT is lower in energy than 3LE.9) Reverse Inter System Crossing(RISC) from T1 to S1.

10) Thermally Activated Delayed Fluorescence (TADF) from lowest lying Charge Transfer singlet (1CT) to S0.

The definition of internal conversion according to the IUPAC compendium of chemical terminology is:

"A photophysical process. An isoenergetic radiationless transition between two electronic states of the same multiplicity. When the transition results in a vibrationally excited molecular entity in the lower electronic state, this usually undergoes deactivation to its lowest vibrational level, provided the final state is not unstable to dissociation."²⁵

Intersystem crossing is similarly defined as:

"A photophysical process. An isoenergetic radiationless transition between two electronic states having different multiplicities. It often results in a vibrationally excited molecular entity in the lower electronic state, which then usually deactivates to its lowest vibrational level."²⁶

It could thus be argued, if one was feeling especially pedantic, that there is no such process as Reverse Inter System Crossing (RISC), as "intersystem crossing" describes isoenergetic transitions between states of both singlet and triplet character in either direction.

Since I am not by nature especially pedantic, and for the purposes of this thesis using terminology which is compatible with the literature, I will use the term "ISC" to refer to an isoenergetic transition from S1 to some higher vibrational mode of the triplet manifold, followed by rapid radiationless relaxation to the T1 state, and I will use the term "RISC" to refer to an excitation in the T1/ 3CT state using thermal energy to explore higher vibrational levels such that it can then undergo an isoenergetic transfer into part of the S1/1CT.

2.5.2 Additional transitions in non-isolated systems

In addition to the intramolecular transitions of an isolated molecule, in systems where optical and electronic transitions are not restricted to *intra*molecular transitions, but *inter*molecular processes are possible, additional transitions must be considered.

For an ensemble where a variety of conformers is present, each individual molecule would not have identical energies and transitions available to it. In this case it would be expected that there would be a broadening of the transitions both in absorption and emission. Another possibility is that absorption and emission events can occur between adjoining molecules via intermolecular transitions.

Depending on whether the adjoining molecules are identical, or different molecules, this can be grouped into aggregate behaviour, or interface states.

Aggregate emission results from delocalisation across pi stacking, and is characteristically red shifted, long lived, and low intensity. Often excitations which have delocalised in this way do not emit, and this results in "concentration quenching" when a material in a solid film has a considerably lower PLQE that when it is dispersed in a host or solution. This is a feature which necessitates a host material for many emitters to function well in devices, adding complexity to the stack architecture and parameter space for optimisation.

Emission from "interface states" arises when the exciton is able to delocalise across neighbouring molecules, and can transition between the HOMO of one molecule and the LUMO of an adjoining molecule.

This type of behaviour is built into some systems intentionally, like bulk heterojunctions of Donor (D) and Acceptor (A) molecules, and is replicated on individual molecules for TADF systems using D-A-D style architectures.

These configurations are avoided in the data presented in this thesis where possible by dispersing samples in wide bandgap polymer hosts for spectroscopic measurement, or by hosting in semiconducting host which will inject excitation onto the dopant for studying device like environments

2.5.3 Mechanisms for exciton transfer

For the cases discussed so far, an excitation emits from the molecule/s on which it formed, however in device applications, electrons and holes are injected, transport layers and host materials are used, and emission from the dopant relies on resonant energy transfer from the host.

There are two main processes for energy transfers which apply to excitons.

Triplet and singlet excitons are able to migrate over short distances via a process called Dexter transfer. Dexter transfer typically occurs over ~10 Angstroms.

Singlet excitons are able to migrate over longer distances by a process called Forster Resonant Energy Transfer. FRET occurs over distances up to 10 nm.

The same process which is used to transfer excitations from a host matrix to a dopant molecule can also be relevant in a film of a single material if there is a distribution of lower energy sites present in the film, like defect sites, aggregates, or lower energy conformers of a material. In this case, the same effect may provide a mechanism for quenching luminescence if these lower energy sites are non-emissive, and act as trap states. This is another factor in concentration quenching.

2.5.3.1 Dexter transfer

Dexter transfer occurs via direct transfer of an excited state electron. This requires the second molecule to be close, typically a few nm.



Figure 2.10 Dexter energy transfer

Figure 2.10 shows a schematic of Dexter transfer, with direct transfer of an excited state electron for a ground state electron by hopping ²⁷

This is characteristically short range, and is not considered in this thesis for selection of host materials or energetic migration within solid films.

Hypothetically speaking, in the case of a material system with a large stokes shift, it could be that this is the only available mechanism to transfer singlet excitons if there is little or no overlap in the absorption and emission bands of a given material, however this is not realised in the material systems studied herein.

2.5.3.2 Forster Resonant Energy Transfer

Forster resonance energy transfer is a transfer of energy between two molecules by dipoledipole coupling. This is distinct to Dexter transfer, where the electrons themselves move. FRET can occur over ~10nm.



Figure 2.11 Forster energy transfer

Figure 2.11 shows a schematic for Forster transfer, where the electron relaxes on the donor molecule, and transfers the energy to a nearby molecule which has a resonant energy level via a virtual photon. ²⁸

This is sensitive to the distance between donor and acceptor molecules, and for energy transfer to be effective from a host material into an OLED dopant, the dopant concentration must be tuned to maximise FRET.

The overlap between the donor emission spectrum and the acceptor absorption spectrum determine the efficiency which FRET can occur by, and makes sense if the energy is thought of as being transmitted by a "virtual photon"



Figure 2.12 FRET overlap

Figure 2.12 shows a schematic of the absorption and emission spectra of the two materials involved in FRET. The overlap of the host/donor emission with the absorption of the guest/acceptor determines how resonant the transition is. ²⁸

Despite singlet excitons being able to undergo both Dexter and Forster transfer; because the length scale for FRET is about one order of magnitude larger, this is the dominant energy transfer process.

There is clearly a large amount of energy lost via 2 stokes shifts between initially exciting the donor/host material and emission from the acceptor/dopant chromophore. This is undesirable for high efficiency systems, and so materials with do not require a host are appealing.

For the materials discussed in this thesis, FRET is the dominant form of energy transfer considered.

2.6 Measurement of excited state transitions

Within this framework, we can consider spectroscopic measurements of these transitions broadly into steady state and time resolved techniques. Steady state measurements providing a measure of the time average, and time resolved measurements for population dynamics.

2.6.1 Absorption

If the HOMO –LUMO energy gap is considered to function like the bandgap of our semiconductor, then it makes sense that this corresponds to the absorption onset.

2.6.1.1 Steady state UV-Vis absorption

Steady state absorption spectra can be considered as a map of available excited states (usually singlet), their respective energy above the ground state and the corresponding oscillator strength of the transition. This is then an incomplete picture of the allowed excited states of a material, and only shows us the singlet excited states, and the respective oscillator strength with transitions to the ground state. This also does not provide any information about the absolute energy of the state relative to the vacuum level, but only about the difference between the ground state and a given excited state. This will be discussed in detail in the Experimental Methods Chapter.

Triplet excited states are not able to be directly populated by optical excitation and thus are not able to be probed in this way. For a triplet excited state to form after optical excitation, there must exist some mechanism for a change of orbital angular momentum in the system. These processes rely on some procession of the angular momentum, and so usually take longer to happen.

2.6.1.2 Time resolved (transient) absorption

In time resolved transient absorption spectroscopy [TA] we are able to probe the transitions between singlet states, but also absorptive transitions between higher lying triplet states can be probed without violating spin conservation once an excited triplet state has been formed by some process other than direct excitation from the ground state by an absorbed photon which allowed a spin flip and the T1 state to form.

The first signature seen in a TA map will correspond to transitions from an excited singlet state which formed directly from the pump pulse.

2.6.2 Emission

Emission occurs from the lowest energy state of a given multiplicity. If an electron is promoted to a higher lying excited state, it rapidly relaxes to the lowest energy excited state of the same spin configuration. This process is called internal conversion where excess energy is lost vibrationally. Emission then only tends to occur from the lowest energy state. This is summed up by Kasha's rule:

*"Polyatomic molecular entities luminesce with appreciable yield only from the lowest excited state of a given multiplicity."*²⁹

2.6.2.1 Direct emission processes

Once an electron is in an excited state, it can either relax by losing the excess energy to vibrational modes of the molecule, or by emission of a photon. For OLED applications this second pathway is desired, as vibrational losses manifest as waste heat and limit the efficiency of the device.

Excitations can either form in singlet or triplet configuration, and emission directly from an excited singlet or triplet state to the singlet ground state is known as fluorescence or phosphorescence respectively.

2.6.2.1.1 Fluorescence

Before discussing devices based on fluorescent materials, it is helpful to clarify what is meant by fluorescence, and quantify the ways in which I will use the term for the purposes of this thesis.



Figure 2.13 fluorescence energy diagram

Figure 2.13 shows an energy level diagram for photo-excitation and fluorescence. The photo-excited singlet in the S1 state either couples radiatively back to the S0 ground state or is decays via non-radiative vibrational pathways.

The IUPAC defines fluorescence as:

"Luminescence which occurs essentially only during the irradiation of a substance by electromagnetic radiation"³⁰

If one was to apply this definition strictly to lighting applications, it would clearly be inappropriate or inadequate to describe emission from an electrically driven system. In this thesis, I will use the term "fluorescence/ fluorescent" in the following manner;

Firstly, in the context of optically excited spectroscopy, I use "fluorescence" to refer to radiation from the recombination of a correlated electron and hole generated on a given molecule subsequent to photoexcitation as per the above definition.

Secondly, in the context of emission from OLED devices, I will more loosely use "fluorescent" to refer to emission from the recombination of uncorrelated electrons and holes which have formed a singlet exciton on a given fluorescent molecule after being injected into the system by an applied bias.

.Since the emission trajectory is identical once the exciton is formed for any given spin configuration the phrase "fluorescent device" is sufficiently unambiguous and captures the physics desired for my purposes.

This definition of "fluorescence" does not seem to strictly exclude emission from triplet excited states, however I take it as implicit in "essentially only during irradiation" that this refers to *fast*, and therefore allowed, direct transitions from the same population initially excited by irradiation.

Since photons are a particle with spin=1, however optical excitation is between states of the same character (ds=0). Most materials have a singlet ground state, thus the spin of the initially excited population is singlet, and subsequent direct radiative transitions are between states of the same, singlet, character.

This is the key point for my purposes; that in either the optically excited or electrically pumped system; that I am referring to emission of photons which occurs via fast, direct, allowed transitions between states of similar, singlet, spin character without any additional transitions to intermediate states, typically on the order of nanoseconds.

2.6.2.1.2 Phosphorescence

Similarly to fluorescent materials, phosphorescence also describes radiation from a set of transitions between states which are material specific, and thus the energy and structure of the emission spectrum are defined by the excited state transitions in a given material rather than other parameters like temperature.



Figure 2.14 phosphorescence energy diagram

Figure 2.14 shows an energy level diagram for photo-excitation in a system where ISC can occur, followed by phosphorescence from the T1 state. Since the T1 state is populated much longer than S1 this will be the dominant contribution to non-radiative losses.

For this to occur, spin orbit coupling effects are required to change the orbital angular momentum of the excitation, allowing some mixing of the singlet and triplet excited states as described in section 1.4.1.

The IUPAC definition of Phosphorescence is:

"From a phenomenological point of view, the term has been used to describe longlived luminescence. In mechanistic photochemistry, the term designates luminescence involving change in spin multiplicity, typically from triplet to singlet or vice versa." ³¹

By this definition, it could be argued that emission from a CT triplet state as in TADF is also "phosphorescent", as it is "long-lived", and the process involves a spin flip.

For the sake of clarity within this thesis when referring to the mechanisms and pathways contributing to delayed emission, I wish to differentiate between emission from locally excited triplet states via direct SOC to the ground state, emission from charge transfer states with triplet character directly to the ground state and emission from a triplet charge transfer state via a singlet excited state.

I will use the term "direct phosphorescence" when I refer to transitions from a locally excited triplet state directly to a singlet ground state, where emission is characteristically structured, long lived, and reduces in intensity with increased temperature.

I will use the term "CT phosphorescence" when the lowest lying triplet state couples directly to the ground state is part of the CT manifold rather than the locally excited triplet, where we see broad, unstructured emission retained even at low temperature, and a temperature insensitive radiative rate is seen below a given temperature.

I will use the term "TADF" for emission originating in a triplet state which then emits via mixing with some singlet excited state, and the intensity of the delayed emission increases with temperature, and the lifetimes become more rapid with increased temperature above some intrinsic rate retained at low temperature.
2.6.2.2 Indirect emission processes

The emission process does not have to be a direct coupling between the excited state an exciton is in and the ground state.

It is possible to have a change of spin character in the excited state, like intersystem crossing from a singlet to a triplet, or reverse intersystem from a triplet to a singlet.

2.6.2.2.1 Thermally Activated Delayed Fluorescence (TADF)

Another more recent approach to harvesting triplet excitations for emission in organic materials is Thermally Activated Delayed Fluorescence (TADF). This term was coined in 2012 by Uoyama et al. and is a rebranding of an effect reported in 1961 in eosin, originally known as e-type delayed fluorescence ^{32 33}.

In TADF, the objective is to allow triplet excitons to undergo a spin flip in the excited state so that they can then emit through the "normal" fluorescent pathway.

As discussed, triplet energy levels are lower than their singlet counterpart in molecular systems which impose additional conditions for TADF to function.

As well as needing some mechanism by which spin orbital angular momentum is changed, that the singlet and triplet energy levels must be close enough in energy to be accessible. At room temperature, thermal energy is ~25meV.



Figure 2.15 TADF energy diagram

Figure 2.15 shows an energy level diagram for optical excitation of a system able to undergo TADF. Excitations promote an electron into the S1 state, which subsequently is able to undergo ISC to the T1 state. RISC then allows emission sometime later via the singlet manifold.

For most applications, this provides an energetic threshold of the exchange energy J being sufficiently small that at room temperature reverse intersystem crossing (RISC) is allowed.

The exchange energy can be thought of as how far "uphill" in energy the S1 state is with respect to the T1 state, and thus both a mechanism for changing spin angular momentum AND sufficient thermal energy to occupy the higher energy state are both required for RISC.

This is distinct to phosphorescent materials, where rapid intersystem crossing from the S1 to lower lying T1 states is possible, but once in the T1 state, the exchange energy is too large, and excitations remain in the triplet state until they either emit, or are lost by some other mechanism.

The rate of reverse intersystem crossing (K_{RISC}) is then dependent on 2 main factors.

Firstly, that the singlet-triplet energy gap is small enough that at room temperature there is sufficient energy to overcome the exchange energy shown in equation {3}:

$$K_{RISC} \propto exp^{\frac{\Delta E_{ST}}{k_B T}}$$

{3}

This allows S1 and T1 to be close enough for thermal access.

This point can be addressed by considering the exchange energy, J.

As J is sensitive to the separation of the charges in the excited state, molecules for TADF aim to have good spatial separation of the HOMO –LUMO wavefunction.

This is achieved by selecting molecular structures with well-defined electron donating and accepting moieties. This can be achieved through various architectures, often including multiple donor moieties, but the principle is the same.

Unfortunately, as the saying goes, "there is no such thing as a free lunch", and by increasing the separation of the HOMO – LUMO wavefunctions to achieve reduction of the exchange energy, the oscillator strength of transitions between the two states is reduced considerably.

The extreme of this would be "charge separation" where distant electrons are able to have exactly the same energy, but do not interact with each other at all.

Geometric changes can result in the structure of the molecule like the donor and acceptor moieties being out of plane with each other, and other twists or deformations can also contribute to breaking the symmetry of the orbitals to facilitate otherwise forbidden transitions. ³⁴

The singlet-triplet mixing coefficient (λ) however also includes a spin orbit coupling term as the remaining aspect of achieving RISC is a change in spin angular momentum of the excited state as shown in equation {4}.

$$\lambda \propto \frac{\widehat{H}so}{\Delta EST} = \frac{\langle S1 | \widehat{H}so | T1 \rangle}{\Delta EST}$$

{4}

So we can say also that:

$$K_{RISC} \propto S. O. C.$$

 $K_{RISC} = [k. \langle S1 | \hat{H} so | T1 \rangle] * e - \frac{EA}{KT}$

{5}

This has provided two sets of design rules for designing TADF materials.

The first is to achieve singlet-triplet mixing entirely by HOMO-LUMO wavefunction separation, without incorporating heavier elements. (Fully Organic TADF)

The second is to try and address both these points, and have systems where in addition to spatial separation of the HOMO-LUMO wavefunctions, spin mixing is also encouraged by the inclusion of heavier atoms (Organo-Metallic TADF). This second approach is utilised in the material systems described in this thesis.

Due to the nature of the CT states involved in this process, TADF materials emit with characteristically broad, unstructured PL. Whilst this can allow more efficient, or more rapid emission from excited triplet populations, this remains an issue for display application where high colour purity is desirable.

It should be noted that most materials which display CT emission are not TADF emitters, and in the absence of a mechanism for RISC, having a lower lying locally excited triplet state acts as a sink for CT excitations, and will non-radiatively quench excitation.

2.6.2.2.2 Additional sources of delayed emission

It is worth noting that there are numerous ways in which delayed emission can be generated apart from phosphorescence in both optically and electrically excited samples. Delayed PL or delayed EL alone is insufficient evidence for TADF (E-type delayed fluorescence).

In photo-excited cases there are three:

P-type delayed fluorescence:

"The process in which the first excited singlet state is populated by interaction of two molecules in the triplet state (triplet-triplet annihilation) thus producing one molecule in the excited singlet state. In this bi-photonic process the lifetime of delayed fluorescence is half the value of the concomitant phosphorescence." ³⁵

TTA requires 2 photons, and so can be ruled in/out by whether the intensity of the signal is linear with excitation power or inverse quadratic. If measurements of the phosphorescence have been possible, comparisons to its energy and lifetime are also instructive.

Recombination fluorescence:

"The first excited singlet state becomes populated by recombination of radical ions with electrons or by recombination of radical ions of opposite charge." ³⁵

Like TTA, this process requires 2 radical ions to recombine, and is therefore non-linear in its dependence on excitation power.

Aggregate emission:

Aromatic planar structure can form pi-stacks. Excitations can delocalise. Characteristically these emit broader and redder with long PL lifetime. (N.B. not Aggregate Induced Emission where in the solid phase the PLQE increases relative to a dilute solution due to steric effects.)

Aggregate emission requires the nearest-neighbour molecules to also be the able to form stacks. A dilution series in a polymer host like polystyrene can help rule this in or out.

Within an OLED context, there are several additional considerations which can result in delayed EL.

RC constant of a diode:

Every device has characteristic times for injection of electrons, as well as its RC constant as a capacitor. Small delayed EL is to be expected on the order of the discharge time of the stack.

Trap sites and carrier pinning at interfaces:

Trap sites and electric field effects also. Delayed EL plot from Polymer OLED where clearly charges were trapped somewhere in the stack and able to recombine after E field removed.



Figure 2.16 TREL showing delayed trap emission

Figure 2.16 shows time resolved electroluminescence, with a large increase in intensity after the driving voltage is turned off due to trapped charges in the stack then recombining. Measurement carried out by author on OLEDs fabricated by Robert Hoye from materials synthesised by the Bronstein group.

To fully demonstrate that delayed emission is TADF, it should be sensitive to polarity of solvent, vary with temperature and scale linearly with excitation power. Oxygen quenching should also reduce total PL and result in faster delayed emission.

2.7 Organic Light Emitting Diodes

The motivation for synthesising and studying new emissive materials is that they may provide improved dopants for lighting and display purposes.

An Organic Light Emitting Diode (OLED) consists of a stack of different material layers between an anode and a cathode which inject holes and electrons through the stack respectively.

In an idealised OLED, these would all reach the dopant molecules and recombine to form light.

For this to happen efficiently, additional layers are added to the stack to ensure that the recombination zone where the electrons and holes meet is within the emissive layer (EML)

Further layers can improve electron or hole transport (ETL/ HTL) into the emissive layer, and try to stop the electron or hole currents propagating through the EML before radiative recombination has occurred.



Figure 2.17 OLED device diagram

Figure 2.17 shows a generalised energy level diagram of the layers in an OLED device including the energy level of the injecting anode (right) and cathode (left), electron and hole transport layers(ETL, HTL), injection and blocking layers(IL, HBL) and the emissive layer (EML)³⁶

The energy of the HOMO and LUMO of the dopant determines what materials are appropriate for the other layers within the device architecture to form an appropriate cascade of energy levels and shown in figure 2.17.

There exists an immense parameter space for exploring device architecture, spanning material combinations, layer thicknesses, deposition conditions, interface characterisation and appropriate host material and dilution regimes to name but a few factors.

In this thesis, I do not present work exploring in any detail the process of selecting or optimising device structures, and work within architectures developed by collaborators as proof of concept that given materials have device potential. For details of the device engineering process I refer the reader to the literature cited in these sections.

2.7.1 Singlet emission from OLEDs

One way to consider the development of lighting technology is by the nature of the process which results in photons being emitted.

Lighting from sources like flames from candles and lanterns or incandescent bulbs rely on thermal radiation from a hot gas, plasma or metal filament to produce continuum, broadband, black-body radiation, with the colour being determined by the temperature of the system.

Gas based bulbs and LEDs rely on a fundamentally different mechanism, with electrons being excited between well-defined energy levels, such that the emission spectrum is material specific and well defined by the energetic gap and broadening of the transitions between the allowed levels. For inorganic systems, this is set by the interface between two semiconductors, and in atomic or molecular systems like halogen bulbs and OLEDs, these levels correspond to the energy levels of a given atom or molecule as described earlier.

The "first generation" of OLED technology can then be defined as devices which rely on purely fluorescent materials for the generation of light.

Currently, the best commercial fluorescent OLEDs achieve efficiencies in the region of 12-14% by using a combination of TTA and oriented deposition of films for enhanced outcoupling.

2.7.1.1 The first OLEDs

The idea of using organic materials for light emitting applications was already being discussed in literature as early as the 1960s, and was considered appealing due to the high luminescence efficiency of many organic materials.

In 1962 Pope, Kallmann and Magnante submitted "electroluminescence in Organic Crystals"³⁷ where they report EL from anthracene crystals, and tetracene doped anthracene crystals between 10-20 μ m thick which had been sublimed from solution. Once silver electrodes had been added, the system was driven at 400V to carry out measurements.



FIG. 1. Enlarged photograph of the recombination radiation from a 5-mm-thick crystal, viewed normal to the horizontal current path through a polished side of the crystal. The region of maximum brightness (=luminous zone) on the right-hand side is in front of the positive electrode.

Figure 2.18 EL in anthracene crystal

Figure 2.18 is reproduced from this paper, showing the electroluminescence from the anthracene crystal. ³⁸

In an article submitted in 1964 by Helfricht and Schneider ³⁸ they open by reporting "the observation of fluorescence due to the recombination of electrons and holes in anthracene single crystals".

The crystals were several mm thick and melt-grown. Charge injection was clearly highly imbalanced in the system, and a photograph is shown of the 5mm crystal with a bright region next to the positive electrode.

These early demonstrations relied on first growing crystalline samples, and then building the device electrodes around them.³⁹ This was sufficient for proof of concept that electroluminescence is possible from organic materials, but perhaps it is not fair to describe as the first reported "devices" if we take that word to mean a functioning stack formed in a repeatable, controlled manner, which can be operated at practical brightness under sensible current and voltage conditions.

2.7.1.2 Small molecule OLEDs

The "first generation" of practical OLED devices were developed at Kodak by Tang and Van Slyke in 1987⁴⁰. The fluorescent organometallic small molecule Alq3 was used to achieve devices with ~1% EQE and brightness exceeding 1000cd/m².

These were produced by a combination of spin coating and sublimation, and represented what is usually considered the first demonstration of industrially relevant OLEDs.

All of these early demonstrations relied on fluorescent materials. These are able to rapidly emit light after excitation from transitions between S1 and S0 states directly, with no limitations imposed by conservation of spin angular momentum between two states of singlet character.

Small molecules are chemically appealing as once an appropriate synthesis is determined, they can be purified, characterised and repeatedly reproduced with significantly less batch to batch variation than polymers and crystalline materials. One of the limitations present in small molecules however is their propensity to form aggregates, which can drastically change their electronic properties.

The two forms of aggregation commonly discussed are denoted as H-type and J-type, and are differentiated by the alignment of the transition dipole moment on adjacent molecules.⁴¹

For H-type aggregation this is predominantly face to face, whilst for J-type aggregates, the alignment is predominantly end to end, or head to tail.

An important result of this is that the transition dipole moment in the H-type aggregate is in alternating directions to minimise the energy of the system. This reduces the net transition dipole for any excitation and quenches the fluorescence, characteristically seen as a red shift in emission, increase in PL lifetime and drop in PLQE with concentration of dopant. ⁴²

Reducing the presence or extent of aggregation is then extremely important for small molecule OLEDs, and is one of the reasons that a host matrix is usually necessary for a "good" device. Another key role the host often serves is one of charge transport and injecting excitations onto the dopant molecules, which may be excellent emitters but have poor bulk conductivity.

This can also be mitigated to some extend by processing conditions to limit the formation of aggregated domains⁴³, but all of these points add complexity to the device fabrication process, which makes industrial reproducibility more difficult.

Another approach to mitigating aggregation exists from a synthetic perspective, if molecules can be designed with sterically bulky groups as positions that block intermolecular packing. ^{44–52}

For molecules where there is no appreciable degree of aggregation, films should not undergo concentration quenching, and pure layers may be possible to use in devices if charge transport is sufficient.

2.7.1.3 Polymer OLEDs

The materials studied in this thesis for light emission are principally small molecules, and the role of polymers has primarily been as a soluble host material, used to make amorphous films with good charge transport properties. Developments of emissive and conducting polymers however occurred alongside that of molecular emitters, and many of the same physical challenges apply.

Polymers offered an appealing work around to the issue of sensitivity to neighbour alignment and aggregation, as electronic transitions available are dominated by the conjugation along the backbone rather than other nearby neighbours.

They also solve the problem of charge mobility, as semiconducting polymers rely on a conjugated backbone, allowing delocalisation of excitations along the chain. This development itself warranted the Nobel Prize in Chemistry in 2000 ⁵³.

It was successfully reported that semiconducting polymers could be used as the emitting layer of a polymer OLED (PLED) in 1990 by Friend, Burroughs et. al. ⁵⁴. As with small molecules, the default allowed radiative transitions in a polymer are from singlet excitations, and unless additional processes are made possible, polymers are fluorescent.

One of the points that is important to draw attention to in the context of developing materials to emit from triplet states, is that for conjugated polymers, the singlet triplet exchange energy was believed to be \sim 700meV ⁵⁵ which would render triplet states energetically inaccessible for reverse inter system crossing, thus acting at a trap for excitations if T1 could not couple directly with the ground state.

Subsequent developments have shown that this does not need to be the case, and that structural design can result in energetically accessible triplet states (which will be discussed in more detail later) however, like small molecule emitters, the first generation of PLEDs relied on fluorescence from singlet states, and shared the 25% limit on IQE imposed by spin statistics. Triplet emission from OLEDs

The largest single hurdle for emitting light from organic materials is that for electrical excitation, 25% of excitations are formed in a spin singlet configuration, and 75% in a triplet configuration and that in the absence of additional processes, only the quarter formed in the singlet configuration can couple radiatively with the ground state.

Fortunately, there are numerous such "additional processes" which can influence the orbital angular momentum of an excited electron, as discussed earlier.

Whilst experimental measures of this ratio are possible and vary slightly, to a first approximation the ratio of 1:3 is sufficient and will be assumed throughout this thesis ⁵⁶, the key point being that triplets remain the vast majority of excitons formed under electrical excitation.

2.7.1.4 Phosphorescent materials in devices

If the "first generation" of OLED technology was fluorescent materials, then the "second generation" of OLED devices can be thought of as those which utilised triplet excitations through direct phosphorescence with materials which were not restricted to radiative transitions between states of only singlet character, and where triplet excited states are able to couple radiatively to the singlet ground state.

The first phosphorescent OLEDs (PhOLEDs) were reported in 1998 developed by Baldo and Forrest ⁵⁷. These uses a platinum containing porphine dye (PtOEP).

In the case of phosphorescent materials, heavy elements are incorporated into molecules to allow spin orbit coupling to effect a change in the orbital angular momentum of an excited electron.

For a material to be an effective phosphor, there are several requirements. Firstly, there must exist some allowed coupling between the T1 excited state and the S0 ground state. The strength of this coupling will determine the probability of a transition occurring. Since this transition only becomes possible when the spin angular momentum of the triplet exciton has processed until it is in a sufficiently singlet-like configuration to couple radiatively to the ground state, for a given excitation at a given instant, this transition is less probable than fluorescence, and therefore the process is usually much slower, on the order of microseconds to milliseconds rather than nanoseconds.

Secondly, to get the most out of the excited population, it should also be possible for an excited singlet to rapidly inter-system cross from the S1 to the T1 state. This is clearly required for any optically excited measurements, and must be possible if T1-S0 coupling can occur, however ISC will be in competition with fluorescence and any non-radiative losses from the S1 state.

I have often pictured this issue in the non-scientific context of the "glow in the dark" stars I had on my ceiling as a child.

These were optically excited during the day from daylight or room light. The excitations formed must have been able to form long lived excited state population, and an excited state population build up. During the night, these excited states emitted extremely slowly, over the course of hours.

The relevant point is that phosphorescence is a *slow* process, which introduces additional requirements for an effective phosphor.

Since the excited state population is long lived, there must be very limited options for nonradiative decay from the excited T1 state. Kinetic competition and excited state population dynamics will be discussed in more detail later, but it should be clear that the presence of a more rapid, non-radiative pathway would depopulate the excited states well before they could emit.

An additional consequence of occupying an excited state for a long time is the probability of exciton-exciton interactions increases. These are doubly problematic for OLED applications, as not only do they result in two excitations being wasted non-radiatively, but they also can provide enough energy to break the carbon-carbon bonds holding our molecules together, resulting in degradation and poor device lifetimes.

The design aim for an idealised phosphor is then a molecule which has rapid ISC from S1 to T1, minimal losses from the T1 state, and can also couple as rapidly as possible with the S0 ground state. This is achieved through the incorporation of heavy metal atoms like iridium and platinum into the molecule. As spin orbit coupling scales with atomic number, this allows rapid emission from the excited triplet state. Current champion phosphors achieve this on the order of μ s. ^{58–63}

There are some examples of molecular systems which achieve delayed emission from a triplet population without the inclusion of heavy elements. Phosphorescence has been shown to arise from fully organic crystals if correctly halogenated ⁶⁴, and small molecule systems containing Boron ⁶⁵, however none of these materials currently compete with the excited state lifetimes of organo-metallic phosphors, and so will not be considered further herein as competitive for device application.

As with small molecules, the next generation of materials developed to solve the problem of accessing electrically generated triplet excitons was phosphorescent polymers. From the early 2000s numerous demonstrations were made of moderately efficient devices across the visible spectrum, and white blends for lighting purposes. ^{66,67}

These materials were susceptible to the same issues facing small molecule phosphors, where long lived excited states are prone to annihilation events, which break chemical bonds, resulting in short lived devices, especially for blue emitting materials where . Work is ongoing to improve PhOLED device lifetimes ⁶⁸, and a key parameter for this is increasing the radiative rate from the excited triplet state. Minimising the time spent in the T1 state directly reduces the probability of unfavourable recombination occurring. ⁶⁹

More recently, advances in polymer design have achieved significant enough reductions in exchange energy that other emission pathways are possible, which will be discussed in more detail later.

Despite these advance, the current state of the art phosphorescent materials have emission lifetimes only approaching a microsecond, and still rely on expensive elements.

2.7.2 TADF OLEDs

The terms TADF rather than e-type delayed fluorescence is predominantly used in the field of organic electronics, despite the processes being the same, and I will use it throughout this thesis.

Despite the improvements over purely fluorescent devices which were made using phosphorescent materials for "second generation" OLED technology, there remained issues with device stability, achieving blue emission and accessing all excitations formed in the film efficiently.

TADF provides a system where emission from either singlet or triplet excitations formed is allowed, and triplet excitation can emit on timescales which are competitive with the best phosphors currently available.

These can also be based on molecules not containing rare and expensive heavy elements like platinum or iridium, so offer a potentially more cost effective solution to global requirements asides from the photophysical differences.

2.7.2.1 TADF small organic molecules

This effect was demonstrated for OLED application by the Adachi group by Uoyama et al in 2012 in the first instance.⁷⁰ The materials were a set of small fully organic carbazole based Donor-Acceptor molecules, and efficient reverse intersystem crossing was achieved a by minimising the singlet-triplet exchange energy.



4CzIPN

Figure 2.19 molecular diagram of 4CzIPN

Figure 2.19 shows a molecular diagram of 4CzIPN, the material reported in the 2012 paper by Uoyama et. al. This uses the approach of having 4 carbazole donor units attached to a central electron accepting unit.

In this molecule, the design rule of using many donor groups well spatially separated from a core acceptor unit proved very effective at minimising the exchange energy. This template proved effective and synthetically versatile, and a large number of variations on this archetype have been synthesised across the visible spectrum.

2.7.2.2 TADF polymers

As with the development of fluorescent materials, polymerisation was also desirable for TADF.

The same logic of minimising the exchange energy by achieving HOMO-LUMO wavefunction separation on Donor and Acceptor units was applied to the design of polymers following two distinct structural templates.



Figure 2.20 TADF polymer architectures

Figure 2.20 illustrates the different strategies employed to achieve Donor-Acceptor wavefunction separation when polymerising TADF materials. ⁷¹

The Adachi group developed polymers of alternating donor-acceptor units forming the polymer backbone ⁷².

A similar logic was applied by the Bronstein group in developing a series of polymers where the donor units were linked on to an accepting TFB like backbone as orthogonal side groups.⁷¹

2.7.2.3 Organometallic TADF materials

Devices based on molecules incorporating metal atoms, where the charge transfer states were between the metal and a ligand (MLCT) rather than intra-ligand (LLCT) were first reported by Ma et al in 1998 on a serious of Osmium based compounds. ⁷³ This was part of the exploration of high SOC interaction for triplet emission via phosphorescence, but the emission was from a MLCT rather than some local triplet state.

