Structural Characterization of the Interfacial Structure of the Working Electrode in Dye-sensitized Solar Cells Using X-ray and Neutron Techniques



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This thesis is submitted for the degree of Doctor of Philosophy

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This thesis is the result of my own work and includes nothing which is the outcome of work done in collaboration except as declared in the Preface and specified in the text. It is not substantially the same as any that I have submitted, or, is being concurrently submitted for a degree or diploma or other qualification at the University of Cambridge or any other University or similar institution except as declared in the Preface and specified in the text. I further state that no substantial part of my thesis has already been submitted, or, is being concurrently submitted for any such degree, diploma or other qualification at the University or similar institution except as declared in the text. I further state that no substantial part of my thesis has already been submitted, or, is being concurrently submitted for any such degree, diploma or other qualification at the University of Cambridge or any other University or similar institution except as declared in the text. It does not exceed the prescribed word limit for the relevant Degree Committee.

Abstract

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Ke Deng

The transparency and low cost of dye-sensitized solar cells (DSSCs) renders this technology promising for the development of electricity-generating windows in future energy-sustainable buildings. Typically, DSSCs contain a working electrode (photoanode) that consists of a dye adsorbed onto the surface of a semiconductor (often TiO_2), where photo-induced electrons are injected into the conduction band (CB) of the semiconductor; the electrical current passes to the counter-electrode, which is often coated with platinum in order to catalyze the electrolytic process. The electrolyte is a redox couple (e.g. I^{-}/I_{3}^{-}) that fills the void between the two electrodes. This thesis examines the interfacial structure of the working electrode in DSSCs using X-ray and neutron techniques.

Chapters 1 and 2 provide an introduction to X-ray reflectometry (XRR) and neutron reflectometry (NR) techniques, i.e., the principal analytic tools used for research carried out in the context of this thesis. Chapters 3, 4, and 5 contain the results obtained from applying *ex-situ* air-solid X-ray techniques to investigate the structure of the dye…TiO₂ interface for three high-performance DSSC dyes: the organometallic dyes **N3** and **N749**, as well as the metal-free organic dye **MK-2**. Chapter 3 discusses how XRR and grazing-incidence small angle X-ray scattering (GISAXS) can be used to explore the molecular packing behavior of these three dyes on TiO₂ as a function of the dye-sensitization concentration. Chapters 4 and 5 examine the relationships between the structure of the dye···TiO₂ interface and the DSSC fabrication parameters based on several case studies using *ex-situ* XRR, and a more systematic study using high-throughput *ex-situ* XRR.

Chapters 6 and 7 discuss the structural aspects of the dye…TiO₂ interface in the presence of solvent and electrolyte based on the results of NR techniques. Chapter 6 examines the structure of the dye…TiO₂ interface and the effect of solvent ingression on the dye…TiO₂ interface in an emulated DSSC, using *in-situ* NR combined with *ex*-

situ XRR. Given that the electrolyte solution plays an important role in the photon-toelectron conversion efficiency, Chapter 7 examines the modulation of the dye…TiO₂ interfacial structure from solvent ingression and in the presence of different levels of electrolyte composition, using high-flux *in-situ* NR with contrast-matching. These aspects are of paramount importance for the determination of various properties of the DSSC working electrode and ultimately of the DSSC device. Chapter 8 concludes the thesis and explores improvements and other potentially feasible techniques to study the structure of the dye…TiO₂ interface based on current research findings. The importance of understanding our sample systems, based on various supporting techniques such as IR spectroscopy, XPS as well as imaging techniques is discussed; the results provide additional structural information for the X-ray and neutron reflectivity analyses (fittings).

Publications

Below is a summary of papers published, under review or in preparation for peerreviewed journals based on the work presented in this thesis:

Deng, K.; Cole, J. M.; Rawle, J. L.; Nicklin, C.; Chen, H.; Yanguas-Gil, A.; Elam, J. W.; Stenning, G. B. G. Dye Nanoaggregate Structures in MK-2, N3, and N749 Dye…TiO₂ Interfaces That Represent Dye-Sensitized Solar Cell Working Electrodes. *ACS Appl. Energy Mater.* **2019**. This paper formed the basis of Chapter 3.

Deng, K.; Cole, J. M.; Stenning, G. B. G.; Nye, D. W.; Stan, L. Establishing Relationships Between Dye…TiO₂ Interfacial Structure and Dye-Sensitized Solar-Cell Fabrication Parameters Using High-Throughput X-ray Reflectometry, under review. This paper formed the basis of Chapter 5.

Deng, K.; Cole, J. M.; Cooper, J. F. K. *et al.* Examining the Structure of the Dye…TiO₂ Interface Structure in Dye-Sensitized Solar Cells by High-flux *In-situ* Neutron Reflectometry, in preparation for submission. This paper formed the basis of Chapter 6 and 7.

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List of acronyms and abbreviations

ACS	American Chemical Society		
AFM	Atomic Force Microscopy		
ALD	Atomic Layer Deposition		
AMI	Adsorption Mass Index		
APM	Area-per-molecule		
ATR	Attenuated Total Reflection		
B3LYP	Becke, 3-parameter, Lee-Yang-Parr		
СВ	Conduction Band		
CCDC	Cambridge Crystallographic Data Center		
CSNS	China Spallation Neutron Source		
DFT	Density Functional Theory		
DSSC	Dye-sensitized Solar Cell		
DTGS	Deuterated Triglycine Sulfate		
FOM	Figure of Merit		
FTIR	Fourier-transform Infrared Spectroscopy		
FTO	Fluorine-doped Tin Oxide		
FWHM	Full-width at Half-maximum		
GISAXS	Grazing-incidence Small-angle X-ray Scattering		
GIXRD	Grazing-incidence X-ray Diffraction		
GIXS	Grazing-incidence X-ray Scattering		
НОМО	Highest Occupied Molecular Orbital		
IPCE	Incident-photon-to-electron Conversion Efficiency		
IR	Infrared Radiation		
ITO	Indium Tin Oxide		
LED	Light-emitting Diode		
LUMO	Lowest Unoccupied Molecular Orbital		
NEXAFS	Near-edge X-ray Absorption Fine Structure		
NIR	Near Infrared		
NR	Neutron Reflectometry		
PCE	Power Conversion Efficiency		
SAM	Self-assembled Monolayer		
SLD	Scattering Length Density		
	AII		

ТВА	Tetrabutylammonium
TD-DFT	Time-dependent Density Functional Theory
TDMAT	Tetrakisdimethylamido-Titanium
TOF	Time-of-flight
TTIP	Titanium Tetraisopropoxide
UV/vis	Ultraviolet-visible
XPS	X-ray Photoelectron Spectroscopy
XRR	X-ray Reflectometry

1. Background

1.1 Abstract

The transparency and low-cost nature of dye-sensitized solar cells (DSSCs) afford this technology with promising prospects for electricity-generating windows in buildings for energy-sustainable cities in the near future¹. Despite the enormous industrial potential of DSSCs, innovation is hampered by the lack of suitable dyes². Therefore, it is of paramount importance to improve our understanding of how the dye···TiO₂ interface of a working electrode in a DSSC functions at the molecular level, in order to generate design guidelines for advanced dyes. To this end, state-of-the-art reflectometry methods supported with advanced materials-characterization techniques are applied herein to study the interface structure (e.g. dye adsorption modes, dye/dye separation, and dye/TiO₂ tilt angles) of several high-performance DSSC dyes on different types of TiO₂ surfaces. Subsequently, the observed structures are correlated to the photovoltaic properties of the corresponding devices. Subsequently, structure-function relationships will be established, which may serve as molecular design principles in order to guide the molecular engineering of new dyes with superior DSSC performance.

1.2 Photovoltaics

The ever-increasing global demand for energy and the growing concerns regarding global warming have stimulated the interest in renewable and sustainable energy sources. In this context, solar energy is particularly interesting, as it has already shown its potential to satisfy the global need for energy in the future³. Figure 1.1 illustrates the efficiency of different types of solar cells and their historical development. DSSCs have received extensive attention as particularly cost-effective conversion devices for solar energy. A central requirement for the commercial use of DSSCs is the development of cost-effective, environmentally friendly, efficient, and sustainable light-absorbing dyes with high flexibility regarding the molecular tailoring.



Figure 1.1 Power conversion efficiency for different types of solar cells and their historical development. Reproduced from National Renewable Energy Laboratory (NREL), 2019.

DSSCs represents an exceptionally fast-growing thin-film solar cell technology. This is not surprising, given their low fabrication costs, their relatively high efficiency, as well as their substantial flexibility regarding shape, color, and transparency. In DSSCs, dyes are usually adsorbed onto a mesoporous semiconductor electrode, which is then joined with a counter electrode. The void between the two electrodes is filled with an electrolyte containing a redox couple. Ruthenium-based dyes have been regularly employed in DSSCs^{4,5}, and subsequent progress has been focused predominantly on improving absorption properties. Initially, dispersed particles were used to increase the interface area. Subsequently, the surface roughness of the photoelectrodes was enhanced in order to generate multiple reflections in order to increase the captured incident light by using a monolayer of dye with a high molar extinction coefficient⁶. Due to the continuous evolution of substrate roughness and morphology, as well as dye photophysics and electrolyte redox chemistry, sensitized nanocrystalline photovoltaic devices reached an incident-photon-to-electron conversion efficiency (IPCE) of 7.1% in 1991⁷. The subsequent discovery of the Ru(II)-based dyes N3 and N749 ('black dye') pushed the IPCE to 10%^{8,9}, while DSSC efficiency values of up to 11.5% have recently been obtained from molecularly tailored Ru(II)-based sensitizers¹⁰. However, despite their good conversion efficiencies, Ru-based sensitizers suffer from relatively high costs, toxicity, and the scarcity of the transition metal sources. Therefore, attention has recently shifted toward metal-free organic sensitizers on account of their low cost, lower environmental impact, high molar extinction coefficients, flexibility with respect to molecular tailoring, and the diversity of suitable molecular structures^{11–13}. Metal-free organic sensitizers are thus arguably regarded as the most promising alternatives to the successful Ru(II) sensitizers.

1.3 Dye-sensitized solar cells (DSSCs)

DSSCs have been studied extensively since their discovery a few decades ago. DSSCs use a dye as the optical absorber to harvest UV/vis light and convert it into electrical power, thus mimicking the natural photosynthesis process¹⁴. Dye molecules can be attached onto the surface of a metal oxide substrate via a multitude of mechanisms, including covalent and hydrogen bonding, electrostatic interactions, hydrophobic interactions, van der Waals forces, or physical entrapment. DSSCs almost exclusively employ covalent bonds between the dyes and the TiO₂ surface in order to ensure strong coupling, a homogeneous dye distribution and device stability¹⁵. Figure 1.2 illustrates the operating principles of DSSCs¹⁶. The maximum potential generated by a cell is determined by the energy difference between the chemical potential of the electrolyte (E_{redox}) and the Fermi level (E_F) of the TiO₂ layer¹⁷.



Figure 1.2 Schematic illustration of the operating principle of DSSCs¹⁶. Adapted from Jasim, K.E. *et al*, 2011.

Specifically, light is absorbed by a sensitizer anchored on the surface of a wide-band semiconductor. The most frequently used DSSC anchors are carboxylic acid and

cyanoacrylic acid groups, and their chemical behavior has a significant impact on their potential in the DSSC applications^{18–20}. At the interface, charge separation occurs, whereby photo-induced electrons are injected from the dye into the conduction band (CB), and carriers are transported to the charge collector in the CB of the semiconductor. In order to harvest a large fraction of sunlight, sensitizers with a broad absorption spectrum are used in conjunction with oxide films of a nanocrystalline morphology. Thus, it is possible to achieve high conversion rates of incident photons into electric current for a wide spectral range from the UV to the near infrared (NIR) region²¹.

A self-assembled monolayer of dye molecules is adsorbed onto a mesoporous TiO_2 photoanode that exhibits a high surface area. The DSSC, which is completed by a Pt-covered FTO counter electrode, is subsequently filled with an electrolyte solution that contains the molecular redox shuttles. The DSSC performance crucially depends on four parameters: 1.) the dye loading; 2.) the fraction of harvested sunlight, which affects the photocurrent of the cell and is determined by the amount of dye absorbed on the TiO₂ surface and its molar extinction coefficient; 3.) the efficiency of the injection of electrons into the semiconductor by the photo-excited dye, which should ideally be effectively regenerated by the redox electrolyte²². For that purpose, a monolayer of the dye is required on the surface, while aggregation or multilayers should be avoided²³; 4.) the recombination between the injected charge in the semiconductor and the oxidized form of the redox couple in the electrolyte should be minimal. Previous studies have shown that molecular co-adsorbates can significantly reduce the recombination rate²⁴.

Charges injected into the semiconductor can recombine with either the dye cations created by electron injection, or with the electron acceptors of the redox electrolyte. Charge recombination between the injected electrons and the dye cations represents a key loss mechanism, while the impact of recombination between the redox electrolyte and TiO₂ electrons is usually negligible in efficient cells. In terms of the time scale, the recombination with a dye molecule typically falls in the order of a micro- to milliseconds, whereas recombination with the electrolyte falls in the range of milliseconds to seconds²⁵.