The initial work from the Adachi group in setting out a design objective for achieving efficient coupling of the T1 and S1 state via reverse inter system crossing considered the singlet-triplet mixing coefficient from first order perturbation theory.

$$\{6\} \qquad \qquad \lambda \propto \frac{\widehat{H}so}{\Delta EST}$$

This property scales with the strength of spin orbit coupling, divided by the exchange energy, and in the fully organic N-Cz-IPN derivatives, only this denominator is considered.

"It follows ... that heavy atoms are not required to achieve efficient spin conversion when a molecule possesses a small ΔE_{st} and H_{so} is not vanishingly small."⁷⁴.

One of the largest issues with fully organic TADF is the necessary compromise between the oscillator strength of the T1 to S1 transition with the minimisation of the exchange energy.

Organo-Metallic TADF molecules address both of these properties, and aim to achieve spatial separation of the HOMO-LUMO wavefunctions, and also have a metal atom at a point relevant to the mixing of these two wavefunctions. By introducing a heavy element, a similar degree of mixing between T1 and S1 should be possible with less spatial separation of the HOMO-LUMO wavefunctions, as the spin orbit coupling of the heavier nucleus perturbs the spin states of the singlet and triplet exciting, reducing the compromise in oscillator strength for the same degree of mixing of character of states.

This also impacts the forward ISC rate as well as the RISC rate, and in Organo-Metallic-TADF molecules there is often a smaller degree of prompt fluorescence visible, as the S1 state is rapidly depopulated by ISC to the T1 state reducing the number of excitations which emit through direct fluorescence. This is the design approach discussed within this thesis.

2.7.2.4 Caution with literature interpretations

A danger in any field which gains rapid success and interest is that once a topic has reached "buzz-word" status, it can be invoked to boost the perceived impact of publications, perhaps when it is not entirely relevant or the data fully digested.

TADF is no exception to this rule, and even reputable groups publishing in well regarded journals are not immune to the allure of impact over accuracy of content.

An example of this is a recent paper on stimulated emission from a set of boron containing small molecules, claiming the first reports of a TADF molecule or phosphor being used as a gain medium under optical excitation ⁷⁵.

Whether or not TADF materials are a promising option for electrically pumped organic lasing materials aside, there are a few aspects of this paper which warrant scrutiny. This is discussed in more detail in Appendix A as an example of the degree of caution required when placing one's own results within the context or interpretations existing in the literature.

2.8 **Processing**

One of the main appeals for organic electronics has always been access to material properties that metals and crystalline materials lack such as flexibility, transparency and also solubility. This has facilitated a revolution not just in the electronic and optical properties of new molecules and polymers but also a revolution in possible manufacturing techniques. Conventional semiconducting crystalline materials require extremely pure single crystal domains, and are very sensitive to defects and doping. This means that they must be manufactured in very controlled conditions to extremely high tolerances, which is expensive.

In contrast to this, the ability to use electrically and optically active inks for spin coating, ink jet printing and roll to roll deposition offers a much less sensitive alternative for manufacturing large area electronics.

For the materials which are relevant to this thesis, the two most relevant processing techniques are solution processing and thermal evaporation.

2.8.1 Solution processing

Broadly speaking, most organic small molecules and polymers should be possible to process from solution unless they have particularly low saturation limits in appropriate solvents. It is also trivial to co-deposit from solution, as a mixture of a host and a dopant can be deposited from the same solution.

There are limitations of solution processing however. Firstly, given that the materials used are usually chemically similar, it is often the case that a solvent used for one layer in a device will also dissolve the layers below. This creates issues with washing away lower lying layers, or the morphology of interfaces between layers being difficult to control. This treatment can result in a concentration gradient forming at an interface which becomes partially dissolved. This effect can result in positive device characteristics, but is difficult to predict, control and reproduce from solution deposition.⁷⁶

Even in the case where orthogonal solvents can be used for subsequent layers in a device, ⁷⁷ ⁷⁸achieving uniform thickness and morphology reproducibly is challenging, with work ongoing to describe this process well. The main parameters which contribute to the film thickness are the viscosity of the solution, the radial forces from the spinning substrate, and the volatility of the solvent.

*"Even assuming idealized hydrodynamic and evaporative behaviour, film thinning and the accompanying solute enrichment is a rather complicated process"*⁷⁹

This means that whilst polymers are appealing for their material flexibility that at least with current deposition techniques they are difficult to control in terms of layer thickness and interface quality, and achieving repeatability is difficult.

2.8.2 Thermal vapour deposition

Another method for depositing thin layers of a material is thermal vapour deposition.⁸⁰

Even in a solution processed device stack, the metal electrodes are usually applied via thermal evaporation.

There are a number of criteria for whether a material will be suitable for evaporation. Firstly, it must be of a sufficiently low molecular weight. Thermal evaporation is carried out under high vacuum (10^{-6} to 10^{-7} mbar) to allow ballistic transport between the source and the substrate, but this also defines the vapour pressure of the material and the temperature at which it will evaporate.

For an organic molecule, this imposes a destructive upper limit on the temperature which can be used, as the molecule will degrade chemically beyond a certain point. This is usually between 200C and 300 C and it is possible to test whether a material will be suitable/unsuitable for processing via evaporation with Thermal Gravimetric Analysis (T.G.A.). T.G.A. is a process where a known weight of sample is heated up gradually, and any change in weight recorded as a function of temperature. Loss of weight with heating implies loss of material, and this usually corresponds to a temperature at which degradation has occurred.

The benefits of thermal vapour deposition are that it is possible to deposit highly reproducible films and achieve sub-nm control on layer thickness. Co-evaporation from multiple sources also facilitates depositing blend films, or carefully including concentration gradients within a film. For these reasons this is the current preferred deposition method for many industrial OLED applications.

Asides from being restricted to molecules which are small enough and thermally stable enough, thermal evaporation also requires much larger volumes of material than solution processing techniques, as the deposition is not directed. This is problematic for new materials which may only be produced on the 10s of mg scale in the first instance, so solution demonstration of OLEDs remains a valuable tool even for molecules which can be evaporated.

2.9 Current models of TADF

To lead the development of new, more efficient emitters, an understanding of the states and processes involved in the spin conversion process is needed.

This allows pre-emptive screening "in silico" of likely candidates for high efficient TADF molecules, rather than a brute force approach of synthesising and screening every conceivable analogue of a known system.

2.9.1 Organic systems

El Sayed's rule would say that there should be no significant spin orbit coupling between states of the same symmetry as there is nowhere to dump spin angular momentum. This would mean that coupling between 1CT and 3CT states would be extremely weak and is true for fully organic TADF molecules.

This clearly does not prevent RISC as efficient organic TADF molecules exist, however an additional step is required via another intermediate state of different character, 3LE, being involved via second order spin vibronic coupling.

In 2016, Etherington et al propose that second order spin vibronic coupling via a local triplet on either the donor or the acceptor is the mechanism by which efficient TADF is achieved in fully organic systems. ⁸¹ Penfold, Dias and Monkman built on this in 2017 summarising these effects for device environments. ⁸²

2.9.2 Organometallic systems

There are two main points to consider for organometallic molecules which differ from fully organic molecules regarding TADF.

Firstly, the heavy atom effect will increase spin orbit coupling in the region of the metal atom.

Secondly; the ground state of the metal will have D orbital character. In the case of coinage metals, this would be D^{10} in the ground state, meaning no metal centred transitions are possible as the metal orbital are full.

This does, however, allow the possibility for Metal-Ligand Charge Transfer states (MLCT).



Figure 2.21 comparison of emission lifetimes

Figure 2.21 illustrates the relationship between emission lifetime and the nature of the transition involved in the states being coupled.⁸³

Given that the orbital on the metal has D character, and nearby atoms will have S or P orbitals, this means that there is no selection rule prohibiting transitions involving the metal. In the terminology of El Sayed's rule, the symmetry of the states is different, so the oscillator strength or transitions can be high.

An intrinsic limitation for fully organic TADF materials is that they must have low oscillator strength transitions by design to achieve reducing in the exchange energy. Organometallics are not constrained by this in the same way.

There have been a number of theoretical descriptions of the CMA molecules over the last few years aiming to explain the involvement of geometric freedom in achieving the low exchange energy between the excited singlet and triplet energy levels. Some have focussed on the role of rotation about the metal nitrogen bond in the excited state geometry, and others have explored the importance of bond stretching and deformation. ^{84–86}

The computational complication of including proper treatment of SOC in the functionals chosen for these calculations has proved an involved process in its own right, however there are points which can inform and support the spectroscopic data.

The data presented in this thesis aims to test the predictive ability of these current descriptions.

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Chapter 3 Experimental methods

In this chapter I set out the techniques which I have used to acquire the data presented in this thesis. This is divided into two themes which could informally be described as the "DOs" and "DON'Ts" of spectroscopic measurement.



Firstly I set out the measurements I have performed and the principles that they function from, with example data sets demonstrating the information that these techniques can access.

The second theme is corresponding experimental artefacts, control measurements, and protocols which can be followed to minimise/ mitigate the presence of additional features within data sets during well considered measurement.

The intended consequence of introducing the measurements in this format is that the data discussed in subsequent chapters has been measured with the same scrutiny, and the discussion can then focus on the interpretation.

For data presented in this thesis which has been measured by collaborators, I refer the reader to literature for full details of techniques.

3.1 Steady state absorption

Steady state absorption measures the energy of the allowed photo-excited transitions relative to the singlet ground state, weighted by their respective oscillator strength. In the diagram show in figure 2.9 this would be a weighted measurement of processes **1** and **2**.

For a given sample, this is measured in units of Absorbance or Optical Density (OD) which is defined as: "Logarithm of the ratio of incident to transmitted radiant power through a sample (excluding the effects on cell walls)."⁸⁷

3.1.1 UV-Vis absorption

A standard UV-Vis absorption measurement is usually carried out by passing broadband light through a sample and an appropriate reference, such as a blank substrate, and comparing the difference between these two spectra.



Figure 3.1 UV vis scematic

Figure 3.1 shows a simplified schematic of a UV-Vis absorption experiment ⁸⁸. Various geometries are possible. The simplest configuration is shown, with one optical path, and the sample and reference objects interchanged and measured separately. More complex setups have 2 paths for light passing through the sample and separately through the reference simultaneously, but the principle is the same.

The result of this is a spectrum which corresponds to the *difference in transmission* of the light which has passed through the sample and through the reference.

Absorption by the sample is the quantity of interest, but it is not the only process which can result in a change in the transmitted signal.

Any reflection from the surface of the sample, any scattering from the sample or waveguiding from the substrate can also result in a change in the intensity of the light reaching the detector.

The detector will also have a range of intensities over which its response is linear to the change in signal, and can also be saturated.

If a UV-Vis spectrum is measured on a dilute solution with an appropriate blank, the dominant contribution to the change in transmitted signal is from the absorption of the molecules.



Figure 3.2 UV vis spectra and energy levels

Figure 3.2 shows (left) the UV-Vis spectrum of a sample of a silicon pthalocyanine in toluene and (right) a schematic diagram of the transitions that correspond to these absorption features. Measurements by author as detailed in reference ⁴³.

The low energy onset of the reddest absorption band is \sim 700nm (1.77eV). This means that the gap between the S0 state and the S1 state is \sim 1.77eV.

The higher energy features between 600-650nm will be coupling to higher vibrational levels of the S1 state.

The onset of the second absorption band is at ~400nm (3.09 eV). This means that the gap between the S0 state and the S2 state is ~3.09 eV.

Additional structure can also be seen at higher energy in this second band from further allowed transitions to vibronic replicas of the S2 state, however these overlap.

Transitions to higher lying singlet states may be possible, however this measurements is limited by the spectra of the lamp used. For the purpose of organic materials, stability tends to become an issue further into the UV so for my purposes this is not a limiting consideration.

Absorption spectra contain information about all transitions which can couple with an incident photon. For our purposes, the optical and electronic bandgap are relevant.

The optical bandgap is the threshold energy at which photons can be absorbed, and is extracted from the red edge of the absorption spectra, i.e. ~ 1.77 eV in figure 3.2.

The electronic bandgap, uses the terminology of electronic band structure and conduction and valence bands, and is the difference between the top of the valence band and the bottom of the conduction band.

In cases where the exciton binding energy is large, this distinction becomes meaningful, and an incident photon may have sufficient energy to form an exciton, but insufficiency energy for the electron and hole to dissociate. This is a more pertinent issue in OPV application.

3.1.2 Assigning state energies

Assigning energies of states from PL and absorption data is not clear cut, as both absorptive and emissive transitions can occur between different vibronic replicas of the states involved.



Figure 3.3 Franck-Condon energy diagram

Figure 3.3 shows a Franck- Condon energy diagram of a singlet ground state(S0) and the first singlet excited state (S1) with corresponding allowed vibronic sub levels ⁸⁹.

Transitions are possible between any of these allowed levels however a system tends to relax to the lowest vibrational level rapidly. Realistically this results in most absorptive transitions being form the 0th S0 state, and most emission occurring from the 0th S1 state.

From this picture we can infer that the lowest energy absorption or the highest energy emission should correspond to the actual gap between the S0 and S1 states.

The Stokes shift is defined as the difference between positions of the band maxima of the absorption and emission spectra of the same electronic transition.

For materials with large stokes shifts, the S0- S1 gap can then be approximated as the intersection of the absorption onset with the high energy edge of the PL.

This method is approximate, and perhaps overly simplistic for describing ensembles of materials, but is sufficient to track changes in the behaviour of the same material in different environments, or to track the result of modifications on a molecular motif. To these ends, this is the method I use within this thesis.



Figure 3.4 small and large stokes shift

Figure 3.4 shows: (Top left) energy diagram of absorption and emission on a molecule between multiple vibronic replicas of the singlet ground (S0) and first excited state (S1)⁸⁹. (Top right) shows an example of small stokes shift in a silicon pthalocyanine ⁴³ like the 0th order absorption and emission shows top right, with some additional vibronic contributions mirrored in both absorption and emission. (Bottom left) shows an energy diagram of absorption and emission on a molecule with a large stokes shift ⁸⁹. (Bottom right) example of larger stokes shift in emission from CMA1 in MTHF where there is a larger stokes shift to CT emission. Absorption and PL measurements by author.

3.1.3 Artefacts in steady state absorption

As with all detectors, it should go without saying that they must be properly calibrated and aligned. I have not needed to carry out calibration or alignment during my measurements, but "sanity checks" for the status of the detector are to firstly check that measuring in the absence of a sample provides a spectrum showing zero change across all wavelengths, and secondly, that a known, commercially available and reproducible object like a glass microscope slide shows absorption features which agree with literature reports of the absorption onset of the material.

3.1.3.1 Linear response of the detector

There exists a range of input intensities for which the detector will have a linear response. Even if other effects like reflection and scattering are mitigated, it is important that the highest optical density measured for the sample is within this range (OD<2).

If this is exceeded, then the intensity of the spectrum will lose physical meaning at the highest values, even if the structure still corresponds to the energy of allowed transitions. This is an issue if calculation of oscillator strength is required, but not a problem is the onset of a transition is what is required.

This also means that artefacts which introduce falsely high readings, like scatter in the UV, cannot be corrected beyond a certain point, as the data recorded has deviated from the physical form of the correction being applied.

3.1.3.2 Scattering

Scattering from a film or solution is largely Rayleigh scattering, which scales with λ^{-4} . For a spectrometer which outputs the spectrum as a function of Optical Density (OD) which
is the logarithm of transmission, simply subtracting weighted λ^{-4} as a baseline zero-offset is not strictly accurate even though it's a good first approximation.

A more rigorous correction can be carried out as shown in equation $\{7\}$:

 $A = A_0 + \log \frac{I_0}{I}$ $= A_0 + \log \frac{I_0}{I_0 - scatter}$ $= A_0 + \log \frac{1}{1 - K^*(\lambda^{-4})}$

Thus

$$A_0 = A - log \frac{1}{(1 - K * (\lambda^{-4}))}$$

{7}

If the absorption measured by the detector (A) is the combination of the actual absorption (A0) and the change in intensity due to scatter, which is measured as the logarithm of the correct intensity (I0) and the measures intensity including contribution from scattered light (I).

This treatment assumes that the measured intensity can then be represented as the correct intensity – light lost to scattering, and expresses this as a function of wavelength with a scattering constant K.

By adjusting the magnitude of K, different degrees of Raleigh scattering can be corrected for in datasets.

The sample in figure 3.6 only absorbs quite far into the UV. This is an example of where an appropriate measurement regime is difficult, as different structures form at increased concentrations and the only optical transitions occur in a region of high scatter.



Figure 3.5 Rayleigh scatter correction

Figure 3.5 shows an example of this form of correction being applied to dilute protein fibrils suspended in water. Measurements by author.

In this case, the scatter correction has helped sharpen up two transitions at ~310nm and 270nm before the signal is no longer correctable.

Fortunately, for the single molecule systems considered in the bulk of this thesis, the transitions occur closer to, or within visible wavelengths so scatter is less present.

Also, studying isolated molecules rather than structures means that there is a greater freedom in adjusting the concentration of the sample to an appropriate OD without changing the chemistry of the sample.

For isolated molecules, the Absorption and PL taken at different concentrations in the same solvent should then be cross comparable.



3.1.3.3 Dilution effects



Figure 3.6 shows a concentration series of the same material demonstrated for the scatter correction, with a blank water comparison. Measurements by author.

This demonstrates how the onset of scattering could be mistaken for an absorption onset. This is again, particularly important for materials with weak optical absorption, extremely dilute samples, or samples which only absorb in the UV.

For the materials discussed in this thesis, the absorption onset was not in a regime where this limited measurements.

3.2 Time resolved absorption

I present Transient Absorption data from collaborators in this thesis to support some of my own data. To put this into context so it can be interpreted, I will briefly introduce how this is measured, and what information about excited states it provides. I refer the reader to the published literature for a full description of the details of these techniques. ⁹⁰

Transient Absorption Spectroscopy commonly referred to as either TAS or TA is measurement which provides data about the population of excited states, and how this changes in time.

This is achieved by passing two pulses through the sample, and varying the time delay between them. Both pulses need to be short in time to achieve high temporal resolution. In the diagram show in figure 2.9 this would be a weighted measurement of processes 1, 2, 4 and 6.

The first pulse, called the pump pulse, is used to excite a population in the sample. This pulse is narrow band and corresponds to some known absorption of the material. This will result in a population of photo-excited singlet excitons.

At some time delay after the pump pulse has excited the sample, a second pulse is passed through. This is called the probe pulse, and is broadband. The transmission of the probe pulse is what is measured.

To account for fluctuations in power, this is compared to a reference portion of the probe pulse which is not passed through the sample.

Measurements are taken at each time delay after excitation by the pump pulse excites the sample, and also with the pump pulse having been blocked. Time delay is achieved by addition optical path to the probe pulse with a mechanical delay stage.



Figure 3.7 Transient Absorption diagram

Figure 3.7 shows a visualisation of a TA setup. The top panel shows the pulp and probe beam spatially overlapped on the sample with some temporal delay, and the transmitted probe light being sampled by a spectrometer. The bottom diagram shows an energy level diagram of the manifolds occupied by an excitation as it is formed, and then proceeds to relax and undergo intersystem crossing. The change is occupancy of these sites can be visualised by the difference spectra changing with different pump-probe delay as shown bottom right ⁹¹. The transmission of the probe pulse is then compared both with the pump pulse having excited the sample, but also with the pump pulse having been blocked.

The difference between these two signals corresponds to how much more or less the probe pulse is absorbed at a given time delay after the pump pulse when the sample is excited.

To fully interpret this data, comparison to the steady state PL and Absorption is needed.



Figure 3.8 TA spectra

Figure 3.8 shows an examples of a TA spectrum at a particular time delay (100fs). This is compared to the steady state absorption of the sample, and its PL spectrum. Reductions in the absorptive transitions from S0 can be inferred from the increase in signal in the area corresponding to the steady state absorption. Additional signal is seen in the same region as the PL are attributed to stimulated emission. The new, negative feature represents absorptions from states not previously populated. Image reproduced from the OE introductory talk on TA data analysis, 2018 by Ture Hinrichsen.

3.2.1 Positive ΔT (reduced absorption)

If this difference in transmission (ΔT) is positive this, implies previously allowed absorptive transitions have been depleted.

3.2.1.1 Stimulated emission

If the pump pulse forms excitations which then emit, there will be positive contributions to the transmitted probe collected from PL. These should be spectrally similar to the emission from the sample, and have the same lifetime as the PL lifetime.

3.2.1.2 Ground state bleach (GSB)

If electrons which were in the ground state of the sample are excited by the pump pulse, then there are fewer electrons which can then be excited from S0 to Sn when the probe pulse arrives.

This will result in a reduction in the absorption in the spectral regions which correspond to the steady state absorption of the sample as this represents ground state transitions.

3.2.2 Negative ΔT (increased absorption)

If the difference in transmission (ΔT) is negative, this implies additional absorptive transitions are present.

3.2.2.1 Photo-induced absorption (PIA)

For there to be an increase in the amount of light being absorbed at a given wavelength, there must be additional allowed transitions present corresponding to that energy. This is called a Photo Induced Absorption (PIA).

An example of this would be that when a molecule is in the ground state, the allowed transitions are from S0 to S1, S0 to S2... S0 to S (n>0), and the weighted average of all of these is our steady state absorption spectrum.

Once a material has been excited, the S1 state could be populated. There would then exist a new set of allowed optical transitions from S1 to S2, S1 to S3... S1 to S (n>1). These new transitions will be possible only whilst the S1 state is populated, and so they provide a measure of the excited state lifetime of the S1 population.

The same will be true, that if an excited triplet state, T1 for example, becomes populated, that transitions to higher lying states in the triplet manifold will be possible.

3.2.3 Transient Absorption summary

- TA is able to probe the population of both excited singlet and triplet states.
- It provides information about the difference in energy between one excited state, and another higher lying excited state of the same multiplicity.
- It provides information about the TOTAL population of this state, and how this changes in time. It should be explicitly noted that this technique is insensitive to how a state is depopulated, and provides no information about whether excitations have emitted a photon of been lost non-radiatively.
- Inferences can be made about processed like intersystem crossing, since it is known that all excitations initially form in a singlet configuration as they are photo-excited. Any contributions to the signal which grow in at some later time must be another form of excited state, like a triplet, which the initially excited singlet population has converted to.
- By comparing the rates at which these transitions decay or grown in with the PL lifetimes of the same samples with comparable pump excitation, correlations can be drawn about which states are emitting.

For my purposes, this technique is used to probe the timescale over which singlets are able to intersystem cross to triplet excited states.

3.3 Photoluminescence Quantum Efficiency

Photoluminescence Quantum Efficiency (PLQE), sometimes called Photoluminescence Quantum Yield (PLQY), is a measure of the probability that a photon is emitted when a material is photo-excited.

This is calculated by comparing the absolute number of absorbed photons to the absolute number of emitted photons. For an ideal emitter, where there are no non-radiative loss mechanisms, this ratio would be 1:1, as every absorbed photon would result in an emitted photon.

This imposes an upper limit on how well a given dopant may perform in an OLED device environment, as if, for example only 50% of excitations result in a photon being produced, this factor then combines with the out-coupling efficiency of the device, and the fraction of excitations formed in the relevant spin configuration.

Various methods exist for calculating PLQE via comparison to known standards, but in this thesis the absolute method described by de Mello et al. is used ⁹². This calculation requires capturing all of the light from both the excitation and the sample in an integrating sphere. This captures all the light from the laser excitation as well as any generated by the PL of the sample.

The laser is shone into the sphere through a small aperture and light collected through a fibre optic cable. The size of the aperture is assumed to be small enough that effectively all light is collected.

Three measurements are required for this calculation:

- 1) Shine the excitation laser into the sphere without a sample in it
- 2) Shine the excitation laser into the sphere directly onto the sample
- 3) Shine the excitation laser into the sphere without directly illuminating the sample

These three measurements allow quantification of the PL as a result of direct excitation, but also PL excited by scattered laser light bouncing around the inside of the sphere which is absorbed by the sample on some later pass.

In each measurement, the total integrated counts from the laser peak and the PL are measured. For this to work well, ideally the excitation wavelength and PL are well separated. By this method, the PLQE is calculated as:

$$PLQE = \frac{PL_2(1-A)PL_3}{Laser_1A}$$

{8}

Where PL_2 is the total integrated PL in measurement 2, PL_3 is the total integrated PL in measurement 3, $Laser_1$ is the total integrated counts from the laser excitation in measurement 1, and A represents the fraction of the laser light which is absorbed during direct vs. indirect illumination.

$$A = 1 - \frac{laser_2}{laser_3}$$

{9}

3.4 Steady state Photoluminescence

Steady state photoluminescence spectra provide a measurement of the energy of all transitions which couple radiatively with the ground state, and their respective relative intensities.

In figure 2.9 this would correspond to processes 3, 7, 8 and 10.



Figure 3.9 monochromator schematic

Figure 3.9 shows a diagram of a diffraction grating monochromator ⁹³.

A monochromator is used to spatially separate the different wavelengths in a signal so they can be read out on a CCD array. This can then be calibrated such that a spectrum can be produced.

If this is functioning correctly, then:

- In the absence of a signal into the detector should produce a flat response
- Light should be collected at the correct wavelength
- The intensity profile should match calibration spectra

These checks and calibrations are carried out on our equipment as a matter of course and I demonstrate these checks for the equipment presented herein.

3.4.1 Artefacts in spectrally resolved measurements

Artefacts pertaining to spectral shape are mostly the same for steady state PL measurements and time resolved measurements, with certain exceptions which will be discussed specifically in the time resolved PL section.

All issues possible for a steady state measurement are also possible in time resolved measurements, and the same controls discussed here are applied to those data sets.

3.4.1.1 Second order grating effects



Figure 3.10 second order diffraction maxima

Figure 3.10 shows the response of a diffraction grating to broadband illumination.⁹⁴

Higher order maxima can overlap with longer wavelengths, so for very broadband signal long pass filters may be required, and multiple measurements needed to produce a correctly weighted spectrum.

If the spectrum is measured correctly, a LP filter should be able to be added at any wavelength without changing the spectral shape of the redder portion of the spectrum.

3.4.1.2 Sample self-absorption

All samples absorb, therefore all samples are filters. In some collection geometries, this effect can be appreciable.



Figure 3.11 self absorption

Figure 3.11 shows an example of sample self-absorption from literature ⁹⁵. The overlap of the absorption (blue line, left panel) and the PL (green line, left panel) results in the sample predominantly absorbing the blue edge of its own emission. The right panel demonstrates that if the PL spectrum is measured further from the point of excitation, that the intensity is reduced, and the blue edge is depleted.

This effect is most prominent in materials with high absorption and small stokes shifts ⁴³.

In geometries where there is a long optical path through the sample like a Luminescent Solar Concentrator (LSC) this is also a serious issue ⁹⁶.

Another geometry where this is prone to occur is measurements of PL spectra carried out within an integrating sphere, as the PL must pass through the sample many times on average before it is collected. This can results in spectral shifts and underestimates of PLQE.

If an excitation geometry is set up such that the sample is excited from one side, and PL

collected from the other side, this is also prone to self-absorption, though only as much as could occur in a single pass, which may be inferred from the UV-Vis.



Figure 3.12 absorption in device stack

Figure 3.12 shows an example of a device architecture where a highly absorbing subpthalocyanine layer is above a green emitting portion of the EML ⁹⁷. The edge of the ALQ3 emission at ~550nm can be seen to be depleted in the region corresponding to the Cl-BsubPc absorption.

In OLED devices, this effect can be important, as light from the emissive layer must pass through the rest of the device stack before escaping the device. If higher layers in the device have absorption where the EML emits, this can shift the spectra and reduce the EQE of the device.

For the data presented in this thesis, thin film samples are measured, and they are excited from the same side which the PL is collected to mitigate this effect.

3.4.1.3 Spectral response of optical elements

It is important to take into account the spectral profile of the optics used in collecting a PL signal. Whilst lenses and mirrors used to steer a laser beam for excitation purposes can result in back-reflections, loss of power or temporal resolution, their spectral profile is not relevant for monochromatic light.

This is not true for optics reflecting or transmitting broadband signal like PL, and every element has some spectral absorption or reflection profile.

3.4.1.4 Optical elements with negligible spectral profile

In some cases, this can be ignored as the effect is small. If an element results in a change of <1% in intensity across the region of spectral interest, then this would only be an issue if a spectra needed to be generated to study features on the scale of 1% of the total intensity, or if the collection geometry resulted in multiple passes between optics such that the effect was compounded to an appreciable level.

In a compound system with many such elements, or for high spectral accuracy, a transmission or reflection profile for each of these elements could be produced and the total effect on the intensity profile corrected for. Similarly, use of a calibration lamp in the sample position would allow of calibration file for the entire optical collection path to be produced, taking into account any angular dependencies in their actual configuration.

A preferable approach is to mitigate the need for this by sensible design of collection optics such that the PL from the sample needs to interact with the minimum number of elements before reaching the detector. In the setups used to measure the data in this thesis, this is usually one lens, and 2 or 3 mirrors, so the compound effect is still considered negligible.

Common optics used which have been considered unnecessary to correct for and their corresponding spectral responses are mirrors⁹⁸, anti-reflection lens coatings⁹⁹ and the windows used on vacuum chambers and cryostats¹⁰⁰. All of these elements have a variation <1% across the visible spectrum, and no sharp features.

3.4.1.5 Optics with non-trivial intensity artefacts

When the spectral response of an optic over the wavelength range of interest exceeds a few percent it is necessary to consider this, and correct accordingly.

An example of an optical element where the spectral profile is not reasonable to ignore is a filter.

3.4.1.5.1 Long pass filter transmission

In the case of long pass filters used to remove residual scattered pump excitation, the "cut on" wavelength is stated where the transmission drops by many orders of magnitude. This means that wavelengths below this threshold are effectively attenuated, but does not mean that there is no effect on transmission above the cut on wavelength.

To determine whether features in PL spectra are the result of actual optical transitions rather than transmission artefacts, it is necessary to take the transmission profile of the filter into account.

The relationship between absorbance and percentage transmission is:

$$A = 2 - log_{10}T\%$$

{10}

$$T\% = 10^{2-A}$$

Where A= absorbance, T= Transmission, %T is percentage transmission

This means that whilst the absorption spectrum seems relatively flat after the cut on wavelength, the effect on transmission is considerable due to optical density being logarithmically related to transmission.

Even after the cut on wavelength, the filter shown in figure π introduces a sharp feature dropping the transmission by over 20% at ~460nm. These features correlate to the structure in the PL spectrum measured.

Especially in the study of TADF materials, the character of the emitting state can be linked to the presence of structure in the PL spectra, indicating whether light is from a locally excited or charge transfer excited state.



Figure 3.13 long pass filter transmission

Figure 3.13 shows (top left) the UV-Vis absorption spectrum of a 425nm Long pass filter, and its corresponding transmission profile. (Top right) shows a scaled comparison of the same quantities demonstrating sharp variations in transmission of ~10-20% across visible wavelengths. (Bottom left) shows this transmission profile overlaid on a PL spectrum measured using this filter to remove scatter from 400nm laser excitation. (Bottom right) shows a correction of the measured PL spectrum by dividing by the transmission profile. This is seen to rapidly increase at the cut on wavelength of 425nm as the correction attempts to divide by a transmission approaching zero. Measured by author.

A correction for this effect can be achieved by dividing the PL spectrum by the transmission profile of the filter.

It should be noted that in the example shown here that this has not fully removed the additional structure or perfectly recreated a broad featureless spectrum characteristic of CT emission. This is because the transmission profile is generated by taking the UV-Vis Absorption spectrum of the filter in question. For high spectral resolution, absorption spectrometers usually have very narrow slit widths.

In this case, the PL spectrum was measured with a 100µm slit width, which is considerably larger. This means that the correction file generated will be spectrally sharper than the effect on the PL after entering the monochromator through the slit.

Given that the correction file is also generated on a different piece of equipment, and these features are spectrally sharp, a correction of this form is also sensitive to even slight differences in the spectral calibration of the respective spectrometers.

For my purposes this correction was sufficient with some degree of smoothing to meaningfully represent the character of the emitting state.

3.5 Effect of oxygen on Photoluminescence

For emission processing involving excitons in a triplet spin configuration, measuring in the absence of Oxygen is extremely important. The reason that triplet excitons are long lived in the first place is that direct coupling to a ground state, which is of singlet character in most materials, in not a spin allowed transition, and so it takes more time for a secondary process to allow some change in the angular momentum of the system before it can decay radiatively.

This is not the case for molecular oxygen O2, which has a triplet ground state. This allows coupling directly between triplet excited states on a given chromophore with the ground state of a nearby oxygen molecule. This results in both a reduction in the total photoluminescence and a reduction in the photoluminescence lifetime.

Given that this process is not a chemical reaction; the presence of oxygen can be thought of almost as a catalyst for increasing non-radiative decay from an excited triplet population. A given oxygen molecule in solution or absorbed into a film has the potential to quench many excitons.

Increasing the number of ways in which a triplet exciton can decay non-radiatively will change the photoluminescence kinetics, which can be mistaken for a higher radiative rate.

Whilst this process is undesirable in the context of our measurements, it can be used as either a measure of the partial pressure of oxygen, ¹⁰¹ or a quick "wire in the blood"¹⁰² test for triplet involvement in photoluminescence by testing for reversible quenching of net PL when cycling between ambient conditions and high vacuum for film, and by cycling through bubbling air and dry nitrogen through a solution, or vacuum-freeze-cycling on a Schlenk line.

Oxygen quenching is much more complete in solutions ^{103,104}, giving a closer estimate of the magnitude of triplet involvement in luminescence, however cycling requires either freeze-vacuum cycles on a Schlenk line, or purging with dry nitrogen both of which are not readily carried out in situ in spectroscopic labs. For this reason, vacuum-air cycling of solid film samples is the method primarily used in this thesis as a test for triplet emission.