The charge recombination in DSSCs can be summarized by^{26,27}:

$$I_3^- + e_{TiO_2}^- \to I^- + I_2^{-\bullet}$$
 (1.1)

This process can either be followed by a second electron transfer to convert the iodide radical anion $I_2^{-\bullet}$ (with an unpaired valence electron) into two iodide anions (I⁻), or by the disproportionation of two $I_2^{-\bullet}$ to form I_3^- and I⁻. The operational principle of a DSSC on the molecular level is shown in Figure 1.3²⁸. Initially, the sensitizing dye absorbs a photon and promotes its transfer from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The excited electron is then injected into the CB of the metal oxide, where it travels to the front electrode. The oxidized dye is reduced by the electrolyte, which is regenerated at the counter-electrode to complete the circuit. For efficient charge injection, the energy level of the LUMO must be sufficiently higher than the edge of the CB of TiO₂, while for efficient dye regeneration, the energy level of the HOMO must be sufficiently higher than the edge of the CB of TiO₂, while for efficient the redox level of the redox electrolyte⁵.



Figure 1.3 DSSC operation principle on the molecular level²⁸. Adapted from Hardin, B.E. *et al*, 2012.

1.4 Scientific context

Previously, the discovery of dyes emanated in many cases from serendipitous discoveries, and a subsequent iterative chemical fine-tuning. However, in order to

overcome the aforementioned bottleneck in the realization of smart materials, a more systematic approach to the design and synthesis of suitable dyes is indispensable.

Such systematic approaches could be accomplished by molecular engineering, which aims at establishing DSSC design rules based on the correlations between the structure of a dye and its optoelectronic properties^{29,30}. As the DSSC working electrode consists of the adsorbed dye molecules on the TiO₂ nanoparticles, a reliable prediction of the DSSC performance of a dye requires the precise determination of the structure of the dye…TiO₂ interface, as well as of the correlation between the structure and the photovoltaic properties.

The dye serves two essential functions in a DSSC: 1.) absorbing the sunlight that propels the molecule into the photo-excited state, and 2.) injecting the electron into the TiO_2 semiconductor, thereby initiating the electrical circuit of the solar cell. The efficiency of this electron-injection process as well as downstream electron recombination issues that can short-circuit a solar cell, depend on the adsorption mode of the dye on the TiO_2 surface³¹. Apart from the adsorption mode, the photovoltaic performance of a DSSC is influenced by the following characteristics of the dye… TiO_2 interface:

- (i) the tilt angle between the dye and the TiO_2 surface;
- the average spacing between dyes molecules on the TiO₂ surface and the homo- or heterogeneity of the dye separation;
- (iii) potential dye aggregation in lateral direction with respect to the TiO₂ surface (as determined by the average thickness and density of the dye layer)^{32,33}. The formation of dye aggregates in self-assembled monolayers (SAMs) strongly affects the electronic and optical properties of organic chromophores in DSSC devices^{34–36}.

Reflectometry and grazing-incidence X-ray scattering (GIXS) are ideal characterization tools for the evaluation of these interfacial structure parameters. Lab-based X-ray reflectometry (XRR) measurements have already been carried out on several TiO₂-adsorbed dyes. While these data are limited with regard to intensity and resolution, they have nevertheless been used to estimate dye thicknesses and to calculate tilt

angles between dye molecules and the TiO₂ surface by comparing results to those of the dye structure³⁷. Considering its importance, the systematic and quantitative examination of the structure of the dye...TiO₂ interface by reflectometry and GIXS at a synchrotron facility such as the Diamond Light Source (UK) represents a desirable research target.

Given that the working electrode of the DSSC is a buried interface within the device, neutron reflectometry (NR) should be particularly useful in this context, on account of the ease and depth of penetration, which is characteristic for neutrons. Moreover, NR is able to discriminate signals arising from the dye and from the TiO₂ surface, as the various DSSC layers exhibit sufficient contrast in scattering length densit (SLD)ⁱ. Accordingly, a pilot project was carried out on the dye…TiO₂ interface in DSSCs to develop a suitable sample environment for these types of experiments, which includes a sample holder that emulates a DSSC device. Initial results were obtained from *insitu* NR experiments. The results revealed information on the dye…TiO₂ tilt angles, the thicknesses of the dye layer, and dye interactions that influence the device performance of two high-performance DSSC dyes. Proof-of-concept results were also obtained from *in-operando* NR experiments, whereby the interface structure of the full DSSC device can, in principle, be obtained in parallel to the photovoltaic properties.

1.5 Dyes of interest

This project aims to determine the structure of the dye…TiO₂ interface and the structure-function relationship for several high-performance DSSC dyes. A few dyes of interest are shown in Table 1.1. Squaraine dye SQ2 represents a particularly promising class of DSSC dyes on account of their very strong absorption properties in the red to near-IR (NIR) regions³⁸.

ⁱThe scattering length density (SLD; sometimes denoted N_b) is a measure of the scattering power of a material. It increases with the physical density (how tightly packed the scattering entities are), as well as the intrinsic scattering power of the 'scattering entities'. For X-rays, the scattering arises from the electron density, which is linearly correlated to the atomic number, whereas for neutrons, the scattering arises from the nuclear scattering lengths.

Name	Molecular Formula	Formula Weight	Description	Structural Formula
MK2	C58H70N2O2S4	955.45 g/mol	High-performance metal-free organic dye	$(\mathbf{C}_{\mathbf{N}})_{\mathbf{C}_{\mathbf{H}_{3}}} = \mathbf{C}_{\mathbf{N}} = \mathbf{C}_{\mathbf{R}} = \mathbf{C}_{$
RK1	$C_{46}H_{40}N_4O_2S_2$	744.97 g/mol	Red metal-free organic dye	C _g H ₁₇ S N S N S N COOH
SQ2	C41H46N2O4	630.81 g/mol	Green metal-free organic dye	$O \xrightarrow{OH} O \xrightarrow{O} O \xrightarrow{N} O \xrightarrow{N} O \xrightarrow{O} C_8H_{17}$
Black dye (N749)	C ₅₃ H ₈₂ O ₆ N ₈ S ₃ Ru	1124.2 g/mol	Panchromatic Ru- based dye	$= \underbrace{\begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 $
N3	C ₂₆ H ₁₆ O ₈ N ₆ S ₂ Ru	705.64 g/mol	Benchmark Ru-based dye	O OH N N N N N N N N N N N N N N N S O O H

 Table 1.1 Selected representative dyes of interest.

Quantum-chemical calculations on **MK2**, **RK1**, and **SQ2** were performed using Gaussian View 5.0³⁹. Geometry optimization on these dyes based on density functional theory (DFT) calculations were carried out using Becke's three-parameter and the Lee-Yang-Parr hybrid functional (B3LYP)⁴⁰ together with a 6-311G⁴¹ basis set. DFT calculations were also carried out on various other metal-free organic dyes in order to estimate the energy levels of their HOMOs and LUMOs as well as the

corresponding band gaps, which are important parameters for the photovoltaic performance in solar cells.



Figure 1.4 HOMOs, LUMOs, and the corresponding band gaps of **MK2**, **RK1**, and **SQ2**; calculated *in vacuo* at the B3LYP/6-311+ G(2d,2p) level of theory (red: positive; green: negative; isovalue: 0.02).

1.6 Research motivation

Since DSSCs function by initiating an interfacial charge separation at the dye...TiO₂ interface, it is crucial to understand the interfacial properties and processes between the dye molecules and the oxide surface. Previous studies have revealed the interface structure of the electrode, especially how dye orientation and molecular packing affects the photoelectric properties and processes. Previous investigations on the orientation of organic molecules on TiO₂ surfaces have focused on single-crystal substrates under high-vacuum conditions using synchrotron X-rays. This project will mainly use XRR and NR in combination with other advanced materials-characterization tools to determine the structure of the dye...TiO₂ interface, the adsorption behavior of dyes, the dye tilt angles relative to the TiO₂ surface, the spacing between dye molecules on this surface, and the degree of homo- or heterogeneity of the dye distribution

thereupon. The ultimate goal of this project is the determination of the structure of the dye···TiO₂ interface within an operational DSSC device.

2. Methodology

2.1 The basic principles of X-ray and neutron scattering

X-rays refer to high-energy electromagnetic radiation (wavelength: 0.01-10 nm; frequency: 3×10^{16} - 3×10^{19} Hz; energy: 100 eV-100 keV) that can interact with the atomic electrons upon scattering off a sample. X-ray scattering techniques are based on recording the intensity of the scattered X-ray beam, which is a function of incident and scattering angles, polarization, and wavelength/energy. The amplitude of the scattered wave is expressed by the atomic form factor $f(\mathbf{Q})$, i.e., the Fourier transform of the electron-charge density, which increases with the atomic number:

$$f(\mathbf{Q}) = \int \rho(\mathbf{r}) \cdot e^{i\mathbf{Q}\cdot\mathbf{r}} d^3r \quad , \tag{2.1}$$

wherein $\rho(\mathbf{r})$ represents the electron-charge density at a distance \mathbf{r} from the nucleus, \mathbf{Q} the scattering vector or momentum transfer vector, ($\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_s$), while \mathbf{k}_i and \mathbf{k}_s denominate the wave vectors for the incident and scattered X-ray beam, respectively.

For neutrons, in analogy to X-rays, $\rho(r)$ represents the spatial density distribution of a nucleus, which is considered an infinitesimal point (δ -function) relative to the neutron wavelength. The Fourier transform of the δ -function affords the constant neutron form factor.

Neutrons differ from X-rays as they have a significant mass, and thus a kinetic energy and an (average) lifetime. In addition to these particle characteristics, neutrons also exhibit a wavelength (~ Å), which is defined by the de Broglie relationship:

$$p = mv = \frac{hk}{2\pi} = \frac{h}{\lambda}, \qquad (2.2)$$

wherein *p* refers to the momentum of the neutrons, *m* and *v* to the mass and the velocity of the neutron, respectively, while *h* denominates the Plank constant (6.62 × 10^{-27} m²kgs⁻¹) and *k* to the wave number of the neutron.

Table 2.1 Properties of Neutrons.

Neutron Properties			
Spin	1/2		
Mass	1.67 × 10 ⁻²⁷ kg		
Magnetic moment	-0.966×10 ⁻²⁶ J·T ⁻¹		
Average lifetime	881.5s		

The simplest scenario for elastic neutron scattering is probably best described by scattering from a single, rigidly fixed nucleus. In this case, scattering depends on the Fermi interaction potential between the neutron and the nucleus; the distance between the latter two is by ca. five orders of magnitude shorter than the wavelength of the neutrons. Accordingly, nuclei can be considered point scatterers⁴².



Figure 2.1 Elastic neutron scattering from a rigidly fixed nucleus⁴². The incident plane wave ($e^{ik \cdot x}$), with the wave vector **k** and unit amplitude, interacts with the point-scattering nucleus at a distance **r**=0. The scattered wave is spherical, with an amplitude of $-\frac{b}{r}$. Adapted from Rinaldi, R., *et al*, 2008.

In the aforementioned scenario, the incident plane neutron wave ψ_i is defined by the wave function:

$$\psi_i = e^{i\mathbf{k}\cdot\mathbf{x}} \,, \tag{2.3}$$

wherein **k** refers to the wave vector that is defined by:

$$k = \frac{2\pi}{\lambda}, \qquad (2.4)$$

while x denominates the distance from the nucleus. The incident wave is scattered isotropically by the nucleus according to:

$$\psi_s = -\frac{b}{r} e^{ik \cdot x} , \qquad (2.5)$$

wherein r is the distance from the nucleus and b is the scattering length, which quantifies the strength of the neutron…nucleus interaction. The negative sign accounts for the repulsive interaction potential arising from a positive value of the scattering length. In fact, the scattering length varies randomly across the periodic table.

For a three-dimensional array of nuclei, the elastically scattered wave can be expressed in the wave function:

$$\psi_{s,a} = -\sum \left(\frac{b_i}{r}\right) e^{i\mathbf{k}\cdot\mathbf{r}} e^{i\mathbf{Q}\cdot\mathbf{r}} , \qquad (2.6)$$

wherein *Q* represents the scattering vector or momentum transfer vector, ($Q = k_i - k_s$), while k_i and k_s denominate the wave vectors for incident and scattered neutrons, respectively.

The refractive index of a material is a dimensionless number that describes the propagation of a wave through the medium. The variation of reflectivity with the momentum transfer vector, Q, depends upon the materials scattering properties, which can be expressed as a function of the refractive index defined as:

$$n = \frac{c}{v}, \qquad (2.7)$$

wherein c denotes the speed of light in vacuum and v is the phase velocity of the wave in the medium. The bulk refractive index of a materials is given by:

$$n = 1 - \delta - i\beta , \qquad (2.8)$$

wherein δ represents the real component related to the scattering properties of the material, while $i\beta$ denominates the imaginary component related to the absorption properties of the material^{ii,43}. As δ is very small for both neutrons and X-rays, the refractive index is close to 1. However, the two characterization methods differ in their calculation of δ and β .

For X-rays, δ and β are defined by:

$$\delta = \frac{\lambda^2}{2\pi} r_0 \rho_{el} , \qquad (2.9)$$

$$\beta = \frac{\lambda \mu}{4\pi} \,, \tag{2.10}$$

wherein λ is the wavelength of incident radiation, r_0 the classical electron radius (2.82 × 10⁻¹⁵ m), ρ_{el} the electron density, and μ the absorption coefficient. The collective term $r_0\rho_{el}$ is typically referred to as the scattering length density (SLD) in analogy to neutrons. For heavier elements with large atomic form factors, β may become significant for X-rays. With increasing X-ray wavelength, β also increases, as lower energy X-rays interact more strongly with a given sample.

In non-magnetic substances, the neutron absorption factor is generally negligible, as $\beta \approx 0$. The refractive index of materials can thus be simplified by removal of the imaginary term:

$$n \approx 1 - \delta = 1 - \frac{\lambda^2}{2\pi} \rho(r)$$
, (2.11)

ⁱⁱ The choice of $\pm i\beta$ depends on the mathematic form by which the waves are represented and must be consistent with wave decay in the presence of absorption. Early X-ray scientists such as Compton used to express plane waves by $\exp[i(\omega t - kr)]$, wherein *n* contains a negative imaginary component in the presence of absorption, and this form still is predominantly used in the X-ray community. In the modern electrodynamics and optical science, plane waves are expressed by $\exp[-i(\omega t - kr)]$, wherein the imaginary component of the refractive index is positive in the presence of absorption.

wherein $\delta = \frac{\lambda^2}{2\pi}\rho(r)$ denotes the nuclear contribution to the optical index, and $\rho(r)$ is typically referred to as the neutron scattering length density.

$$\rho = \sum_{i} b_{i} n_{i} \tag{2.12}$$

$$n_i = \frac{1}{V} = \frac{N_A \cdot \rho}{M} \,, \tag{2.13}$$

wherein b_i represents the experimentally determined neutron scattering length, n_i the number density, *V* the molecular volume, N_A the Avogadro constant, ρ the mass density, and *M* the molecular mass.

Evidently, the neutron refractive index decreases with increasing SLD. Total reflection occurs when neutrons pass from a medium of higher refractive index to a medium of lower refractive index, i.e., when neutrons pass from a medium of lower SLD to a medium of higher SLD. Clearly, a medium with a positive SLD exhibits a refractive index of less than unity, i.e., the medium is optically sparser than the vacuum. Accordingly, a neutron beam that interacts with a medium surface from the vacuum would be totally reflected at grazing incident angle.

When considering the magnetic contribution with the optical index, while neglecting the absorption, the value of the refractive index is given by:

$$n \approx 1 - \delta \pm \delta_M = 1 - \frac{\lambda^2}{2\pi} \rho(r) \pm \delta_M , \qquad (2.14)$$

wherein δ_M refers to the magnetic contribution, which depends on the relative orientation of the neutron spin with respect to the magnetization (parallel or anti-parallel).

Some examples of scattering length values of nuclei of different elements with low atomic numbers are shown in Table 2.2⁴⁴. The apparent substantial difference of these is a major advantage for the examination of organic chemicals and biological materials^{45,46}, especially in so-called isotope-labeling experiments, wherein molecules or parts thereof are enriched with a specific isotope of an element, e.g. by replacing hydrogen with deuterium.

Nucleus	Scattering length/fm	Nucleus	Scattering length/fm
¹ H	-3.741	0	5.803
² H (or D)	6.671	Si	4.149
С	6.646	CI	9.577

Table 2.2 Neutron scattering lengths of selected nuclei of elements with low atomic numbers.

2.2 The basic principles of X-ray and neutron reflectometry

In this section, the theoretical basis of XRR and NR for the investigation of the specular reflection from a uniform layer is outlined. The theory provides highly instructive information and bears much practical importance for the understanding of XRR and NR. Specifically, reflectometry is governed by the principles of scattering and those of classical optics, i.e. that waves are subjected to reflection and refraction when incident upon an interface in between two sides of different refractive indices.

Figure 2.2 illustrates the reflection of a plane wave upon incidence with a onedimensional stratified medium, whereby the region z < -d is air, the region -d < z < 0is the film, and the region z > 0 is the uniform bulk medium, i.e., the substrate. The unit vector, *i*, represents the direction of propagation for the incident plane wave, which lies in the y/z plane and includes a grazing incidence angle, θ , relative to the y-axis. The wave is reflected in the specular direction, \hat{o} , including the same angle, θ , relative to the y-axis.



Figure 2.2 Schematic illustration of the reflection of a plane wave upon incidence with a one-dimensional stratified medium⁴⁷. Adapted from Zhou, X.L. *et al*, 1995.

For elastic scattering, energy transfer does not occur between the neutrons and nuclei, and the incident and reflected wave vectors and directions are thus described by:

$$\boldsymbol{k}_{i} = k\hat{\boldsymbol{i}}, \, \boldsymbol{k}_{o} = k\hat{\boldsymbol{o}} \tag{2.15}$$

$$\hat{\imath} = \hat{\imath} \cos \theta + \hat{z} \sin \theta \qquad (2.16)$$

$$\widehat{\boldsymbol{o}} = \widehat{\boldsymbol{y}} \cos \theta - \widehat{\boldsymbol{z}} \sin \theta \tag{2.17}$$

wherein k_i and k_o refer to one-dimensional wave vectors for the incident and reflected wave ($k_i = k_o = k = \frac{2\pi}{\lambda}$). Therefore, the momentum transfer vector is defined by:

$$\boldsymbol{Q} = \boldsymbol{k}_i \cdot \boldsymbol{k}_o = k(\hat{\boldsymbol{i}} - \hat{\boldsymbol{o}}) = \hat{\boldsymbol{z}} 2k \sin \theta \qquad (2.18)$$

$$Q = |\mathbf{Q}| = \frac{4\pi}{\lambda} \sin\theta \qquad (2.19)$$

Similarly, Figure 2.3 shows the incidence and reflection of a plane wave from a uniform layer (the SLD of the film is denoted by ρ , with a thickness of *d* on top of a substrate with the SLD of ρ_s). This geometry is very similar to the real structure of the dye…TiO₂ interface on silicon substrates. The bottom of Figure 2.3 depicts the corresponding one-dimensional spatial trajectory of the SLD from air through the film and the substrate. The amplitudes of the incident, reflected, and transmitted waves are 1, R, and T, respectively, whereby R and T denominate the Fresnel reflectance and transmittance.



Figure 2.3 Schematic illustration for the incidence and reflection of a plane wave from a uniform layer⁴⁷. Adapted from Zhou, X.L. *et al*, 1995.

The vertical wave numbers in air (k_0) , the film wave vector (\mathbf{k}) are defined by:

$$k = \sqrt{k_0^2 - 4\pi\rho} \quad , \tag{2.20}$$

while ρ is the scattering length density of the film. Neglecting the film thickness, this model can be simplified to a more prevalent situation, in which the wave impinges on the bulk medium, wherein Fresnel reflectance and transmittance can be quantified as:

$$R = \frac{k_0 - k_s}{k_0 + k_s}$$
(2.21)

$$T = \frac{2k_0}{k_0 + k_s},$$
 (2.22)

wherein k_0 is the vertical wave number in air ($k_0 = 2\pi \sin \theta / \lambda$), and k_s is the vertical wave number in the substrate.



Figure 2.4 Schematic illustration of the incidence of a plane wave from air onto a bulk medium with a smooth surface⁴⁷. Adapted from Zhou, X.L. *et al*, 1995.

For substrates with a negative SLD, the substrate vertical wave number k_s would remain a real number for any value of k_0 , as $k_s = \sqrt{k_0^2 - 4\pi\rho_s}$, wherein ρ_s is the SLD of the substrate. The Fresnel reflectance is quantified by:

$$R = \frac{k_0 - k_s}{k_0 + k_s} , \qquad (2.23)$$

which shows that total reflection (R = 1) is theoretically not possible, and that the incident wave will propagate into the substrate. However, below the critical point ($k_0 < \sqrt{4\pi\rho_s}$), k_s is imaginary, while *R* remains unity, i.e., total reflection occurs⁴⁷.

Reflectometry is a scattering technique used to measure the structure of thin films and interfaces by exploiting the small angle (< 5°) for the specular reflection of X-ray or neutron radiation from a surface as a function of Q; a simplified geometry that shows only the reflection from the surface of a thin film is illustrated in Figure 2.5.



Figure 2.5 Geometry of a specular reflectivity experiment. The scattering wavevector, Q, is oriented perpendicular with respect to the plane of the thin film.

The specular reflection of neutrons provides information on interface inhomogeneities ⁴⁸. The basis of the specular neutron reflection method is that the variation in specular reflection with Q, ($Q = 4\pi \sin \theta / \lambda$, wherein λ is the neutron wavelength and θ the glancing angle of incidence) is related to the surface and interface structure, including the thickness and roughness of the layers, and the composition or density profile in the direction normal to the interface.

The more complex geometry of reflection and refraction in a reflectivity experiment is shown in Figure 2.6.



Figure 2.6 Schematic representation of the geometry of reflection and refraction in a reflectometry experiment.

The incident wave impinges upon the interface of two materials of different refractive index (*n*) at an angle θ_1 . The angle of the reflected beam relative to the surface is equal to that of the incident beam. A part of the incident beam is refracted into the material

layer (thickness *d*), at an angle of θ_2 , which is determined by Snell's law (eq. 2.24). At subsequent interfaces, this beam can be further reflected and refracted at an angle of θ_3 . The intensity of the initially reflected beam is determined by Fresnel's law (eq. 2.23). As Q is oriented perpendicular to the interface, the sample structure out-of-plane can be determined.

Given the refractive index for neutrons and X-rays (n < 1), the incident beam could be totally reflected from most materials. The critical angle, below which the total reflection happens, can be determined by Snell's law:

$$\cos(\theta_c) = \frac{n_2}{n_1} , \qquad (2.24)$$

wherein n_1 is the refractive index of the medium from which the incident beam impinges upon the interface, while n_2 is the refractive index from which the incident beam is refracted. For X-ray and neutron radiation on a sample through air of refractive index approximate unity, the critical angle for the film or substrate can be determined as:

$$\theta_c = \lambda \sqrt{\frac{SLD}{\pi}}$$
, (2.25)

wherein λ is the radiation wavelength and SLD the scattering length density of the film or substrate.

Given the relationship between the Q and the angle of incidence, the Q_c value known as the critical edge can be determined by:

$$Q = \frac{4\pi \sin \theta}{\lambda} \tag{2.26}$$

$$Q_c = \sqrt{16 \cdot \pi \cdot SLD} \tag{2.27}$$

2.3 Reflectivity profile

On the basis of classical optics, the intensity of the reflected beam is defined by Fresnel's law:

$$R = \left| \frac{n_1 \sin \theta_1 - n_2 \sin \theta_2}{n_1 \sin \theta_1 + n_2 \sin \theta_2} \right|^2 \quad , \tag{2.28}$$

wherein parameters are defined in Figure 2.6.

The reflectivity can also be expressed as the kinematic approximation:

$$R(Q) = \frac{16\pi^2}{Q^2} \left| \int \rho(z) e^{-iQz} dz \right|^2 , \qquad (2.29)$$

which is a convenient form that is extensively used to discuss reflectivity measurements in the analysis of thin adsorbed layers⁴⁹. The reflectivity profile of a thin film at the interface between two bulk phases can also be determined without approximation by optical matrix methods⁵⁰. In that case, the reflectivity can be expressed as:

$$R = \frac{r_{01}^2 + r_{12}^2 + 2r_{01}r_{12}\cos(2\beta)}{1 + r_{01}^2 r_{12}^2 + 2r_{01}r_{12}\cos(2\beta)} , \qquad (2.30)$$

wherein the subscripts 0, 1, and 2 refer to the upper phase, the thin film, and the lower phase, respectively. The optical path length is then defined by:

$$\beta = \left(\frac{2\pi}{\lambda}\right) \cdot n \cdot d \cdot \sin \theta \quad , \tag{2.31}$$

wherein *n* denotes the refractive index of the thin film, λ the wavelength in the thin film, *d* the film thickness, and θ the refracted angle from the interface with Fresnel coefficients of ⁵¹:

$$r_{ij} = \frac{p_i - p_j}{p_i + p_j}$$
, wherein $p_i = n_i \sin \theta_i$ (2.32)

For $Q \gg Q_c$, which is the momentum transfer of the critical angle for total reflection, the reflectivity can be simplified to:

$$R(Q) \approx \frac{16\pi^2}{Q^4} \left[(\rho_1 - \rho_0)^2 + (\rho_2 - \rho_1)^2 + 2(\rho_1 - \rho_0)(\rho_2 - \rho_1)\cos(Qd) \right], \quad (2.33)$$

wherein ρ_0, ρ_1 , and ρ_2 are the SLD values of the upper phase, the thin film, and the lower phase respectively.


Figure 2.7 Simulated reflectivity profile showing the oscillation of reflectivity. In this case, a 100 Å layer of TiO₂ with an SLD of 31.2×10^{-6} Å⁻² was deposited on a silicon substrate. For comparison, the dashed trace shows the bare silicon substrate. All subsequent layer parameters were fixed around calculated values and all roughness values were fixed at 2 Å.

The oscillations of the reflectivity profile are called Kiessig fringe and are caused by the interference of waves reflected from the top and the bottom of the thin film. Accordingly, the period of these fringes furnishes an immediate approximation of the thin film thickness:

$$d \approx \frac{2\pi}{\Delta Q}$$
, (2.34)

wherein ΔQ is the difference in momentum transfer between two consecutive maxima or minima, which is inversely proportional to the film thickness. Simulating the reflectivity curves with more sophisticated methods will afford more accurate information including the thickness of the layer and the roughness of the interface.



Figure 2.8 Simulated reflectivity profile showing how the thin film thickness affects the reflectivity. In this case, a thin film of TiO_2 (thickness: 300 Å, SLD of $31.2 \times 10^{-6} Å^{-2}$) was added on a silicon substrate. For comparison, the dashed trace shows a TiO_2 layer with a thickness of 80 Å. All subsequent layer parameters were fixed around calculated values and all roughness values were fixed at 2 Å.

However, as most real surfaces are not ideal and exhibit a degree of surface roughness, adding the root-mean-square Gaussian roughness amends the reflectivity and the Fresnel coefficient.

$$R(Q) = R_0(Q) \cdot e^{-Q_n \cdot Q_{n+1} \cdot \sigma^2}$$
(2.35)

$$r_{ij} = \frac{p_i - p_j}{p_i + p_j} \exp\left(-0.5Q_n \cdot Q_{n+1} \cdot \sigma^2\right), \qquad (2.36)$$

wherein $R_0(Q)$ is the reflected intensity without surface roughness, Q_n and Q_{n+1} are the momentum transfer for the media on either side of the interface, while σ is the rootmean-square Gaussian roughness⁵². Thus, a rough surface will result in a more rapid decaying rate of the reflectivity compared to that of an ideally flat surface.