Figure 3.14 vacuum-air cycling

Figure 3.14 shows (top) Au-Cz demonstrating reversible quenching with minimal sample degradation between measurements by comparing total counts measured in a given interval under uniform illumination. (Bottom) Cu-Cz demonstrating reversible quenching with a meaningful amount of sample degradation between data points. Measured by author

Between each measurement, the beam is blocked, and the sample allowed to equilibrate in vacuum or ambient conditions for 5 minutes to allow oxygen to either degas or be absorbed into the film.

To better separate the effects of photo-degradation from oxygen quenching in a sample like this, multiple points can be taken for each environment in the cycle so that the degradation in the presence of oxygen can be compared to that in a vacuum.

E.g. Air 1a, air 1b, air 1c, vac 1a, vac 1b, vac 1c, air 2a, air 2b, air 2c... and so on

This method would allow the quenching factor to be separated from the two degradation factors, and also to track whether or not these degradation factors are actually constant if the exposure time to the beam is kept constant.

Whilst there may be cases where these were the metrics of interest, for the purposes of the materials studied herein, it implied that a far better approach to measuring these materials would be rigorously excluding oxygen from the measurements.

3.5.1 Spectral information from oxygen quenching

A large amount of information can be extracted from steady state PL spectra without resorting to time resolved or cryogenic techniques.

For emitters where there is PL from fluorescence and also from a triplet state, like TADF, estimating the contribution to the total emission from these 2 pathways is very important.

By comparing the steady state spectra measured in air to a similar measurement carried out in vacuum, we expect the change to be due to quenching of emission from triplet states.

The difference spectrum obtained by subtracting the measurement carried out in air from the measurement carried out in vacuum thus should correspond to the emission spectrum from triplet contributions to the total PL.

If this is spectrally distinct from the fluorescent contribution, is it possible to perform a weighted subtraction from the spectrum measured in vacuum and quantify what percentage of the total emission was from fluorescence versus triplet contributions.

This also provides a measure of the state energies from the S1 and T1 /3CT states.

In the case where there are multiple contributions to the PL from triplet emission, oxygen quenching can also provide a quantitative tool for spectral analysis.



Figure 3.15 oxygen quenching spectra

Figure 3.15 shows that the structured room temperature phosphorescence (blue) can be separated from the broad CT emission (green). These are in good agreement with phosphorescent measurements and time resolved data on the same material. Data measured by Antti Reponen.

Given that oxygen quenching is a process which is in kinetic competition with emission from a triplet state, the extent to which emission from a given pathway is depleted is proportional to its PL lifetime.

This means that if two triplet processes exist, like CT emission and room temperature phosphorescence, that these are not depleted equally in the presence of oxygen.

3.5.2 Measuring in the absence of oxygen

A series of different approaches were explored to measure sample in the absence of oxygen. For solid films this was achieved by carrying out measurements with the samples under hard vacuum (10⁻⁶mbar) where possible, and either encapsulated or in a nitrogen environment where vacuum chambers were not practical.

Samples of solutions proved much more problematic to keep devoid of oxygen. Whilst preparing solutions in a glovebox environment using degassed solvents meant that oxygen free samples were possible to produce, keeping them that way during measurement proved difficult. Given that solutions are more prone to oxygen quenching than solid samples, I needed to develop robust methods to work around this repeatably.

3.5.2.1 PL and TA on oxygen free solutions

During the course of this PhD, I have explored seven methodologies for excluding oxygen from solutions:

-1) Comar cells with dust cap and para film (effectively pointless)

- -2) Hellma cells with stopper and para film (few hours)
- -3) Hellma cells with supraseal cap and argon balloon (few hours)
- -4) Aireka cells with PTFE screw top (hours to days depending on seal)
- -5) Cuvettes in existing vacuum chamber (at least a day)

-6) Cuvettes sealed within in secondary glass vial in glovebox environment (at least a day)

-7) Cuvettes sealed with parafilm within bespoke atmospheric chamber (at least a day)

Methods 1-4 were either entirely ineffective, or did not guarantee measurements could be carried out before ingress occurred.

Method 5 was highly effective, keeping out air indefinitely, however the existing vacuum chambers were too large to fit through the small glovebox antechamber, so this was highly inconvenient for sample changes.

Method 6 also kept air out repeatably over the course of many hours, and was much more convenient for sample loading. The downsides of this approach are that the glass bottles used would glow if UV excitation was required, alignment was difficult to achieve manually and as the sample was on an angle, transmission measurements were not practical.



Figure 3.16 methods of preventing oxygen ingress

Figure 3.16 shows (left) cuvette of solution sample prepared in glovebox environment sealed within a secondary glass bottle of nitrogen i.e. method 6. (Centre) small atmospheric chamber on optical post designed to fit through glovebox antechamber i.e. method 7. (Right) shows a 1mm path length Hellma quartz cuvette which has been flame sealed to a Young's tap, property of the Bronstein group. To solve the above issues, I fabricated a small atmospheric chamber (method 7). This was designed to mount on an optic post for reliable alignment, have 2 parallel windows made from UV Quartz so that transmission measurements were possible and remove PL from glass under UV excitation. The dimensions of this chamber were designed to be compatible with all our glovebox antechambers with the optic post still attached.

During collaboration with a synthetic group also studying TADF materials, quartz cuvettes which had been flame sealed to a Young's tap were used, which provided a very elegant solution to this problem as the sample can be freeze-pump-thaw cycled directly. Sadly they would not let me keep it. I did ask.

Method 7 has proved suitable for measuring solutions in the absence of oxygen for both PL and TA.

3.5.2.2 PLQE of oxygen free solutions

The protocol adopted for PLQE measurements where the sample could not be kept as per methods 5-7 was to prepare the sample in the glovebox, seal with parafilm, transport to the integrating sphere within secondary containment in a glovebox atmosphere (as per method 6), and then transfer the sample into the integrating sphere flooded with nitrogen, so it only is exposed to ambient conditions for a matter of seconds, and subsequently is not in the presence of oxygen long enough for a meaningful amount to diffuse through the parafilm. Tests carried out over several hours using this method showed no noticeable drop in PL intensity, and since this was much longer than the duration of a measurement, these measurements are assumed to represent an oxygen free environment.

3.6 Andor ICCD spectral characterisation

3.6.1 ICCD monochromator input slit

As a sanity check for PL measurements, it can be good practice to deliberately measure some amount of the scatter from the excitation laser pulse. This serves two purposes.

Firstly, it allows for a confirmation of the spectral calibration in that region of the spectrometer i.e. Does the scatter from a 400nm laser appear at 400nm?

The second purpose of carrying this out is that the broadness of the scatter feature in wavelength space is a direct indication of the spectral resolution of a measurement, and sets a lower limit on the width of features which can be considered to be "resolved" in a measurement.

This is important for well-considered experimental work, as to minimise sample degradation it is good to acquire signal at the lowest power necessary, and as fast as possible. Choosing an appropriate input slit width facilitates achieving this balance.

The width of the input slit to the monochromator governs the spectral sensitivity of the measurement, but also the amount of light collected. This introduces a trade-off between SNR and experimental run time with spectral sensitivity achieved.



Figure 3.17 input slit characterisation

Figure 3.17 shows (left) scatter from 400nm laser light on a blank glass substrate measured as a series of input slit widths. (Right) the FWHM of the measured laser scatter as a function of slit width. Measured by author.

For the processes I have studied, none of the transitions are very spectrally narrow, and an input slit width of $100\mu m$ -150 μm was used to get as much light into the detector as possible before significant broadening or spectral mismatch occurred.

A FWHM of 5nm is an order of magnitude sharper than any emission I report, and was therefore considered sufficient. The spectral position of the laser scatter is also within 1nm of 400nm, which I considered sufficiently accurate as this was well within the FWHM.

3.6.2 Detector spectral sensitivity

Another source of structure in measured spectra can be the detector itself. No material has a spectrally flat response, and in a properly designed and calibrated system this is corrected for.

Structure can be artificially introduced in the spectra we measure by the sensitivity of the spectrometer, the centre wavelength of the grating selected, and the response function of the detector itself.

The Andor ICCD I used for many of my measurements uses a silicon CCD. The bandgap of silicon is 1.14eV which corresponds to ~1080nm. In the photomultiplier before the CCD however, there is a phosphor screen with a sensitivity cut-off around 900nm.

The key features to mark here are that there is a well-defined cut on and cut off of the sensitivity based on where the grating is positioned, and also that there is some structure introduced between 850nm and 900nm, and no light is detected after ~900nm.

It is important to take this into consideration when setting up a measurement, as the features to be resolved need to lie within ~ ± 200 nm of the centre wavelength of the spectrometer (most clearly seen for the turquoise line in figure 3.19 for 650nm centre trace which shows signal between 450 and 850nm).

In the case where very broadband emission is to be measured, or emission from a wide ranges of states such as a host: guest blend with incomplete quenching of host excitations, or a low temperature measurement where fluorescence and phosphorescence are both measured simultaneously, it can be necessary to repeat the measurement with several centre wavelengths and later stitch the data in the overlapped region.

The materials I have measured emit across the visible spectrum, and in this region, no significant structure is introduced. This confirms that the intensity profile of my measurements is accurate over the wavelength region considered.



Figure 3.18 Andor ICCD spectral response

Figure 3.18 shows (top left) the wavelength response of Andor ICCD intensifiers ¹⁰⁵, (top right) spectra of Ocean Optics calibration lamp used, (bottom left) the measured spectrum of calibration lamp when measured at a series of different centre wavelengths on the monochromator, (bottom right) the calibration lamp spectrum compared to the range of centre wavelengths which I measured at for the samples discussed in this thesis. Bottom panels measured by author.

3.6.3 Room light

If the scatter from the laser is in the correct position, it can still be a useful exercise to compare to the spectra of the room lights in the lab to check that the entire spectral width is calibrated. If these are fluorescents, these have sharp, well defined emission peaks across the visible spectrum, and can be used to verify wavelength calibration across a spectrometer in one measurement. This confirms that the spectral calibration of my measurements is accurate across the entire spectral region considered.



Figure 3.19 fluorescent buld spectrum

Figure 3.19 shows a comparison to the measured (by author) room light spectrum in the lab using the ICCD (top) with the published spectrum of a fluorescent bulb (bottom) ¹⁰⁶.

3.6.4 Profile of electronic gain

Another source of non-physical structure in the spectra measured on an ICCD is the spectral profile of the electronic gain. The gain applies across roughly the centre two thirds of the range of the CCD in a highly nonlinear fashion. This means that for measurements taken at high gain, such as low intensity long live PL, emission from low PLQE samples or samples excited at very low intensities this can be an appreciable portion of the signal measured.



Figure 3.20 ICCD PMT

Figure 3.20 shows a schematic of the intensifier in an ICCD. This is placed in front of the CCD array and all light measured has been generated by this device. No photons from the actual sample PL are recorded on the CCD.¹⁰⁷

Asides from creating non-physical structure in the spectra measured, this results in an additional problem for kinetic analysis, as this signal is equivalent to a baseline amount of emission which is temporally invariant. If the integrated PL is considered, this manifests as a

nonphysical upwards trend at long time, which is analogous to integrating an exponential decay with a small constant offset.

This feature can be corrected for by carrying out a blank measurement with the beam blocked for subtraction. Due to the increased noise level at high gain, it is advisable to take at least 10 scans of this to generate an average correction file to be subtracted from the data set. In the example presented this also corrects for a small ingress of room light into the sample enclosure, which can also become problematic at extremely low intensities.



Figure 3.21 ICCD gain correction

Figure 3.21 shows (top left) blank measurement on 150 gain. 2 lobes at either extreme of the spectrum represent the shape of the response. A small amount of room light is also detected; sharp peaks at 540nm and 620n. (Bottom left) shows a spectrum measured with this level of gain overlaid on the blank measurement. (Right) shows this spectrum corrected by subtracting this background. The 2 non-physical lobes and the small amount of room light have been removed and the average in areas where emission is not occurring is at zero so will not interfere with integration. Measured by author.

In the case of data processed for kinetic comparison, or integrated PL, this artefact can be mistaken for wrap-around. The frequency of the laser used for most of our time resolved PL measurements is 1 KHz, meaning a pulse to pulse time of 1ms. Some very long lived phosphorescent emitters, even at room temperature, may not be totally finished emitting by 1ms, and at low temperature emission lifetimes from triplet states slow down considerably and this can become a meaningful limitation, as for most time resolved measurements we work under the assumption that all excitations have relaxed before the arrival of the next pulse, and so multiple sampling of subsequent pulses should recreate the behaviour of an individual decay.

In the measurements I have carried out, this method of subtraction has been used to only include real signal in measurements and processing.

3.7 **Time Resolved Photoluminescence**

One of the key metrics in the field of light emitting materials is measuring the time taken to emit light once an excited state is formed. In the context of the diagram in figure 2.9, this represents transitions 3, 7, 8 and 10.

The measured photoluminescence lifetime, in conjunction with the PLQE of a material, allows for calculation of the radiative and non-radiative rates of the transitions accessible to excitons on the material. In addition to this, in systems where the emission behaviour varies with temperature, the change in the PL lifetime with temperature gives insight into the activation energy of the emission process as the thermal distribution of the energy of excited states varies. The relationships between PL lifetime (τ) , radiative rate (\mathbf{K}_{rad}) , non-radiative rate ($\mathbf{K}_{non-rad}$) and *PLQE* are expressed in equations {11to 14}.

$$\frac{1}{\tau} = K_{rad} + K_{non-rad}$$

{11}

$$PLQE = \frac{K_{rad}}{K_{rad} + K_{non} - rad}$$

{12}

$$\frac{PLQE}{\tau} = K_{rad}$$

{13}

$$\frac{1}{\tau} - \frac{PLQE}{\tau} = K_{non-rad}$$

{14}

Clearly these are key quantities for describing the intrinsic photophysical behaviour of a material, as well as for cross comparison between a given material in a series of environments, or tracking the effect of changes to a molecular structure.

3.7.1 Measuring Time Resolved Photoluminescence

There are two ways in which time resolved measurement of an event can be achieved.

Firstly, many subsequent measurements of the same, individual event can be taken, like a video. This requires the ability to sample *much* faster than the event is occurring, and carry out a large number of measurements over the duration of the event.

Secondly, many individual measurements of a series of separate, but nominally identical events can be carried out, and compiled to recreate the dynamics of the event which is repeated for subsequent measurements.

This approach is required when the duration of the event is shorter than the time over which a large number of subsequent measurements would be possible.

This second approach is how we measure TRPL.

There are a number of methods available to measure TRPL; there are Intensified CCD cameras (ICCDs), streak cameras, Time Correlated Single Photon Counting (TCSPC) and ultrafast transient grating techniques. All of these techniques have their respective strengths and weaknesses; however they all share common elements which are required for any time resolved measurement.


Figure 3.22 generalised TRPL setup

Figure 3.22 shows a schematic representation of an arbitrary TRPL experiment.

These key elements are:

- Pulsed excitation source with suitable short excitation pulses and pulse-pulse times
- A detector which can be triggered in synch with the excitation pulses
- A means of achieving temporally resolved measurement
- A means of adding temporal delay between the trigger pulse and the measurement
- Some manner of beam delivery and PL collection is also required.

For the subsequent events to be "nominally identical" the pulse to pulse variation in the laser power must be small, and the samples should be chemically stable over the duration of the measurement.

To resolve an effect, you ideally require a sampling rate and resolution which is an order of magnitude more rapid than the effect. This was famously demonstrated in 1878 when the development of (at the time...) high speed cameras allowed it to be proved that whilst horses ran, there were moments when all 4 feet are off the floor.

To resolve the processes relevant for the absorption and emission of light, we therefore require apparatus which can sample across the timescales of femtoseconds-picoseconds-nanoseconds – microseconds as the processes of absorption, excited state conversions and subsequent emission span many orders of magnitude in time.



Figure 3.23 "The horse in motion"

Figure 3.23 shows images from "The horse in motion" by Eadweard Muybridge¹⁰⁸

To achieve this range of temporal resolution, a number of different physical effects are required for the gating process.

These include electronic gating delay (ICCD), electronic time of flight measurement (TCSPC) and changing optical path length (TA and transient grating PL).

In this thesis I present measurements which I have carried out using ICCD and TCSPC techniques. I include transient grating PL data measured by Johannes Richter and Sascha Feldman to aid in the interpretation of some of the data sets.

These different techniques will be discussed individually below.

3.8 ICCD time resolution

The ICCD achieves temporal resolution electronically. As shown earlier, the photons reaching the CCD are not those from the sample, but actually those which have been generated by a phosphor screen struck by electrons accelerated from a photocathode on which the sample PL is incident.



Figure 3.24 ICCD detection harware

Figure 3.24 shows a diagram of the ICCD camera¹⁰⁵

The Photo Multiplier Tube (PMT) only accelerates the electrons from the photocathode whilst a voltage is applied across is, otherwise the CCD receives no signal.

This is referred to as "gating" the camera, and is the mechanism by which temporal resolution is achieved.

The shortest time that this can be gated for electronically is ~5ns, as this is the limit on electronic resonance in the circuits gating the camera and the time taken for the voltage to be switched on/off across the PMT.

The accelerating voltage across the PMT determines the energy with which the electrons from the photocathode strike the phosphor screen, and thus the signal to the CCD can be increased for low intensity PL, or when measuring over longer timescales. This is referred to at the gain. Time resolved measurements are achieved by changing the delay between the ICCD receiving the trigger pulse, and when the gate voltage is applied.

By adding increments to this delay, measurements of subsequent emission events at a series of delays can be achieved building up a picture of what an individual decay would have looked like, from a series of identical subsequent measurements.

To achieve better SNR, it is possible to take a number of accumulations at a given temporal delay, before adding the next step to the gate delay time.

By varying the duration of the gate pulse, the number of accumulations at each time step, and the electronic gain, it is possible to carry out measurements over >6 orders of magnitude in intensity, (see figure 3.390). This is extremely important for the sorts of measurements needed on TADF systems, where early time emission can be very intense and short lived, often orders of magnitude more counts per second, but for only a few ns, and most of the emission occurs over the next few hundred microseconds at much lower intensity.

These techniques are used for the measurements presented herein, with data measured in different time and intensity regimes stitched together by overlapping time regions and matching intensities.

3.9 Time Correlated Single Photon Counting

3.9.1 TCSPC time resolution

The mechanism by which the TCSPC achieves time resolution "time of flight" and relies on an individual photon reaching the detector relative to a high frequency trigger signal.



Figure 3.25 TCSPC time of flight histogram

Figure 3.25 shows a diagram of how temporal resolution is achieved with a TCSPC, and a histogram is compiled which correlated to the optical temporal waveform 109

The delay between receiving this trigger pulse and the arrival of the photon is used to measure the "time of flight", and by carrying a large number of such measurements, a histogram is produced which represents the PL decay rate.

This means that if a series of kinetics are measured at different wavelengths, it is important to set the count rate at the brightest wavelength so that only one photon is detected per trigger pulse. A count rate of 1-5% of the trigger rate is sufficient for this to occur a small fraction of the time.

3.9.2 Appropriate TSCPC measurement

One of the strengths of the TCSPC is that the laser excitation and detector can be triggered at a variety of frequencies; making is a versatile tool for measuring samples with different brightness radiative lifetimes in an efficient manner without needing to compromise on SNR or duration of experiment.



Figure 3.26 example TCSPC data

Figure 3.26 shows (left) steady state PL spectrum of an evaporated film and (right) the TCSPC trace measured at a series of different wavelengths. Measured by author.

Unlike with the ICCD, the TCSPC does not measure spectrally resolved measurements, but either a total count rate, or single wavelength at a time.

If there is only one species emitting, this is not an issue, however if there are multiple states emitting at different wavelengths at different rates, then it is necessary to take a number of TRPL scans.

In the example in figure 3.27, two distinct features are present in the steady state PL spectra. The time resolved measurements at these different wavelength regions show clear differences in the lifetimes of the emission of these 2 states.

In addition to the count rate not being too high compared to the trigger rate such that a meaningful fraction of photons are not counted, it is also important to consider the time window between excitation pulses and ensure that this is long enough for the excited states to have depopulated fully.

In the case where emission is from a singlet state, this does not tend to be a problem, as emission happens over 10s of ns.

For materials emitting from triplet states, this can become an issue if the PL lifetime is of the same order as the time interval between laser pulses, or longer. This can lead to the sample still emitting when the next laser pulse arrives, and the camera is triggered for the next collection window. This results in signal from previous excitations being recorded in subsequent time bins.

This is called "wrap around" and resembles the noise floor of the measurement having some finite offset from zero. In figure 3.28, a sample is measured with 400ns between excitation pulses, and the PL lifetime of the material is of the order of μ s. We see that the noise level before the pulse arrives is different for each wavelength, as the stop condition used in this case was a set collection time rather than peak counts, and so the counts scale with the intensity of that given wavelength in the PL spectrum.



Figure 3.27 TCSPC data with wrap around

Figure 3.27 shows TCSPC measurements at a number of wavelengths for a sample which has a longer emission lifetime than the time between laser pulses (400ns in this case). Measured by author.

Despite the issues with wrap around changing the intensity, information can still be extracted about the PL lifetime even if the experimental window is shorter than the time taken for the signal to decay. If the prompt fluorescence is omitted from the above kinetics, then all the wavelengths display highly mono-exponential decay.

If the intensity from a single excitation event is:

$$I(t) = I_0 e^{-kt}$$
$$\frac{dI}{dt} = -k I$$

{15}

Then if a single species is emitting, the decay constant is easily obtained.

The intensity of a measurement including the contributions from previous pulses could be thought of as a sum of this term with different time offsets. (Δt)

$$I(t) = I_0 e^{-kt} + I_0 e^{-k(t+\Delta t)} + I_0 e^{-k(t+2\Delta t)} + I_0 e^{-k(t+3\Delta t)} + \cdots$$
$$\frac{dI}{dt} = -k I$$

{16}

A sum of exponentials with same rate constant but time offset produces modified amplitude but the same rate constant, so the PL lifetime can still be extracted.

For this assumption to hold, it would need to be possible for subsequent pulses to excited the same number of carriers each pulse, i.e. the excited state lifetime is not so long compared to the repetition rate that a ground state bleach is achieved.

Even though kinetic information can still be extracted if the PL lifetime exceeds the repetition rate of the laser, this measurement condition is not ideal, as information about additional processes can be distorted.

To avoid this is it important to set the repetition rate of the laser such that the PL will have decayed by as many orders of magnitude in intensity from the noise level as are desired for the measurement.

Whilst this may seem like a "chicken and egg" scenario, as to choose an appropriate frequency you must already know the PL lifetime, which you are in fact setting out to measure, this should be considered part of the setup of any well considered experiment.

3.10 Transient grating PL spectroscopy

Transient grating PL spectroscopy is the highest time resolution technique used in this thesis. These measurements were carried out by Johannes Richter and Sascha Feldman. To aid in interpreting their data, I will provide an overview of the functional principles of this technique. A full description of the technique can be found in the literature. ¹¹⁰

The mechanism for achieving temporal resolution is that two gate beams are overlapped on a crystal, or gate medium. These overlapping beams form an interference pattern, which sets up a diffraction grating due to the optical Kerr effect, where local variation in refractive index is induced due to the high variation in local electric field.

The Kerr effect is a change in the refractive index of a material in the presence of an applied electric field where the change in the refractive index n is proportional to the square of the intensity of the E field. This can either be achieved by applying a large external electric field, or the Optical Kerr effect, when very high intensity light passing through any media, the change in the E field results in a change in the refractive index. This this can be appreciable for laser illumination, and can be enhanced by focussing 2 beams such that the temporal and spatial overlap results in much higher intensities.

By overlapping 2 "gate" beams, an interference pattern of high intensity E field, and thus higher refractive index is created. This regular pattern of alternating refractive index can act as a diffraction grating, and PL passing through this gate medium can be deflected by this diffraction grating. Since this grating only exists whilst the gate pulses overlap, a mechanism exists to selectively divert PL from a very well defined time window. This sets the temporal resolution of the technique to the temporal overlap of the 2 gate pulses, which in our case is 100-200fs, and temporal evolution of the signal is achieved by adding optical path to either the gate or sample path. Much like the ICCD, time resolution is achieved by adding a series of delays, and building up a series of snapshots from subsequent measurements.



Figure 3.28 transient Grating PL diagram

Figure 3.28 shows a schematic of the setup of a transient grating PL experiment. ¹¹⁰

The limits on the spectral resolution of this technique are set by the gate pulse and excitation wavelength. In our setup, the gate pulses are 800nm, and excitation 400nm providing a spectral window between 420nm and 750nm which can be measured, which is ideal for most OLED materials emitting in the visible spectrum. The spectral response was calibrated for using the white light quasi-continuum of a sapphire crystal, and corrected for directly within the measurement software.

3.11 Artefacts in time resolved measurements

To trust the lifetimes generated by TRPL measurements it is important to be able to identify and exclude sources of error in time resolved measurements.

These have 2 origins; firstly, changes to the balance of processes available to an excitation formed on a given molecule and secondly artefacts arising from the instruments used to achieve the time resolved measurement.

3.11.1 Kinetic artefacts due to sample conditions

If the environment or nature of the sample changes during measurement, then the assumption that subsequent events are "nominally identical" breaks down and the composite picture which is constructed of the behaviour will not represent the intended process.

3.11.1.1 PL kinetics in the presence of oxygen

In this comparison we see that the photoluminescence lifetime for the same spot on a sample of CMA1, is markedly more rapid in ambient conditions than in vacuum. When the chamber is purged with dry nitrogen after the vacuum measurement, we see that the emission kinetics are closely comparable between nitrogen and vacuum, though there is a slight drop in net PL intensity, possibly resulting from sample degradation, or residual air in the nitrogen plumbing.



Figure 3.29 effects of oxygen on PL kinetics

Figure 3.29 shows (left) normalised integrated emission kinetics of a film of CMA1 measured using an Andor ICCD. (Right) shows the same data presented as raw data so that the relative intensities can be seen as well as the emission rates. Measured by author.

This supports the use of measurements carried out under a nitrogen purge as being a close proxy for vacuum conditions, though possibly representing a slight under estimate. It is important to purge for an appropriate amount of time, and this can be tested by taking a spectrum every minute after either venting the sample chamber or beginning a nitrogen purge. Once the PL has plateaued in either case, the sample has reached whatever level of oxygen depletion is achievable.

3.11.1.2 Sample degradation during measurement

If a sample is damaged in the process of a measurement, then the number of emitting sites is reduced.

In addition to reducing the number of emissive molecules, molecular fragments can act as non-emissive trap sites and further quench excitations which form on remaining intact molecules.

This means that later in the experiment, a lower signal will be recorded than would initially have been.

If the time resolution is achieved through subsequent measurements at longer time delays, this will generate an artificially rapid emission kinetic, which is a convolution of the PL decay rate in the experiments time frame and the degradation in real-time.

3.11.1.3 Radical Oxygen

One of the non-reversible issues which can arise from the presence of oxygen in organic samples in chemical degradation. When molecular oxygen is excited, like when a triplet excitation transfers to it, it forms radical oxygen species, which is extremely reactive with organic material, to the extent that it is used in plasma medicine to remove tissue.

"The production of oxygen based radicals is the bane to all aerobic species" ¹¹¹

This is addressed by measuring in the absence of oxygen, even when triplet excitons are not involved in emission.

3.11.1.4 Photo-degradation

Catch 22 for organic blue light emitters, is that the energy of carbon double bond in near UV, and host emission for FRET needs to be at this energy to host deep blue emitters. This remains a topical issue, and is part of the motivation for faster emitters, as the probability of degradation events increases with the amount of time spent in the excited state.

3.11.1.5 Photo-bleaching test



Figure 3.30 photobleaching of host guest film

Figure 3.30 shows photo-bleaching of a host: guest blend film. The sample was exposed to 405nm laser light, and measured every 3 minutes for 30 minutes. Measured by author.

A method for testing the photo-stability of a material is to measure it during prolonged illumination. Ideally the signal should not change at all if the material is stable. In the example shown here, a host-guest film of a small molecule in F8BT is tested. The dopant, which emits at ~675nm is seen to degrade, and host emission from the F8BT grow back in.

This supports that the degradation product in this instance does not form a trap site to quench excitations from the host.

3.11.1.6 Testing for degradation before and after measurement

Since Cryogenic measurements over many orders of magnitude in time are invariably measurements involving extended exposure to high power laser pulses, it is also best practice to check for sample degradation with an identical "before and after" measurement. This should compare total PL, PL kinetics and spectral shape.



Figure 3.31 sample photo-degradation

Figure 3.31 shows before and after measurements of two materials measured cryogenically. (Left) shows a small amount of degradation, ~10% and no change in spectral shape. (Right) shows considerable degradation of ~90% compared to the original intensity, and broadened, redder emission. Measured by author.

In the case shown here, 2 samples are compared before and after cryogenic measurement. This consisted of 11 subsequent measurements of 30-40 minutes. For the material on the left, a total drop of 10% would mean ~1% variation in intensity during a measurement set at a given temperature. This is the limit of what I would consider acceptable to extract PL kinetics from reliably.

The data shown on the right has degraded significantly, and kinetic or spectral data from this measurement must be treated with caution.

This control of "before and after" measurements is absolutely imperative for cryogenic measurements, as if a series of measurements are taken at a series of temperatures, then degradation risks being mistaken for the effect of cooling or heating. For all cryogenic data presented in this thesis, this control measure was used.

3.11.1.6.1 False kinetic from degradation:

If photo-degradation is rapid, and a time resolved measurement is carried out over a long time compared to the rate of degradation, there is the possibility for this to produce non-physical kinetics.

The two main ways to achieve time resolution are either taking a series of accumulation as a given delay and then stepping that delay forwards in time relative to your trigger signal like an ICCD, or carrying out one scan at a time and then repeating this like time of flight measurements for single photon counting.

In the case where degradation only renders some portion of the molecules non emissive, but does not introduce traps or other emissive states from molecular fragments, then each successive pulse of the experiment would excite a slightly reduced population of emitters which retained the same spectra and kinetics.

For a time resolved and spectrally resolved measurement on an ICCD, this would result in the time slices measured later during the measurement being of lower intensity, and so the kinetic measured would be a convolution of the emission kinetics of the sample with the degradation rate in real time projected onto the time for each accumulation at a given time bin. This would result in artificially rapid kinetics, though the true form of the spectra would be retained.

In the case where the result of degradation is not only a reduction in the number of chromophores, but a new emissive reaction product the result would be different.

For a time resolved and spectrally resolved measurement on an ICCD, this would result in the time slices measured later during the measurement having a lower intensity contribution from

the original material as before, but also including a contribution from some spectrally distinct species. This would manifest as an artificially rapid kinetic with additional exponential contributions, with a spectral shift with time.

For a time of flight measurement this would only manifest in the signal rate decreasing, and not impact the kinetics, however if multiple TRES scans are taken at some wavelength interval to reconstruct a steady state spectra or heat-map via integration then the result would be susceptible to an apparent depletion of the red/ blue edge depending on the order of the measurement.



Figure 3.32 PL and integrated TRES mismatch

Figure 3.32 shows a comparison of the steady state PL measured for a sample (black) and the integral of the TCSPC tract at various wavelengths. If the TCSPC detector has a flat spectral response, this should overlap the steady state PL. Measured by author.

It is possible to identify if there has been any degradation, and if so which form, by carrying out before and after measurements on the same spot of a sample under identical conditions.

Once again, it is possible to construct a simple model of the form of degradation by carrying out a photo-bleaching experiment, but it is vastly preferable from the perspective of data integrity to carry out measurements in a regime where degradation is absent, or minimal.

3.11.1.7 Additional decay kinetics at high excitation density

When excited at high powers densities, the excited state density in a sample can become high enough that it becomes probable for the average distance between excitations to be small enough for interaction between excitations, and exciton-exciton annihilation introduces an additional non-radiative pathway for depopulating an excited population.



Figure 3.33 excitation power dependent kinetics

Figure 3.33 shows the dependence of the emission kinetic of a film of CMA1 on excitation power. Data measured by Patrick Conaghan and Emrys Evans.

Much like the effect of the presence of oxygen on emission from a population of triplet excitons, this can be thought of as shifting the balance between the radiative and non-radiative terms in a rate equation describing the excited state population of a molecule or material.

The threshold at which this occurs is a function of the optical density of the sample at the excitation wavelength, and the average lifetime of an exciton. It should be noted that this means that a measurement at a given power is not appropriate for any sample of the same material.

In the case of a pure film, or a film in a dilute wide bandgap host where the excitation wavelength directly pumps the guest material and not the host, the OD at the pump wavelength may be considered directly as all excitations will form on the chromophore.

In the case of a host: guest system when the host if being pumped and excitations form on the chromophore solely via resonant energy transfer from the host, this optical density at the excitation wavelength must be scaled for the FRET efficiency.

In a system where the excitation wavelength corresponded to absorption features for both host and guest, for example a narrow stokes shift host, or guest with additional high energy absorption features, a combination of the two approaches above would need to be considered with a weighting for the proportion of the absorption at the excitation wavelength directly into the guest versus into the host matrix. This approach would break down in the case where the absorption spectrum of the blend film is not a linear superposition of the absorption features of the two pure materials, as would be the case in the formation of some exciplex state, or if the host encouraged the formation of aggregates or crystal domains within the film.

In a host guest system pumped in a high fluence regime it is possible to reach a point where all guest sites are excited, and the dopant population is saturated. In the case of a semiconducting host, this can result in residual emission from the host material as not all excitations formed on it can be quenched be the guest. This effect can create a bottleneck in energy transfer from the host to the dopant, and must be considered for determining dopant concentration in devices.

A estimate of this threshold could be calculated by considering the spot size, film thickness, extinction co-efficient of the host at the pump wavelength, average spacing between dopant molecules, FRET efficiency, and guest PL lifetime, however for our purposes, we take it that this regime is avoided in optical and device environments where host emission has been completely quenched in steady state illumination(see figure 6.16), and this is determined experimentally by carrying out concentration series in the prospective host.

Dilute solutions are considerably less sensitive to this effect, as the average distance between molecules is great enough that they can be considered in isolation, and it is statistically unlikely for two excited molecules to close enough together for annihilation processes to occur.