Figure 2.9 A simulated reflectivity profile showing the reflectivity decay on a silicon substrate with surface roughness of 5 Å. In comparison, the dashed trace shows an ideal reflection on the silicon substrate. All subsequent layer parameters were fixed around calculated values.

For multi-layer systems, the reflectivity can be calculated in matrix form, using the Abeles method⁵³. The phase factor is used to account for the thickness of each layer:

$$\beta_p = k \cdot d , \qquad (2.37)$$

wherein *k* is the vertical wave vector through the layer, and *d* its thickness. The phase factor of the incident medium for the radiation, β_0 , equals 0.

Subsequently, a characteristic matrix, C_n , can be calculated for each layer:

$$C_{n} = \begin{bmatrix} e^{\beta_{p,n}} & r_{n}e^{\beta_{p,n}} \\ r_{n}e^{-\beta_{p,n}} & e^{-\beta_{p,n}} \end{bmatrix},$$
 (2.38)

wherein r_n is the Fresnel coefficient of each layer expressed as:

$$r_n = \frac{k_n - k_{n+1}}{k_n + k_{n+1}} \tag{2.39}$$

The reflectivity can be calculated based on the resultant matrix for the overall system defined as the product of the characteristic matrices:

$$M = \prod_{1}^{n} C_n \tag{2.40}$$

$$R = \left|\frac{M_{11}}{M_{21}}\right|^2 \tag{2.41}$$

In the following chapters, simulations based on these calculations will provide information on the surface and interface structures of multi-layer systems. Figure 2.10 shows the model that has been adopted for the ex-situ reflectivity analysis of the $dye\cdots$ TiO₂ system.



Figure 2.10 The model for reflectivity analysis used in subsequent chapters of this thesis. 'Superphase' refers to the incident medium for the radiation, while 'Subphase' refers to the bottom phase with assumed infinite thickness. In the context of ex-situ reflectivity analysis, the former refers to air, while the latter refers to the silicon substrate.

2.4 Analytical methods

This project aims at determining the dye \cdots TiO₂ interfacial structure and the structurefunction relationship of three high-performance DSSC dyes that are adsorbed onto several forms of TiO₂ substrate via a combined experimental and computational approach.

Reflectometry techniques are important tools for the characterization of structured interfaces on the nanoscale (1-5000 Å)⁵⁴, and they are particularly suited to the study of the internal properties of layered film structures on surfaces, yielding data on subsurface structure and material properties.

When X-rays impinge on a stratified sample, reradiating dipoles are induced in individual electrons in the sample material⁵⁵. These dipoles generate reradiated electromagnetic waves in specular direction with regard to the plane of stratification of the surface structure. The intensity of the reflected rays provides information on the spatial distribution of the electron density perpendicular to the surface. If the composition of the sample is known, the electron density distribution can be obtained from its chemical profile or its atomic/molecular structure. When a neutron beam strikes a stratified sample, the neutrons interact in a similar way with individual atomic nuclei and magnetic induction is caused by the spin of the vertical SLD profile of the sample. If the isotopic composition of the sample is known, the SLD profile of a sample can be related to its chemical and/or magnetic profile using the known scattering length values of various isotopes⁵⁷.

In general, the beam flux of synchrotron-derived X-rays is higher than that of neutron sources, which shortens exposure times and provides higher spatial resolution with improved statistics. Compared to X-rays, neutrons exhibit a higher penetration depth, which allows the incident beam to propagate in a solid medium before reaching the solid-liquid interface that is highly important in DSSCs. Neutron-based experiments are susceptible to isotope labeling, which can enhance contrast⁵⁸, and neutron beams damage the samples to a lesser degree than X-rays⁵⁹, which may allow the recording of several successive measurements using the same sample. Moreover, neutrons are capable to detect magnetic interactions in samples. Despite these differences, XRR and NR experiments complement each other in the specific characterization or magnetic profiling of a sample.

Specifically, XRR is capable of characterizing single- and multi-layered thin film structures (layer thicknesses ~nm). XRR spectra are obtained from varying the grazing incident angle while measuring the specular reflected X-ray beam. Although the shape of the resulting angle-dependent curve does not provide direct information on the presence or distribution of chemical elements within the sample, it can be used to infer changes of the electron density in the sample, which contains information on the depth distribution and mass density of the elements in the sample⁶⁰. Overall, XRR is an

extremely useful technique for examining organic molecules adsorbed on atomically flat surfaces.

X-rays interact with electrons, and the classical formalism used in the transmission of X-ray diffraction is based on two approximations. Firstly, the diffraction at one point does not depend on the diffraction at other points (Born approximation), while the incident field is identical everywhere on the sample. Therefore, only single-point scattering is considered. However, absorption by the sample is also taken into account. Secondly, the scattering length of an electron is assumed to be independent of the incident angle (small-angle approximation) and equal to:

$$r_e = \frac{e^2}{4\pi\varepsilon_0 mc^2} = 0.282 \times 10^{-14} \,\mathrm{m}$$
 (2.42)

wherein r_e denotes the Bohr electron radius. As far as the X-rays are concerned, any material is therefore characterized by an SLD that is equal to the local electron density multiplied by r_e^{61} .

$$SLD = \frac{r_e Z}{v} \quad , \tag{2.43}$$

wherein *Z* is the sum of atomic numbers, i.e., the total number of electrons for the molecules in each layer, and V the molecular volume obtained from the diffraction data.

Nominal values for the SLD of each layer were used to construct initial structural models using a three-layer approach. The molecular footprint of each dye can be obtained from normalizing the molecular volume with the measured dye layer thickness:

Area per molecule (APM) =
$$\frac{r_e Z}{d(SLD)}$$
, (2.44)

wherein *d* represents the dye layer thickness.

According to basic trigonometric considerations, the tilt angle between the dye and the TiO₂ surface can be calculated by using the molecular mean plane, d_{max} , and the dye layer thickness, d_{obs} , obtained from the XRR measurements (Figure 2.11).



Figure 2.11 Trigonometric considerations for the tilt angle between dye molecules and the TiO₂ surface.

The intermolecular spacing between parallel planes can thus be calculated according to:

$$l = \frac{APM}{w}, \qquad (2.45)$$

wherein w denotes the molecular width of the dye, and APM the measured average projected area per dye molecule on the TiO₂ surface (*cf.* eq 2.44)

XRR can thus be very useful to determine the average thickness of continuous or nanoparticle layers on atomically flat substrates. The interference between the waves scattered by the surface and the interface yield maxima and minima known as the Kiessig fringes, which are related to the film thickness (eq 2.36)⁶². Modeling of the reflectometry data can also be used to determine the surface and interfacial roughness as well as the electron density. Upon roughening of the interface and surface, the interference between scattering from the surface and interface loses coherence and the fringes consequently broaden and eventually disappear.

Apart from the analysis of experimental results, theoretical investigations based on DFT and time-dependent DFT (TD-DFT) will be applied to various sensitizers within the remit of this project, including Ru(II)-based sensitizers and metal-free sensitizers. DFT is a quantum-mechanical modeling theory used to investigate the electronic structure of the subject dyes in order to provide information on mechanisms that are difficult to investigate experimentally. DFT is a highly versatile method to determine the properties of many-body electron systems by using the spatially dependent electron density. However, DFT is limited to ground-state properties and in order to determine the features of excited states such as excitation energies, TD-DFT methods have to

be employed. TD-DFT is an extension of DFT to handle time-dependent external perturbations, and if the external perturbation does not completely change the groundstate structure of the system, a combination of linear response theory with TD-DFT allows the accurate calculation of excitation energies.

2.5 Sample preparation

In order to prepare amorphous or nanocrystalline TiO₂ substrates with atomically flat surfaces, which are for XRR and NR measurements, atomic layer deposition (ALD) was employed. ALD is based on a sequential reaction of gaseous precursors to deposit thin films, the thickness of which can be precisely controlled on the Angstrom scale. All TiO₂ substrates were sensitized by immersion into dye solutions, followed by solvent washing. Sensitization was achieved by immersing the TiO₂ films for 20 h in 0.5 mM dye solutions. The resulting films were rinsed with neat acetonitrile and dried under a flow of nitrogen gas prior to being subjected to XRR measurements³¹.

For the experiments performed in this thesis, we used several batches of TiO_2 thin films prepared using different precursors as listed in Table 2.3. The TiO_2 thin films demonstrate uniform structural parameters within each batch of samples.

Batch number	1	2	3	
Source of production	ANL	ANSTO	ANL	
Precursor	TTIP	TiCl ₄	TDMAT	
Density (g/cm ³)	3.18	3.65	3.98	3.85
Thickness (nm)	15-20	11	10	12
Surface roughness (Å)	<2	<2	<2	<2
Chapter for use	3	6	4 and 5	7

Table 2.3 Batches of TiO₂ thin films prepared using different precursors.

Batch 1

Atomically flat thin films of amorphous TiO₂ were prepared using atomic layer deposition (ALD) at Argonne National Laboratory (ANL), USA. Titanium tetraisopropoxide (TTIP) and water were used as ALD precursors. The deposition took

place in a viscous flow reactor under a N₂ background pressure of 1 Torr and a substrate temperature of 150 °C, corresponding to conditions that are known to lead to amorphous TiO₂ films. Exposure times of 5 s and 1 s were used for TTIP and water, followed in each case by a 5s purge times. These TiO₂ thin films prepared using this method shows a uniform density of 3.18 g/cm^3 (confirmed by XRR) and were used for the study of Chapter 3.

Batch 2

In order to prepare phosphorous-doped silicon (100) wafers (diameter: 2 inches; El-Cat) that contain an amorphous TiO_2 film with an atomically flat surface, which is necessary for NR measurements, we employed an atomic layer deposition (ALD) technique which was performed at the Australian National Science and Technology Organization (ANSTO). Vaporous $TiCl_4$ and H_2O precursors were delivered from Peltier-cooled reservoirs, following a sequential dosing scheme of 0.4 s $TiCl_4$, a 1.0 s N₂ purge, a 1.0 s H_2O pulse, and a final 1.5 s N_2 purge. These TiO_2 thin films prepared using this method shows a uniform density of 3.65 g/cm³ (confirmed by XRR) and were used for the study of Chapter 6.

Batch 3

Amorphous TiO₂ films with atomically flat surfaces were deposited on silicon wafer and substrates using an Arradiance Gemstar ALD instrument at ANL. Tetrakisdimethylamido-titanium (TDMAT, 99.999%, Strem Chemicals) was reacted with H₂O. The TDMAT precursor was heated to 60°C while the H₂O was kept at room temperature. High purity nitrogen gas (99.999%) was used as a carrying and purging gas with a flow rate of 40 sccm and 100 sccm, respectively. The reactor chamber and the sample holder temperatures were maintained at 200 °C. During exposure-mode ALD process, the evacuation valve was closed before introducing the precursor in the chamber and opened after a delay time. A cycle consisted of 0.7 s TDMAT pulse, 1.3 s delay, 23 s N₂ purge, 0.022 s H₂O pulse, 1 s delay, and 28 s N₂ purge. The TiO₂ deposition rate was about 0.38 Å/cycle. These TiO₂ thin films were used for the study of Chapter 4, 5 and 7. These TiO₂ thin films prepared using this method shows a uniform density of ~ 4 g/cm³ (confirmed by XRR) on silicon substrates for the use of Chapter 4, 5, and a uniform density of ~ 3.85 g/cm^3 (confirmed by XRR) on n-type silicon wafers for the use of Chapter 7.

2.6 Initial structural models

- i) Nominal values for the SLD of each layer were used to prepare the initial structural models.
- ii) For the silicon substrates used in the ex-situ XRR measurement, a three-layer approach was adopted to construct initial structural models, whereby SLD values of 20.1 × 10⁻⁶, 18.9 × 10⁻⁶, and 31.2 × 10⁻⁶ Å⁻² were used for the silicon wafer, the native oxide layer, and TiO₂, respectively. The SLD of the subphase silicon was set to 20.1 × 10⁻⁶ while the SLD of the other two layers were allowed to vary. The thickness of the native oxide layer was fixed at 5 Å. Molecular volumes for N3 and N749 were obtained from the data of the Cambridge Crystallographic Data Center (CCDC)^{63,64}.
- iii) For the silicon wafers used in the *in-situ* NR measurement, a three-layer approach was also adopted to construct initial structural models, whereby SLD values of 2.07×10^{-6} , 3.48×10^{-6} , and 2.39×10^{-6} Å⁻² were used for the silicon wafer, the native oxide layer, and the TiO₂ layer, respectively. The SLD of the superphase silicon was set to 2.07×10^{-6} while the SLD of the other two layers were allowed to vary. The thickness values of the native oxide layers were set at 5 Å for samples used in OFFSPEC NR related experiments while refined around 15 Å for samples used in INTER NR related experiments. The SLD of the subphase solvent d₃-MeCN or d₄-MeOH was used as 4.92×10^{-6} Å⁻² or 5.80 × 10⁻⁶ Å⁻² respectively.
- iv) Interfacial roughness values for individual layers were estimated and refined in accordance with XRR results, whereby R values of 1 Å, 2.5 Å, and 3.5 Å were initially set for the silicon, the native oxide, and the TiO₂ surface, respectively. The dyes and possible water adsorbates attached to the bare TiO₂ substrate were attributed a surface roughness of 4 Å. However, after the dye sensitization, the water adsorbates on TiO₂ are assumed to be negligible as they are expected to be removed by the solvent during sensitization anyway. To start with the

fitting, the fitted SLD values were set close to their theoretical values, assuming a surface coverage of 100%. The dye volume fraction of a dye layer is defined by:

$$\varphi = \frac{\rho_{fit}}{\rho_{ref}} \tag{2.46}$$

wherein ρ_{fit} is the fitted density of the dye layer in GenX (unit/Å³), and ρ_{ref} is the theoretical (calculated) density of the dye layer in GenX (unit/Å³).

	Material	Chemical Formula	Mass Density /g cm ⁻³	Molecular Volume /ų	Xray SLD (10 ⁻⁶) /Å ⁻²	X-ray iSLD / (10 ⁻⁶) /Å ⁻²
	MK2	$C_{58}H_{70}N_2O_2S_4$	1.24	1284.34	11.3	0.063948
Dye	N3	$C_{26}H_{16}O_8N_6S_2Ru$	1.10	1063.82	9.42	0.13475
	N749	$C_{53}H_{82}O_6N_8S_3Ru$	1.28	1462.75	11.6	0.11167
	TiO ₂	TiO ₂	3.84	34.5374	31.2	1.5315
Substrate	Native Oxide	SiO ₂	2.20	45.3519	18.9	0.2504
	Silicon	Si	2.33	20.016	20.1	0.47304
Adsorbate	Water	H ₂ O	0.998	29.9753	9.45	0.031495

Table 2.4 Nominal SLD components for the materials of interestⁱⁱⁱ.

Table 2.5 Initially set roughness values used for modeling of the materials of interests.

	Materials	Surface and Interfacial Roughness/ Å
	MK2	4
Dye	N3	4
	N749	4
Substrate	TiO ₂	3.5

 $\ \ \, \ \ \, Molecular \ volume = \frac{unit \ cell \ volume}{number \ of \ molecules \ per \ unit \ cell}; \ \ data \ taken \ from \ the \ CCDC.$

	Native Oxide	2.5
	Silicon	1
Adsorbate	Water	4

2.7 Simulating layer roughness and thickness

Based upon previous theoretical analyses and simulations, Figure 2.12 summarizes the effect of film thickness, density, as well as of surface and interface roughness on the X-ray reflectivity profile of a thin film deposited on the substrate.





However, when multiple layers are deposited onto the substrate, the effects of film thickness, density, as well as surface and interface roughness on the reflectivity profile become complicated. Figure 2.13 shows how the variation of the roughness of a dye layer of interest affects the reflectivity profile of the dye…TiO₂ system. In the modeling system, which is close to our real electrode, the reflectivity decays more rapidly with increasing interfacial roughness (*cf.* Figure 2.10). However, no obvious systematic pattern changes are observed upon variation of roughness values in the employed model.





The simulated reflectivity profiles for various dye layer thickness values, which are close to the dye monolayer thickness of our interest, are shown in Figure 2.14. It clearly depicts obvious differences in reflectivity profiles for different dye layer thickness values, indicating that XRR is effective in resolving the structure of the dye...TiO₂ interface at this scale. In fact, due to the complex nature of the structure of the dye...TiO₂ interface, arising from e.g. surface roughness, density, background, and condensed water layers, as well as from imperfectly flat surfaces, the real reflectivity profile slightly deviates from the simulated profile, which renders the fitting results ambiguous. In the subsequent chapters, the understanding of our sample systems will improve based on various supporting techniques such as GISAXS, IR spectroscopy, XPS as well as imaging techniques; the results will provide additional structural information for the X-ray and neutron reflectivity analyses (fittings). Independently, the accuracy of the data analysis will be enhanced by e.g. improving the angular resolution, reducing background noise, and prolonging collection times.



Figure 2.14 Simulated reflectivity and (inset) SLD profiles for a 100 Å layer of TiO_2 sensitized with a layer of an arbitrary dye with varying thickness, which exhibits an SLD (10 ×10⁻⁶ Å ⁻²) similar to that of **MK2.** All subsequent layer parameters were fixed around calculated values and all roughness values were fixed at 2 Å.

The figure of merit (FOM) function is used to compare how well the simulation matches the measured data. As for the fitting errors in reflectivity, they are calculated based on a (default) 5% increase in the optimal FOM. In this thesis, the weighted FOM function logbars that takes into account the measurement data, error and simulation was used for fitting the NR data, while the unweighted FOM function logR1 that takes into account only the measurement data and simulation was used for fitting the XRR data which do not have valid error bars. The use of logarithm of square as opposed to sum of squares is because the logarithm provides scaling results in a more similar weighting of high-intensity and low-intensity reflectivity data points that can span several orders of magnitude.

Specifically, the weighted FOM function logbars represent the absolute logarithmic (base 10) difference, taking errors into account:

$$FOM_{logbars} = \frac{1}{N-p} \times \frac{\sum_{i} |\log_{10}(Y_i) - \log_{10}(S_i)|}{E_i * \ln(10) * Y_i}$$
(2.47)

Where Y_i denotes the measurement data, S_i denotes the simulation, and E_i denotes the error. The total number of data points is given by N, while p is the number of free

parameters in the fit. The unweighted figure of merit (FOM) function logR1 is calculated using the scaling decadic logarithm difference of the data and simulation according to:

$$FOM_{logR1} = \frac{\sum_{i} \left| \log_{10} \sqrt{Y_{i}} - \log_{10} \sqrt{S_{i}} \right|}{\sum_{i} \log_{10} \sqrt{Y_{i}}}$$
(2.48)

It is worth noting that the thickness and density are not totally independent parameters in the fitting, i.e., the change of FOM caused by the thickness increase/decrease could be offset by the density decrease/increase, and in fact the integration of density along the depth profile is a more reliable fitting parameter. Therefore, the correlation of errors between thickness and density should be calculated in some cases, e.g. by covariance matrix, to assess the confidence level of fitting results.

3. Dye nanoaggregate structures of MK-2, N3, and N749 at the dye...TiO2 interface, which represent the working electrode of dye-sensitized solar cells

The working electrode of a dye-sensitized solar cell (DSSC) consists of dye molecules adsorbed onto nanoparticles of a semiconductor such as TiO₂. A reliable prediction of the DSSC photovoltaic performance of a given dye requires in-depth knowledge about the precise structure of the dye... TiO_2 interface. X-ray reflectometry (XRR) and grazing-incidence small angle X-ray scattering (GISAXS) are herein employed to determine the dye...TiO₂ interfacial structure and associated dye aggregation behavior of three high-performance DSSC dyes: the organic metal-free dye MK-2 and the two archetypal ruthenium-based organometallic dyes, N3, and N749 ('black dye'). The obtained results show that all three dyes form nanoaggregates at the dye... TiO_2 interface. In order to examine this aggregation behavior, we examined the separation, size, distribution density, and the extent of short-range order within each of those selfassembled dye nanoaggregates in longitudinal and lateral directions. Dye...TiO₂ composites fabricated using dye solutions of varying concentrations were also analyzed. We found that nanoaggregates of the three dyes are separated by several hundred nanometers (158-203 nm) at dye...TiO₂ interfaces that had been fabricated using concentrated dye solutions (0.5 mM or 1.0 mM). Interestingly, MK-2 and N749 dves also display smaller inter-particle separations. The observed dve nanoparticle diameters (156-198 nm) are comparable to the largest hitherto reported inter-particle separations. Accordingly, extraneous dye particles cannot be fitted into the gaps between the nanoaggregates, i.e., the dye self-assembly is saturated. Self-assemblies of all three dyes exhibit both lateral and longitudinal short-range order; N3 displays a particularly short coherence length along the TiO₂ surface, with extensively structured disorder in longitudinal direction. The operation of DSSC working electrodes would therefore seem to be dependent on a dye self-assembly that may exhibit several levels of structural granularity and dye-aggregation effects.

3.1 Introduction

DSSCs represent a next-generation of photovoltaic technology with commercial niche prospects for 'smart window' applications^{66–68} and as passive energy harvesters in wearable devices and textiles^{69–72}. In order to generate more efficient dyes to realize

industrial and commercial applications, a better understanding of how the dye…TiO₂ interface of the DSSC working electrode operates at the molecular level is indispensable. To this end, we have applied state-of-the-art X-ray reflectometry (XRR) and X-ray grazing-incidence scattering methods to investigate the molecular packing behavior of several high-performance DSSC dyes adsorbed onto amorphous TiO₂ surfaces.

The operation of DSSCs is initiated by an interfacial charge separation at the dye...TiO₂ interface. It is therefore crucial to understand the interfacial properties and processes between dye molecules and the semiconductor surface. Various parameters that influence the charge-transfer kinetics in DSSC devices have been extensively studied, including the dye structure^{73,74}, the chemical interactions between the anchoring groups on the dye molecules and the oxide surface^{75,76}, as well as the electronic character of the oxide substrates⁷⁷. Previous studies have shown that the molecular packing parameters such as dye-layer thickness, density and the spacing between adsorbed dye molecules affect key interfacial properties and processes, including the photovoltaic charge-transfer rate^{78,79}, the interfacial surface potential⁸⁰, and undesired recombination reactions⁷⁴. Specifically, the molecular packing behavior of the dye molecules influences the availability of binding sites on the TiO₂ surface, which determines the dye surface coverage that, in turn, affects the short-circuit current density $(J_{sc})^{81}$. The molecular packing behavior of dye molecules on the TiO₂ surface also defines the exposure of the latter to the redox electrolyte, whereby the electron recombination may be accelerated by the proximity between the redox electrolyte and TiO₂, hence reducing the open-circuit voltage (V_{OC})⁸². Overall, given that the molecular packing behavior of dye molecules in working electrodes strongly influences the performance of photovoltaic devices, it is highly desirable to obtain detailed structural information on this fundamentally important interface.

Previous structural investigations on dye…TiO₂ interfaces have used spectroscopy techniques that include near-edge X-ray absorption fine structure (NEXAFS)⁸³, X-ray photoelectron spectroscopy (XPS)⁸⁴, and polarized Fourier-transform infrared (FTIR) spectroscopy⁸⁵. Moreover, diffraction⁸⁶, imaging^{87,88}, and computational tools^{4,89} have been used to postulate dye…TiO₂ interfacial structures. Meanwhile, XRR has been successfully employed to interpret the structure of self-assembled monolayers of dyes

on TiO₂ surfaces; *cf.* the structure of a zinc-porphyrin dye on a TiO₂ substrate⁹⁰, and the successful determination of the molecular orientation and packing density of a range of metal-containing and metal-free organic dyes^{31,91}.

The work herein employs XRR as well as grazing-incidence small-angle X-ray scattering (GISAXS) to determine the molecular packing behavior of three highperformance dyes on thin films of amorphous TiO₂: the metal-free organic dye **MK-2** as well as the two archetypal ruthenium-based organometallic dyes, **N3** and **N749** ('black dye'). Their dye…TiO₂ interfacial structures were also determined as a function of the dye-sensitization concentration used for their fabrication. In particular, we will show that dye nanoaggregates form along the dye self-assemblies in both lateral and longitudinal direction. We employ GISAXS data to afford the separation and size of these nanoaggregates in longitudinal direction. The GISAXS signal also provides evidence of the lateral dye aggregation that is suggested by the XRR findings. Whilst it is rarely quantified, dye aggregation is well known to exist in working electrodes of DSSCs⁹². Herein, we show, using three high profile DSSC dyes, how this aggregation can be quantified through combined XRR and GISAXS measurements.

3.2 Materials, fabrication, and characterization methods

Materials. Three high-performance DSSC dyes were selected for the case studies presented in this study: the metal-free organic sensitizer **MK-2**, and the two archetypal ruthenium-based organometallic dye sensitizers, **N3** and **N749** (Scheme 3.1).

Even though **N749** exhibits better photovoltaic performance, **N3** is the current industry standard DSSC dye. Ruthenium-based organometallic dyes are commonly employed in DSSCs^{4,5}, although improving their absorption properties has remained a focus of research in this area. Despite their good conversion efficiencies, ruthenium-based sensitizers suffer from relatively high costs, toxicity, and the scarcity of the transition metal sources. They also have moderate molar extinction coefficients compared to organic chromophores. Therefore, attention has recently shifted towards metal-free organic sensitizers on account of their low cost, low environmental impact, high molar extinction coefficients and high flexibility with respect to molecular tailoring, as well as the diversity of organic molecular structures^{12,13,17}. **MK-2** represents one of the highest

performing organic DSSC dyes under traditional device manufacturing conditions, e.g. using an I₃-/I⁻ redox electrolyte.



Scheme 3.1 Chemical structures of MK-2, N3, and N749.

Preparation of thin films of amorphous TiO₂. The batch 1 TiO₂ thin films (*cf.* Chapter 2.5 for preparation method) were used for this study with the film thickness (15-20 nm) verified through *ex-situ* spectroscopic ellipsometry, and the homogeneity of film deposition over 40 cm, expected from a fully saturated self-limited process, was experimentally verified.

The atomically flat nature of these amorphous TiO_2 films is necessary in order to generate a good signal in the XRR measurements. Meanwhile, it is suitable to approximate a TiO_2 surface in a DSSC to that of a flat TiO_2 surface in these measurements owing to the scale of the dye \cdots TiO₂ interfacial structure: dye molecules are very small (a few nm) relative to a typical DSSC TiO₂ nanoparticle (50-100 nm) such that the radius of curvature of a TiO₂ nanoparticle will appear flat at the molecular scale.

Dye sensitization of TiO₂ to form dye···TiO₂ interfacial structures. All TiO₂ films were sensitized by immersion of the substrates into solutions of the respective dyes for 20 h, followed by washing with pure solvent. TiO₂ films were sensitized with **MK-2** (95%, Sigma Aldrich) in MeCN:*t*-butanol:toluene (1:1:1, v/v), while sensitization with **N3**·2H₂O (95%, Solaronix) and **N749** (95%, Solaronix) was carried out in MeCN:*t*-butanol (1:1, v/v) (Sigma Aldrich, ACS reagent grade). The resulting films were rinsed with neat acetonitrile and dried under a flow of N₂ prior to being subjected to XRR measurements³¹.