Whilst all the solution measurements discussed in this thesis are carried out in a dilute case, for the sake of completeness it is worth mentioning that this assumption may cease to be valid for highly concentrated samples, for example those used to study singlet fission, where higher excitation density and intermolecular interaction is explicitly required. In that case a treatment more similar to the solid state would be required.

It is important to distinguish that whilst this process is spin ambivalent, and also present in a purely fluorescent sample, the threshold at which it becomes an appreciable factor in a kinetic competition for excitations will be orders of magnitude higher as the radiative lifetime increases.

For spin allowed transitions from a singlet excited state this is usually on the order of ns, compared to µs to ms for excited state lifetimes in triplet states emitting via phosphorescence or TADF. This means that particularly in the study of emitters using triplet excitations care must be taken to operate within an appropriately dilute population of excitations, as the threshold for high excitation density will be more easily reached, and also that annihilation processes will be a more significant competition for a process with a slower radiative rate.

Measuring in a regime where PL intensity is linearly proportional to the power of the sample excitation at a given wavelength ensures that the sample is within a regime where the excitation density is not sufficiently high for exciton annihilation processes to occur between a meaningful proportion of the total excitations.¹¹²

When a new sample is being measured, testing a number of excitation powers and verifying that the total PL scales linearly with power, and that the decay rate is power independent will mitigate this effectively. All data presented in this thesis was measured in this manner.

3.11.2 Hardware based TRPL artefacts.

The second potential source of error in time resolved measurements is that there are variations in the hardware which result in a slow drift in signal.

3.11.2.1 Fluctuation in laser power

For subsequent events to be "nominally identical", not only does the sample have to be the same, but the excitation must be also.

Variation in power, alignment, or beam mode can all manifest in a change in the PL signal produced, or it's in-coupling into the detector spatially.

This problem is solved by spending a large amount of money on a good laser, and keeping it in an environmentally controlled lab.

3.11.2.2 Variation in excitation/collection geometry

Collection optics are very sensitive to small changes in sample position or excitation spot.

If something like an optical post delivering the laser beam is slightly loose, this can result in beam wander if there is a source of mechanical vibration, like a vacuum pump running.

Testing that all optics are firmly bolted in place is sufficient to eliminate this.

3.11.2.3 Fogging of windows

In low temperature measurements, if correct levels of vacuum are not used to insulate the cryostat, then the outer housing and windows can cool down. This can result in condensation forming on the windows very gradually, which during a long TRPL measurement can introduce false kinetics.

This is mitigated by using an appropriate level of vacuum for insulation (10⁻⁶mbar was used for my measurements), and visual inspection of the windows if the signal changes drastically.

3.11.2.4 ICCD kinetic artefacts

Part of the photomultiplier in an ICCD is a phosphor screen which the photoelectrons generated from light from the sample striking the photocathode are accelerated onto. The applied voltage bias across the vacuum tube onto the phosphor screen determines how many photons the phosphor creates, which are then read out by the CCD.

This is the mechanism by which very low intensity signals can be amplified, and what gives the ICCD its large range of sensitivity over many orders of magnitude of signal intensity; however the physical response of the phosphor screen to excitation must be considered.

3.11.2.4.1 Phosphor glow

If the phosphor receives too high a flux of photo electrons, then it no longer responds linearly to signal in over the duration of one measurement bin. Higher excited states in the phosphor are much longer lived, and the phosphor physically glows for some amount of time.

Since the phosphor screen is positioned after the MCP, these long lived excitations have the same spatial distribution as the signal which created them, meaning that an artificial signal which is spectrally identical to your PL signal is added to the measurement, and that it decays at an independent rate, corresponding to how the physical cooling of the phosphor in real time overlaps with the duration of each accumulation and the time step it represented.

This effect can best be demonstrated by deliberately over-pumping the phosphor, and then taking a time resolved measurement with the beam blocked where the background includes the signal from the phosphor. What is seen is then a signal which starts at zero as the glow from the phosphor is correctly subtracted in the background correction, but as the phosphor cools, the background correction over corrects this signal, and so we see a negative signal emerge representing the extent of the overcorrection, which will eventually plateau when the phosphor has totally cooled.





Figure 3.34 shows a screen shot of the Andor ICCD software when the phosphor screen has been deliberately over exposed, and then a TRPL measurement taken with the beam blocked whilst it cooled. Measured by author.

An appropriate method to be sure that this effect is mitigated if you are measuring at high intensity is to start the measurement, and after the first several data points which would be the most intense, stop the measurement, block the beam and then start again with the same background file as before. If the phosphor is not glowing there should be no signal, and then it is fine to measure in these conditions.

Similarly, the first several steps of a measurement can be taken, the measurement stopped, and a fresh background measured to perform the same check.

It is extremely important in the study of prompt delayed emitters like TADF materials to recognise that this artefact has the potential to generate signal of identical form to what we may be expecting to see.

If one was to measure a purely fluorescent material at an inappropriate intensity such that the phosphor was over-pumped and glowed, we would measure a rapid high intensity decay, followed by a considerably slower, much lower intensity, spectrally identical signal which could mistakenly be interpreted as delayed fluorescence from reverse inter system crossing from the T1 to the S1 state.

As with all such artefacts, it is clearly preferable to carry out measurements in a regime where they are not generated rather than try to later apply correction for them, which requires understanding them well enough to test whether such a condition has been met.

The S.O.P. for measurements discussed in this thesis follows this format, with fresh background measurements being taken after the first several data points which include the highest counts per bin.

3.11.2.5 TCSPC

3.11.2.5.1 Multiple photon "pileup" from high a signal rate

Unlike with an ICCD where the limiting factor is charges being swept out of bins on the CCD, this readout technique can only produce a response of "did not receive a photon in this time interval" or "received a photon at some delay".

This gives rise to the possible artefact whereby if the rate of photons incident on the detectors is on above the trigger frequency, photons which arrive in the same time interval between trigger pulses when a photon has already been detected are missed.



Figure 3.35 TCSPC photon "pile up"

Figure 3.35 shows (left) a visualisation of how if multiple photons arrive during one gated interval, that they are not counted. (Right) shows a demonstration of the effect of this by increasing the power on a sample and measuring its PL decay. Data from Xinyu Bai, from OE group TCSPC training material.

This means that some portion of the emission is not registered, and thus the histogram of the collected photons against time of flight will produce an underestimate of the amount of signal, and the overestimate the rate at which it is emitted.

As more photons are emitted directly after the excitation pulse, the influence of this effect is most pronounced at early time, and we can see that a mono-exponential decay which should be a straight line on a log-lin axis, becomes concave and "sharper at the top".

To mitigate this effect being present in a measurement, it is important to set the count rate to smaller than the trigger rate, usually in the region of 1%. As this is still a statistical process, it is always possible that photons are double-counted, however if there are several orders of magnitude difference between the count rate and the trigger rate, this does not represent a large enough portion of the total photons to result in the measured trend deviating from the actual kinetics.

3.11.2.5.2 TCSPC spectral ambiguity

Despite its high temporal resolution, measurements on a TCSPC do suffer from the possibility of there being ambiguity about what signal is being measured. In this example, appropriate filtering to remove scatter of the excitation laser pulse has not been used, and rather than measuring the PL decay lifetime, instead, the response function of the TCSPC has effectively been measured and mistaken for unexpectedly rapid PL, which remained temperature invariant between 4K and room temperature.

Mitigation of this form of artefact is trivial, and appropriate long pass filters should always be used to remove scattered laser excitation. Even if laser scatter had been correctly filtered, the correct interpretation of this data would have been that the process was instrument limited, rather than thermally invariant.



Figure 3.36 TCSPC instrument response comparison

Figure 3.36 shows (left) the IRF of the TCSPC measured by Xinyu Bai, compared with (right) the TRPL measured on this instrument ¹¹³.

It is possible to apply a time-domain deconvolution to a measured signal if a good measurement of the instrument response function exists, however for our purposes, since we have access to higher temporal resolution experiments, I opted to combine transient grating, TCSPC and ICCD measurements to build up the picture of the emission at varying time scales.

3.12 Putting a measured lifetime in the context of PLQE

In addition to ensuring that a PL lifetime is measured within the correct operating conditions of the camera and in an environment where it is representative of the intrinsic photophysics of the system it must also be considered in the context of the PLQE of that given sample to infer the radiative and non-radiative rates from the PL lifetime.

Whilst there do exist physical processes like singlet fission where one absorbed high energy photon can result in two lower energy photons being emitted, allowing PLQE values between 100% and 200%, for the materials described in this thesis, this does not apply, and an upper bound of 100% is the relevant physical limit.

In a system with 100% PLQE, the radiative rate and photoluminescence lifetime would contain analogous information, and be the reciprocal of each other, as every excitation results in the generation of a photon, and thus a measurement of the rate of emitted photons would be the same as the rate at which the excited state population is depopulated.

In a more physically realistic system with less than 100% PLQE, the excited state population is also being depopulated by processes which do not result in the emission of a photon, and thus the photoluminescence lifetime as measured would be faster than the radiative rate.

This means that to properly interpret any photoluminescence lifetime, a PLQE measurement is needed which is representative of the sample in the same environment and excitation regime.

Achieving identical sample condition is not always experimentally practical, as ideally PL measurements are carried out in vacuum, whereas it is not practical to operate our integrating sphere in these conditions. If it can be demonstrated that one environment acts as an appropriate proxy for the other with respect to excited state dynamics however, this becomes a reasonable cross comparison.

Measurements carried out using CW excitation versus pulsed laser excitation can be hard to compare directly with respect to average power and steady state excitation density, however operating in a regime where net PL is linearly proportional to excitation power implies both are in a regime where exciton-exciton annihilation processes are not present. Both the PLQE measurement and time resolved PL measurements should be taken in this condition for any inferences about radiative rates to be valid.

Understanding the physical processes used in the hardware we use to measure photoluminescence and TRPL is crucial to understanding the limitations and strengths of a given setup, as well as recognising what artefacts it is possible for that system to generate, and how to avoid these, or separate them from our data.

3.13 Exponential and non-exponential emission kinetics

One of the metrics commonly used for comparison purposes in this thesis is the photoluminescence lifetime of a state, from which we infer the radiative rate.

In an ideal system, like a dilute solution, the assumption can be made that each molecule is in an identical environment, and is sufficiently dispersed that intermolecular interaction is negligible as each molecule cannot interact with others.

Since quantum transitions between a given pair of states are intrinsically probabilistic, the total number in a given time interval is proportional to the excited state population, and thus the excited state population as a function of time is given by:

$$P_{(t)} = P_0 e^{-kt}$$

Thus

$$\frac{dP}{dt} \propto P_{(t)} = -kP_0e^{-kt} = -kP_{(t)}$$

Where both radiative and non-radiative decay are probabilistic,

$$\frac{dP}{dt} = k_1 P_{(t)} + k_2 P_{(t)} = k_{rad} P_{(t)} + k_{non-rad} P_{(t)} = K P_{(t)}$$

Where $K = k_{rad} + k_{non-rad}$

Given that the intensity of emission is proportional to the change in excited state population, the change in intensity of the signal we measure with time is a combination of both the radiative decay rate(k_{rad}) and the non-radiative decay rate ($k_{non-rad}$).

$$\frac{dP}{dt} \propto I_{(t)} = I_0 e^{-Kt}$$

Time resolved PL measurements in isolation then can only provide a lower bound for the radiative rate, and the ratio of k_{rad} : $k_{non-rad}$ must be known to extract radiative rates from photoluminescence lifetimes.

This is measured using a technique called Photo Luminescence Quantum Efficiency (PLQE) as described in section 3.3.

In the absence of non-radiative decay (100% PLQE) the radiative decay rate and the PL decay constant directly comparable.

The radiative rate is a key metric for emissive materials, and it is either discussed directly from measurements of PLQE and PL lifetime, or a proxy is used when emission is from a number of similar states simultaneously.



Figure 3.37 solution vs. film kinetic comparison

Figure 3.37 shows a comparison of 4 molecules in dilute toluene solution (left) and a in a solid polymer hosted film (right). Measured by author.

In the case of a solid film, these assumptions break down. Each individual molecule will be in a subtly different environment. This could be a change in the proximity or orientation relative to other nearby host/ dopant molecules, or to be locked into some non-energetically favourable configuration if there is any degree of aggregation or crystallisation present in the film.

The result of this is that it is usual for emission from a solid sample to not be comprised of pure exponential contributions.

3.13.1 Characteristic emission Timescale versus rate constant

For the treatment of the CMA family of materials, a metric was developed to allow meaningful comparison between changes in the nature of emission between different molecules and across a large range of environments.

As shown above, a solid film deviates from the pure mono-exponential form of PL decay even in the case where there is only one state emitting as in a fluorescent compound.

This deviation from a convenient mathematical treatment is increased when the material emitting has a number of different states which can emit light, and the energy and time scales which it happens on are highly dependent on morphology, like the CMA materials which display prompt fluorescence from the locally excited singlet on the nanosecond timescale, TADF from the CT manifold on the µs time scale, and phosphorescence from the local triplet states on the hundreds of µs timescale in some instances.

Whilst it may seem reasonable to adopt a double or triple exponential treatment of a system with three states, each emitting with a well-defined rate and energy, the variation in each of these rates introduced by the range of morphologies results in this being a poor fit to experimental data.

Higher order exponential fits, polynomial fits, or a power law description all offer methods for generating some fit which more closely matches the data, but at the expense of the fitting parameters not having a meaningful or obvious physical interpretation.

I would not advocate using any fitting function which has not been selected to represent real physical aspects of the emission process, for example, bi-exponential decay if there are 2 emissive states in a dilute sample. To this end, I developed another metric for comparing emission lifetimes between CMA molecules, where solid samples often displayed non-exponential kinetics due to a range of conformations locked in the ensemble.

In CMA molecules, for the majority of the emitters studied, the dominant emission pathway is via the CT state, rather than fluorescence of phosphorescence form the S1 or T1 locally excited states. This motivated a metric being developed where we treat all the emission as

though it had resulted from a perfect single exponential decay, and extract a characteristic time to characterise the emission, rather than a decay constant.

This time is set to be when the emission reached 1-(1/e) of the total emission. In the case of a perfect mono exponential, this is the time value which corresponds to the decay constant.



Figure 3.38 cumulative PL metrics

Figure 3.38 shows (left) the PL kinetic of a dilute solution of CMA1 in THF. This is highly mono-exponential over 6 orders of magnitude in intensity. (Right) is shown the cumulative PL as a function of time. This has clearly plateaued by the end of the measurement. A dashed line shows when 63% of emission has occurred. Measured by author.

In the example shown here of a dilute solution of CMA1 at 1mg per ml in THF, the emission is highly mono-exponential over 6 orders of magnitude in intensity, with a time constant of 1314ns.

By integrating the count rate as a function of time, it is possible to demonstrate the cumulative PL, even for measurements taken with discontinuities in the sampling interval, without requiring more complicated treatment ¹¹⁴.

If the integral of this is plotted, the time at which the threshold of 1- (1/e) is reached is 1294ns which is within ~1% of the exponential time constant obtained from the fitting

Another benefit of this treatment is that by plotting the data in its integral form, we are able to ascertain whether the experiment has captured all the emission of the material over the time window, and also to then meaningfully characterise what proportion of the emission has come from the different radiative channels. This obviously cannot be quantified unless the sum of the total emission is known.

3.14 Temperature dependent measurement

Energetically speaking, there is no such thing as a free lunch, balls do not roll up hill, and entropy always wins.

Whilst this may be cause for speculation about the inevitable heat death of the universe, in the meantime, there is sufficient thermal energy in solid matter that it is able to explore both exothermic and endothermic processes, and some of them are rather useful.

In figure 2.9, there is one arrow, number 9, pointing upwards which does not correspond to a photoexcitation, but that a transition to a higher energy state is possible using excess thermal energy.

To determine just how far "uphill" that arrow is pointing, energetically speaking, cryogenic measurements can be used to limit the thermal energy in a system to test the relationship between temperature and the rates with which these transitions are accessed.

From the perspective of an excited state wavefunction, temperature has a number of effects on the vibrational freedom of a molecule, with different stretching, bending and twisting modes being explored with increased thermal energy. This effects the potential seen by the electron, and thus can change the energy, or distribution of energies explored in the excited state. Additional factors like glass transitions in polymeric materials can also change the steric effects of the local environment, also changing the conformational (and thus energetic) freedom of the excited state. At a given bulk temperature, the molecules in the sample will explore a Boltzmann distribution of local energies, and thus information extracted at different temperatures must be read as a distribution of local state conditions.

3.14.1 Continuous flow cryostats

A continuous flow cryostat can be used to regulate the temperature of a sample environment by balancing the flow of a coolant with the current passed through a resistive heater.

If a fixed flow rate is used, then a PID controller can vary the current supplied to the heater until the system stabilises at the desired temperature.

The lowest temperature which can be achieved in this configuration corresponds to the coolant used. In my case this was liquid helium, which is 4K. Realistically this means that measurements down to 5-10K are achievable.

For the data presented in this thesis, I used Oxford Instruments Optistat Static, and Dynamic flow cryostats. The difference between these two models was whether the coolant gas was drawn through the sample chamber (dynamic) or passed through a heat exchanger with the sample area in an independent atmosphere (static). My measurements have either been carried out with the Static configuration with the sample in vacuum, or in the Dynamic with a helium environment after vacuum purging the sample chamber of air.

3.14.2 Cryogenic TRPL

Below is the same treatment for an evaporated film of CMA1 at a range of temperatures as described in section 3.15.



Figure 3.39 temperature dependent TRPL example

Figure 3.39 shows the integrated TRPL for a neat film of CMA1 at different temperatures. Measured by author.

From this we can see that the vast majority of the emission occurs over the 100s of ns to μ s regime at room temperature, and that this slow down to the 10s or 100s of μ s at low temperature. We can also see that even at the lowest temperature no meaningful amount of the PL results from fluorescence at early times, or a phosphorescent regime emerging at lower temperatures.
3.14.3 Control measurements and sanity checks

When carrying out low temperature measurements of photoluminescence, either steady state or time resolved, it is important that we are able to attribute changes seen at different temperatures to a given process.

In order to make an unambiguous statements about the dependence of the radiative rate, and how the conversion between different energy levels varies with temperature we must either demonstrate that this is the only variable changing with temperature, or account for other variations.

3.14.3.1 Allow time for temperature stabilisation

The measurement of the sample temperature is indirect from nearby thermocouple. This means what the TCU is actually reading is the temperature NEAR the sample.

It is important to let the temperature of the system settle, and the PID stabilise before measuring so that the temperature is not being varied during the course of the measurement and also so that the thermocouple reads a temperature representative of the sample.

This usually takes 20-30 minutes. No measurements were carried out until the envelope of the temperature fluctuation read by the TCU was within ± 0.2 K.

3.14.3.2 Temperature dependence of absorption

In the case of a neat film or dilute solution, the trajectory of the excitation would be:

photon absorbed \rightarrow excitation forms on chromophore \rightarrow rad. or non-rad. decay

And in the case of a doped film where the host is pumped it becomes

photon absorbed by host \rightarrow FRET \rightarrow excitation forms on chromophore \rightarrow rad. or non-rad. decay

Any variation in the optical density of the film at the excitation wavelength would be directly manifest in a proportional change in the number of excitations formed, or the efficiency of FRET overlap with the host, and therefore directly scale the magnitude of the total PL.

Two examples are shown here of CMA1 in a neat film and dilute solution in MTHF. In the case of the solid film we see that between 5K and 300K there is no prominent change in the intensity or form of the absorption features. The solution however demonstrates a clear blue shift and sharpening of the CT absorption band upon cooling.



Figure 3.40 cryogenic solution vs. film UV vis

Figure 3.40 shows a comparison of the temperature dependence of the absorption of CMA1 in solid film (left) and MTHF solution (right). Measured by author.

If both of these samples were to be excited at 410nm and their emission process was otherwise insensitive to temperature, the total PL would look like it increased drastically in the solution but not in the sample, whereas in fact the real change would be more excitations had formed in the solution at higher temperature rather than the PLQE having changed.

In the case where the absorption is temperature invariant, and in the absence of sample degradation of fluctuation in excitation power, both the total PL and PL rate should be indicative of the same activation energy.



Figure 3.41 cryogenic radiative rate vs. total PL

Figure 3.41 shows a comparison of the temperature dependence of the radiative rate (black) and the total PL (red) of an evaporated film of CMA1. 295K initial and final are almost identical (the 2 points overlap in this figure), so degradation is minimal. Measured by author.

In the case where degradation is minimal and the kinetics remain unchanged, either the net PL or the PL lifetime is suitable to calculate an activation energy.

In the case of modest reduction in net PL before and after and no change in kinetics, a scaling factor could be applied to scale the net PL for calculation of activation energy. This assumes that OD is constant for all T and the photo-degradation is temperature independent.

The method of calculating an activation energy from only the net PL remains sensitive to sample degradation, changes in OD with temperature and fluctuation in excitation power. Whilst in an ideal case it can be shown that both metrics provide the same activation energy to within a very small margin, it is far more robust to work primarily from the kinetic argument and use net PL as support for whether additional non radiative processes are also temperature sensitive.⁷¹

This supports the interpretation in cryogenic measurements of solid films that we can assign increase in PL with temperature to an increase in PLQE rather than simply a change in OD with absorption features narrowing or shifting at low temperature. In conjunction with the similar trend in activation energy seen in the emission rate, this comprehensively supports the low temperature film studies as being indicative of the photophysical processes for emission from these samples.

3.15 Sample preparation

3.15.1 Solution processed thin film samples

Solution processes samples were spin cast onto 13mm round quartz substrates at 2000rpm using a spin coater with a vacuum chuck. 25μ l was dropped onto the substrate once it was spinning, and both solution preparation and deposition were carried out in ait. Solutions were prepared at 10mg/ml in in THF. After deposition the back of the film was cleaned using acetone to remove any mark from the vacuum chuck.

Films were stored in the dark in a glovebox environment between production and measurements, and purged in vacuum (10⁻⁶ mbar) prior to measurement. Substrates were cleaned prior to deposition by ultra-sonication for 10 minutes in acetone followed by 10 minutes in isopropyl alcohol.

3.15.2 Evaporated OLEDs and thin film samples

OLED devices were fabricated on ITO-coated glass substrates with sheet resistance of 15 Ω/\Box . Substrates were cleaned prior to deposition by ultra-sonication for 10 minutes in each of deionized water with non-ionic detergent, deionized water, acetone, and isopropyl alcohol.

After blow drying with nitrogen, the substrates were exposed to an oxygen plasma treatment for 10 minutes.

An Angstrom Engineering EVOVAC 700 system was to deposit the organic layers and the cathodes through high-vacuum (10⁻⁷ Torr) thermal evaporation at rates between 0.1 and 2 Ås⁻¹.Layer thickness was determined using a quartz crystal monitor, having tooled for deposition of specific compounds by comparing pure films to elipsometry measurements. Thin film samples were produced in a similar manner on 15mm square glass substrates. Substrate cleaning and evaporation procedures were otherwise identical.

CMAs were produced and sublimed by Alexander Romanov at UEA, all other materials were purchased commercially (Sigma Aldrich) and were used as received.

3.15.3 Solution samples

Solutions prepared in an argon glovebox environment using degassed, anhydrous solvents purchased from Sigma Aldrich. Samples were then sealed in Hellma 1mm path length quartz cuvettes using PTFE stopper and parafilm. Solutions for spectroscopic measurements prepared at 1mg/ml or such that the optical density at excitation wavelength was between 0.1-0.3. Cuvettes were cleaned between use by firstly soaking in whatever solvent had last been used, then immersed in acetone and rinsed 5-10 times internally and blown dry with dry nitrogen. Oxygen was kept out of the samples by the methods described din section 3.5.2.

Chapter 4 Photophysics of CMA 1

Defining our own "gold standard"...



In this chapter I introduce what has become the archetypal example of the new set of CMA materials. It is currently the most comprehensively studied experimentally, in device applications and from calculation.

Subsequent experimental chapters are discussed in the context of exploring the effect of variations on this molecular structure, and tracking the impact of molecular modification on the excited state energies, ISC/RISC rates and coupling between states.

4.1 The Carbene-Metal-Amide archetype

The gold-carbazole derivative of this family was one of the first of this set of compounds to be subjected to extensive spectroscopic studies and provided some of the differences from the conventional model of TADF. I will refer to this molecule as CMA1 as in literature.



Figure 4.1 CMA1 molecular structure

Figure 4.1 shows (top left) the chemical structure. (Top right) crystal structure as measured by XRD powder diffraction. (Bottom left and right respectively) shows HOMO and LUMO wavefunction from DFT calculations; red (green), positive (negative) sign of wave function]. Synthesis and crystal structure from Alex Romanov, UEA. As reported in ¹¹⁵. HOMO and LUMO calculations carried out by Mikko Linholati, University of Eastern Finland using MN15 functional. Existing organo-metallic light emitting compounds had largely featured three-coordinate or four-coordinate copper complexes where Metal to Ligand Charge Transfer (MLCT) states offered the lowest lying energy triplet state, facilitating emission from triplet excitons either via phosphorescence or TADF[56–69].

The first luminescent gold 1 complex (a phosphorescent material) had already been reported as early as 1970¹³⁰ and a number of 3 coordinate gold complexes have also been reported previously as phosphorescent materials ^{131–134}.

Reports of phosphorescent 2-coordinate copper complexes ^{135,136}, were published relatively contemporaneously with our first report of the CMAs. These reports included symmetric and asymmetric substitutions on either side of the copper, in a similar geometry as the linear donor-metal bridge-acceptor architecture of the CMAs, including CAAC electron accepting units. Emission is shown from both local, and charge transfer triplet states in the materials reported, however they go so far as to clarify:

"(TADF) does not contribute significantly to the luminescent properties of these complexes." 135

At the time of our first report there were not yet any reports of group 11 2-coordinate organometallic TADF materials to that I am aware of, making the CMA family the first example of a linear, 2 coordinate group 11 metal complex being used for TADF style emission.

The donor-metal-acceptor architecture allows a high extent of spatial separation of the HOMO-LUMO wavefunctions, which is desirable for CT excited states as discussed earlier and also provides a versatile template for molecular modification.

As discussed in section 3.14, temperature has a large effect on molecules, which except at very low temperature are not static. This geometry has a large number of possible distortions and conformational changes including bond length, twist angle, folding modes, and vibronic replicas of the local excited states in conjunction with local phonon modes. The additional freedom to explore this continuum of conformations changes the overlap of the HOMO and LUMO wavefunctions, and thus can affect the oscillator strength of transitions between different states.

4.2 Absorption and emission

In the steady state emission and absorption of a neat film of CMA1, we see broad, unstructured emission and a corresponding broad feature in the absorption, characteristic of CT transitions.



Figure 4.2 CMA1 absorption and PL

Figure 4.2 shows the UV-vis absorption (black) and the steady state photoluminescence in vacuum (red) of a spin cast film of CMA1. Measured by author.

The broad feature in the absorption at ~380nm is assigned to the CT absorption. Local structure from the carbazole groups is also seen at ~370nm on top of the CT band. PL is broad and unstructured. It is common in molecular emitters that aggregation can quench fluorescence efficiency, however in pure films of CMA1 high PLQEs of 80% + are achieved, comparable to those of dilute oxygen free solutions in toluene (95%) and also when dispersed in a host material in the solid state for both polymer and small molecule hosts (75% in PVK and 72% in TSPO1 at 10% weight concentration). The published crystal structure shows that there is not significant overlap of the metal orbitals between molecules¹¹⁵ ¹¹³, which would be consistent with the lack of significant self-quenching from metal-metal interaction.

4.3 Solvatochromic effects on CT absorption and emission

To test whether the broad features visible in the emission and absorption spectra are from CT transitions, a series of solutions in solvents of varying polarity were compared.

Given that a charge transfer excited state exists between spatially separated moieties, either two separate molecules for intermolecular charge transfer states, or between regions like the donor and acceptor moiety on the same molecule for intramolecular charge transfer states, this means that a dipole is set up when the excited state forms.

In solution, solvent molecules have the freedom to re-orient relative to this local dipole if they are close to the excited molecule, and in doing so can change the energy of the excited state. Solvents with higher polarity can act to stabilise the energy of the state to a greater extent, whereas nonpolar solvents like benzene should have no response to this dipole, and effect no change.

This process is known as solvent dipole screening, and can be used to identify absorption and emission as being from a CT state, rather than a local excitation.

When CMA1 is places into a series of different polarity solvents and compare the absorption and PL, we see that the sharper features in the absorption spectra corresponding to the local carbazole transitions are seen to remain relatively unchanged, whilst the broad absorption band responds by moving to higher energy in increased polarity environment.

The CT absorption blue shifts with increased solvent polarity, with features assigned to local absorption to the carbazole not changing. For the steady state PL, the emission is shown to red shift slightly with increased solvent polarity.

This demonstrates that the transitions involved are indeed CT states. It should be noted that the direction of the solvatochromic shift in the absorption and PL are in opposite directions. This is explained by the dipole moment of the molecule being reversed and greatly reduced in the excited state geometry which is in agreement with calculations. ⁸⁵



Figure 4.3 solvatochromism of CMA1



This alone is not sufficient to demonstrate the involvement of triplets in emission, or TADF.

4.4 Oxygen dependence of film and solution PL

One of the key points of comparison for a TADF material is demonstrating the involvement of triplets in the emission process and producing a measure of what fraction of total excitations emit via the delayed triplet contributions. This can be done with varying degrees of precision.

In solution, the degree of quenching of triplet excitation by molecular oxygen is much higher than in a solid sample ¹⁰³. Due to the requirement to either bubble argon or nitrogen through a solution to purge oxygen, or vacuum-freeze cycle on a Schlenk line, solid films are used to demonstrate this as they can be cycled through different atmospheres whilst in situ for spectroscopic measurement.

4.4.1 Oxygen quenching of steady state PL

In the first instance, triplet involvement in luminescence can be demonstrated via reversible quenching of steady state emission from a solid film sample cycled in the presence/absence of oxygen.



Figure 4.4 vacuum-air cycling of CMA1

Figure 4.4 shows quasi-reversible quenching of total PL demonstrated for a spin cast film of CMA1. The slight decrease in subsequent scans is attributed to a small amount of degradation of the film during each measurement in the presence of air. Between each measurement the film was left for ~10 minutes in the new atmosphere for oxygen to permeate/evacuate the film. Measured by author. As discussed in the methods section, the presence of oxygen will introduce a competing non radiative pathway for triplet excitations, as well as potentially an additional degradation from reactive oxygen species.

Given that this process is in kinetic competition with emission through RISC, and also that permeation of oxygen into a film may not place every chromophore close to an oxygen molecule, this provides strong circumstantial evidence supporting triplet involvement in the luminescence, but cannot provide accurate quantification, only as a lower bound to the triplet contribution to total PL. ¹³⁸The extent to which Oxygen permeates a sample can also vary considerably. Oxygen ingress is greatly reduced in host blend films as the host material acts as an encapsulant to some degree. However for the measurements presented herein, a vacuum environment is used. As in figure 4.4

4.4.2 **Response of emission kinetics to presence of oxygen**

Having demonstrated that triplet excitons are contributing to the emission of this material, the next point was to determine what portion of the emission came from triplet excitations versus singlets, and also how rapidly this occurred.

Figure 4.5 shows the film in air to have more rapid decay of PL intensity, and that a nitrogen purged environment is a close proxy for vacuum. The trend in emission rates is also seen in the total PL, supporting the introduction of a non-radiative pathway rather than genuinely more rapid emission. It can be seen that there is no large initial drop in intensity, and that \sim 80% of the total emission has occurred by 1µs, and by 10µs effectively all emission has occurred.

It is clearer in the kinetic comparison that the delayed emission originating from the excited triplet population is reduced in its intensity, rather than suppressed entirely, as a considerable amount of delayed emission is retained. This emission has an artificially rapid decay lifetime due to the presence of an additional non-radiative rate depopulating the triplet reservoir.



Figure 4.5 CMA1 emission in different atmospheres

Figure 4.5 shows the effect of atmosphere on the emission of spin cast film of CMA1 at room temperature with 400nm excitation. A normalised comparison of the emission kinetics is shown (top left). The total emission is presented (top right.) The decay kinetics in vacuum are presented (bottom left) compared to the integrated total PL (bottom right). Measured by author.

To quantify the proportion of emission originating from the triplet contributions, it is necessary to carry out a time resolved measurement where effectively all the light is captured. If the signal is then integrated with time, we can see when this plateaus, and also quantify what timescale different fractions of the total emission occur over as shown in figure 4.5. For the case of CMA1, we see that effectively all of the emission occurs over the hundreds of ns to μ s range, and the contribution of early time fluorescence to total emission is small (~1%).

This behaviour is markedly different to fully organic TADF molecules where there is a considerable contribution from fluorescence from the initially photo-excited S1 population before ISC occurs.



Figure 4.6 organic TADF - CMA1 comparison

Figure 4.6 shows emission from a thin film sample of TXO-TPA a fully organic TADF molecule (top left) compared to a thin film sample of CMA1 (top right). Inset top right is the first 100ns of the PL decay plotted on a linear intensity axis, showing ~15% drop in intensity. Below each are energy level diagrams showing the depletion of donor fluorescence by rapid ISC which governs the difference in emission trajectory. Both films measured in an analogous manner at room temperature. Measured by author.

A small initial contribution of prompt fluorescence is seen in the first time bin only for CMA1, with a drop of intensity less than ~15% in the first 100ns, whereas there is a

considerably larger contribution from prompt fluorescence for the fully organic molecule, with ~2 orders of magnitude drop in intensity over the first 100ns before the delayed regime. Since there is not a significant portion of the entire emission from fluorescence, or indeed an initial decay over an appreciable drop in intensity from the prompt fluorescence, this suggests that at room temperature there is extremely rapid ISC depopulating the S1state.

4.5 Temperature dependence of delayed emission

There are a number of mechanisms by which delayed fluorescence may occur. Demonstrating triplet involvement in the delayed fluorescence is necessary but not sufficient to separate between phosphorescence, E-type (TADF) and P-type delayed fluorescence (Triplet-triplet annihilation).

To determine which form of delayed emission is present in CMA1, I carried out temperature dependent TRPL measurements on neat films and films at 20% weight concentration in PVK which display thermal activation of the delayed emission with an activation energy in the region of 80-85meV.