X-ray reflectometry (XRR). XRR measurements were conducted using a Rigaku SmartLab reflectometer with a rotating anode (9 kW), a Cu-K α X- ray source (λ = 1.541 Å), and a Ge (220 × 2) monochromator. Reflectivity data were collected in increments of 0.01° for a detector range of 0.1° < 2 θ < 8°. The results were refined using GenX⁹³, which uses the differential evolutional algorithm to perform robust optimizations and avoids local minima to reveal associated structural parameters. The X-ray reflectivity was plotted as a function of the momentum transfer vector (Q) perpendicular to the TiO₂ surface, which is defined by:

$$Q = \frac{4\pi \sin \theta}{\lambda} \tag{3.1}$$

As far as the X-rays are concerned, any material can be characterized by a scattering length density (SLD) that is equal to the local electron density multiplied by the classical electron radius r_e (2.82 × 10⁻¹⁵ m) according to:

$$SLD = \frac{r_e Z}{V} = \frac{r_e N_A \rho Z}{M},$$
(3.2)

wherein *Z* is the sum of atomic numbers, i.e., the total number of electrons for the molecules in each layer, *V* is the molecular volume obtained from the diffraction data deposited in the Cambridge Structural Database and the literature^{63,64}, *N*_A is the Avogadro's constant, ρ is the mass density, and *M* is the molecular mass.

Nominal values for the SLD of each layer were used to construct initial structural models using a three-layer approach. For the substrates, values of 20.1 × 10⁻⁶ Å⁻², 18.9 × 10⁻⁶ Å⁻², and 31.2 × 10⁻⁶ Å⁻² were used for the silicon wafer, the native oxide layer, and the TiO₂ layer, respectively. The thickness of the native oxide layer was set to 5 Å^{31,94–96}.

Grazing-incidence small-angle X-ray scattering (GISAXS). GISAXS experiments were conducted on amorphous TiO₂ thin films sensitized with **MK-2**, **N3**, or **N749** using X-ray irradiation ($\lambda = 0.992$ Å; E = 12.5 keV) from beamline I07 at the Diamond Light Source (UK) with the following apparatus parameters. For the detector positioning system, an independent mounting system was used for the Pilatus 2M area detector. The sample-detector distance was set to 3017 mm, whereby the detector was allowed to move in horizontal and vertical directions. Measurements were carried out as a

function of the incidence angle, with angular increments of 0.05° between 0.15 and 0.40°, encompassing the critical angle for the film and providing some depth sensitivity. The GISAXS flight tube on the path between the sample and the Pilatus 2M detector was filled with helium to prevent air scattering. Mica entrance and Kapton exit windows were installed, while two internal, remotely movable, beamstops were employed for the direct and the reflected beam. BornAgain simulations, which use a distorted-wave Born approximation to model multilayer samples, were used in support of the GISAXS experimental data analysis⁹⁷. Associated BornAgain fitting was performed using Python scripts (see Appendix A) that employ a Genetic Algorithm to roughly locate the global minima and a Minuit minimizer to efficiently detect the nearby local minima⁹⁸.

Grazing-incidence X-ray diffraction (GIXRD). GIXRD measurements were conducted using a Rigaku SmartLab reflectometer with a rotating anode (9 kW), a Cu-K α X- ray source (λ = 1.541 Å), and a Ge (220 × 2) monochromator. The employed GIXRD measurements in this study avoided intense signals from the substrate in favor of stronger signals from the thin film by using a detector scan with a fixed grazing angle of incidence (0.7°); this was chosen to be slightly above the critical angle for total reflection of the film material.

Attenuated total reflection (ATR)-Fourier-transform infrared spectroscopy (FTIR).

ATR-FTIR measurements were performed using a Nicolet iS 10 FTIR spectrometer. Measurements were performed on dye solutions of the three high-performance DSSC with different concentrations. The dye solutions were trapped between the Smart iTX tip and the crystal, through which the evanescent wave of IR light was transmitted, and incident onto the dye solutions, before it was reflected internally multiple times, finally exiting the sample to be collected by a fast recovery deuterated triglycine sulfate (DTGS) detector.

3.3 Results and discussion

3.3.1 Thickness and density of dye layers on thin films of amorphous TiO₂ and levels of lateral dye aggregation as a function of dye-sensitization concentration

The thickness and packing density of dye layers fabricated using different sensitization concentrations were investigated by XRR (Figure 3.1). In these experiments, the sensitization time remained constant ($t_s = 20$ h).



Figure 3.1 Reflectivity profiles (offset for clarity) of the (a) **MK-2**, (c) **N3**, and (e) **N749** dye layers as well as fitted XRR parameters: thickness and density for (b) **MK-2**, (d) **N3**, and (f) **N749** dye layers on amorphous thin films of TiO₂ ($d_{TiO2} = \sim 3.18$ g/cm³; $t_s = 20$ h; $c_{dye} = 0.05$ -1.00 mM). Fitting error bars are not visible where they are smaller than the symbols.

Figure 3.1 indicates that the dye-layer thickness of dye...TiO₂ interfaces for N3 are fairly constant when fabricated with increasing dye-sensitization concentration up to 0.5 mM. For MK-2, the thickness increases more linearly with concentration, while for N749, the thickness is maximal at 0.25 mM. In particular, the thickness of the MK-2 and N3 dye layers increases substantially when fabricated using the highest dye-sensitization concentration presented in this study (1.0 mM) (Figures 3.1(b), 3.1(d)). This is presumably a consequence of the TiO₂ surface becoming saturated with the dye to the

point that it cannot adsorb any more molecules. Hence, dye molecules will tend to stack on top of each other instead.

In accordance with these expectations, Figure 3.1(b) shows that the dye-layer thickness of **MK-2** on TiO₂, fabricated using a 0.5 mM dye solution, is almost doubled when a 1.0 mM dye solution is used instead. The formation of **MK-2** dye aggregates or multilayers in lateral direction (along a trajectory perpendicular to the TiO₂ surface) appears to be responsible for this difference; *cf.* the maximum possible dye-layer thickness for a monolayer of **MK-2** is ~28 Å⁹⁹.

Figure 3.1(d) shows that the dye-layer thickness of **N3** on TiO₂ is generally stable at ~16 Å for sensitization concentrations up to 0.5 mM. Given that the maximum possible dye-layer thickness for a monolayer of **N3** is ~16 Å¹⁰⁰, monolayers of almost upright **N3** geometry are deemed to form for 0.05-0.5 mM dye-sensitization conditions. However, upon increasing the concentration of the dye-sensitization solution to 1.00 mM, the dye-layer thickness increases to 20.10 Å. The **N3** dye^{...}TiO₂ interface must therefore exhibit some form of an "over-stacking structure" of dye aggregates in lateral direction relative to the TiO₂ surface.

Unlike **MK-2** and **N3**, the dye-layer thickness of **N749** does not exhibit a clear trend of variation upon increasing the sensitization concentration from 0.05 mM to 1.00 mM (Figure 3.1(f)). The errors associated with these measurements are comparatively large, especially for the 0.25 mM data point, which skews a fair analysis. One can nonetheless gauge that monolayers of **N749** form when fabricated using more dilute dye-solutions, given that the maximum possible dye-layer thickness for a monolayer of **N749** is ~16 Å.⁶⁴

3.3.2 Dye nanoaggregate structures and their extent of order within dye selfassemblies on TiO₂ in lateral and longitudinal directions as a function of the dyesensitization concentration

3.3.2.1 Determining the critical angle, Yoneda peak position, and Q_y profiles at different horizontal cuts, Q_z , from the GISAXS geometry and XRR fitting

The effects of dye aggregation on TiO_2 , and the extent and nature of its ordering within the self-assembled dye····TiO₂ interfacial structure, were studied using GISAXS. Such experiments were performed on dye-sensitized thin films of TiO_2 on silicon substrates fabricated using different sensitization concentrations. The detailed GISAXS sampledetector geometry relative to the incident X-ray beam is shown in Figure 3.2.



Figure 3.2 (a) GISAXS geometry; (b,c) side and top view of the approximated scattering geometry of this GISAXS experiment, where the detector is aligned perpendicular to the direct beam; (d) example of the extraction of Q_y at a horizontal cut at the Yoneda peak position.

According to the GISAXS geometry shown in Figure 3.2(a), the scattering wavevector, q, is defined in three dimensions by:

$$q = \frac{2\pi}{\lambda} \begin{bmatrix} \cos(\alpha_f) \cos(2\theta) - \cos(\alpha_i) \\ \cos(\alpha_f) \sin(2\theta) \\ \sin(\alpha_f) + \sin(\alpha_i) \end{bmatrix}$$
(3.3)

The approximated scattering geometry of this GISAXS experiment, wherein the detector is aligned perpendicular to the direct beam, is shown in Figure 3.2 (b,c). This situation is only applicable to very small angles of α_r and small values of Q_z , as the surface normal and detector plane are not absolutely parallel to each other. The side view of the GISAXS experiment geometry (Figure 3.2(b)) shows that the position of the Yoneda peak is based on the critical angle of the layered substrate, α_c , and the specular reflection angle, α_r , of the X-ray beam. By performing a horizontal cut at the Yoneda peak position at a specific Q_z value, the position of peaks along the corresponding Q_y profile allows determining average inter-particle separations; in this case, particles presumably refer to dye aggregates. Specifically, the Q_z positions for different Yoneda peaks were calculated according to eq 3.4, based on the approximated GISAXS geometry:

$$Q_{z-Yoneda} = \frac{2\pi}{\lambda} \sin(\alpha_f + \alpha_c) \tag{3.4}$$

where $\lambda = 0.992$ Å for the 12.5 keV synchrotron X-ray irradiation employed.

The critical angle of the dominant TiO₂ layer was calculated based on parameters fitted from the XRR data. In this case, the α_c for the dominating Yoneda peak was calculated to be 0.165°, which is equal to the critical angle of the TiO₂ layer used for this experiment (density: ~3.2 g/cm³). Accordingly, the Q_z positions of the Yoneda peaks for different incident angles of the X-ray beam were calculated (Table A4). The calculated Q_z positions agreed very well with the experimental observations.



Figure 3.3 Intensity of Q_y revealed by horizontal cuts at the Yoneda peak positions as a function of the angle ($\alpha_i = 0.15^\circ$; 0.40°) of the incident X-ray beam for (a) **MK-2**, (b) **N3**, and (c) **N749** dye layers fabricated using different sensitization concentrations. Q_y for $\alpha_i = 0.15^\circ$ was cut at $Q_z = 0.035$ Å⁻¹, while Q_y for $\alpha_i = 0.40^\circ$ was cut at $Q_z = 0.063$ Å⁻¹. Intensity of Q_y obtained from a horizontal cut at the Yoneda peak position for different angles of the incident X-ray beam for (d) **MK-2**, (e) **N3**, and (f) **N749** dye layers fabricated using the sensitization concentration that produced the most obvious peak along Q_y , i.e., 1.00 mM for both **MK-2** and **N3**, and 0.50 mM for **N749**. Plots are offset for clarity.

3.3.2.2 Structural interpretation of experimental GISAXS data: separation of dye aggregates

Figure 3.3 shows that the most structured Q_y profiles along the Yoneda line belong to the dye…TiO₂ interfaces that were created using the following dye-sensitization concentrations: 1.00 mM for **MK-2** and **N3**, and 0.50 mM for **N749**. These concentrations correspond to the dye…TiO₂ interfacial structures where the XRR data showed that the least dense dye layers form, as discussed in the previous section. Dye…TiO₂ interfaces featuring the most diffuse GISAXS data will exhibit nanostructures with the richest short-range order. Accordingly, the results suggest that dye…TiO₂ interfaces that exhibit a low dye-layer density will tend to feature selfassemblies of dyes with the most significant levels of short-range order.

Figure 3.3 also reveals that one or more broad diffraction peaks are observed along the Q_y profiles corresponding to an X-ray beam incident angle of $\alpha_i = 0.15^\circ$. This is just below the critical angle of the TiO₂ layer, but above that of the dye layers, as calculated from the fitted XRR structural information (Table A7). Accordingly, the broad diffraction signal from GISAXS data acquired at $\alpha_i = 0.15^\circ$ should arise predominantly from the dye layer. Inter-particle separations, *d*, can be calculated according to eq 3.5, which is based on the peak position, *q*, in the scattering,

$$d = \frac{2\pi}{q} \tag{3.5}$$

Given that *d* involves the dye layer and that the scale of q involved corresponds to a few hundred nanometers, these inter-particle separations presumably represent some form of dye-nanoaggregate separation. Indeed, a recent study used Atomic Force Microscopy (AFM) to show that dye nanoaggregates of the three subject dyes form rows of fairly regularly spaced particles on TiO_2^{101} ; this sort of particle structure would invoke the type of diffraction peaks that are observed herein.



Figure 3.4 The Gaussian fit full width at half-maximum (FWHM) and center (x_c) for peaks of the intensity profile along Q_y (obtained from a horizontal cut at the Yoneda peak position) at $\alpha_i = 0.15^\circ$, for (a) **MK-2**, (b) **N3**, and (c) **N749** dye layers fabricated using the sensitization concentration that produced the most obvious peak along Q_y , i.e.,1.00 mM for both **MK-2** and **N3**, and 0.50 mM for **N749**.