4.5.1 Rate of emission from neat films at different temperatures

Figure 4.7 cryogenic TRPL neat CMA1

Figure 4.7 shows the temperature dependent TRPL of a spin cast film of CMA1 excited at 400nm in vacuum (10⁻⁶ mbar). The normalised decay kinetics are shown (left) and the integrated cumulative PL for the same data (right). Measured by author.

Delayed contribution to the emission occurs more rapidly at higher temperatures, and the relative magnitude of the drop in intensity at early time from prompt fluorescence is larger at

lower temperature. A consistent trend is seen, with total emission from the film becoming more rapid with increased temperature.

Despite the reduction in the rate at which delayed emission occurs at low temperature, the relative increase of the intensity of prompt fluorescence seen in the measurements at lower temperature is still modest, and even at 50K is only measured over the first 10ns and contributes < <1% of total emission.

Figure 4.7 presents a normalised comparison of the emission, and hence the magnitude of the early time prompt fluorescence seems larger. This is due to the RISC being slower, and so the intensity of the delayed emission being less, and the actual magnitude of the prompt PL does not change significantly. A quantified comparison of the early time donor fluorescence is presented in section 4.10 where the spectra and magnitude of the early time contribution are shown to have minimal temperature dependence. This supports very rapid ISC even at the lowest temperatures as the absence of a significant quantity of fluorescence implies the initially photo-excited S1 population is being depleted at a rate which is able to outcompete and quench fluorescence.

4.5.2 Intrinsic triplet emission rate

Below a given temperature of ~150K for CMA1 in both spin cast and evaporated films, there is little change to the total PL or emission rate. This regime represents the intrinsic coupling of the excited triplet "reservoir" population with the ground state, which I refer to as "CT Phosphorescence".

For a spin cast film at 50K, the time for 1-(1/e) of total emission to have occurred is 37.8 µs, giving an intrinsic phosphorescence rate of 0.02 per µs. For evaporated films, the rate of intrinsic phosphorescence is the same 0.02 per µs.

This will be discussed in more detail in chapter 5, where the effect of the metal bridge atom is compared.

4.5.3 Control experiments for CMA1 absorption

As mentioned when these techniques were introduced in the methods section, it is important to keep track of which photophysical properties are varying with temperature, and what metrics are used to calculate thermal activation.

For CMA1, temperature dependent absorption measurements have been carried out for both neat thin film and dilute solution in MTHF.

The intensity and position of the CT absorption feature in the neat film are close to temperature invariant, in the MTHF solution, there is considerable narrowing and blue shifting of the CT absorption band upon cooling, as well as a shift in intensity relative to the local carbazole absorption peak.

It is worth noting that this is a continuous process down to ~100K rather than a discrete change upon freezing (180K). Comparing the OD at, for example, 410nm, it can be seen that for the film there is virtually no change, whereas in the solution the OD has changed by roughly 1 order of magnitude.

This supports that for solid samples, in the absence of photo-degradation, that the total PL and the radiative rate could be used to generate a measure of the activation energy directly.

This also demonstrates that for variable temperature solution measurements of this class of materials, there could be an appreciable change in OD at the excitation wavelength, resulting in the change in total PL being the product of the increase in OD and any thermally activated increase in PLQE. It would be possible to reduce this effect by exciting one of the carbazole local transitions at ~360nm, however, the broad CT absorption feature still has varying intensity here. This is mitigated by comparing both the kinetics and total PL when determining the changes at different temperature.



Figure 4.8 cryogenic absorption of CMA1

Figure 4.8 shows UV-vis absorption spectra at different temperatures for CMA1 in a neat spin cast film (left) and dilute solution in MTHF (right). Measured by author.

For these reasons, as well as the relevance to device environments, the activation energies presented in this thesis are measured from solid samples of either pure films or host guest blend films, and determined from the variation in emission kinetics. Dispersing in a host film also reduces the variation in morphology between samples, and ensures a dilute environment with minimal aggregation. Cryogenic measurements of solutions have been used for steady state emission only.

Another aspect of the behaviour of the CMA system that this result helps clarify is that we are seeing a continuum of states being explored, corresponding to molecular conformation.

In other systems which exhibit intramolecular charge transfer, different conformers can exists, for example a planar and a twisted version of a molecule, and a two state approach can be used to explain the photophysics¹³⁹. Twisted and Planar Intramolecular Charge Transfer (TICT and PICT) was one of the early interpretations we considered for the CMA family, however, the characteristic transitions indicative of a 2 state system are not seen here.

This set of control measurements has only explicitly been carried out on CMA1, and is assumed to hold true for the low temperature film measurements measured in other chapters, as the photophysical behaviour of the solid films is otherwise similar.



4.6 Temporal and thermal evolution of spectra

Figure 4.9 CMA1 spectral variation with time and temperature

Figure 4.9 shows the spectral changes in an evaporated neat film of CMA1 at different temperatures and time delays. The top panels show the red shifting and broadening of the steady state PL with increased temperature (top left) with the peak position plotted against temperature (top right). The lower two panels show the temporal evolution of the PL spectrum at 50K, with time slices at increasing gate delays being shown (bottom left) alongside the peak position as a function of time after excitation (bottom right). The distribution of peak wavelengths explored at 50K can be seen to be either side of the average of ~507nm shown (top right). Measured by author. One aspect of the emission of CMAs which has made applying simple exponential fits to the emission inappropriate is that in the solid state, they do not emit from states of well-defined energy and lifetime, but rather from a continuum of state both for energy and lifetime.

This behaviour had been noted, but was not yet fully characterised in the early reports of these materials, and contributed partially to the assignment of state energies which did not capture the full extent of energetically disordered sites accessible at low temperature.

This was further evidence that the TICT/PICT model considered early in the project was insufficient to describe the emission processes in CMA1, where the rotational freedom about the metal bridge allows many different dihedral angle to be explored, rather than having two distinct preferred states with some energetic threshold associated between exploring one versus the other. ¹³⁹

We see that in a solid film, the peak wavelength of the PL migrates over time, and the rate at which this spectral diffusion takes place increases with temperature.

Even at temperatures as low as 50K however, if the system is measured for long enough, the emission relaxes to a state which is spectrally similar to the emission in dilute toluene. This is taken to be representative of the most relaxed possible state in a relatively non polar environment with complete rotational freedom.

This same degree of relaxation is seen at 300K in the neat film, but the migration to lower energy sites happens within hundreds of ns rather than taking tens of μ s, which is consistent with a diffusional process becoming more rapid with temperature.

Given this, it should be noted that the kinetics used in calculations of radiative rates and activation energies are the kinetic of the integrated PL over all wavelengths. In figure 4.9 it is clear that a kinetic taken at the early time peak wavelength would seem to decay faster than it should due to the red shift in PL with time. Similar comparisons are used in the ultrafast TRPL datasets.



Figure 4.10 range of CMA1 emission energy

Figure 4.10 shows how the emission from CMA1 varied with time, temperature and environment. (Left) compares steady state PL from a toluene solution (black), and shows that at both 50K and (purple) and room temperature (green) that after an amount of time (250µs at 50K and 100ns at room temperature), emission of from a state of the same energy as the toluene solution. At the same time delay of 100ns at 50K, the emission has not yet settled to this lowest energy (blue). An estimate of the prompt fluorescence is included from the difference spectrum of the first data point and the delayed emission (red). (Right) shows our initial report of this behaviour in the literature, showing spectral migration with time at various temperatures for the first 10 µs. ¹¹⁵ Measured by author.

Spectral migration changes rapidity with temperature, but even at low temperatures, a pure film can emit from lower energy sites. By comparing room temperature and cryogenic spectra from the same time delay of 2 μ s and 10 μ s in our initial report, we concluded that the emission energy at low temperatures had stabilised at a higher energy than the 300K emission.

"This phosphorescence redshifts by \sim 5 nm over the first 3 µs, consistent with diffusion of triplets to lower-energy sites." ¹¹⁵,

This did not capture the full behaviour of the triplet diffusion being thermally activated across the density of states. The rate of diffusion having significantly slowed was interpreted as the

energy of the states accessible having plateaued at longer times, which was interpreted as the DOS narrowing upon cooling attributed to reduced torsional freedom in the ensemble.

In my later work, measurements were carried out in high vacuum to the hundreds of μ s – ms range, which significantly improved our understanding of the triplet behaviour. This showed that even at temperatures at low as 50K emission was seen which matched the delayed emission at room temperature.

Comparison with the emission from toluene solutions shows that the reddest emission from the film at either room temperature or cryogenic conditions is in good agreement with the emission from toluene solution, supporting some fraction of the molecules in the film being locked in their most relaxed geometry, and the rate or diffusion to them is what is varying with temperature, rather than the lowest energy conformers being inaccessible below a certain temperature.

This changes the picture to the density of states retaining the same lowest energy sites, but that the mean of which sites are explored shifts with temperature, rather than any extremes being frozen out. This is consistent with literature on triplet diffusion.

The energetic migration of triplet excitations in phosphorescent materials was described in 1986 by Richert and Bässler¹⁴⁰ and temporal migration of peak emission energy subsequently reported by Lange, Ries and Bässler¹⁴¹. This same behaviour has been observed in more contemporary reports of phosphorescence and triplet migration in solid films of by Jankus et. al ¹⁴².

In the original calculations, the energy surface of the triplet was relatively flat with dihedral angle; one of the original assumptions which contributed to our interpretation was that there was therefore no particular energetic incentive for migration of triplet excitations to lower energy sites.

Subsequent calculations ¹⁴³ suggested that the increased dihedral angle resulted in a destabilisation of the ground state, which provided the minimisation in the energy of given states in population locked into a series of geometric arrangements in the solid film.

4.7 Photophysics in device-like conditions

The primary application for this class of emitting materials is as dopants for high efficiency OLEDs. With that context in mind, it is necessary to consider the photophysical behaviour of these emitters not just from the perspective of isolated molecules or abstract theory, but also in environments which are relevant to the conditions they would need to operate under in an OLED device stack.

This has therefore been a guiding consideration in my work, which has explored whether the properties which contribute to efficient emission of isolated molecules are retained in different host environments and films processed via different processing techniques.

The device work on this material set has primarily been the work of collaborators, and I refer the reader to our published works for information on the chemical synthesis and device fabrication.

Full details of the solution processed device studies have been published in Science by Di et al in 2017¹¹⁵. Full details of the evaporated devices are reported in Advanced Materials by Conaghan et al. in 2018¹⁴³.

4.7.1 Effects of dilution on spectral migration

The existence of temporal spectral migration raised the question of its origin. In the case of a solid film, there are two possible mechanisms which could give rise to this behaviour; either that the emission results from isolated molecules in different local conditions, or that the behaviour represents an ensemble which is able to explore local energetic minima via some diffusional mechanism.

For the first case of emission from isolated molecules to be true, it would be required that there was some reaction coordinate which corresponded to a reduction of the emission energy, and also a reduction in oscillator strength, and so emission from lower energy sites in the film would be slower.

The second case would require that an excitation formed on a given molecule can either emit from the molecule where it originated, or had some probability of hopping to an adjoining site which was energetically permitted, which on average would be lower in energy, hence result in a gradual average reduction in emission energy down to some average global minima.

The extent of this spectral red shift with time at room temperature has been shown to be significantly reduced with dilution in polymer hosted films.

From this it can be inferred that of the two mechanisms suggested to account for the spectral migration with time that the diffusional case seems to be dominant, as there is no reason that the distribution of conformers that dopant molecules would be locked in would be concentration dependent, and an exponential reduction in hopping rate with concentration is predicted for the case of triplet diffusion.

Given that this process is observed in both neat and films hosted in PVK and other hosts, the long lived emission which red shifts in time is attributed to emission from CMA1. Control films of PVK were measured under similar conditions, and no contributions beyond initial fluorescence were seen, ruling out low intensity host phosphorescence. The phosphorescence from free carbazole is also presented in figure 4.20 and is distinctly structured, unlike the long-lived emission from the CMA samples.



Figure 4.11 CMA1 PL in PVK

Figure 4.11 shows the behaviour of a series of films of CMA1 in increasing weight concentration in a PVK host. (Top left) shows measurements (by author) of CMA1 at 20% weight in PVK spin cast films demonstrating spectral migration similar to that displayed in the pure sample presented in figure 4.10. This demonstrated that this behaviour persisted in a polymer host, and prompted a more detailed investigation by my colleague Jiale Feng. I present his measurements alongside mine in this section for comparative purposes. (Top right JF) the normalised PL kinetics. (Bottom left JF) shows the peak PL migration as a function of time and (bottom right JF) shows a separate measurement of the steady state peak energy on a fluorimeter displaying the same trend with concentration. Bottom right inset is the peak energy in eV. Pure PVK films measures in similar conditions did not demonstrate this long lived emission, so it does not originate from the host material. This provides one method of blue-shifting the steady state emission without molecular modification or using different host materials by using dilution to reduce the availability of lower energy sites which an exciton formed on a given molecule may diffuse to.

CMA1 / PVK	Delayed Lifetime	PLQE
5% CMA1	1040 ns	67%
10% CMA1	1000 ns	75%
30% CMA1	920 ns	76%
50% CMA1	850 ns	94%
80% CMA1	840 ns	81%
100% CMA1	970 ns	80%

Table 4.1 CMA1 PL lifetime in PVK

Table 4.1 shows the PL lifetimes and PLQE for the same weight concentration series of CMA1 in PVK as described in section 3.13.1. The PL lifetimes are within ~10% of each other across the set, and high PLQEs are maintained. Data measured with Jiale Feng.

There is very little change in the lifetime of the emission even with a 60meV shift in steady state PL peak energy. To compare 10% and 100% weight, there PLQE is 75% and 80% respectively, the lifetimes 1000ns and 970ns, and yet there is a 50meV shift in PL peak energy, and migration over sites with ~40meV lower energy than in the 100% weight film.

This can be thought of as changing what portion of the density of states is explored by reducing diffusion by dilution, in a similar manner to cooling the film reducing the average diffusion length. The diffusion length of a given exciton would not change, but the average nearest neighbour distance does, resulting in the same trend.

The energies of steady state emission explored in this concentration series lie between the extremes seen in a dilute solution and solid film, as expected.

This seems to contradict the prediction that the ISC and RISC rates are dependent on the energy of the CT state and the exchange energy, and I will discuss this in more detail later.

4.7.2 Effects of host polarity

The effect of the host polarity in the solid state is not as pronounced as in a solution, where there is complete freedom for solvent molecules to respond to the electric field of the excited state dipole, and reorganise to minimise the energy of the excited state via solvent dipole screening.



Figure 4.12 CMA1 dilution kinetics

Figure 4.12 shows the shift in peak emission energy with time for a series of films of CMA1 in different concentrations in a polymer vs small molecule host. 10% and 50% by weight in the small molecule host TSPO1. 10% in PVK and CMA1 pristine 100% are included as a visual guide to compare to figure 4.11. Data measured with Jiale Feng.

"Crucially, this is not the case in device relevant media, *i.e.* an amorphous thin film organic solid, where the host is not free to reorient"⁸²

It has already been demonstrated that in solution, the emission of CMA1 is red shifted in higher polarity environments. In addition to varying the concentration of dopants in a host film to minimise excitonic migration to lower energy sites, the polarity of the host provides an additional degree of control on the emission energy. Both of these effects are clearly demonstrated when time evolution of peak emission energy is cross compared between dilution series in different polarity hosts.

CMA1 / TSPO1	Luminescence Lifetime	PLQE
5% CMA1	1400 ns	65%
10% CMA1	1330 ns	72%
30% CMA1	1190 ns	78%
50% CMA1	1180 ns	70%
80% CMA1	1010 ns	75%
100% CMA1	970 ns	80%

Table 4.2 CMA PL lifetime in TSPO1

Table 4.2 shows the lifetime and PLQE for a concentration series of CMA1 in the small molecule host TSP01. Similarly to the data shown in table 4.1, high PLQEs are retained, and emission lifetimes between ~1- 1.5µs are retained despite a considerable shift in PL peak energy. Data measured by Jiale Feng.

Here we see that rather than dilution shifting what portion of the DOS is explored, that the higher polarity host has moved the entire DOS higher in energy.

A comparison of the 10% weight films in PVK and TSPO1 shows that the emission in the small molecule host is considerably higher in energy at the same dilution.

Comparing between the 10% and 50% weight in TSPO1 shows the same trend of dilution shifting what portion of the DOS can be explored by diffusion, but that this entire DOS has been shifted up in energy.

4.7.3 Effects of host rigidity and steric effects

An additional effect which is necessarily present when considering a concentration series is that the rigidity/effective glass transition of the host will change with higher dopant concentration, as will the average polarity of the environment of a given dopant molecule (the bounds for this being a pure host/ pure dopant film). Work in ongoing on the impact of these environmental factors with J. Feng and forms a separate investigation to this thesis.

It has been shown that dynamic reorganisation of the host is possible, though with less freedom to reorganise than in a solution. Solid State Solvation (SSS) links the polarizability of a host matrix with the stabilisation of the energy of the excited state, and has the same relevance to the CT excited state energy of TADF molecules.¹⁴⁴

In addition to the ability of the host to reorganise in response to an excitation on the guest molecule, there are many examples in the literature of triplet emission being sensitive to conformational freedom of the emissive molecule, and that TADF can be restricted by the addition of steric blocking groups, resulting in phosphorescence.¹⁴⁵¹⁴⁶

The polycrystalline powder represents the highest emission energy as molecular deformation is restricted in the crystal environment. Being locked in a close packed structure means that rotation of the donor and acceptor moieties across the bridge is impeded, and the molecule is not able to undergo conformational change to minimise the energy of the dipole introduced upon excitation. Similarly the solution (toluene) represents the most freedom for geometric relaxation. The intermediate points represent weight percent dilution in PVK film, where diffusion to lower energy emitting sites is reduced between these two bounds.

For studies of the CMA materials, polymer hosts have included PVK and PS, despite the fact that concentration quenching is not seen in neat films, these environments still provide a handle to reduce diffusion, or improve charge transport.



Figure 4.13 CMA1 emission energy morphology dependence

Figure 4.13 shows the steady state PL peak energy of CMA1 in a number of different sample environments. Polycrystalline powder is compared thin spin cast films at 1.5% and 20% weight in PVK, 100% CMA1 spin cast film, and dilute toluene solution. Evaporated neat films display similar peak emission to the powder phase. Measured by author.

As well as providing a degree of encapsulation from oxygen, the role of polymer hosts is also discussed in the literature as a method to achieve improved triplet quantum yields for fully organic room temperature phosphors. This is reported as resulting from the polarity and rigidity of the polymer host suppressing non-radiative decay pathways. ¹⁴⁷

Given that the excited triplet population is able to emit on much more rapid timescales in CMA molecules, they are less sensitive to kinetic competition from vibrational losses from the excited CT triplet or 3LE state, so potential improvements in triplet yield due to polymeric rigidity are likely not so extensive.

4.7.4 Solution and thermal vapour deposition

Films and devices which were processed via vacuum deposition achieved similar maximum efficiencies, considerably improved average EQEs and greatly reduced batch to batch variance, largely due to the improved control of layer thickness compared to spin cast devices. EQEs of 23% were achieved in host free emissive layers and 26.9% in hosted active layers as described in our published works. ¹⁴⁸¹⁴³



Figure 4.14 CMA1 deposition comparison

Figure 4.14 shows how the normalised cumulative total PL varies with temperature, for two films of CMA1 prepared by spin casting (left) and thermal vapour deposition (right). The dependence of PL emission rate on temperature is functionally similar, and at room temperature, but films have emitted ~90% of the total photons by 1µs. Measured by author.

The emission from evaporated neat films is blue shifted relative to a neat film which has been prepared via solution processing, suggesting that during deposition, the film may solidify

faster and lock molecules in the ensemble into a configuration which on average is less energetically favourable. The PL peak from neat evaporated films closely matches the polycrystalline powder.

Temporal spectral migration is still seen in evaporated films, as shown in figure 4.9, but the range of energies explored narrows due to the change in the distribution of conformers available with vacuum deposition.

In neat films at room temperature the PL steady state peak of evaporated film =2.33eV versus 2.25eV for the solution processed neat film. Both trends discussed already for tuning the steady state PL or EL of this material are clearly demonstrated here, with the additional benefit of increased constraint of angular freedom imposed by vapour deposition.


Figure 4.15 CIE plot of evaporated CMA1 devices

Figure 4.15 shows the CIE coordinates for emission from OLEDs made from CMA1 in different hosts, as different concentration, and by different deposition techniques¹⁴³. The emission colour can clearly be tuned between blue-green and sky-blue by environmental factors rather than chemical modification, with the bluest devices being achieved at 5% weight concentration in a polar small molecule host. Reference [4] in this figure is to the paper on solution processed devices ¹¹⁵.

The progression towards bluer emission with decreasing concentration in the mCP host clearly shows that migration to lower energy sites has been reduced. Comparable weight concentration in PVK and MCP at 20% weight also clearly demonstrates the effect of host polarity.



Figure 4.16 evaportated CMA1 cryogenic data

Figure 4.16 shows (top left) transient PL decay kinetics of an evaporated neat CMA1 film at varying temperature ¹⁴³. (Top right) Transient PL characteristic decay rates (black, lefthand axis) and integrated PL intensity (red, right-hand axis) as a function of 1/Temperature. The fitted curve yields an activation energy EA = 79 meV. (Bottom left) steady state PL spectra at varying temperature and (bottom right) the shift in PL peak position as a function of temperature. A similar dependence on temperature for the red shift and broadening of the steady state PL as for the solution processed film is seen. Measured by author.

The effects of temperature on the photophysics of the evaporated films shown in figure 4.17 closely resembles that of the spin cast samples shown in figures 4.7 and 4.9, supporting that the emission mechanism has not fundamentally changed upon vapour processing. The gradual shift of emission energy and broadening both also support the interpretation of a continuum of conformers rather than a two state TICT/PICT interpretation.

At the lowest temperature the high energy edge of the emission is slightly concave, as the donor fluorescence is a larger portion of the total emission. This is in good agreement with the ps-TRPL presented in section 4.9 and consistent with the spectra obtained in section 4.10 estimating prompt donor fluorescence contribution.

4.8 Direct measurement of local state energies

Another limitation of the data set used to generate the initial model of the photophysics of this system is that it lacked a measurement of the energy of the 3LE state since emission at 4K was still clearly residual CT phosphorescence. It was possible to directly measure an estimate for the S1 energy from prompt fluorescence either from the rise of the long-time TRPL data, or the ps time resolved measurements of initial fluorescence, however we did not have an experimental value for the 3LE energy. An upper bound was provided by values stated in the literature for free carbazole phosphorescence of 3.09 eV ¹⁴⁹ however the extent to which coordination with the metal would lower the energy of the local triplet had not yet been demonstrated.

This effect is clearly important for the relative energy of excited states as clear differences between charge transfer emission and phosphorescence from locally excited triplet states have subsequently been observed in solid film samples of the silver analogues of this material which are discussed in more detail in chapter 5.



Figure 4.17 CMA1 state energy estimation

Figure 4.17 shows the changes in absorption and PL of a solution of CMA1 in MTHF with temperature. (Top left) shows the absorption and (top right) shows the steady state PL. The lower panels show the absorption (black) and steady state emission (red) of the same solution of CMA1 in MTHF at 60K (bottom left) and 300K (bottom right). Excitation was at 375nm indicated with a dashed blue line, and the energy of the state emitting approximated from the intersection of absorption and emission. Data measured during research visit to the Köhler lab in Bayreuth. Thanks to Anna Köhler and Fabian Panzer for hosting me. Measured by author.

The absorption narrows and blue shifts upon cooling, whereas the steady state PL stays close to the room T spectrum until the solution freezes, and then the energy of the CT state emission blue shifts with cooling. At the point then the onset of the CT state energy passes

the onset of the local state, emission is seen then primarily from the locally excited state. This would be consistent with geometric relaxation and solvent dipole screening being arrested upon freezing.

It is worth noting, that in both the absorption and PL presented in the top panels of figure 4.18 that a continuum of peak absorption and emission energy is seen progressing with temperature and NOT an isobestic point, which would be expected is there was a transition between a pair of well-defined states rather than a continuum of conformers. I take this as further support for the interpretation that a TICT/PICT description does not apply to this system.

Subsequent measurements on frozen solutions of CMA1 in MTHF shift the CT energy sufficiently that structured phosphorescence from the local triplet can be separately observed. The high energy edge of this emission is used to assign the energy of the local triplet [415nm = 2.99eV], rather than part of a distribution of CT state energies.

The CT- PL onset can be seen to approach 400nm as the sample is cooled. When this passes the onset of the local emission, structured PL is seen instead as the CT state ceases to be the lowest energy emission.



Figure 4.18 TXO-TPA frozen solution PL

Figure 4.18 shows steady state PL (left) of TXO-TPA measured in Toluene at various temperatures. The same data is normalised for visual comparison (right). Measured by author.

Since the energy of the local triplet state should not be sensitive to the polarity of the environment, this allows direct experimental insight into the extent to which the 3CT state energy is below this in different environments. This is not necessarily the case in all TADF molecules.

When normalised for spectral comparison, a shift is seen either side of the melting point at ~180 K, but emission is still from a CT state even when solvent dipole screening is frozen out. No further blue shifting is seen of the high energy edge of the CT emission below the freezing point, unlike CMA1.



Figure 4.19 CMA1 local emission in frozen solutions

Figure 4.19 shows a comparison between the local emission from solutions of CMA1 in MTHF and toluene with the emission of free carbazole. The top panels show a comparison between the structured PL of CMA1 in MTHF between 60K and 300Kwhen excited at

375nm (top left, Measured by author) and free carbazole in similar conditions (top right). Free Carbazole data measured by Alexander Romanov. (Bottom left) shows CMA1 in toluene at room temperature displaying a small contribution from local emission when excited at 292nm. Inset is a magnified portion of the graph showing the structure of the emission. (Bottom right) shows the absorption and emission or the same sample when excited at 292nm after the solution has been oxygenated. Toluene CMA1 data measured by Antti Reponen.

The local emission of CMA1 in MTHF at 60K and 300K share 2 peaks in the near UV, overlapping well, and show 2 additional peaks seen at 300K. This is attributed to local transitions from carbazole, and is in good agreement with emission from free carbazole in THF and MTHF at 77K and 300K (top right)

The structured emission at 60K is interpreted as arising from the carbazole 3LE state, and has an onset at 415nm (2.99eV), and the CT emission seen at 300K has an onset on 455nm(2.72 eV).

For the oxygenated toluene solution of CMA1 there is a considerable quenching of the CT emission such that its intensity is comparable to the local emission. This is presented for ease of visual comparison with the symmetry of the absorption bands. This does not clearly resemble the same local emission which is seen in figure 21 because it is not truncated by 375nm excitation and LP filter, and results from direct excitation of the 280-310nm band corresponding to local carbazole absorption, closely resembling that of free carbazole at 300K as shown in figure 4.20.

4.9 **Picosecond timescale behaviour**

To understand the processes giving rise to the behaviour we observe in steady state and ns – ms time resolved measurements, it is necessary to probe on the timescale on which the excited states form.

Femtosecond- picosecond time resolved Transient Absorption (TA) spectroscopy, and transient grating PL spectroscopy provide information on the timescale of the formation of the different excited state populations, and molecular relaxation events.

The following ultrafast datasets were measured by Jasmine Rivett (TA), Johannes Richter (TRPL), Heather Goodwin (TA), Antti Reponen (TA) as part of the wider experimental investigation into the photophysics of the CMA materials, and are presented to provide context for discussion and interpretation of measurements I have carried out.

For details on the experimental details of these techniques, please refer to our published works.¹⁵⁰

4.9.1 Transient grating PL spectroscopy

Emission on the ps timescale provides information about the dynamics of the initially formed singlet state.

This is the timescale on which molecular re-organisation and ISC take place, and these two processes are separately discernible as a spectral shift in emission peak energy, and as decay of the total PL.

The latter should not be mistaken for a radiative rate, but the convolution of the fluorescence lifetime with the ISC rate which depopulates the initially photo-excited singlet population. If the fluorescence lifetime is assumed to be much larger than ~ps, then this is a good measure of the timescale of ISC.

4.9.2 Transient Absorption

Transient Absorption (TA) spectroscopy provides insight into the formation, interconversion and subsequent depopulation of excited states in a material.

Unlike PL spectroscopy techniques, TA is sensitive to excited state populations which do not couple radiatively to the ground state (dark states).

As with all photo-excitations, the initial excitation formed must be singlet in character, though not limited to the first excited state. Subsequent intersystem crossing is possible if there are mechanisms by which spin angular momentum can be changed.

As has been mentioned previously, this data seeks to not only provide insight about the behaviour of the molecule as an isolated system, but also to guide interpretation of the transitions and states which are accessed in a device context.

All of the processes which the electrically-excited singlet undergo will then be identical for a film in similar conditions, and the excitons which form directly in the triplet configuration will behave in an identical way to an exciton which had inter system crossed from the S1 state in the first few ps. In short, with the exception of the first 5ps or so, this should be a very close representation of the dynamics of an electrically excited ensemble.

We see in the longer time resolved PL measurements that effectively all the light is emitted on considerably longer timescales. If the initial ISC is an efficient process, and does not result in the loss of a meaningful fraction of the excitations formed, then the transitions and states shown in the TA can be taken as representative of device-like conditions. The high PLQE of solutions and solid films under optical excitation supports this assumption being appropriate.



4.9.3 Comparison of picosecond processes

Figure 4.20 CMA1 ps TA and TRPL

Figure 4.20 shows a comparison of the ps-resolved TA and TRPL of CMA1 in film and solution. ¹¹⁵ (Top left) shows a heat map of early time fluorescence from a solid film and (top right) shows the same measurement of a toluene solution, (bottom left) shows the TA map of a neat spin cast film of CMA1. (Bottom right upper) shows a comparison between the spectral migration at early time between the film and solution samples compared top left and right. (Bottom right lower) shows the correlation between the decay of the initial PIA in the TA map and the ps-TRP. Data measured by Johannes Richter (TRPL) and Jasmine Rivett (TA).

In figure 4.21, the TA heat-map is presented for a solid film of CMA1 over ps to us timescales. At early time, we see the formation of the singlet state directly after excitation, and then the long lived reservoir of triplet excitations after ISC. The initial PIA is centred at ~680nm and within the first 5-10ps has decayed entirely. On the same timescale of the first 5-10ps we see the growth of a second feature not initially present centred at ~650nm. This second feature exists from ps-ns and is seen to decay on the hundreds of ns timescale, being essentially depleted by 1µs, consistent with the long-time PL at room temperature shown for films of CMA1. This is consistent with the initial formation of a singlet population upon photo-excitation, followed by rapid intersystem crossing into a long lived triplet state, acting as a reservoir for delayed emission. Since this sample was pumped at 400nm, the initial short lived PIA is assigned to the 1CT state, since the oscillator strength of transitions to the 1LE state at that energy is much less as shown in figure 4.20. The second feature is assigned to the 3CT state as the emission on these timescales is from a charge transfer state, and no other PIAs are observed. A conservation of excited state population argument thus supports this assignment. In the upper two panels we see a comparison of the prompt fluorescence from a film and solution of CMA1. In the solution, there is a clear red shift at early time as molecules are free to undergo geometric relaxation.

We see that during the initial ~2ps in neat films at room temperature that this relaxation is greatly inhibited where geometric reorganisation is prevented by the host matrix.

By 5ps, this has slowed significantly in both samples on this time scale. Longer time measurements already presented in figures 4.9 and 4.10 show that in the solid samples, spectral diffusion continues over much longer timescales.

The extent of the red shift seen at longer time via triplet diffusion in the solid film supports that conformers corresponding to the most relaxed rotated states are available in the film since the extent of the reduction in the emission energy seen in the early time fluorescence in solution as a result of molecular relaxation is comparable to the extent over which delayed emission relaxes from triplet migration to lower energy states. This supports the extent of the red shift in the delayed emission being attributable in solid films to a distribution of

conformers locked in different geometries with respect to some molecular relaxation coordinate like distribution of dihedral angles locked into the film.

The timescale of early time fluorescence from the film is also in good agreement with the time taken for the PIA assigned to S1 state to decay, and the corresponding growth of the T1 PIA in the TA, supporting that the emission is from the same state probed in the TA, and not one which is not present in this spectral region. From this we infer that this early-time emission represents fluorescence from S1 being quenched by ISC.

A point which had not been compared in our initial report of CMA1 was whether there was a change in the forward ISC time between solid films and solutions.



Figure 4.21 CMA1 TA in toluene solution and PS film

Figure 4.21 (left) shows the transient absorption spectrum of a toluene solution of CMA1, with 400nm pump and broadband probe. (Right) shows the transient absorption spectrum of CMA1 in a dilute polystyrene hosted film measured in an analogous manner. Data measured and analysed by Heather Goodwin and Antti Reponen.

As in the initial report, two distinct features separated spectrally and temporally are seen. Initially there is the presence of a Photo-Induced-Absorption at ~680nm. This is assigned to the singlet 1CT state excited at 400nm. At later time a lower energy feature at ~650nm is seem to grow in and stabilise. This is assigned to the excited state triplet population which acts as a reservoir for delayed emission. The intersystem crossing time is taken as the time taken for the first PIA to decay, and for the formation of the second feature. In dilute solutions, this is ~4ps.

In the solid film, the same two features are clearly seen on similar time scales, supporting the intersystem crossing still occurring on the order of 4ps in the solid state, so the ISC time remains virtually unchanged at ~4ps.

There is a considerable red shift of ~350meV in the emission of solutions compared to the solid powder due to the freedom to occupy energetically minimised conformations as shown in figure 4.13; however the forward ISC time remains unchanged between dilute solution and solid film.

For these measurements, the samples have been optically excited with a 400nm pump, and so are initially in a singlet CT configuration. In a device context where charge carriers are injected with random spin alignment, singlet and triplet excitons will both be randomly formed initially in a ratio of 1:3.

4.10 Dependence of intersystem crossing on temperature

Intersystem crossing in organo-metallic compounds does not behave in the exact same manner as fully organic compounds ¹⁵¹. It has been clearly demonstrated that the RISC in CMA 1 is highly dependent on temperature. If the same states and processes are involved in ISC as RISC, it follows that the magnitude/rate of ISC should scale in the same manner. Performing the same ultrafast measurements for both ps-TA and ps-TRPL is not necessary to measure trends in ISC with temperature, as the information is captured in the ns-TRPL data. To estimate forward intersystem crossing in films, the following inferences can be made:

- 1) The absorption of the film has been shown to not vary with temperature.
- 2) At room temperature, there are ps resolved measures of ISC from the TA.
- 3) Corresponding quenching of fluorescence from the photo-excited 1CT State has been shows by ps-TRPL to correspond to ISC.
- 4) In the first one or two time slices of the ICCD ns-TRPL, the prompt fluorescence can be separately identified, and agrees well with the ps-TRPL spectra.
- 5) It is thus possible to estimate the total contribution from the prompt fluorescence in the first time bins(s) of the cryogenic TRPL measurement.
- 6) The OD and excitation power are constant, and there is no reason that the emission rate from the 1CT would have changed.
- 7) I assume that on the 5ps time scale that vibrational losses from the 1CT are outcompeted by ISC, and these can only be reduced at low temperature.

The amount of prompt fluorescence from the 1CT state at different temperatures before it is quenched by ISC thus provides an indirect measurement of the dependence of the forward ISC rate on temperature.



500

Wavelength (nm)

Figure 4.22 prompt fluorescnece of CMA1

700

450

500

550

Wavelength (nm)

800

650

Figure 4.22 shows how an estimate of prompt fluorescence was generated for an evaporated film of CMA1 at 295K (left top and bottom) and 50K (right top and bottom). The top panels shows the total PL in the rise and the maximum time bin summed together (black) and the spectrum after 10 or 15 ns (red)when none of the blue edge remains. The prompt fluorescence estimate (blue) is then obtained by carrying out a weighted subtraction of the delayed spectrum from the prompt + maximum. The lower 2 panels show a normalised comparison of the three spectra, with a clearly resolved higher energy contribution isolated for the prompt estimate. In terms of total counts, this contribution was ~2.8 times larger at 295K than at 50K. Measured by author.

By this estimate, there is ~ 2.8 times more fluorescence at room temperature than 50K, though it is worth noting that this metric would not be sensitive to the emission blue shifting or narrowing at low temperature.

The room temperature difference spectrum used to approximate the emission from the prompt singlet fluorescence is in good agreement with the fs- TRPL. In addition to this, the low energy edge of the difference spectrum is not seen to shift much with temperature, as shown in figure 4.24, so this is considered a reasonable first order approximation as had there been a significant narrowing or blue shift, the low energy edge of the state would likely be sensitive to this also.



Figure 4.23 CMA1 prompt 50K and RT comparison

Figure 4.23 shows a comparison between the normalised difference spectra generated for 50K and 295K as estimates of prompt fluorescence. The red edge and structure match quite closely, which supports the interpretation that significant blue shifting or narrowing has not occurred to this emission upon cooling. Measured by author.

If the initial population excited into the singlet does not change with T as is suggested by the OD not changing significantly with temperature (A change from 0.1 to 0.11 OD as seen at the excitation wavelength would only result in a $\sim 2\%$ drop in transmittance), this then suggests that ISC is not changing by the same extent at RISC.

In the top right panel of figure 4.17, it is shown that the quantities associated with RISC, i.e. the total PL and rate of delayed emission for the same film of CMA1 are both highly temperature dependent, and increase by approaching 2 orders of magnitude over the same temperature range of 50K to 300K, in contrast to the factor of ~2.5 seen in the change in prompt luminescence. This is consistent with the time kinetic data presented in section 4.5.1.

This demonstrates that the states and transitions involved in ISC and RISC do not have the same dependence on temperature.

Whilst it makes sense that a process which is downhill in energy may not be as sensitive to a reduction in the thermal energy of the system, this has implications on which states and vibrational modes are involved in ISC and RISC, and that these may not need to be the same.

4.11 CMA1 Conclusions

4.11.1.1 CMA1 can have the emission tuned without chemical modification

The first point to make about CMA1 as an emissive molecule is that it has been shown that its emission can be tuned to a considerable extent by either dilution restricting triplet diffusion to lower energy sites, changing the polarity of the host environment or by sample morphology locking molecules in a more sterically restricted configuration such as crystalline powders.

This has been shown to be true for both samples measured for the isolated photophysics, but also in functional device contexts with high efficiency demonstrations. ¹⁴³ ¹⁵⁰

The calculations on CMA1 carried out by prof. Mikko Linnolahti show that this is largely due to stabilisation of the HOMO. This suggests that in addition to morphological control of emission from CMA1 that further control emission from CMA molecules should be possible from analogues of CMA1 designed with electron donating and withdrawing groups on the donor carbazole unit.

This forms the basis of the investigation in chapter 6, and will be discussed fully therein.

4.11.1.2 Existing TADF theory does not fully describe the behaviour of CMA1

Literature treatment using the methods reported by Yersin of the emission from organotransition metal complexes as discussed in the literature review builds in certain assumptions resulting in the average emission time of the ensemble decaying exponentially with the exchange energy. In the literature I have found, it describes the triplet emission rate as being linked to the difference in energy of the S1 and T1 states.

In a concentration series where the peak emission shifts by ~50meV, we see very little change in the emission lifetimes as shown in figure 4.11.

It has also been shown that in a range of different polarity host environments, where the emission from the CT state is blue shifted by ~200meV that the PL lifetime is largely unchanged as shown in figure 4.12. If we are changing the CT emission energy, and retaining a similar rate constant, this suggests that this treatment may not fully account for the behaviour of CMA1.

If this is compared to the high energy edge of the emission from the 3LE state seen in frozen solutions of MTHF, we see that shifting the CT energy relative to the 3LE state does not significantly change the rate of RISC. The emission from CT states has been identified by its characteristic broad, unstructured spectrum, and the sensitivity to the polarity of the environment of the molecule in both solid and solution samples.

As mentioned earlier, if Yersin and Penfold are correct that the 1CT and 3CT energy levels are the correct/ relevant levels, then this result is not in agreement with this.

Current models of organic TADF have an explicit dependence on the exchange energy being linked to the ISC/ RISC rate, being exponentially dependent either as a function of Δ Est or the difference in energy between the 3CT triplet and the 3LE. In either case, this would result in a meaningful change in the lifetime of the delayed emission, either from films of varying concentration, or from higher polarity hosts which have raised the energy of the CT emission.

It would also be predicted that the rate for ISC would scale similarly to that of RISC, whereas in CMA1, I approximate the contribution at room temperature from prompt fluorescence to be \sim 2.8 times larger than at 50K, whereas the delayed emission lifetime, which can be considered a proxy for the RISC rate, increases by nearly 2 orders of magnitude.

Clearly these behaviours cannot be fully explained independently using either the existing theory of organic TADF, or the existing models of heavy metal phosphors and suggest for the class of organo-metallic molecules, that both mechanisms must be considered simultaneously.

This places the photophysics of the CMA family at the intersection of current TADF theory and heavy metal phosphors, and to understand the photophysics facilitating the rapid and efficient emission from triplet excited states, both SOC and Donor-Acceptor tuning must be considered.

To study the importance of SOC, and the phosphor-like aspects of this system, an investigation was carried out to probe the importance of the metal bridge atom on forward and reverse intersystem crossing rates for gold, copper and silver analogues of CMA1, both with a carbazole donor unit or with a carbazole unit with 2 tBu groups substituted to modify the overlap of the HOMO and LUMO on the metal bridge atom. This work is discussed in detail in chapter 5.

The second mechanism for singlet and triplet mixing via minimising the exchange energy using a Donor-Acceptor molecular architecture is studied by comparing a large number of donor substitutions, primarily on the Au bridged version. This includes a set of carbazole dendrimerised versions which considerably increase the spatial separation of the HOMO wavefunction compared with CMA1, and 6 new donor moieties of varying electron withdrawing strength.

Between these two chapters I separately probe the mechanisms for excited state spin conversion, and also assess the effects of these modifications on the energy of the emitting states.

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Chapter 5 Spin orbit coupling effects on intersystem crossing in metal bridge series



5.1 Coinage metal analogues of CMA1

One of the parameters which can be varied in the CMA architecture is the metal atom used in the bridge between the donor and acceptor units.¹⁵²

With the valence of the existing carbazole donor group, we are bound to group 11 elements, practically limited to the coinage metals; copper, silver and gold as heavier group 11 elements are radioactive. Similar substitutions have been explored in three coordinate geometries for TADF style emitters ¹⁵³, including work on ISC in the coinage metal series ¹⁵⁴.

From DFT calculations of the excited state carried out by Mikko Linnolahti, it has been shown that there is considerable overlap of the HOMO and LUMO wavefunctions on the metal bridge atom, CMA1 and a number of other derivatives, as shown in figure 4.1¹¹⁵.

Part of the reason we attribute the rapid emission from triplet excitons in the CMAs to is the contribution of spin orbit coupling to the singlet-triplet mixing strength, facilitating rapid ISC and RISC, in a similar manner to existing heavy metal phosphors. The combination of the effect of the metal atom with the reduction in the exchange energy achieved by separating the HOMO and LUMO wavefunctions on the Donor and Acceptor moieties is key to the highly efficient, rapid delayed emission seen in CMA1, but the balance of how these two effects combine cannot be demonstrated from one molecule.

To investigate the importance of spin orbit coupling strength of the metal bridge atom, and how this determines the RISC rates in CMAs, a set of 6 molecules were compared, where the metal bridge atom is swapped between Copper, Silver and Gold with Carbazole and tBu Carbazole donors.¹⁵⁵



Figure 5.1 metal bridge CMA variants

Figure 5.1 shows molecular diagrams for coinage metal analogues of Copper (left), Silver (centre) and Gold (right) of CMA1 with both carbazole (top) and bi-tertiary butyl substituted carbazole (bottom) donor units. The top right Au-Cz is CMA1, as discussed in chapter 4.

For discussion within this chapter, these will be referred to in the format of the bridge metal atom, and the donor unit, e.g. Au-Cz for CMA1, and Au-Cz-tBu for the version with 2 tert. Butyl groups attached. This varies from the labels used in the literature, but is used for the sake of clear cross comparison within this thesis.



5.1.1 Photophysical behaviour of metal bridge variants

Figure 5.2 metal bridge Abs. and PL

Figure 5.2 shows a comparison of (top left) extinction coefficient in toluene, (top right) steady state PL in toluene, (bottom left) steady state PL at 20% weight in PVK film, (bottom right) integrated PL from PVK host guest films. Measured by author.

This set of 6 molecules retain the characteristic charge transfer features seen in CMA1 in both their absorption and the PL, and exhibit delayed PL from both solution and solid state samples, demonstrating that the nature of the emission has not been changed entirely by varying the bridge metal atom, or adding tBu groups to the carbazole.

5.1.1.1 Steady state emission

A consistent trend is seen in the steady state PL spectra, in that the addition of the tBu group red shifts the PL by ~30nm relative to the emission from the Carbazole donor versions. This is consistent with a slightly more delocalised wavefunction, consistent with the stabilisation of the HOMO of the donor unit.

The extent of this red shift changes between solution and solid films samples, but the trend remains the same that the tBu group slightly reduces the energy of the emission.

5.1.1.2 Steady state absorption

The strength of the CT absorption band seen in dilute toluene solutions is strongest for the Au derivatives, followed by Cu and weakest in the Ag analogues. This does not entirely follow the order of atomic weight of the bridge atom, as the Cu variants show stronger CT absorption than the Ag variants. This could result from the donor-acceptor distance being slightly larger in the Ag analogues which would be expected to reduce the oscillator strength of charge transfer transitions.

When the Tertiary Butyl side groups are added, relatively small changes are seen in the intensity of the coupling of the ground state to CT state, and the magnitude and order of these absorption features in the tBu analogues is largely the same as for the Cz versions. A small red shift of the CT absorption band is also observed with the addition of the tBu groups for all 3 of the metals.

The trend in the absorption is then that the metal bridge atom determines the strength of the CT absorption feature, and addition of the tBu groups red shifts this slightly, as would be expected by stabilising the energy of the HOMO on the donor group.

5.1.1.3 Changes in emission kinetics

The trend seen in the TRPL is not so clear cut. We see that for gold and copper, the heavier metal has more rapid delayed emission, and that addition of the tBu groups makes this slightly more rapid, as could be expected if we believe the RISC rate to depend on SOC, and more electron density has been pushed toward the metal bridge.

The results from the Ag analogues do not follow this trend. Firstly, the emission lifetime for the Ag-Cz is faster than the Au-Cz or Cu-Cz analogues, which would not be predicted from a simple dependence on higher SOC strength from atomic weight resulting in more rapid RISC.

In addition to the order of emission lifetime having changed, the effect of the tBu substitution is also different for the Ag analogues, in that the Ag-Cz-tBu emits slightly slower than the Ag-Cz.

5.1.1.4 Processes on intersystem crossing timescales

From the steady state data, and long-time resolved measurements it is not possible to identify the origin of the deviation from this trend for the silver analogue. Clearly there is more to the changes in the behaviour than the weight of the metal bridge atom, and the energy of other states involved in forward and reverse ISC must be considered to form a complete picture of how these modifications affect the photophysical behaviour.

To this end, ps resolved TA and PL measurements were carried out. TA data presented was measured by Heather Goodwin. Picosecond TRPL measured by Sascha Feldman.

5.2 Tertiary Butyl substitution to CMA1

First, let us consider the addition of the tBu groups on the gold variants. In the initial reports on solution processed devices, both the Au-Cz and the Au-Cz-tBu performed well, with EQEs > 25%.¹¹⁵ The steady state absorption and PL are similar, and the longer time TRPL also follows the same form as the Au-Cz molecule.

The emission at longer times is slightly faster in the Au-Cz-tBu analogue, supporting slightly faster RISC, but only by a small amount.



Figure 5.3 effect of tBu on Au HOMO-LUMO

Figure 5.3 shows calculated HOMO-LUMO wavefunctions for Au-Cz and Au-Cz-tBu. Calculations by Mikko Linnolahti.

5.2.1 Picosecond TRPL of Au-Cz-tBu

For CMA1, the prompt fluorescence is seen to rapidly red shift during the initial decay in solution over ~5ps. This is consistent with a small contribution from the 1LE state alongside the 1CT population rapidly undergoing ISC. It can be seen in the kinetics from the blue edge decaying faster than the centre, which in turn in faster than the red edge which is seen to grow in.



Figure 5.4 Au-Cz ps-TRPL

Figure 5.4 shows ps resolved TRPL data of Au-Cz (CMA1) in toluene solution.(top left) shows time slices of the first 10ps of emission (0.5-1 in 0.1ps steps, and 1-10in 1ps steps). (top right) shows the same data for the first 10ps normalised to more clearly show the early time red shift. (Bottom left) shows the kinetics compared over 3 spectral regions for the blue edge (460-480nm) centre (500-520nm) and red edge (580-600nm). (Bottom centre) shows a normalised comparison of these same kinetics, (bottom right) shows the position of the PL peak wavelength over time, settling after the first ~5ps. Data measured by Sascha Feldman.



By comparing the total PL to the peak shift, it is possible to decouple the times over which molecular relaxation occurs versus fluorescence from the 1CT being quenched by ISC.

Figure 5.5 Au-Cz-tBu ps-TRPL

Figure 5.5 shows Au-Cz-tBu in toluene. (Top left) shows the rapid quenching of the fluorescence and blue shift over ~5ps. (Top Right) shows the PL peak wavelength shifting over the first ~5ps and stabilising after ~10ps. (Bottom left and right) shows a comparison of the kinetics for the blue edge, central region, and red edge of the PL on linear and logarithmic intensity axis respectively. Data measured by Sascha Feldman.

A similar trend is seen for Au-Cz-tBu in toluene solution. There is a rapid reorganisation on the order of 5ps, followed by a decay in the total luminescence on the order of 10ps. These observations are in good agreement with existing spectroscopic measurements of CMA1. The decay of the total PL, taken as a proxy for ISC, occurs over ~4ps, supporting that the emission is from the state observed in the TA.

5.2.2 Transient absorption of Au-Cz-tBu

At early time a PIA forms which we attribute to population photo-excited into the S1 state. Sometime after this a second PIA forms which we attribute to the T1 state being populated by excitons intersystem crossing from the S1 to the T1 state, which is then long lived.



Figure 5.6 Au-Cz-tBu TA

Figure 5.6 shows Au-Cz-tBu in toluene. When compared with figure 4.21 in chapter 4 (Au-Cz) we see that the behaviour is similar. Data measured by Heather Goodwin.

The PL shows rapid quenching of the fluorescence over 5-10 ps, consistent with kinetic competition from the S1 state being depopulated by ISC, along with a rapid red shift of PL peak as the ensemble relaxes to lower energy excited state conformations. All of this is functionally similar to CMA1 / Au-Cz, and the addition of the tBu groups has not drastically changed the behaviour of the molecule in the excited state, or the emission process or states involved in ISC and RISC in the gold variants beyond achieving a slight red shift in the PL.

5.2.3 Effects of the tBu substitution on CMA1

On the gold bridged analogue, the addition of the tBu groups has only significantly changed one aspect of the emission.

The PL has been redshifted by ~30nm, which is consistent with a greater degree of spatial delocalisation the HOMO wavefunction.

There is a slight increase in the PL emission rate, but only ~10% from 915ns for Au-Cz to 805ns for Au-Cz-tBu in PvK hosted films.

The forward intersystem crossing occurs on a similar timescale for both Au-Cz and Au-Cz-tBu.

This particular modification then, reduces the energy of the excited state of the molecule without significantly changing the photophysics, states, or transitions involved.

This raises the question about whether further donor group modification may be a way to red shift the emission whilst retaining rapid ISC, RISC, high PLQE and low concentration quenching in the solid state, and is discussed in greater detail in chapter 6.

5.3 Changing the metal bridge atom

The strength of spin orbit coupling depends on the size of an atom which an electron is near. This is the same logic which has gone into developing many of the phosphorescent molecules which incorporate heavy metals like platinum and iridium discussed earlier in the literature review.

By varying the metal bridge atom in the CMA architecture, it should be possible to test how much effect the strength of spin orbit coupling has on the ISC and RISC rates, and how much these processes are facilitated by the spatial separation of HOMO and LUMO wavefunctions by molecular design.

5.3.1 Structural changes with metal bridge substitution

It is important to note that whilst this set of molecules is as close as synthetically possible to only changing one factor in the motif, that some additional parameters have also varied between the different metal bridge variants.

This will have some impact on spatial separation of the HOMO- LUMO wavefunctions in addition to the change in strength of SOC from the metal bridge atom, and this will be discussed later for meaningful cross comparison.



Figure 5.7 crystal structure of Ag-Cz and Ag-Cz-tBu

Figure 5.7 shows published crystal structure calculations for Ag-Cz and Ag-Cz-tBu¹⁵⁵. These show several differences between the different metal bridge atoms.

These differences between the two silver analogues and the copper and gold carbazole versions are summarised in table 5.1 below.

Bond length/compound	Cu-Cz	Ag-Cz	Au-Cz
M1–C1 (Å)	1.884(2)	2.085(2)	1.991(3)
M1–N2 (Å)	1.862(1)	2.067(1)	2.026(2)
C1–N1 (Å)	1.305(2)	1.294(2)	1.299(4)
Angle C1–M1–N2	174.34(6)	178.55(7)	178.78(11)
Torsion angle N1–C1–N2- C28	7.8	19.9(4)	17.6

Table 5.1 metal bond lengths

Table 5.1 shows the differences in bond lengths and torsion angles for Au-Cz, Cu-Cz, Ag-Cz and Ag-Cz-tBu according to the calculations presented in ¹⁵⁵. Calculations by Mikko Linnolahti.

In the case of the silver the metal-carbon bond length is ~10% longer than for Gold and copper, which are very similar. Bond lengths for the tBu analogues are nominally identical.

This in itself does not explain why we would see more rapid emission from the Ag analogues, or the effects of the tBu substitutions reversed, as a larger HOMO-LUMO spatial separation would result in a reduction in oscillator strength.


5.3.2 HOMO- LUMO calculations

Figure 5.8 metal bridge series HOMO-LUMO

Figure 5.8 shows HOMO-LUMO calculations for the full Cz and Cz-tBu metal bridge series. Calculations by Mikko Linnolahti.

If we are considering the role of the metal bridge atom, then clearly the wavefunction overlap on the bridge will determine the extent to which an electron in that state experiences the effect of the metal. If the magnitude of the HOMO and LUMO are compared either side of the metal bridge on atoms C1 and N2, we see that due to the longer carbon-metal bond in the silver bridge version, that the overlap on the metal bridge varies considerably.

The largest amount of wavefunction overlap is on Au-Cz, followed by Cu-Cz with silver showing the greatest HOMO-LUMO separation. This implies there will be the least involvement of metal orbitals in transitions on the silver analogue, followed by copper, with the largest involvement in the gold analogues. This parameter did not vary meaningfully with the addition of the tBu side groups.

5.3.3 Picosecond TRPL of metal bridge series

As has already been compared for the Au-Cz and Au-Cz-tBu analogues, the timescale over which the initial fluorescence decays over provides information about the timescale of forwards ISC.



Figure 5.9 ps TRPL of metal bridge series

Figure 5.9 shows a comparison of the ps TRPL of the 6 variants in toluene solution. All show rapid red shifting; however the rate of quenching of the fluorescence varies considerably with metal bridge atom. Data measured by Sascha Feldman.

The addition of the tBu group did not significantly change the ISC time between Au-Cz and Au-Cz-tBu, both of which occurred over ~ 9ps if the total PL is considered or ~ 15ps if the low energy edge is considered.

As the tBu side groups do not seem to have a large effect on the ISC rate, I will discuss only the carbazole derivatives in detail, as the statements hold true for the Cz-tBu analogues also.



5.3.3.1 Ag-Cz

Figure 5.10 Ag-Cz ps TRPL

Figure 5.10 shows a comparison of the emission from Ag-Cz and the timescale for PL shifting. Data measured By Sascha Feldman.

In the silver bridged version, relaxation and red shift occurs rapidly within the first 2.5ps.

Despite this, subsequent emission is much slower, supporting conformational freedom being similar, but the forward intersystem crossing rate, inferred from the total emission, being lower than for the gold analogue.



5.3.3.2 Cu-Cz

Figure 5.11 Cu-Cz ps TRPL

Figure 5.11 shows a comparison of the emission from Cu-Cz and the timescale for PL shifting. Data measured By Sascha Feldman.

In the copper bridge version, the initial red shift is slower than both the silver or gold analogues, implying that molecular reorganisation is impeded.

The ISC time as inferred from the decay of the PL after this initial reorganisation is faster than the silver analogue, but slower than for the gold.

5.3.3.3 Forward intersystem crossing

If we compare across the different metal variants, we see that the addition of the tBu side groups does not have a large impact on the reorganisation time or the decay of the low energy edge of the emission for a given metal bridge atom.

Molecule	T _{early} (ps) peak shift	T _{late} (ps) red edge	T _{overall} (ps) total
Cu-Cz	4.5±0.6	67.4	11.3±0.7
Cu-Cz-tBu	4.4±0.3	62.7	36.3±2.2
Ag-Cz	2.5±0.4	84.6	62.4±11.5
Ag-Cz-tBu	2.3±0.3	79.5	42.4±6.6
Au-Cz	2.9±0.1	14.7	9.7±0.2
Au-Cz-tBu	3.1±0.3	15.9	9.2±0.3

Table 5.2 metal series ps-trpl times

Table 5.2 shows a comparison of the timescale of the PL peak shift, the red edge of the PL decay and the decay of the total integrated PL.

There is a larger disparity in the decay of the total PL, however the same trend is seen that for either the red edge, or total PL decay, forward intersystem crossing occurs fastest in the gold bridged analogues, followed by copper, and then silver.



Figure 5.12 atomic weight decay time comparison

Figure 5.12 compares the ISC time inferred from the decay of the red edge (left) with the decay of the total PL (right) as a function of atomic number.

This result would seem to contradict the dependence of SOC on atomic weight as discussed in the theory section, which would predict SOC rate to scale with Z within a given group on the periodic table. This points to additional factors in the molecular geometry and excited state wavefunctions driving the ISC time. The factors which have changed with the substitution of the metal bridge atom include the length of the C-M-N bridge, and the increased rotational and conformational flexibility with greater Donor-Acceptor separation.

When the strength of SOC from the metal atom is considered also in the context of wavefunction overlap on the metal, this trend makes more sense, as the forward ISC is in the same order as magnitude of the calculated HOMO-LUMO wavefunction overlap on the bridge atom.

5.3.3.4 Molecular relaxation

We also see that the early time red-shift in PL does not scale in order of metal atom weight.



Figure 5.13 reorganisation:bridge length comparison

Figure 5.13 shows a comparison of the timescale over which molecular relaxation occurs with the donor-acceptor bridge length.

If the early time red shift is considered to be indicative of the molecule undergoing conformational change in the excited state to minimise the excited state dipole, then it follows that this would scale with the torsional freedom of the molecule.

If the bridge length, i.e. C1-M1-N2 is compared to the reorganisation timescale, this seems to be in agreement, supporting the inference that the rapid red shift corresponds to conformational reorganisation of the molecule.

5.3.4 Transient Absorption of metal bridge series

In the full set, the growth of the second triplet PIA feature is well defined in the Au derivatives. A similar transition is also seen in the Cu variants growing in over a longer time. Both Ag analogues show different behaviour with less clearly defined transitions, and the transition occurring on a longer timescale. For the Ag derivatives, there seems to be greater spectral overlap between the singlet PIA and triplet PIA in the region of ~650nm. For this reason, the decay of the feature at ~600nm is used to approximate the ISC time.



Figure 5.14 metal bridge series TA

Figure 5.14 shows a comparison of the TA spectra for the 6 analogues, with a visual guide of where the second PIA has grown in. Data measured by Heather Goodwin.

The order and magnitude of the timescale over which the singlet PIA decays and the triplet PIA grows in is in close agreement with the ps-TRPL. This is consistent with the rapid decay of the fluorescence attributed to the depletion of the 1CT state via ISC being fastest in the gold, followed by the copper, and markedly slower in the silver. The order of ISC from the

TA data is in good agreement with the longer time TRPL measurements, where we see a larger portion of the total emission in the Ag analogues, and no appreciable contribution to total PL in the Au variants, and a slight presence of prompt emission in the earliest time slice for Cu. As shown in figures 5.16, 5.17 and 5.18.

5.4 Comparing ISC and RISC

The ps-TRPL and TA both provide information about the forwards intersystem crossing time, and are in good agreement for the order of rates, and agree on approximate magnitude.

The order of ISC time is not in the order of atomic number, however it does scale with wavefunction overlap on the metal bridge.

Similar investigations have been carried out in the literature on the effect of heavy atom substitution on forward intersystem crossing rates in phosphors, and have concluded:

"The results conclude that, along the same family, how much a metal d-orbital is involved in the electronic transition plays a more important role than how heavy the metal atom is, i.e. the atomic number, in enhancing the spin–orbit coupling" ¹⁵⁶

This reports Cu with faster ISC than Ag and Au. We see faster ISC for Au and Cu with Ag slower however, this is a result of the molecular architecture, and both sets depend on orbital overlap.

5.4.1 Trends in reverse intersystem crossing

Whilst the trend in forward intersystem crossing goes in the order of gold, followed by copper, followed by silver, as explained by orbital overlap, reverse intersystem crossing does not.

Using the proxy of delayed emission lifetime to infer the RISC rate, the order is that silver is fastest, followed by gold, with copper slowest.

These quantities are not exact measures of the ISC and RISC times, but both approximations should be the correct magnitude and track the trend produced by changes in ISC and RISC.

Material	M atomic number	ISC time TA (ps)	ISC time PL (ps)	RISC time PVK PL
				(ns)
Cu-Cz	29	20	11	2889
Cu-Cz-tBu	29	70	40	1748
Ag-Cz	47	~100	60	402
Ag-Cz-tBu	47	~100	40	550
Au-Cz	79	5-10	9.7	915
Au-Cz-tBu	79	5-10	9.2	805

Table 5.3 metal series ISC and RISC times

Table 5.3 shows a comparison of the ISC and RISC times for the coinage metal series, as obtained by ps-TRPL, TA and delayed PL lifetime.

This forward ISC trend seems to be contradictory to the trend seen in the delayed PL, where the silver is the fastest. If we take the time for the second PIA to appear in the TA data, and the early time quenching of the fluorescence as indicative of the ISC timescale, and the timescale of the delayed emission as representative of the RISC process, then if these molecules are coupling the excited states in the same way, the trend should be in the same order.

To explain the trend in RISC it is useful to consider the differences and similarities between fully organic and organo-metallic TADF systems.

In the field of fully organic TADF molecules where spatial separation of the wavefunction across a number of donor and acceptor units reduces the exchange energy, direct spin orbit

coupling between 1CT and 3CT states is suppressed, as the orbitals which make up the HOMO and LUMO are similar, as outlined in El-Sayed's rule:

"the rate of intersystem crossing is relatively large if the radiationless transition involves a change of orbital type"¹⁵⁷

The corollary of this is clearly that the ISC rate is small if the states involved are of similar orbital symmetry.

In the literature on RISC mechanisms for fully organic TADF compounds, it is asserted that there are a number of regimes in which TADF can occur as set out by Etherington et al., determined by the relative energy levels of the 3CT and 3LE states.

Given that direct spin orbit coupling between states of similar character is largely suppressed, it follows in this treatment that:

"that the intersystem crossing (ISC) and reverse intersystem crossing (rISC) between ${}^{1}CT$ singlet and ${}^{3}CT$ triplet states is a more complicated second order process. This second order process is mediated by vibronic coupling of the ${}^{3}CT$ to the local exciton triplet ${}^{3}LE$ states to allow spin–orbit coupling to the ${}^{1}CT$ state"⁸¹

The process of RISC relying on 2nd order vibronic coupling would predict that this contribution can be "frozen out", and at very low temperatures, any delayed emission remaining must primarily result from direct coupling of the excited triplet to the ground state by phosphorescence. The amount of delayed emission which persist below the activation energy can thus be taken as a proxy for the effect of the metal atom acting more like a metal containing phosphor than a purely TADF molecule.

This allows us to separate the presence of the two existing mechanism by which emission from triplet excitations is utilised, i.e. organic TADF systems, and heavy metal phosphors, and explore a quantified comparison of the respective contribution in the CMA systems. For the set of molecules which I am studying where a metal atom is included, this treatment is not sufficient, as El Sayed's rule does not describe the contribution of metal D orbitals to what transitions are allowed by symmetry. Extensions to this treatment have been explored in literature to describe organo-metallic compounds¹⁵¹.

If the first order singlet-triplet mixing coefficient is:

$$\lambda = \frac{\langle S1 | \widehat{H} so | T1 \rangle}{\Delta EST}$$

{16}

And the RISC rate is:

RISC rate =
$$[k.\langle S1|\hat{H}so|T1\rangle] * e - \frac{EA}{KT}$$

{17}

It would be expected that the trends in forward and reverse intersystem crossing with metal should be in the same order if this is mediated by first order, direct spin orbit coupling.

This would not have to be the order of the metal bridge atoms atomic weight, but the trend should be the same in both directions.

If only copper and gold were being compared, this would seem to hold, however silver does not fit this trend. Since this is not the case, we must consider second order spin-vibronic coupling, and whether local triplet states act as intermediaries for RISC.

5.5 Low temperature behaviour of metal bridge variants

In addition to providing information about the thermal activation of RISC by measuring TRPL at a number of temperatures, cryogenic measurements can also provide information about the energy of the lowest lying triplet state by measuring direct phosphorescence below the regime where RISC is thermally accessible.

The lowest lying triplet state could either be a charge transfer state (3CT) or a locally excited state (3LE). In the regimes laid out by Etherington et al. the lowest energy triplet state is I) 3LE, II) isoenergetic 3LE and 3CT and regime III) 3CT.



Figure 5.15 3CT vs 3LE alignment

Figure 5.15 shows a schematic of the alignment of 3CT and 3LE energy levels in the 3 regimes of TADF described by Etherington et al.⁸¹

From Kasha's rule, we expect to see luminescence from the lowest energy state of a given multiplicity, thus phosphorescence measured below the threshold temperature for RISC should allow us to identify which of these regimes applies, and therefore infer whether second order spin vibronic coupling is a possible explanation for the differences between ISC and RISC.

5.5.1 Lowest triplet state and phosphorescence

In the CMA materials, emission is seen at a large range of energies from a number of different states. By comparing the blue edge of early time emission, the range of delayed emission in the solid state at various temperatures, and emission from a dilute, low polarity solvent, the different energy levels can be compared.

5.5.1.1 Au-Cz spectral comparison



Figure 5.16 Au-Cz spectra

Figure 5.16 shows the range of emission energies from Au-Cz as shown in figure 4.10. Measured by author.

In CMA 1, the distribution of conformers in the solid state is able to explore the lowest energy emission at all temperatures. This is clearly demonstrated by the delayed 100ns PL at room temperature (green) overlapping with both the toluene solution (black) and the 250µs emission at 50K. The 3CT and 1CT states have considerable energetic offset. It is also clear that the lowest energy triplet state is CT, and this corresponds well to the emission from dilute solution.



5.5.1.2 Cu-Cz spectral comparison

Figure 5.17 Cu-Cz spectra

Figure 5.17 shows the range of emission energies from Cu-Cz. Measured by author.

In copper, we also see that the range of conformers in the solid film approaches the energy of the emission from toluene solution eventually. As the bond length is similar to that of Au, this is consistent with the interpretation that the allowed range of conformers in the solid state explores the energetic minima. Spectral migration in the solid film is slightly slower than for Au-Cz, and the delayed PL takes longer to resemble the toluene spectra, however after 500ns it matches well.

All delayed emission is also charge transfer in character, and retains broad, unstructured emission, supporting the 3CT state being the lowest lying triplet. There is a suggestion of a shoulder on the 50K data after 250 μ s, however this represents a vanishingly small portion of the total PL the 3CT and 1CT states have considerable energetic offset, as for Au-Cz.