Figure 3.4 presents a Gaussian fit to the full width half-maximum (FWHM) of the diffraction peaks in these Q_y profiles for each dye where the diffraction peaks are most

evident ($c_{MK-2} = 1.00 \text{ mM}$, $c_{N3} = 1.00 \text{ mM}$, $c_{N749} = 0.50 \text{ mM}$). The center, x_c , of the strong first-order diffraction peak lies at $Q_y = 0.00309 \text{ Å}^{-1}$ and 0.00398 Å^{-1} for the **MK-2** and **N3** layers ($c_{dye} = 1.00 \text{ mM}$), and at $Q_y = 0.00316 \text{ Å}^{-1}$ for **N749** ($c_{N749} = 0.50 \text{ mM}$). These scattering vectors translate to an average dye-nanoaggregate separation of 203 nm, 158 nm, and 199 nm, respectively.

Figure 3.3 shows that the first-order peak in the Q_y profile appears for the **MK-2** dye···TiO₂ interfacial structure even where dye-sensitization concentrations are as low as 0.05 mM; corresponding data for **N3** and **N749** show no or a less obvious structure, respectively. This indicates that at least **MK-2** forms nanoscale aggregates on TiO₂ even when fabricated at medium to low sensitization concentrations.

The presence of higher-order peaks in the Q_y profiles for **MK-2** and **N749** further suggest that these dyes also form shorter dye-nanoaggregate separations; again, such peaks are particularly evident in Figure 3.3 for the 0.5 mM **N749** and 1.0 mM **MK-2** data measured at $\alpha_i = 0.15^\circ$. Conversely, such higher-order peaks were not observed for **N3**, which means that **N3** dye nanoaggregates do not afford a significant number of multiple, distinct, inter-particle separations, as opposed to their **MK-2** and **N749** dye counterparts. Gaussian fits to the FWHM of the higher-order diffraction peaks in the Q_y profile for each dye at $c_{MK-2} = 1.00$ mM and $c_{N749} = 0.50$ mM are given in Figure 3.4. The center, x_c , of the second- and third-order diffraction peaks corresponds to the respective inter-particle separations of 67 nm and 61 nm for **MK-2** and 104 nm and 46 nm for **N749**.

3.3.2.3 Structural interpretation of experimental GISAXS data: particle size of dye aggregates

The Guinier approximation is a commonly used analysis method to determine the particle size from GISAXS data^{102–105}. The low-q_y data of the Yoneda cut were analyzed within the Guinier region, which is the part of the Q_y profile before the onset of the first diffraction peak in Figure 3.4; this onset lies at 0.00309 Å⁻¹ for **MK-2**, 0.00398 Å⁻¹ for **N3**, and 0.00316 Å⁻¹ for **N749** ($\alpha_i = 0.15^\circ$). Based on the Guinier law, the radius of gyration (R_g) for each dye nanoaggregate was determined using eq 3.6:

$$\ln(I_q) = \ln(I_0) - \frac{1}{3}R_g^2 \cdot q^2$$
(3.6)

where q is the scattering vector, I_q is the scattering intensity at low-q, and I_0 is the zeroangle scattering intensity which provides information about the mass and the structure of molecule(s).





Figure 3.5 Guinier plots and linear approximation (slope of the linear fit: $-1/3 R_g^2$) for the low-q intensity profile along Q_y , obtained from a horizontal cut at the Yoneda peak position for (a) **MK-2**, (b) **N3**, and (c) **N749** dye layers ($\alpha_i = 0.15^\circ$) fabricated using different sensitization concentrations. Due to the limited data available at low-q range, the error bars on the values may be quite large.



Figure 3.6 Calculated R_g values at $\alpha_i = 0.15^\circ$ for **MK-2**, **N3** and **N749** dye layers as a function of dye-sensitization concentration. All values are presented but those encircled are declared void on account of poor reliability in their derivation owing to: a lack of sufficient (< 4) data points available for the linear fit used to determined R_g ; or data points that deviate substantially from a linear trend such that the fit to determine

 R_g lacks validity. The horizontal band contains the region of all valid R_g values, based on which, a range of dye nanoparticle radii was declared.

Thereby, R_g values were calculated from the plots of q_y^2 as a function of $ln(I_q)$ shown in Figure 3.5. These present linear fits to the data acquired for each dye at all dyesensitized concentrations studied. The gradient of each slope is -1/3 R_g^2 , assuming that eq 3.6 is valid. It is important to consider the extent to which the Guinier law is valid for these datasets, given its following known limitations¹⁰⁶.

The fact that the Guinier plots are nearly straight lines for all **N3** results, except that pertaining to the 0.25 mM dye-sensitization data, suggests that the dye self-assembly is essentially monodisperse. This finding corroborates our earlier results (*cf.* section 3.3.2.2), where **N3** nanoaggregates exhibited uniform inter-particle separations. In contrast, all Guinier plots for **MK-2** and **N749** are concave upwards, suggesting that their nanoaggregates are polydisperse¹⁰⁷. This corroborates other results from section 3.3.2.2, i.e., that multiple inter-particle separations of nanoaggregates were found for **MK-2** and **N749**. Marked deviations of the Guinier plots from linearity for **MK-2** and **N749** make it difficult to calculate R_g with a high level of reliability for their self-assemblies. Nonetheless, a linear fit to these regions can afford rough values of R_g .

All dye^{...}TiO₂ interfaces fabricated using 0.25 mM dye solutions, including **N3**, show the worst deviations from linearity for each dye. The reason for this is unclear, but all associated data points were classified as outliers.

 R_g values are also heavily influenced by the number of data points, as there are often few¹⁰⁸. All linear fits that contain less than four data points in Figure 3.5 were declared void owing to this concern. In fact, it was for this reason that our supplementary calculations of R_g (**MK-2**: 1.00 mM, **N3**: 1.00 mM, **N749**: 0.50 mM) were also derived from GISAXS data with $\alpha_i = 0.20^\circ$, 0.30° and 0.40° since these contain at least four data points (Figure A22). However, fits to plots of q_y^2 as a function of I(q) for data with these incident angles all deviate significantly from linearity. Moreover, data corresponding to $\alpha_i = 0.15^\circ$ were maintained for the final results since they afford scattering that arises exclusively from the dye layer.

The maximum *q* that is generally acceptable within the Guinier approximation ranges from $q < 1.1/R_g$ to $q < 1.3/R_g$, depending on the extent by which particles exhibit elongated or globular shapes, respectively¹⁰⁹. The dye self-assemblies presented in this study are highly elongated in the direction (Q_y) that our data is analyzed; thus, a limit of q < 1.1/R_g should probably be reasonable. The thus calculated maximum limits of *q* that are applicable for linear approximation are q < 1.57 × 10⁻³ Å⁻¹ for **MK-2**, q < 1.18 × 10⁻³ Å⁻¹ for **N3**, and q < 1.53 × 10⁻³ Å⁻¹ for **N749**. These *q* ranges are lower than the aforementioned *q* ranges used for the Guinier plots, all of which are ~3 × 10⁻³ Å⁻¹, indicating some limitations of using linear approximation to calculate R_g .

Given all of these considerations, a 'band' of R_g values that denote the radii of gyration for our dye aggregates were classified according to the shaded region in Figure 3.6. Thereby, R_g values from fits with too few (< 4) data points (Figure 3.6, solid encircled points) were declared void as were those determined from data that poorly resembled a linear fit (Figure 3.6, dotted encircled points). Having identified these outliers, a band of R_g values that span 55-70 nm covered all remaining data points in Figure 3.6. Hence, it seemed most appropriate to consider this band as the representative R_g values for all three dyes. A distinction between R_g values was not made for individual dyes since the level of accuracy in determining R_g did not merit such fine detail.

Having determined R_g , the overall particle diameter was calculated, which naturally depends on the particle shape. The aforementioned AFM study showed that these dye nanoparticles essentially form 2-D circular disks on a TiO₂ surface¹⁰¹. Thus, the particle radius (*R*) of each dye is related to R_g according to eq 3.7, which is based on the moments-of-inertia calculation for a 2-D thin disk model:

$$R = \sqrt{2}R_g \tag{3.7}$$

The band of R values thus spans 78-99 nm, i.e., particle diameters for the dye nanoaggregates range from 156-199 nm.

3.3.2.4 Structural interpretation of experimental GISAXS data: determining the extent of order along the dye self-assemblies

3.3.2.4.1 Extent of structural order in dye self-assemblies in longitudinal direction

The FWHM values of the diffraction peaks shown in the Yoneda cut of the Q_{v} profile for each dye (Figure 3.4) are essentially a form of coherence length of the dye selfassembly in longitudinal direction, i.e. running parallel to the TiO₂ surface. A quantitative analysis of absolute FWHM values, Δq , is difficult to justify in this study given that their interpretation depends heavily on innumerable factors such as the particle shape, instrument specifics and the intrinsic limits of these data. Nevertheless, a qualitative assessment can be made since the peak width, Δq , is inversely related to the extent of longitudinal order of the nanoaggregates. In the Scherrer equation, $\xi =$ $2\pi K/\Delta q$, wherein ξ is the "crystallite size" (or 'coherence length' in this case), Δq denotes the peak width, and K represents the Scherrer constant¹¹⁰. For **MK-2**, the FWHM of the n^{th} -order diffraction peak of the Q_v profile along the Yoneda cut increases with increasing n; and as mentioned earlier, the inter-particle separation decreases with increasing n. Thus, the extent of structural order, or 'coherence length', of the dye self-assembly in (longitudinal) direction running parallel to the TiO₂ surface, decreases as the inter-particle separation of nanoaggregates decreases. The situation for N749 is more complicated. Its FWHM value increases from the 1st to 2nd-order diffraction peak (as per the case for MK-2) but decreases between the 2nd and 3rd-order diffraction peak. This suggests that the coherence length of the N749 dye self-assembly is greatest where nanoaggregates with the largest inter-particle separation reside but is tentatively the shortest in regions that are occupied by the intermediate inter-particle separation. This tentative level of interpretation is important given that the accuracy of the higher-order diffraction peak signatures is less clear and thus harder to model. The case of **N3** is simple since it only contains a 1st-order diffraction peak, whose FWHM value is larger than those for MK-2 and N749, except perhaps for the highest (3rd) order diffraction peak of MK-2. The N3 dye self-assembly thus exhibits the lowest overall coherence length of the three dyes, i.e., N3 shows the highest extent of structural disorder in longitudinal direction relative to its dye assembly.

3.3.2.4.2 Extent of lateral and longitudinal dye nanoaggregation in the dye selfassemblies

While the FWHM analysis indicates the nature by which the dye nanoaggregates selfassemble along the TiO₂ surface trajectory (longitudinal direction), the portrayal of the full extent of the GISAXS features permits a qualitative analysis of both lateral and longitudinal order.

To this end, Figure 3.7 shows the experimental GISAXS patterns ($\alpha_i = 0.4^\circ$; data collection time = 4s) for **MK-2**, **N3**, and **N749** dye layers with dye…TiO₂ structures that were fabricated at sensitization concentrations of 0.50 mM or 1.00 mM ($t_s = 20$ h).

GISAXS data acquired at $\alpha_i = 0.4^\circ$ exhibit contributions from the dye and TiO₂ composite structure as well as the silicon substrate. GISAXS signals from the TiO₂ and silicon structures are nonetheless expected to be uniform, such that any differences in scattering between the dye...TiO₂ interfaces will be due to variations in the dye structure. This structure may nonetheless be influenced by the TiO₂ surface since the data window available using an incident X-ray angle of $\alpha_i = 0.4^\circ$ will capture lateral and longitudinal expanses of the dye molecules on TiO₂ surfaces as well as the core dye monolayer. This contrasts with GISAXS data from $\alpha_i = 0.15^\circ$, which were used in the previous section to determine structural information that involves just the dye layer.

GISAXS data acquired at $a_i = 0.4^\circ$ can thus assess the extent by which dye aggregates expand upwards from or along the TiO₂ surface, i.e., in the lateral or longitudinal direction, respectively. The pertinent GISAXS features for this assessment are the bulbous shapes that lie just above the origin in the images of Figure 3.7. These features exist in all samples measured along both the Q_y and Q_z directions, and their shapes are symptomatic of nanoaggregate structures. Thus, nanodomains of dye molecules on TiO₂ appear to exist along and upwards from the TiO₂ surface in all samples studied. This is consistent with the peak-width analysis of the diffraction signatures in section 3.3.2.4.1 and the XRR findings described in section 3.3.1 that indicated longitudinal and lateral dye aggregation, respectively.

The bulbous features in Figure 3.7 display a distinct level of dispersive signals along Q_y , especially where it corresponds to the Yoneda line. This level of dispersion

manifests the extent of short-range order in the dye \cdots TiO₂ interface along the TiO₂ surface, i.e., in longitudinal direction. The GISAXS signal intensity associated with the height of this bulbous features (along Q_z) describes the extent of order of the dye \cdots TiO₂ interface in lateral direction. The bulbous feature in the Q_z direction is harder to define as it can constitute multiple distinct features, i.e., essentially several layers of bulbous shapes and a long tail. This study uses the point on the long tail that intersects with the bulbous feature as the reference mark for estimating the 'height' of each GISAXS signal in Figure 3.7. This provides a relative-scale metric for qualitatively assessing the extent of short-range order from lateral dye aggregation in the dye \cdots TiO₂ interface.