5.5.1.3 Ag-Cz spectral comparison

Figure 5.18 Ag-Cz spectra

Figure 5.18 shows the range of emission energies from Ag-Cz. Measured by author.

For silver, a very different picture is seen. At earlier time

The delayed emission at 50K and room temperature also converge, supporting that the distribution of conformers locked in the solid film explore the same energy range, however, this does not include the minimised energetic configuration of the dilute solution.

This may be a result of the longer donor-acceptor bridge being locked into energetically nonminimised conformers in the solid state whereas more torsional freedom is explored in the solution.

Another clear difference is that the low temperature extremely delayed emission at 250µs, which I assign to direct phosphorescence from the carbazole donor, is clearly structured and

from a local state. This is in close agreement with the phosphorescence measurements for free carbazole presented in figure 4.20.

Clearly the alignment of the 3CT and 3LE states in the silver analogue is different to the gold and copper analogues, and the 3LE state is the lowest lying triplet for this molecule.

In the terminology of figure 5.15, this would state that the silver analogue is operating in "type 1" TADF in some configurations where the 3LE state drops below the 3CT state.

The high energy edge of the phosphorescence from the 3LE state is very close to the edge measured for the prompt fluorescence. In this case they are limited by the 425nm long pass filter used, however clearly the energetic spacing is less than for the Au or Cu versions.

5.5.2 Correcting phosphorescent wrap around

Another result of the lowest triplet state being 3LE in character is that coupling with the ground state is reduced, and emission takes much longer than phosphorescence form the 3CT states.

From an experimental perspective this introduced the issue that wrap around occurred at low temperature, and the ICCD and laser I measured on are triggered at 1 kHz, so have a maximum experimental window of 1ms.

This introduces a non-zero background which becomes problematic when calculating the integrated PL, as integrating a non-zero background tends to infinity, as seen in the blue and red lines in the left panel of the figure above.

To allow comparison with the Au and Cu analogues for activation energy calculation, I applied the following correction.

- Extrapolate the PL value to what would be present at 1ms when the next pulse arrives (from last data point at 800µs)
- Use this value as a linear offset, and subtract it from the entire data set, which sets the data to be zero at 1ms
- This then means we are comparing the activation of emission occurring within <1ms



Figure 5.19 correcting phosphorescence wrap around

Figure 5.19 shows (top) a comparison of the PL kinetics with spectra inset for (top left) Au-Cz and (to right) Ag-Cz. The structure of the long-time emission is clearly CT in Au-Cz and 3LE in Ag-Cz. (Bottom) shows the integrated PL for a solid film of Ag-Cz-tBu. (Bottom left) is the raw data including phosphorescent wrap around. (Bottom right) shows a corrected version of this. Measured by author.

Since the 3CT emission is the process of interest for thermal activation, this should be an appropriate comparison. This then could be considered the activation of PL which occurs in less than 1ms.

5.5.3 Activation energy

In this comparison, the Ag-Cz-tBu analogue is compared, as the photo-stability of the Ag-Cz analogue was poor, and significant degradation occurred over the course of the measurement.

This is calculated using an Arrhenius relationship, where the logarithm of the decay rate is plotted against 1/T. A mono-exponential decay is then fitted to this on top of a linear offset representing thermally invariant emission. The activation energy (EA) is extracted from the decay constant divided by Boltzmann's constant (KB). i.e.:

Compound	Activation energy (meV)		
Cu-Cz (spin cast)	166		
Ag-Cz-tBu (spin cast)	84		
Ag-Cz (spin cast)	108		
Au-Cz (spin cast)	80		
Au-Cz (evaporated)	79		

 $ln(decay \ rate) = ln(intrinsic \ phos. \ rate) + A \ exp^{(\frac{-E_A}{K_BT})}$

Table 5.4 metal series activation energies

Table 5.4 shows activation energies measured for a range of CMA samples. Measurements and calculations by author.



Figure 5.20 metal series activation energy

Figure 5.20 shows integrated PL (left) and activation energy (right) for Au-Cz (top), Cu-Cz (centre row) and Ag-Cz-tBu corrected for wrap around (bottom). Measured by author.

In the silver, $\sim 5\%$ of the emission comes from a temperature invariant contribution from the prompt fluorescence in the first ~ 10 ns. This is consistent with the slower forward intersystem crossing times measured in both the TA and ps-TRPL allowing more fluorescence from S1 before excitons cross to the triplet manifold.

Despite having forward intersystem crossing rate ~10-20 times slower than for the gold, the activation energy for Ag-Cz-tBu is almost identical to Au-Cz, and room temperature emission more rapid.

Both the copper and gold versions display all emission from states of CT character across all temperatures measured, and have no significant contribution from prompt fluorescence from the S1 state. The silver analogues however shows clear phosphorescence from a local state, in keeping with the 3CT energy level being well below the 3LE as in type III TADF in figure 5.15.

If we compare the rate of phosphorescence below 100K, we have:

Au= 2.5 x 10⁴/s, Cu= 2.2 x 10⁴/s Ag = 8 x 10³ s

Thus we see that the intrinsic CT phosphorescence is governed by the involvement of the metal atom in direct coupling in the absence of 2^{nd} order processes, and that both the forwards intersystem crossing time and the intrinsic phosphorescence scale together in response to Z and metal bridge length.

This is in good agreement with the intersystem crossing time on the order of 10s of ps outcompeting singlet fluorescence.

Au-Cz seems ambivalent to energy of 3CT state for thermal activation, as relative to spin cast samples, emission from evaporated and films in a polar host shifts considerably, however the activation energy does not seem to change.

This result would seem to contradict the work of Etherington et. al. where the balance of 3CT and 3LE energies is sensitive to the local environment, and thus for a given molecule, would change with host polarity and rigidity.

The fact that for Au-Cz considerable chromatic shift can be achieved by changing the morphology of the film by thermal vapour deposition, or blue-shifting the CT emission in a highly polar small molecule host without changing the emission lifetime or activation energy supports the interpretation that TADF in the gold versions of this molecule is mediated by direct SOC rather than predominantly through second order spin-vibronic coupling as for the silver analogue.

5.6 Similar behaviour in literature

The CMA family is not the only time the trend of RISC with bridge metal varying in this order has been observed. In addition to our reports of the behaviour of the gold, copper and silver compounds separately in the literature, ^{115,143,155} there has also recently been a publication by the Thompson group ¹⁵⁸ on a very similar material system directly comparing Cu, Ag and Au bridged molecules which corroborates our earlier reports of this trend with metal bridge atom in reverse intersystem crossing inferred from delayed PL.

This set of materials is strikingly similar to the CMA family, incorporating a carbazole donor unit, coinage metal bridge atom, and only slightly different acceptor moieties are used.



dipp = 2,6-diisopropylphenyl

Figure 5.21 molecular structures of CMA-like emitters

Figure 5.21 shows chemical structure of materials reported by the Thompson group. ¹⁵⁸

In this report, the forward intersystem crossing times are reported in toluene follow the same trend, but are not well defined as they are decoupled from the IRF of a TCSPC with considerably poorer time resolution.

As I have demonstrated, the PL kinetics at a particular wavelength are not a robust measurement of forward intersystem crossing time, as there is a considerable degree of conformational reorganisation on the ps timescale. Spectrally resolved TRPL combined with TA provides a much more rigorous measure of this process.

5.7 Coinage metal series conclusions

From this comprehensive cross comparison of the effect of the metal bridge atom for both carbazole and bis-tertiary butyl modified carbazole donor moieties, I have demonstrated that different aspects of the molecular design govern forwards and reverse intersystem crossing, and also effect the intrinsic coupling of the 3CT state to the ground state by direct phosphorescence.

Utilising features from both heavy metal phosphorescence, by having meaningful wavefunction overlap on a heavy element, as well as incorporating the spatial separation of the HOMO and LUMO wavefunctions used in organic TADF Donor-Acceptor molecules, the rates or both forward and reverse intersystem crossing can be tuned, as can the relative energies of the local vs. charge transfer triplet state.

The weight of the metal bridge atom is linked to the direct spin orbit coupling strength which contributes to ISC and RISC, however wavefunction overlap plays a defining role in this also, as demonstrated by the silver analogues having slowing ISC than the copper analogues as shown in figure 5.13, in proportion to the bridge length and reduced HOMO-LUMO overlap on the metal atom.

The factors contributing to RISC include bridge atom weight, HOMO-LUMO overlap on the bridge atom, and also the energy of the local triplet state relative to the charge transfer triplet state, which will be linked to the metal bridge length. The result of the silver analogues achieving the most rapid RISC are thus consistent with the enhanced vibronic coupling achieved by the 3LE and 3CT being close to degenerate energetically, whereas mixing with the 3LE state was less efficient in the Au and Cu variants, as the state was much higher in energy, as demonstrated by the lack of phosphorescence from the 3LE, and the frozen solution measurements in MTHF presented in figure 4.18.

The RISC being more rapid in the Au versus Cu variants is also consistent with this, as with similar carbon-metal bond lengths, the higher Z atom in the Au analogues contributes more to the mixing of states, allowing more rapid RISC despite the reduced coupling to 3LE compared to the Ag analogues.

The effect of the metal bridge atoms in the intrinsic coupling between the 3CT and the S0 ground state is also consistent with the intersection of orbital overlap and SOC strength, with the largest residual phosphorescence seen in the Au variants, followed by Cu and with the Ag analogues displaying the least coupling between the 3CT and S0 at low temperatures, with emission from the 3LE state outcompeting the 3CT state.

This set of materials demonstrates that the principles set out for achieving efficient ISC and RISC in fully organic systems can, in part, be brought into consideration for organometallic emitters also. This is distinct to conventional phosphors achieving emission directly from the 3LE state to the S0 state.

If the local triplet energy of the Au and Cu CMA molecules can be appropriately tuned, perhaps the "best of both worlds" could be achieved, and rapid ISC from direct SOC combined with efficient RISC involving intermediary local transitions. Existing organometallic literature has found the balance between improving TADF, and rendering a material phosphorescent challenging,¹⁵⁹ so progress on informed design rules would be a positive step for the field.

In the solid state, the freedom of conformers to occupy a distribution of energy levels clearly varies with metal bridge atom, suggesting that future synthetic work exploring either distorting the donor-acceptor bridge, or locking it into a favourable configuration has the potential to blue shift and sharpen the emission in the solid state.

Modification to the donor group has successfully shifted emission energy to the red by ~30nm for all metal bridge variants without interfering with desirable photophysical parameters.

The Au-Cz-tBu variant provided the combination of the largest red shift in the solid state, slightly faster emission than Au-Cz, as well as superior photo-stability to the Ag-Cz-tBu, which whilst it was slightly redder in solution proved more prone to degrade.

To this end, I will explore whether the Au-Cz-tBu analogue can be used in vacuum deposited OLEDs. This will be discussed in detail in chapter 6.

Chapter 6 Exploring CMA donor modification

All that is gold does not glitter (with a significant delayed contribution...)

After one of the poems by J.R.R. Tolkien from The Lord of the Rings

One of the design trajectories for exploring the new CMA family of emitters was determining to what extent different modifications on the molecular motif could retain the desirable photophysical properties displayed by CMA 1 as discussed in chapter 4.

The 3 core components of the CMA structure are the Donor, the metal bridge atom, and the Acceptor.

In chapter 5, the effect of varying the metal bridge is systematically investigated, and shown to have great effect on the spin conversion rates of the molecules.

The addition of two tertiary butyl groups to the donor unit is also explored in parallel, and shown to achieve a modest red shift without significantly changing other aspects of the photophysics for any of the metal analogues.

In this chapter I will explore the effects of more extensive modification to the donor group on a series of 13 new variations on the CMA motif.

The aim is to explore the impact of changing Donor- Acceptor wavefunction separation on effective triplet-singlet spin mixing for rapid, efficient delayed emission and to establish which properties can be retained or selectively modified by different forms of modification to the donor moiety, and identify viable candidates for both solution and thermal vapour processed OLEDs.

6.1 Recap of properties of CMA1

6.1.1 Desirable properties of CMA1

Some of the properties of CMA1 were desirable for OLED applications:

- Rapid (sub microsecond) emission from excited triplet states
- High PLQE
- Lack of concentration quenching
- High thermal stability
- Light enough to evaporate at chemically stable temperatures
- High solubility, sufficient for solution processing
- Good energy transfer in host-guest films

This combination of properties allowed highly efficient devices to be made by both solution processing and TVD.¹⁴³¹⁵⁰ These devices included host-free/self-hosted emissive layers being utilised in device architectures allowing fabrication of high efficiency devices with simpler device stacks.

6.1.2 Limitations of CMA1

Other properties of CMA1 were either limiting, or did not address the areas where progress is most desirable for application currently:

- Broad CT emission, non-ideal for display application
- High efficiency green emitters already exist ^{160–164}
- Even with morphological tuning, not blue enough for display CIE targets
- Not shown to be able to tune into red emission
- Limited to hosting orange-red emitters

To expand on the scope of application of this family of materials for display purposes, the full range of RGB emission would be desirable. Narrow band red emission can be very useful even outside the visible range for a number of imaging and medical purposes.

If the CMA family was to be considered as a hyperfluorescent host or co-dopant, it would need to have its emission matched to the absorption of whatever fluorescent co-dopant is chosen. Bluer versions would be required to host narrow green fluorescent hosts, and deep blue versions would need to be matched to low Stokes shift blue dyes to achieve hosting narrow band emission across visible wavelength.

Beyond the visible spectrum, narrow band NIR emission is also of interest for device applications, so broad deep red emission would be ideal for FRET to porphyrins or pthalocyanines emitting in the NIR.⁴³

6.2 Donor group modification

In chapter 5, I have shown that the addition of two tBu groups in the 3-6 positions on the Carbazole donor unit result in a red shift of the PL without interfering with the states involved in the emission process, or the ISC and RISC rates.

This demonstrated that the PL could be successfully red-shifted whilst retaining the characteristics of CMA1 by only modifying the donor group.

This makes Donor modification an appealing place to start for systematically exploring modifications to this motif as it has already been demonstrated to function to some extent.

The geometry of the Carbazole also provides a large degree of freedom for modification, as there are a number of sites where substitution can be made. Since it is symmetric, this provides the option of exploring single substitution, symmetric additional groups, as shown in chapter 5, or asymmetric modifications.

The donor group is attached at the final stage in the synthesis. ¹⁵² This means that final yield is not sensitive to the modification, and purification etc. can all be carried out without interfering with the acceptor chemistry. Donor modification is thus appealing from a synthetic perspective.

6.2.1 Choosing the parameter space for initial investigation

In this initial screening of donor modification, the aim is to be able to clearly determine the effect of the chemical substitution on the performance of the molecule and the energy levels of the HOMO. For this reason, not all sites for substitution will be explored, and only symmetric substitutions will be tested in the first instance to limit the parameter space.

Gold bridged variants have thus far been the most promising candidates, and so all donor modifications will be demonstrated on Au bridged CMAs. Cu analogues will be produced for some modifications, as the metal nitrogen bond is closest in length to Au.

Blue materials introduce the issue of chemical stability in the excited state. The need for high energy UV pumps for spectroscopic study, and the stability in devices both make it difficult to infer the effect of the chemical modification without simply observing degradation.

To this end, to best understand the role of donor modification, this initial investigation will be limited to symmetric substitutions tuning emission from the green to the red on gold bridged molecules, with some copper analogues.

6.2.2 Constraints imposed by donor group modifications

Any modification to a molecule can have effects on a large number of the material and electronic properties beyond the parameter targeted for tuning.

The properties we do not wish to interfere with in this instance are:

- Torsional freedom
- Thermal stability
- Solid state packing without concentration quenching

To further refine the parameter space explored in this investigation, some of these aspects were considered.

6.2.2.1 Steric considerations of modification on torsional freedom

One of the aspects of CMA1 which we have attributed its desirable photophysical properties to is the freedom to rotate around the Metal-Nitrogen bond.¹¹⁵



Figure 6.1 structure of CMA1

Figure 6.1 shows the structure of CMA1 and the positions available for substitution on an isolated carbazole unit. In CMA1, position 9 is occupied by the bond to the metal bridge.

This introduces a constraint on the positions where substitutions could be made without adding steric bulk which could interfere with the rotational freedom around this bond, or change the average torsion angle between the donor and the acceptor moieties.

To that end, modifications explored in this investigation are limited to avoid positions *1*, *2*, *7* and *8* on the carbazole unit (shown above), as disruption of the rotational freedom is not the parameter intended to be considered in this screening.

Symmetric substitutions can then be made in positions 6 and 3, 5 and 4 or by replacing the 4a to 4b bond with another atom or group.

6.2.2.2 Size constraint on donor modifications

Another limitation on what modifications are possible to explore whilst retaining the full versatility of CMA1 with respect to processing and photophysical properties is whether the molecule becomes too large to evaporate without breaking apart.



steric bulk of donor group substituent

Figure 6.2 donor bulk limitations

Figure 6.2 shows examples of published variations on CMA1 and their suitability for TVD. Beyond a certain bulk on the donor group, the molecule loses the additional side groups before it can evaporate. ¹⁶⁵

These bulkier side groups are not stable up to high enough temperatures to evaporate, as mass loss is seen via Thermal Gravimetric Analysis (TGA) in several stages as the molecule decomposes. This introduces a constraint on what modifications can be explored regarding the photophysics without restricting what processing techniques remain possible.

In this investigation, I will compare 2 sets of donor modifications:

One set of bulky dendritic substitutions (shown above) aimed at producing variants suitable for inclusion in solution processed polymer OLEDs.

The other, a set of modifications with more restricted bulk, intended to be suitable for evaporation as well as solution processing. TGA or evaporation trials have only been carried out on the candidates which displayed desirable photophysical properties. The thermal stability of the other donor modified analogues was not tested.

6.2.2.3 Functional considerations of position of donor modification

The same substitution at different positions on a molecule will not necessarily have the same effect due to the distribution of the excited state wavefunction not being uniform.



Figure 6.3 electrostatic potential CMA1

Figure 6.3 shows the electrostatic potential map of CMA1 as calculated by the MN15 functional by Mikko Linnolahti.

Of the available positions for substitution on the carbazole which do not interfere with the torsional freedom, the largest change in electron density is at positions **3** and **6**, and the **4a-4b** bond.

To maximise the effect of the modifications, positions **3** and **6**, and the **4a-4b** bond will therefore be the sites targeted for modification rather than **4** and **5**.

6.3 Large steric bulk donor modification

The first set of modifications I will discuss is the addition of two further generations of carbazole units at the 3 and 6 positions on the original carbazole donor.

This set of materials aims to retain the desirable photophysical properties of CMA1 for application in solution processed polymer based OLEDs where homogenous mixing with the polymer host is desirable.

Good energy transfer and device properties were achieved in a PVK host for CMA1, so the addition of carbazole side groups should retain good energy transfer from this host.

Within this section, for consistency with literature the gold and copper carbazole versions are referred to as CMA1/AuG0 and CMA2/CuG0. ¹⁵⁰¹⁶⁵

6.3.1 Addition of carbazole dendrimers

Variations on CMA1 and its copper analogue were synthesised with additional carbazole donor groups in the 3-6 positions.



Figure 6.4 CMA dendrimers

Figure 6.4 shows the first (G1) and second (G2) generation carbazole dendrimers of the gold and copper bridged CMA molecules made by Alex Romanov at UEA.¹⁶⁵

The addition of further carbazole side groups improved mixing with polymer hosts, as well as impede aggregation and therefore concentration quenching effects.

There are two effects which are being explored with this modification. There is the change in the spatial separation of the donor and acceptor wavefunction, and there is the strength of SOC from the metal bridge atom.
Firstly, the ability to form a CT state requires that an electron excited on one part of the molecule, like the donor, is able to delocalise onto the spatially separated accepter moiety when excited.

To take this to the logical extreme, if a large number of generations were added, for argument sake 5, then an electron excited from the ground state on the most distant Dendron would have virtually no probability of occupying an excited state orbital on the acceptor unit.

How far away from the acceptor moiety can an electron be before it forms local rather than CT excitation?

The second comparison is the strength of SOC from the metal bridge, and over what length scale the influence of the metal atom is able to alter spin angular momentum in the excited state.

To use the same extreme scenario, one would not expect that an excitation formed on a carbazole very distant from the metal bridge would be able to phosphoresce at room temperature or have appreciable rates of forward or reverse ISC.

Over what length scale does the metal bridge atom couple with excited state orbital angular momentum?

6.3.2 UV- Vis Absorption



Figure 6.5 dendrimer UV-Vis

Figure 6.5 shows absorption spectra carried out in dilute toluene (black), neat film (red) and 20% weight dilution in PVK(blue) for CuG1(top left), CuG2 (bottom left), AuG1(top right) and AnG2 (bottom right). Measured by author. ¹⁶⁵

The absorption spectra in toluene solution and neat film show that the CT absorption has been retained. The carbazole local absorption feature at ~350nm aligns well with the PVK film; however at 20% weight the CT absorption feature is less intense. As expected, the G2 versions show a stronger absorption in the region of the local carbazole transitions, which makes sense as there are now 3 Cz units per molecule. This is most clearly seen comparing between G1 and G2 in toluene solution.

In addition to the larger intensity of the carbazole local transitions, the CT absorption band has also changed relative to the Au G0 and Cu G0 presented in figure 5.2 where a single broad CT band is seen. In both the Cu and Au analogues, we see that the CT band has split, including a new shoulder around 410nm. This is assigned to a 2nd charge transfer transition to the Dendron donor, and is this lower in energy as it is more spatially separated from the acceptor moiety. These are most clearly seen in the G1 spectra, and highlighted in the top two panels of figure 6.5. This supports that the modification has not disrupted the CT transitions between the donor and acceptor moieties.



6.3.3 Dilute toluene solution

Figure 6.6 dendrimer PL

Figure 6.6 shows (top left) a comparison of the steady state Pl in toluene of the 3 Cu generations, (to right) the same comparison for the 3 Au generations. (Bottom left) an excitation emission map for Cu G2 in dilute toluene and (bottom right) the same comparison for Au G2 in dilute toluene. Heat-maps measured by author in collaboration with Bluebell Drummond. ¹⁶⁵

There is little change in the emission energy between the zeroth and first generation dendrimer for either the copper or the gold variants, which both blue shift by ~2nm between G0 and G1.

Both the copper and the gold variants experience a further blue shift of ~20nm with the addition of the second generation of Dendron.

The effect of the metal is clearly less strong in the copper analogues as in the 2nd generation, considerable amounts of local emission are seen from the Dendron when excited between 320 and 360 nm at the Carbazole local absorption.

	Peak PL	PL lifetime	PLQE	K _{rad}	Knon-rad
	(nm)	(µs)	(%)	$(10^{5}s^{-1})$	$(10^5 s^{-1})$
Au G0	528	1.25	98	7.8	0.16
Au G1	526	0.67	51.5	7.7	7.2
Au G2	505	.79	78.2	9.9	2.7
Cu G0	513	2.1	71	3.3	1.3
Cu G1	511	.79	27.7	3.5	9.1
Cu G2	491	.83	2.6	0.3	11.7

Table 6.1 dendrimer PL lifetimes in toluene

Table 6.1 compares of photophysical characteristics in toluene solution.¹⁶⁵

For the Gold versions the PLQE values in dilute toluene were 51.5% for G1 and 78% for G2. This was not quite as high as CMA1 which displayed near unity PLQE in dilute degassed toluene.

The copper versions did not retain high PLQE, dropping from 71% for G0 to 27.7% with the addition of the first generation of Dendron ligands, and only retaining 2.6% PLQE for G2.

One result which is not yet well understood is the difference in the trend with additional dendrons being different between Au and Cu. Specifically, the Au G1 dendrimer seems to break the pattern, having lower PLQE, also borne out by the shorter PL lifetime. This will require further investigation if polymerisation of these materials is attempted, but went beyond the scope of this investigation.

6.3.4 PVK hosted films

As mentioned, one of the motivations of investigating dendrimerisation is for incorporation into flexible electronics and homogenous mixing in polymer hosts. To this end, it was important to verify whether the photophysical properties are retained in an appropriate polymer host. PVK was chosen for good energy transfer to from the carbazole side groups to the Dendron donor units as had been demonstrated in chapter 4.



Figure 6.7 dendrimer: PVK kinetics

Figure 6.7 shows the TRPL of solid films hosted at 20% weight in PVK for CuG1 (top left), CuG2 (bottom left), AuG1 (top right) and AnG2 (bottom right).) ¹⁶⁵ Measured by author.

An increase in prompt contribution with additional Dendron generation compared to G0 and also between G1 and G2 is seen for both Cu and Au.

This is consistent with a higher contribution from fluorescence from the S1/1CT state as forward ISC will be slower for excitations formed further away from the metal atom.

From this we can infer that the RISC rates would also be sensitive to this, which is consistent with the CuG2 displaying the highest contribution from prompt fluorescence and the lowest PLQE.



Figure 6.8 dendrimer: PVK spectra

Figure 6.8 shows (top left) a comparison of the steady state PL from Cu G0, G1 and G2, (top right) a comparison of the steady state PL from Au G0, G1 and G2, (bottom left) a comparison of the cumulative PL for Au and Cu G1 and G2. (Bottom right) shows the structure of the polymer host PVK with carbazole units attaches orthogonally along a polymer backbone. ¹⁶⁵ Measured by author.

	Peak PL (nm)	PL lifetime (μs)	PLQE (%)	K _{rad} (10 ⁵ s ⁻¹)	Knon- _{rad} (10 ⁵ s ⁻¹)
Au G0	512	0.92	86	9.3	1.5
Au G1	510	0.66	68	10.3	4.9
Au G2	508	1.06	47.5	4.5	4.9
Cu G0	502	2.89	69.4	2.4	1.0
Cu G1	502	3.0	33	1.1	2.2
Cu G2	498	1.97	6	0.3	4.8

Table 6.2 dendrimer PL lifetimes in PVK

Table 6.2 compares of photophysical characteristics in PVK film. ¹⁶⁵

The emission lifetimes for the gold compounds when hosted in PVK remained favourable, with both G1 and G2 derivatives retaining emission lifetimes of a microsecond or less at high PLQE.

The PL lifetimes for the copper remained comparable to G0 (2-3 μ s) however when considered alongside the drop in PLQE, the corresponding radiative rates reduced considerably, and are about an order of magnitude lower than the corresponding generation for the Au bridged analogue.

This is in keeping with the interpretation that there will be a reduction in the HOMO-LUMO overlap on the metal bridge atom, and thus slower rates of RISC, leading to a higher proportion of excitations decaying non-radiatively. For the Cu analogue, even for comparable overlap the SOC perturbs the electron spin less than Au will, so the RISC rate will be even less, corresponding to the crash in PLQE.

6.3.5 Cryogenic behaviour

The molecule with the highest radiative rate in a hosted film was Au G1, despite the Au G2 performing slightly better in the dilute toluene environment. To verify whether this molecule still displayed TADF, I carried out cryogenic testing of the emission rates.



Figure 6.9 dendrimer cryo. PL

Figure 6.9 shows (top left) normalised TRPL kinetics of Au G1 at various temperatures, (top right) a comparison of the emission spectra at different temperature and times, (bottom left) cumulative PL at various temperatures and (bottom right) activation energy calculation from decay rate. ¹⁶⁵ Measured by author.

This characterisation was also carried out on Au G2, Cu G1 and Cu G2, however the photostability of the Cu variants was not as good, and their less favourable emission characteristics meant they were not considered promising for device application. For that reason I will only discuss the AuG1 data here.

The emission comprises of three clear regimes. At early time, there is bluer contribution from donor fluorescence, which emits over the first ~10 ns. The fluorescence contribution does not change appreciably with temperature, and comprises ~8% of total emission as seen in the cumulative PL. This contribution is spectrally distinct, and matches the emission seen in the PVK hosted films over this timescale well, which I attribute to fluorescence from the 1CT state excited at 400nm

At 100K, before thermal activation of RISC has started, we see structure to the emission from the additional Cz dendrons, which is in good agreement with the measurements of free carbazole phosphorescence presented in figure 4.20, however, at room temperature CT emission dominates the steady state emission, and the delayed PL does not display any local character. This is distinct from AuG0, where CT emission is retained to the lowest temperatures, and supports the interpretation of reduced wavefunction overlap on the metal bridge atom. The activation energy calculated from the PL lifetimes is 92 meV, which is close to the values calculated for Au G0/CMA1 in a range of environments of ~80 meV.

In summary then, Au G1 displays clear TADF behaviour, alongside donor phosphorescence from the dendron at low temperature. Even though there is a larger contribution from local fluorescence than for Au G0, the dominant emission at all temperature is still delayed emission from triplet states. At room temperature there is sub-microsecond emission with high PLQE and radiative rates, and effectively all emission is CT.

This is the best example of the role of increasing the spatial separation of the HOMO – LUMO wavefunction to compare the different roles that reduced exchange energy versus SOC play in facilitating efficient triplet emission from the CMA system, and will be discussed later.

This was considered a good candidate to test for solution processed devices. This work was carried out by collaborators and is summarised below.



6.3.6 Development of solution processed OLEDs

Figure 6.10 dendrimer OLEDs

Figure 6.10 shows (left) EQE as a function of current density with EL spectra inset and (right) Luminance as a function of voltage. Solution processed devices made by Le Yang and Dawei Di according to the methods reported in the literature ¹⁶⁵.

The best candidate identified from this screening was the Au G1. In PVK hosted films at 20% weight, this retained PLQE near 70%. This also produced the best devices. In solution processed devices, these achieved 10.3% EQE. Devices for the Au G2 (EQE~3%) and Cu G1 (EQE~5.5%) were also successfully demonstrated.

Emission from all these devices was broad and unstructured; supporting the interpretation that emission from the triplet CT population was achieved.

For Au G1, and EQE of 10.3% implies a device IQE in the region of 30-40%

Full details of these devices may be found in our published report ¹⁶⁵.

6.3.7 Conclusions from dendritic donor modification

This proved to be a neat demonstration that the dendrimerisation did not result in a fundamental change in the PL processes, however the PL metrics and device efficiencies were both lower than the unmodified version of CMA1 previously published.

Positives:

- Au G1 and G2 retained high PLQE
- Au G1 and G2 retained rapid delayed emission
- TADF behaviour with similar activation energy for Au G1
- Decent solution processed devices achieved from Au G1

Negatives:

- Not suitable for vapour deposition
- Copper variants performed poorly
- Little chromatic shift in the solid state

The local emission from the Dendron in both the Au and Cu G2 analogues suggested that any more extensive donor group modification would reduce the ability to form charge transfer excitation with a high fraction of excitations formed. This set of modifications also allows us to consider the balance between achieving triplet emission via spatial separation of the HOMO-LUMO wavefunction to minimise exchange energy versus increased SOC. Alongside the effect of the additional dendron, we see that the range over which the metal bridge atom effectively modifies spin orbit angular momentum is different for Au and Cu. This will be compared to the other modifications to the CMA later. If polymerisation of these compounds is to be attempted, this supports that side groups with larger spatial separation from the backbone would be possible with Au bridge atoms than Cu, but that orthogonal side-groups should not be more than the length of 2 carbazole units from the polymer backbone and bridge.

This could facilitate improvements on solution processing without the need for polymer hosts, and simplify the stack architecture if a homogenous polymerised version of the CMA archetype could be added to something like a PVK backbone.

6.4 Less bulky donor modifications for higher thermal stability

Whilst the carbazole dendrimers retained several of the desired photophysical characteristics, they were not suitable for thermal evaporation, and also did not demonstrate a mechanism for significant tuning of emission energy. The second set of modifications tested focussed on less bulky substitutions, with the aim that thermal stability could be retained allowing processing via thermal vapour deposition.



Figure 6.11donor modifications

Figure 6.11 shows the chemical structures of the 9 donor modified analogues. 6 are variations of the Au-Cz version, CMA1, and three are copper analogues of the same modification as a cross comparison.

In this case, we also explore the synthetic objective of being able to tune emission energy from the green into the red by modifications to the donor group, and to what extent the HOMO energy level can be changed before this interferes with the states and transitions required for emission from a CT state and TADF to function.

Acceptor modification has been shown in the literature to shift the energy levels of Carbazole-pyrimidine compounds sufficiently at room temperature to switch between TADF and room temperature phosphorescence. ¹⁶⁶

As has been demonstrated in chapters 5 with the tertiary butyl additions to the CMA1 motif, the addition of electron donating groups to the donor moiety can stabilise the energy of the HOMO, reducing the energy difference between HOMO and LUMO, resulting in a slight red shift. In the case of two tBu groups, a peak red shift of 30nm from 525nm to 555nm is seen in both toluene and PVK hosted films, with little appreciable change to the photophysics.

A series of analogues of Au-Carbazole (CMA1) were synthesised by Alexander Romanov at UEA with modifications to the donor unit which changed the energy of the HOMO level by modifying the electron withdrawing strength of the donor unit.

This set compares 6 modifications to the donor group on the gold bridged CMA1 motif, and compares between Au and Cu bridged molecules for 3 of these.

For ease of discussion within this chapter, these 9 compounds will be referred to using the label which denotes the order in which they were synthesised in the format *P-N*, rather than their more cumbersome chemical labels.

A full list of the chemical names for the modified donor moiety is provided in table 6.2 below.

6.4.1 Screening of neat films

One of the desirable properties demonstrated in evaporated OLEDs of CMA1 was the ability to have a host free active layer. ¹⁴³

To ensure that candidates with limited self-quenching were identified as a priority, the initial screening of these 9 compounds was carried out on neat spin cast films.

In the initial screening, 3 sets of spectroscopic measurements are compared for neat films of compounds P49-P57.

The measurements compared in the first instance are:

- UV-Vis absorption spectrum
- Steady state PL
- TCSPC time resolved PL at various wavelengths (405nm pump)

This screening aimed to test the presence/ absence of the following characteristics:

- CT absorption band
- CT like PL
- Structure in Absorption and PL
- Rapid red shift at early time
- Delayed component to PL
- Wrap around in baseline counts
- Instrument limited prompt.

An overview of this initial screening is presented in figure 6.12

Figure 6.12 shows a comparison of the initial spectroscopic screening of solid films of these 9 new compounds. The features of interest would be any molecules demonstrating evidence of a strong CT absorption feature and corresponding broad, unstructured emission with a significant delayed component. Since these are all neat films of the molecules, any candidate showing high PLQE will have also demonstrated that it is not highly sensitive to concentration quenching.

In addition to this, information about local transitions can be extracted from the emission and absorption data. By measuring TCSPC traces at a number of different wavelengths across the emission spectrum, it is possible to determine whether there is any spectral shift over the timescales sampled here even though the measurement is not spectrally resolved.

The time window for this measurement was limited to 400ns by the rep-rate of the laser, which means that extracting a complete picture of significantly longer lived emission processes is not possible. This does not however rule out making statements about whether longer processes exist, as long-lived, low intensity emission will manifest in a shift in the background count rate, even if it is not possible to resolve any decay over these timescales.

One of the other features characteristic of CMA1 was that the quenching of fluorescence happened extremely rapidly, so little emission is seen from direct fluorescence from the initial photo-excited S1 state, and that which is decays over ~10ps.

The instrument response of this TCSPC drops by ~3 orders of magnitude over the first 3ns as shown in the experimental methods section.

To a first approximation then, we may also comment on whether forwards ISC in these molecules is significantly slower than CMA1 depending on whether the initial rapid decay of singlet fluorescence is instrument limited, or occurs at a rate which can be temporally resolved by this TSCPC.



6.4.2 Overview and cross comparison





Au- Acridone



Cu- Phenoxazine

Figure 6.12 (continued over page.)







Cu-Dibenzoazipene



Au-Dibenzoazipene

Figure 6.12(cont.)







Au- Phenothiazine



Au-Dinitrophenazine

Figure 6.12 photophysical screening of donor modifications

Figure 6.12(cont.) shows (left) the UV-Vis absorption (red) and steady state PL (black) of neat films, molecular diagram inset. (Middle) first 10ns of TCSPC trace at various wavelengths. (Right) 400ns of the same TCSPC experiments. *Measured by author*.

Characteristic	P49	P50	P51	P52	P53	P54	P55	P56	P57
CT feature in Absorption	No	No	Yes	Yes	No	Yes	Yes	Yes	Yes
CT feature in PL	No	No	Yes	Yes	No	Yes	No	Yes	No
Structured Abs. and PL	Yes	Yes	Yes	No	Yes	No	Yes	No	No
Early time blue shift	Yes	Yes	No	No	No	Yes	No	No	No
Delayed component in PL	No	No	Yes	Yes	No	Yes	No	Yes	No
Phosphorescence wrap around	No	Yes	NM	No	Yes	NM	No	NM	No
ISC fluorescence IRF limited	Yes								

6.4.3 Comparison of effects of donor group modification

Table 6.3 donor modification screening overvies

Table 6.3 shows a comparison of the metrics of interest for the 9 samples tested.

There are a number of features to consider in this cross comparison which help identify the changes in the photophysics from these modifications.

Firstly, if we consider the absorption spectra, in several samples, P49 and P50 with the acridone donor unit, additional structure is seen around 400nm, corresponding to local transitions on the donor group, with symmetric contributions to the emission suggesting a new set of fluorescent transition on the donor unit.

The low PLQE supports that P49 and P50 have retained rapid ISC, but that RISC has not been maintained. P50 is unique in this set as it displays a clear second, redder, structured emission feature at ~600nm, and if we look at the PL lifetime for that spectral region (inset in figure 6.12) we see the redder feature is very long lived. This suggests that this is direct

phosphorescence from the Acridone 3LE state, and it is consistent that this is seen in the Au and not the CU analogue as the heavier metal atom has more direct SOC between the 3LE and S0 states. This room temperature phosphorescence contributes~50% of the emission, but is still a very inefficient process when weighted by the low sample PLQE.

Molecule	Bridge	Donor	Peak PL	PLQE	PL lifetime	Delayed
	metal	moiety	(nm)	(%)	(ns)	lifetime (ns)
P49	Cu	Acridone	500	0.2%	12	NA
P50	Au	Acridone	477 + 581	<0.1%	13	NA
P51	Cu	Phenoxazine	642	0.1%	18	130
P52	Au	Phenoxazine	658	<0.1%	17	NA
P53	Cu	Dibenzoazipene	560	<1%	12	NA
P54	Au	Dibenzoazipene	597	38%	36	350
P55	Au	Dihydrophenazine	729	<0.1%	12	NA
P56	Au	Phenothiazine	657	0.4%	11	67
P57	Au	Dinitrophenothiazine	712	<0.1%	14	NA

Table 6.4 donor modification PL rates

Table 6.4 compares the PL peak energy, PLQE and emission lifetime(s) of P49-P57.

Some amount of charge transfer character seems to persist in both the abs and PL, but given the timescale of the emission, this is dual fluorescence from the 1CT state, with contributions from 1LE. From the rapid blue shift shown by the inversion of the TRPL traces, I infer that the higher energy 1LE fluorescence is more rapid that the emission from the lower energy 1CT state.

No other candidates displayed this structured local fluorescence, with the corresponding early time spectral shift, suggesting the local singlet state is close to degenerate in energy with 1CT. For this reason, and the 3LE state also being below the 3CT as demonstrated by the room temperature phosphorescence, neither P49 nor P50 were investigated beyond the initial screening.

A number of the samples display additional broad absorption features, and the three samples with delayed contributions to the signal (P51, P54 and P56) have retained the CT absorption and broad emission of CMA1. In the case of P51 and P56, only a small amount of delayed emission occurs, but it is broad, and so assigned to inefficient TADF from the 3LE state. Despite being the majority of the emission, the PLQE of P51 and P56 is very low. All three of these also display a slight red shift, consistent with the transition from prompt fluorescence to delayed emission from a lower energy 3CT state.

In the case of P57 and P55, another absorption feature exists centred at ~570nm, which corresponds to an additional intra-ligand transition of the donor, rather than a CT feature.

This is shown to be insensitive to changes in polarity in our subsequent publication, confirming the character of the new state. ¹⁶⁷

According to Kasha's rule, this low energy state is there the sharper red emission originates. In this case, the acceptor moiety is not participating in the emission trajectory.

This has rendered both P55 and P57fluorescent in neat films, and have dropped by over 3 orders of magnitude in PL intensity within the first 4ns, which is approaching the IRF of the detector.

All materials seem to have retained rapid forwards ISC as evidenced by the very low PLQE and rapid emission, suggesting ISC is outcompeting fluorescence from the 1CT state.

The only candidate which retained a large contribution from delayed emission as well as high PLQE in neat film was P54, which has also successfully been red shifted in emission relative to CMA1 and this was selected for further screening and device trials.

6.4.4 Limitations on energy level assignment

Accurate allocation of state energies is not entirely possible from this screening, as most samples have probably undergone aggregation to some extent.

It is worth specifically acknowledging that all of the emission which I have attributed as phosphorescence may simply be aggregate emission, however discussing the exact nature of the transitions which have made eight out of nine of these candidates extremely poor emitters in the solid state was not considered a priority.



Figure 6.13 CIE of modified donor CMAs

Figure 6.13 shows the CIE co-ordinates corresponding to the PL spectra of P49-P57.

With combination of fluorescence, CT emission, Phosphorescence and possibly aggregate emission, ordering these in terms of "redness" is unlikely to capture any meaningful physics about the order of HOMO energy levels with the different donor modifications.

Further work has included dispersing these in various hosts, which has identified other candidates which still function well for high efficiency emission from triplet states when chromophores are isolated. This further work is presented in the literature ¹⁶⁷.

	1	I	1
Molecule	Fluorescence	Phosphorescence	TADF
P49	Y	Y	Ν
P50	Y	Y	Ν
P51	Y	Ν	Y
P52	Y	Ν	Y/N
P53	Y	Y/N	Ν
P54	Y	Ν	Y
P55	Y	Ν	Ν
P56	Y	Ν	Y
P57	Y	Ν	N

6.4.5 Summary of P49- P57 screening

Table 6.5 donor modification emitting states

Table 6.5 shows my assignment of the states contribution to the emission of P49-P57.

The aim of screening this second set of modifications was to determine if any molecules could achieve red shift CT emission, retain rapid triplet emission, high PLQE in solid state and be suitable for both evaporated and solution processed devices.

Most candidates did not achieve this, however P54 has successfully demonstrated that modification of the electron withdrawing strength of the donor group can be a functional synthetic handle on tuning the energy of the emission for this class of molecule.

The substitution of the carbazole unit for Dibenzoazipene analogue resulted in stabilisation of the HOMO without disrupting the nature of the excited state transitions to the CAAC across the metal bridge. The solid state packing was also not changed to the extent that concentration quenching occurred.

More thorough photophysical characterisation of P54 was carried out to test whether it would be suitable for application in vapour deposited OLEDs emitting via TADF.

6.5 Photophysical characterisation of Au-Dibenzoazipene (P54)

Having identified P54 as a promising candidate in the initial screening of the second round of less bulky donor modifications, the next step was more advanced characterisation of its emission behaviour. The aims of this more detailed investigation was to confirm that P54 is functioning as a TADF emitter, and verify it's suitability for incorporation in various hosts via both solution processing and TVD.



6.5.1 Demonstration of triplet involvement in PL

Figure 6.14 P54 vacuum cycling

Figure 6.14 shows PL from P54 during vacuum cycling. (Left) shows PL does not change form. (Right) shows PL recovery on subsequent cycles. Measured by author.

Like CMA1, there is clearly triplet contribution to the PL demonstrated by reversible PL quenching in the presence of Oxygen.

As discussed in chapter 2, delayed PL and response to oxygen are not sufficient evidence of TADF in isolation.



6.5.2 Emission of P54 in solution and film

Figure 6.15 P54 solvatochromism

Figure 6.15 shows (left) comparison between PL rom toluene solution and neat film and (right) PL in a series of different polarity solvents. Measured by author.

P54 shows higher energy emission when restricted in film like CMA1. Some degree of steric freedom is implied in the emission of the material as it is shown that in dilute non-polar environments that the emission energy is relaxed relative to a solid film, supporting the interpretation that a continuum of conformers is present in the solid state compared to the energetically minimised ensemble free to rotate and reorganise in solution. The broad, unstructured emission also showed solvatochromism, supporting emission from CT state like CMA1.

6.5.3 Compatible with polymer host



Figure 6.16 P54 in PVK

Figure 6.16 shows a concentration series of P54 in PVK under UV illumination demonstrates energy transfer from host, resulting in orangey-red PL. Data measured in collaboration with Leonardo Buizza

As a comparison to how well CMA1 is incorporated into a polymer host environment, P54 was tested in PVK hosted films at 20% weight concentration.

Effective energy transfer was achieved, however FRET efficiency does not seem to be as efficient from PVK to P54 which makes sense as its absorption band has been red shifted compared to CMA1, reducing FRET overlap.

If this was to be considered for solution processed device application, a redder polymer host could be explored, however since the intended application was for evaporated devices, this was not considered further in this investigation.



6.5.4 Cryogenic TRPL and activation energy

Figure 6.17 P54 cryo. TRPL

Figure 6.17 shows (top left) neat film cryo-TRPL, (top right) activation energy from the PL rate, (bottom left) room temperature spectral migration, (bottom right) total PL as function of T, broadens and red shifts with warming. Measured by author.

In solid films of P54, this same energetic migration with time is present as seen in CMA1. Across all temperatures, the PL is broad and unstructured from CT emission, suggesting that the local triplet energy level has not been lowered enough to outcompete the 3CT state.

The red shift and broadening of the PL with increasing temperature is consistent with both increased spectral migration to lower energy sites, and also increased steric freedom for conformers to adopt lower energy configurations. An activation energy of 94 meV is obtained from the temperature dependence of the characteristic emission time, as is shown above.

6.6 Testing redder candidates for evaporated OLEDs

Chapters 5 and 6 have both identified candidates which retained the positive photophysical properties exhibited by CMA1 whilst achieving some degree of red shift to the emission.

In chapter 5 the Au-Cz-tBu analogue retained rapid intersystem crossing and efficient delayed emission whilst achieving ~30nm red shift.

In this chapter the Au-Acridone (P54) has demonstrated the PL can be shifted by 75-80nm relative to CMA1 in toluene and PVK whilst retaining highly efficiency, rapid emission from triplets.

Our earlier work lead by Patrick Conaghan ¹⁴³ has already demonstrated that CMA1 can be processed into highly efficient OLEDs via TVD, including host free architectures. To test whether these two candidates are suitable for TVD, I tested them in variations of the architecture developed for CMA1 in collaboration with Patrick Conaghan.



Figure 6.18 CMA 1 TVD OLED architecture

*Figure 6.18 shows the device structure developed by Patrick Conaghan for CMA1 OLEDs made via thermal vapour deposition.*¹⁴³



6.6.1 Demonstration of Au-Cz-tBu OLEDs via TVD

Figure 6.19 Au-Cz-tBu TVD OLEDs

Figure 6.19 shows (left) energy level diagram of the device stack modified to include Au-Cz-tBu and (right) EL spectra from Au-Cz-tBu in 3 different active layers. NB. P38 is the in house name for Au-Cz-tBu used in these diagrams as it is more concise. EL spectra measured using fibre-coupled Labsphere spectrometer. The structure in the spectra was a result of issues calibration issues from the fibre couple, and not indicative of emission from different states. This is clarified in later publication. Devices fabricated by author in collaboration with Patrick Conaghan.

Three variations of the emissive layer in the architecture used for CMA1 as per our previous report were tested:

- a pure layer of Au-Cz-tBu
- Au-Cz-tBu at 20% weight in mCP as per the previous report
- Au-Cz-tBu at 20% weight in TCP



Figure 6.20 Au-Cz-tBu EL

Figure 6.20 shows (left) chemical structures of mCP and TCP, with the HOMO – LUMO values as quoted by Ossila and (right) CIE coordinates of the EL corresponding to the 3 different active layers. Devices fabricated by author in collaboration with Patrick Conaghan.

EL from the 3 emissive layers tested was yellowy green:

-Pure Au-Cz-tBu EML was the reddest, peaking at 550nm and achieved peak EQE ~10-12%.
-mCP hosted EML was the greenest, peaking at 520nm, and achieved peak EQE ~18%.
-TCP hosted EML was between these, peaking at 540nm and achieved peak EQE ~20%.

Examples of J-V characterisation, luminance –V and EQE as a function of applied current measured by Patrick Conaghan are presented in *Appendix B*.



6.6.2 Demonstration of P54 OLEDs via TVD

Figure 6.21 P54 TVD OLEDs

Figure 6.21 shows (left) energy level diagram of the device stack modified to include P54and (right) EL spectra from P54 with varying thickness of MoO3. EL spectra measured using fibre-coupled Labsphere spectrometer. Devices fabricated by author in collaboration with Patrick Conaghan.

Three variations of the device stack were also trialled for the P54 TVP OLED demonstration.

In this case, a hole blocking layer was added to the architecture used on CMA1 to try reduce leakage currents in the stack. MoO3 was chosed as a vapour processible, high work function material.

Three layer thicknesses of 1nm, 6nm and 10nm of MoO3 were tested.



Figure 6.22 P54 EL

Figure 6.22 shows (left) structure of MoO3 and HOMO-LUMO and (right) CIE coordinates of EL from P54 hosted in mCP. Emission spectra did not vary with thickness of MoO3.

EL did not vary spectrally with the different thicknesses of the MoO3 layer, and devices with all 3 layer thicknesses achieved peak EQEs in the range of 10-12% suggesting that a charge imbalance from leakage of the hole current was not limiting the performance of this device stack.

6.7 Donor modification conclusions

The first set of modifications were aimed at moving towards polymerised versions of the CMA materials, and exploring the effect of greater HOMO-LUMO wavefunction separation on spin mixing in the excited state, like in organic TADF systems.

This demonstrated that as long as the acceptor unit and the metal bridge atom are not more than 2 Cz units away from where excitations form, that rapid excited state spin conversion could be retained, and reasonable solution processed OLEDs were demonstrated. ¹⁶⁵ This supports that this class of materials could be incorporated into a polymerised format for flexible solution depositions, and work is ongoing towards this synthetic objective. This comparison allowed the balance between the contributions of spatial separation of the HOMO-LUMO wavefunction and the SOC from the metal bridge atom to be explored, and it is clear that Cu bridged variants would not be functional for more extended systems.

The second set of modifications aimed at molecules which would still be viable for TVD, and explored to what extend the emission could be tuned into the red by donor modification only, whilst retaining the desirable photophysical properties. Whilst it has successfully been demonstrated that chromatic shifting is possible whilst retaining favourable photophysical and device metrics, only modest red shifting was achieved, and all the deep red versions did not work in solid films.

What has been shown so far suggests that donor group modification alone is not sufficient for achieving the desired chromatic shift into deep red without either influencing packing in such a way which introduces aggregation quenching, or altering the electron donating strength of the entire donor moiety to the extent that reverse intersystem crossing no longer happens efficiently and the triplet state becomes a trap, and the dopant becomes poorly fluorescent.

This screening prompted further development of a subset of these materials into a device trial. All except P49 and P50 used as these had both lose the charge transfer emission.

It is possible that in the correct host environment, some of the redder candidates may function well as deeper red dopants, and work is ongoing exploring this. Given that one of the overarching trajectories for TADF OLEDS for display application is to host narrow band fluorescent dyes within a triplet harvesting host or co-dopant, this degree of chromatic tuning


may already be sufficient to achieve deep red devices by hosting an appropriate fluorescent co-dopant.

Figure 6.23 Summary of donor modified CMAs

Figure 6.23 shows a summary of the further screening subsequently published¹⁶⁷ including OLED trials.

The parameter space for modification of this architecture has by no means been exhausted, as this initial investigation only considered a very limited set of locations and modifications, and did not modify the acceptor moiety at all. The effects of a host material, both on preventing aggregation and in tuning the polarity of the environment to modify the energy of the CT state also promises to provide another handle for tuning emission properties in future studies.

To me, this suggests there is scope for improvements on these results if donor and acceptor modifications can be explored together in conjunction with the effect of the host environment, and this is also being developed further by our synthetic collaborators.

Chapter 7 Conclusions

"Everything should be made as simple as possible, but not simpler"

Albert Einstein.

In this thesis I have presented a number of investigations introducing the Carbene Metal Amide family of molecules, studying the processes involved in the excited state spin transitions, and tracking the effects of molecular modification.

In this chapter I will summarise the key findings of these investigations, and discuss the future work motivated by these results.

7.1 Carbene metal amides

Carbene Metal Amides have been identified as a new class of organometallic emitting molecules with considerable potential. They exhibit rapid, sub-microsecond emission from triplet excited states and can retain high PLQE even in solid films. They have been demonstrated to produce OLED devices with record efficiencies, both via solution processing and thermal vapour deposition techniques.

I have shown this to be a versatile motif for chemical modification, with analogues retaining favourable photophysical characteristics and good device demonstrations being achieved spanning the coinage metal series and extensive donor group modification, including steps towards polymerised versions.

Emission from triplet excited states had previously been achieved via phosphorescence from molecules containing heavy metal atoms like iridium⁶⁰, allowing direct SOC between triplet excited states and the singlet ground state, or via low exchange energy organic systems utilising donor and acceptor moieties for HOMO-LUMO wavefunction separation, where the term TADF was first coined.³²

The CMA class of molecules seems to span the "best of both worlds" in terms of current understanding of high efficiency phosphorescent emitters incorporating heavy metal atoms to change an electron's spin angular momentum in the excited state, but also achieving a high degree of HOMO-LUMO wavefunction separation like in the best organic TADF systems by using bridged donor-acceptor architecture. This has allowed PL efficiency approaching 100% in sub-microsecond timescales to be achieved, and record efficiency devices approaching 100% IQE have clearly demonstrated these properties in an applied context. ^{150 168} The inclusion of a second contribution to singlet-triplet spin mixing seems to allow higher oscillator strength to be retained than in other TADF systems, where there is an intrinsic compromise between minimising wavefunction overlap to reduce exchange energy, and reducing the oscillator strength of these states mixing i.e. tending to charge separated rather than charger transfer character in the excited state.

The effect of the metal bridge atom is absolutely intrinsic to the states involved in forward and reverse intersystem crossing, and we see that reduced orbital overlap correlated with slower forward ISC. I have also demonstrated that the processes involved are not necessarily the same in forward ISC and RISC, and that an intrinsic direct coupling between the triplet manifold and the ground state persists, even at very low temperature. This is not the same as the dominant delayed emission seen at room temperature, and so whilst direct coupling from 3CT to S0 is possible, the majority of the delayed emission results from a spin conversion between the singlet and triplet excited state manifolds, as seen in the TA.

The ability to tune the balance between direct spin orbit coupling and second order spin vibronic effects setting the rates of reverse intersystem crossing is extremely novel, and suggests scope for future investigation tuning the local triplet energy of gold bridged variants to retain forward intersystem crossing on 5-10ps timescales but accelerate RISC even more than has currently been achieved in current Au analogues. This would have extreme relevance for device application, as the excited state lifetime is a factor which determines how prone the material is to annihilation events in the excited state, which induce degradation, limiting device operational lifetimes.

There is ongoing debate as to which state energies are the appropriate states to consider when trying to model or predict RISC behaviour in new materials. Whether the singlet triplet energy gap is considered between local excited states S1 and T1, or whether the singlet and triplet CT states are the relevant energy scale to compare.

The differences in behaviour between the Au-Cz and Ag-Cz molecules suggest that for organometallic emitters, there is no single answer for this, as different mechanisms for reverse intersystem crossing are possible in parallel. We must instead consider both the reduction in exchange energy from HOMO-LUMO wavefunction separation as well as the contribution of D-orbitals from the metal atom in facilitating change in spin angular momentum.

The observation that the PL lifetime and activation energy of CMA1 remains virtually unchanged despite considerable shifting in the emission energy from the CT state in different film conditions further suggests that the current TADF models do not yet fully describe systems which are dominated by direct SOC, as all second order processes would predict a dependence on the energy of the emitting state being coupled to.

Moving forward, several avenues of investigation are clearly highly relevant.

Firstly, using this motif, there is a large parameter space to explore for design of new molecules. The successful demonstration that donor modification can result in red-shifting emission raises the question of whether blue shifting of the emission can be achieved with electron withdrawing donor modification. Work is ongoing toward this synthetic objective, with promising results.¹⁶⁹

In parallel to this, the alignment of the 3CT energy with the local triplet is likely to impose a limit on how far the CT state can be blue shifted before the 3LE state becomes the lowest lying triplet, as seen in the metal bridge series and CMA1 in frozen MTHF solution. To push further into the blue, acceptor modification must be explored. Early trials involving removing the adamantyl group from the acceptor moiety have resulted in enhanced aggregation due to the removal of steric hindrance to the formation of pi-stacks, however other variations of the CAAC acceptor moiety are being trialled.

Molecular motifs exploring different symmetries, like AlQ3, may allow versions of the CMA family with multiple donor-meta bridges from a core acceptor unit, which have not yet been explored, but based on the finding of this thesis may be possible without sacrificing rapid spin mixing in the excited state, as seen in chapter 6.

From a device perspective, several avenues of investigation remain of interest.

Simplicity of device structure to reduce the parameter space for optimised deposition on industrial scales is highly desirable, and the CMAs have shown record efficiency for self-hosted EMLs in the visible range. ¹⁶⁸ ¹⁶⁹

The steps towards polymerisation in the donor dendrimerisation trial suggest that the desirable photophysical properties may be retained as side-groups from a carbazolate polymer backbone, which would be of interest for solution processed, large area roll-to-roll devices where a higher degree of plasticity is required.

The efficient rapid harvesting of triplet excitations to emit across the green-orange part of the visible spectrum combined with the lack of aggregation quenching suggests that the CMA family may provide candidates for hyperfluorescent hosts with simpler two part emissive layer blends than are currently achieved with three part host materials combining phosphorescent and fluorescent co-dopants. Being able to have a "host free" or CMA hosted emissive layer of small molecule NIR dopants, this material system may be of interest for photodynamic therapy, or other NIR sensors.

To conclude, I have shown the CMA family to be not only versatile dopants for OLED application, but also an extremely relevant system to help develop our theoretical understanding of organometallic emitters, which incorporate aspects of both existing heavy metal phosphors and organic TADF systems. The nature of the states involved in forward and reverse intersystem crossing, as well as direct triplet coupling to the ground state can all be tuned, which may facilitate the design of the next generation of high efficiency dopants, and potentially also provide a new class of triplet harvesting host materials for hyperfluorescent OLEDs.

Appendix A

Non-obvious conclusions in TADF literature

In a recent paper "Light amplification in molecules exhibiting Thermally Activated Delayed Fluorescence"⁷⁵ there are several points which seem incongruous with other literature. Figures are reproduces directly from the supporting information of this paper for discussion.



Supplementary Figure 1 : (a) Time-resolved PL decay curve of a 6wt%-DABNA-2:mCBP codeposited film at 300 K. Inset: The PL spectrum of a 6wt%-DABNA-2:mCBP co-deposited film at 300 K. (b) Arrhenius plot of the reverse intersystem crossing (RISC) rate from the triplet state to the singlet state of DABNA-2.

Figure A.1 TRPL and activation energy of DABNA-2

The room temperature delayed emission reported in the SI is on the order of hundreds of microseconds. As mentioned before, Boron compounds are reported for exhibiting unusual high temperature phosphorescence, and this is extremely long lived for any system being

branded as TADF. If K_{RISC} has decreased by a further 2 orders of magnitude by the time the system is only cooled to 200K, it is far from obvious that this material is behaving like a usual TADF material, even if the delayed lifetime is more rapid at higher T.

The same paper goes on to show TA data which it attributes to the singlet and triplet excited state absorptive transitions, based on the temporal delay.



Supplementary Figure 4: TA spectra of **3CzTRZ** in dilute solution $(2.4 \times 10^5 \text{ mol } L^1 \text{ in toluene})$. The blue and red circles are singlet and triplet excited-state absorption spectra. The solid line shows the steady-state PL spectrum of the co-deposited film.

Figure A.2 TA of 3CzTRZ

The "triplet excited-state absorption spectrum" has a negative feature which could be interpreted as stimulated emission as it overlaps the PL well, but comparison to the S1 Δ OD in that region is not possible as only positive values are plotted, which for a paper on stimulated emission seems a concerning omission, though the onset matches the edge of the PL. Apart from that, the T1 "spectrum" is a flat line nearly 1000nm broad, at Δ OD ~0.001.

The authors do not suggest a mechanism which could result in a range of real electronic transitions resulting in a flat 1000nm wide absorption band, and this could simply be a feature of whatever background correction has been applied not describing the response of the measurement system perfectly.

In the main text, the "singlet" and "triplet" spectra are assigned by a delay of 1ns and 100ns respectively, though with the resolution provided, at least to a crude comparison, these seem spectrally similar, and not yet on the timescale of the decay kinetics reported for the delayed emission which occurs over hundreds of microseconds.



TA spectra of **DABNA-2** in dilute solution (7×10^{-5} mol L⁻¹ in toluene). The blue and red circles are singlet and triplet excited-state absorption spectra, which were identified by comparing the time constants of transient PL and the TA at 860 nm (Figure S3, Supporting Information). The solid line shows the steady-state PL spectrum of the codeposited film.

Figure A.3 TA of DABNA-2

A drop of ~50% in intensity also seems modest compared to the two and a half orders of magnitude drop in the PL intensity between fluorescence and delayed emission seen in figure 8.1. To me, it seems that some of the inferences drawn from this data set are not entirely self-consistent, or at the very least, control measurements which would support these interpretations are not presented .

Appendix B

OLED characterisation

OLED characterisation of P54 and P38 (Au-Cz-tBu) vapour processed OLEDs.

OLEDs fabricated in collaboration with Patrick Conaghan.

Characterisation carried out by Patrick Conaghan.

P38 mCP hosted



Figure B.1 Au-Cz-tBu mCP OLED data

P38 TCP hosted

Figure B.2 Au-Cz-tBu tCP OLED data

P38 Self-hosted

Figure B.3 Au-Cz-tBu host free OLED data

P54 with 1nm MoO3

Figure B.4 P54 mCP 1nm MoO3 OLED data

P54 with 6nm MoO3

Figure B.5 P54 mCP 6nm MoO3 OLED data

P54 with 10nm MoO3

Figure B.6 P54 mCP 10nm MoO3 OLED data

List of publications

Below are listed the academic publications which I have contributed to during the course of my PhD. Those which include data directly discussed within this thesis are marked with a *.

7.2 Published works

* High-performance light-emitting diodes based on carbene-metal-amides, Science, April 2017

Dawei Di, Alexander S. Romanov, Le Yang, Johannes M. Richter, Jasmine P. H. Rivett, **Saul T. E. Jones**, Tudor H. Thomas, Mojtaba Abdi Jalebi, Richard H. Friend, Mikko Linnolahti, Manfred Bochmann, Dan Credgington

2) * Carbene Metal Amide Photoemitters: Tailoring Conformationally Flexible Amides for Full Color Range Emissions Including White-Emitting OLED, Chemical Science, November 2019

Alexander S. Romanov, **Saul T. E. Jones**, Qinying Gu, Patrick J. Conaghan, Bluebell H. Drummond, Florian Chotard, Leonardo Buizza, Morgan Foley, Mikko Linnolahti, Dan Credgington and Manfred Bochmann

3) Highly efficient luminescence from space-confined charge-transfer emitters, Nature Materials, June 2020

Xun Tang, Lin-Song Cui, Hong-Cheng Li, Alexander J. Gillett, Florian Auras, Yang-Kun Qu, Cheng Zhong, **Saul T. E. Jones**, Zuo-Quan Jiang, Richard H. Friend & Liang-Sheng Liao

4) Highly efficient blue organic light-emitting diodes based on carbene-metal-amides, Nature Communications, April 2020

Patrick J. Conaghan, Campbell S. B. Matthews, Florian Chotard, **Saul T. E. Jones**, Neil C. Greenham, Manfred Bochmann, Dan Credgington & Alexander S. Romanov

5) * Efficient Vacuum-Processed Light-Emitting Diodes Based on Carbene–Metal– Amides, Advanced Materials, July 2018

Patrick J. Conaghan S. Matthew Menke, Alexander S. Romanov, **Saul T. E. Jones**, Andrew J. Pearson Emrys W. Evans, Manfred Bochmann, Neil C. Greenham, Dan Credgington

6) Efficient and Stable Deep-Blue Fluorescent Organic Light-Emitting Diodes Employing a Sensitizer with Fast Triplet Upconversion, Advanced Materials, April 2020

Dongdong Zhang Xiaozeng Song Alexander J. Gillett Bluebell H. Drummond **Saul T. E. Jones** Guomeng Li Hanqing He Minghan Cai Dan Credgington Lian Duan

7) * Mononuclear Silver Complexes for Efficient Solution and Vacuum-Processed OLEDs, Advanced Optical Materials, October 2018

Alexander S. Romanov, **Saul T. E. Jones**, Le Yang, Patrick J. Conaghan, Dawei Di, Mikko Linnolahti, Dan Credgington, Manfred Bochmann

8) Environmental Control of Triplet Emission in Donor–Bridge–Acceptor Organometallics, Advanced Functional Materials, January 2020

Jiale Feng Lupeng Yang Alexander S. Romanov Jirawit Ratanapreechachai Antti-Pekka M. Reponen **Saul T. E. Jones** Mikko Linnolahti Timothy J. H. Hele Anna Köhler Heinz Bässler Manfred Bochmann Dan Credgington

9) * Dendritic Carbene Metal Carbazole Complexes as Photoemitters for Fully Solution-Processed OLEDs, Chemistry of Materials, April 2019

Alexander S. Romanov, Le Yang, **Saul T. E. Jones**, Dawei Di, Olivia J. Morley, Bluebell H. Drummond, Antti P. M. Reponen, Mikko Linnolahti, Dan Credgington, Manfred Bochmann

10) A simple molecular design strategy for thermally activated delayed fluorescence towards 1000 nm, Journal of the American Chemical Society, November 2019

Daniel G. Congrave, Bluebell H. Drummond, Patrick J. Conaghan, Haydn Francis, **Saul T. E. Jones**, Clare P. Grey, Neil C. Greenham, Dan Credgington and Hugo Bronstein

11) Silicon phthalocyanines as dopant red emitters for efficient solution processed OLEDs, Journal of Materials Chemistry C, October 2017

Andrew J. Pearson, Trevor Plint, **Saul T. E. Jones**, Benoit H. Lessard, Dan Credgington, Timothy P. Bender and Neil C. Greenham

12) Star-shaped fluorene–BODIPY oligomers: versatile donor–acceptor systems for luminescent solar concentrators, Journal of Materials Chemistry C, January 2017

Nathaniel J. L. K. Davis, Rowan W. MacQueen, **Saul T. E. Jones**, Clara Orofino-Pena, Diego Cortizo-Lacalle, Rupert G. D. Taylor, Dan Credgington, Peter J. Skabara and Neil C. Greenham

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16) Short hydrogen bonds enhance non-aromatic protein-related fluorescence, PNAS Proceedings of the National Academy of Sciences of the United States of America. March 2021

Stephens, Amberley; Qaisrani, Muhammad; Diaz Miron, Gonzalo; Ruggiero, Michael; Morzan, Uriel; González Lebrero, Mariano; **Jones, Saul**; Poli, Emiliano; Bond, Andrew; Woodhams, Philippa; Kleist, Elyse; Grisanti, Luca; Gebauer, Ralph; Zeitler, J.; Credgington, Dan; Hassanali, Ali; Kaminski Schierle, Gabriele

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Saul T. E. Jones, Andrew J. Pearson, Jeremy D. Dang, Neil C. Greenham, Timothy P. Bender, and Dan Credgington

19) Exploring the photophysics of carbene metal amides, SPIE conference presentation, September 2018

Saul T. E. Jones, Dan Credgington.

7.3 Submitted pending publication

1) Hyperfine Spin Conversion in Thermally Activated Delayed Fluorescence Molecules

Yuttapoom Puttisong, Emrys W. Evans, William K. Myers, S. Matthew Menke, Alexander J. Gillett, Tudor H. Thomas, **Saul T. E. Jones**, Irina A. Buyanova, Weimin M. Chen, Richard H. Friend and Neil C. Greenham

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