Figures 3.7(a) and 3.7(b) allow a comparison of the relative levels of such GISAXS signals along Q_y and Q_z for **MK-2** ($c_{MK-2} = 0.50$ mM) and **MK-2** ($c_{MK-2} = 1.00$ mM). While similar, the dispersion along Q_y appears to be slightly higher where a higher dye-sensitization concentration was employed. Meanwhile, dye nanoaggregate structures extend further along Q_z at the higher dye-sensitization concentration, which suggests that dye nanoaggregates of **MK-2** molecules self-assemble on TiO₂ along and upwards from the TiO₂ surface. Given the inverse relationship between Q and the real-space size of a structure, shorter-range order will exist where dye···TiO₂ interfaces are fabricated at higher dye-sensitization concentrations, i.e., the longitudinal and lateral order of **MK-2** dye self-assemblies shorten as a higher dye-sensitization concentration is used to fabricate DSSCs. These GISAXS results for Q_z profiles also concur with the XRR results for **MK-2**, which revealed dye layers with lower densities, yet larger thicknesses that surpass dye monolayer limits, for dye···TiO₂ interfaces that were fabricated using 1.00 mM **MK-2** (Table 3.1).



Figure 3.7 Experimental GISAXS patterns ($\alpha_i = 0.4^\circ$) for dyes on TiO₂-covered Si substrates fabricated using (a) $c_{MK-2} = 0.50$ mM; (b) $c_{MK-2} = 1.00$ mM; (c) $c_{N3} = 0.50$ mM; (d) $c_{N3} = 1.00$ mM; (e) $c_{N749} = 0.50$ mM; (f) $c_{N749} = 1.00$ mM plotted on a logarithmic intensity scale; for all samples: $d_{TiO2} = \sim 3.18$ g/cm³; $t_s = 20$ h. The Q_z of origin (0, 0) was set at the point of intersection between the beam and the detector.

Figures 3.7(c) and 3.7(d) show that **N3** nanoaggregates exhibit substantially increased short-range order in longitudinal direction when **N3** molecules on TiO₂ are fabricated at higher dye-sensitization concentration. This is evident from the large and extended nature of the bulbous feature along Q_y in the GISAXS image for $c_{N3} = 1.00$ mM, which is approximately 3 times that of its counterpart image for $c_{N3} = 0.50$ mM. Thus, **N3** dye self-assemblies fabricated at 1.00 mM dye will feature nanoaggregates in longitudinal direction whose short-range order is about 1/3 that of those fabricated at 0.5 mM. The lateral order of **N3** dye self-assemblies appears to be slightly shorter for that fabricated at 1.00 mM **N3**, judging from the Q_z 'height' metric. The XRR results concur with these GISAXS findings for the lateral aggregation of **N3**, for reasons akin to the case of **MK-2** (*cf.* Table 3.1 and section 3.3.1). While the longitudinal order for **N3** self-assemblies is much shorter than that of **MK-2** self-assemblies, judging from comparisons of Figures 3.7(a)-3.7(d), the conceptual findings and structural trends for **N3** and **MK-2** are the same.
In contrast to the situation for **MK-2** and **N3**, the GISAXS data for **N749** (Figures 3.7(e) and 3.7(f)) indicate that the extent of order of the nanodomains in **N749** self-assemblies is *higher* in longitudinal direction when the dye····TiO₂ interfaces are fabricated at 1.00 mM **N749** rather than at 0.5 mM **N749**. While the difference is comparatively low in the Q_z direction, the same trend is observed for the short-range order in lateral direction. Thus, the short-range order behavior of **N749** self-assemblies is contrary to that of its **MK-2** and **N3** counterparts in both longitudinal and lateral directions. These contrasting findings between dyes regarding their lateral aggregation effects are corroborated by the XRR results. The XRR-fitted SLD for **N749** (Table 3.1) is 60.6% higher for **N749** self-assemblies fabricated at 1.00 mM **N749**. These calculations suggest that the denser layer of **N749** formed at 1.00 mM corresponds to a surface coverage of 86.9%; which stands in contrast to 54.2% for 0.50 mM **N749** (Table 3.1). This higher density and greater surface coverage of **N749** on TiO₂ stands to augment the longitudinal order of dye self-assemblies adsorbed onto the TiO₂ surface; this conclusion is consistent with the GISAXS patterns observed.

	с _{мк-2} (mM)		С _{N3} (mM)	с _{N749} (mM)	
Concentration (mM)	0.50	1.00	0.50	1.00	0.50	1.00
Thickness (Å)	24.2	38.1	16.1	20.1	15.2	16.0
Error (Å)	(-0.3,0.4)	(-0.4,0.5)	(-0.3,0.3)	(-0.5,0.3)	(-0.3,0.3)	(-0.3,0.4)
Density (10 ⁻⁴ unit/Å ³) ^a	6.85	4.24	12.05	4.87	3.70	5.95
Error (10 ⁻⁴ unit/Å ³)	(-0.26,0.21)	(-0.24,0.17)	(-0.84,0.60)	(-0.38,0.53)	(-0.48,0.32)	(-0.50,0.65)
SLD (10 ⁻⁶ /Å ²)	9.93	6.15	12.08	4.88	6.26	10.07
Error (10 ⁻⁶ /Å ²)	(-0.37,0.30)	(-0.35,0.25)	(-0.84,0.6)	(-0.38,0.53)	(-0.81,0.54)	(-0.85,1.10)
Dye volume fraction (φ ; %)	87.6	N.A. ^b	76.7	N.A. ^b	54.1	87.0
Error (%)	(-3.3,2.7)	N.A.	(-5.3,3.8)	N.A.	(-7.0,4.7)	(-7.3,9.5)

Table 3.1 Fitted density and SLD values for **MK-2**, **N3**, and **N749** on thin films of amorphous TiO₂.

^a: The unit is defined as one dye molecule. ^b: N.A. indicates that the dye volume fraction of a monolayer is not applicable due to the formation of a multilayer structure. The dye volume fraction of a monolayer structure is defined by:

$$\varphi = \frac{\rho_{fit}}{\rho_{ref}} \tag{3.8}$$

wherein ρ_{fit} is the fitted density of the dye layer in GenX (unit/Å³), and ρ_{ref} is the reference density of the dye layer in GenX (unit/Å³) (*cf.* Table A6).

3.3.3 Corroborating experimental findings with simulations of GISAXS data

3.3.3.1 Simulations of GISAXS data using the distorted-wave Born approximation: establishing model parameters

As the structure of the dye \cdots TiO₂ interface can be resolved by XRR fittings, the structural information thus obtained enables the application of BornAgain simulations, in which the sample models are constructed using a three-layer approach on a silicon substrate containing a native oxide layer, TiO₂, and the dye layers (bottom \rightarrow top). The thickness of the native oxide layer was set to 5 Å. The refractive index for the dye molecules was converted from the X-ray SLD using:

$$\delta = \frac{\lambda^2}{2\pi} Re(SLD) \tag{3.9}$$

$$\beta = \frac{\lambda^2}{2\pi} Im(SLD) \tag{3.10}$$

wherein δ denotes the real component of the complex refractive index related to the scattering properties of the material, and β the imaginary component of the complex refractive index related to the absorption properties of the material. The detailed parameters for layer modelling and simulation are summarized in Table A5.

3.3.3.2 Simulations of GISAXS data using the distorted-wave Born approximation: determining the extent of short-range order in dye self-assemblies on TiO_2

The simulations displayed in Figure 3.8 exhibit the GISAXS patterns at $\alpha_i = 0.4^\circ$, which are based on the X-ray optical parameters of each layer obtained from the XRR simulation.



Figure 3.8 Simulated GISAXS patterns ($\alpha_i = 0.4^\circ$) for the dyes on TiO₂-covered Si substrates with the dye-layer density and thickness equal to those of the experimental samples fabricated using a) $c_{MK-2} = 0.50 \text{ mM}$; b) $c_{MK-2} = 1.00 \text{ mM}$; c) $c_{N3} = 0.50 \text{ mM}$; d) $c_{N3} = 1.00 \text{ mM}$; e) $c_{N749} = 0.50 \text{ mM}$; f) $c_{N749} = 1.00 \text{ mM}$ plotted on a logarithmic intensity scale; for all samples: $d_{TiO2} = \sim 3.18 \text{ g/cm}^3$; $t_s = 20 \text{ h}$.

The simulated pattern for the **MK-2**···TiO₂ interface fabricated using 1.00 mM of **MK-2** (Figure 3.8(b)) extends substantially further along the Q_z direction than that of the comparative pattern for 0.50 mM (Figure 3.8(a)). This suggests a shorter range of lateral order for the **MK-2**···TiO₂ interface fabricated at the higher dye-sensitization concentration. The corresponding patterns for **N3** show a similar comparative trend along the Q_z direction, indicating that the **N3**···TiO₂ interface fabricated using 1.00 mM exhibits shorter range lateral order than its 0.50 mM counterpart.

Conversely, the more *compressed* GISAXS signature along the Q_z direction for the **N749**...TiO₂ interface fabricated using 1.00 mM compared to that using 0.50 mM means that it is *not* the highest dye-sensitization concentration that affords the shortest range lateral order for **N749**.

These GISAXS patterns of variation are consistently observed in both simulation and experiment and they correspond well to the density variations of all three dyes, as determined independently via XRR data. Therefore, it seems feasible to conclude that a strong correlation exists between the lateral short-range order, dye-sensitization concentration, and the density of the dye layer. For **MK-2** and **N3**, the lateral short-range order of the dye self-assembly decreases with decreasing dye-layer density. In contrast, their dye-layer density is only weakly correlated to their longitudinal short-range order. These findings suggest that the dye self-assembly process is more disorderly in lateral direction for increasing dye-sensitization concentration, resulting in a less efficient packing of dye molecules on the TiO₂ surface.

Analogous simulations of all of these GISAXS patterns were also performed using an incident X-ray angle of $\alpha_i = 0.15^\circ$ (Figure A1). Overall, the results are consistent with the simulation for the $\alpha_i = 0.40^\circ$. These results validate the assumption that GISAXS data acquired at $\alpha_i = 0.40^\circ$ inform the influence of dye structure on TiO₂, while the same results can be obtained by considering the dye in isolation using GISAXS data at $\alpha_i = 0.15^\circ$.

3.3.3.3 Simulations of GISAXS data using the distorted-wave Born approximation: considering particle distribution densities and particle form factors for the **N3** dye…TiO₂ interface

In general, the GISAXS simulations agree well with experimental observations, except for **N3** fabricated at $c_{N3} = 1.00$ mM, where some aggregation-induced particle effect tentatively plays a significant role. In Figure 3.8, the distortion of the simulated patterns in the Q_y direction for the patterns pertaining to 1.00 mM and 0.50 mM dye-sensitization concentration is relatively small compared to their experimental counterparts shown in Figure 3.7. The difference suggests the probable occurrence of an aggregationinduced particle effect that is not considered in the GISAXS simulations. Indeed, the simulations shown in Figure 3.8 do not consider the particle distribution density and the particle form factors such as particle size, particle shape, polydispersity, aggregate size, and inter-particle structure factors (e.g. particle-particle interactions). Figure 3.9 illustrates the effect on the simulated GISAXS patterns for N3···TiO₂ on silicon substrates when density and form factors for spherical particles *are* taken into account. BornAgain could not simulate particle sizes that are as large as those encountered in our experimental study. Nonetheless, these simulations can present insights into the prevailing trends by forming and comparing structural models with increasing or decreasing particle sizes of arbitrary radii. Clearly, the particle distribution density and form factors exert a strong influence on the GISAXS pattern along all directions in the Q_z - Q_y plane, particularly on the Yoneda peak.



Figure 3.9 The effect of the particle distribution density (particle geometry: full sphere; particle radius: 1.000 nm) on **N3** GISAXS patterns ($\alpha_i = 0.4^\circ$) obtained from BornAgain simulations for **N3** using the full sample model ($d_{TiO2} = \sim 3.18$ g/cm³), with dye-layer density and thickness values that are identical to those of the experimental sample ($c_{N3} = 1.00 \text{ mM}$; $t_s = 20 \text{ h}$) with a particle distribution density of (a) 0.01 a.u.; (b) 0.05 a.u.; (c) 0.10 a.u.; the effect of the particle radius (particle geometry: full sphere; particle distribution density: 0.01 a.u.) on the **N3** GISAXS patterns ($\alpha_i = 0.4^\circ$) obtained from BornAgain simulations using the full sample model ($d_{TiO2} = \sim 3.18 \text{ g/cm}^3$) with dye-layer density and thickness values that are identical to those of the experimental sample (c_{N3} = 0.10 a.u.; the effect of the particle radius (particle geometry: full sphere; particle distribution density: 0.01 a.u.) on the **N3** GISAXS patterns ($\alpha_i = 0.4^\circ$) obtained from BornAgain simulations using the full sample model ($d_{TiO2} = \sim 3.18 \text{ g/cm}^3$) with dye-layer density and thickness values that are identical to those of the experimental sample (c_{N3}

= 1.00 mM; t_s = 20 h) with a particle radius of (d) 1.000 nm; (e) 1.200 nm; (f) 1.500 nm. All dye particles are assumed to sit on the surface of the dye layer.

GISAXS simulations that incorporate particle distribution density values and form factors for spherical particles were in fact performed on all three subject dyes at their 0.50 mM and 1.00 mM dye-sensitization concentrations. The particle distribution density, assuming an arbitrary spherical particle with a radius of 1 nm and density as nominal, was fitted using Python scripts in BornAgain (*cf.* Figures A5-A7). All dye particles were assumed to be located at the bottom of the dye layer. The results shown in Table 3.2 suggest that the density of the dye layer increases with increasing distribution density of particles of constant size. Moreover, a fitting of the size of a spherical particle, assuming an arbitrary particle distribution density of 0.01 a.u. (*cf.* Figures A8-A10), suggested that the density of the dye layer increases with increasing size of particles of constant distribution density (Table 3.2). The strong correlation between the dye-layer density and the particle-distribution density or the particle size (Figure 3.10) indicates that these two parameters represent well the structure of the dye layer. This is probably due to the fact that the dye particles are located almost inside the dye layer given the size and the position of the particles (Figure 3.11).

In comparison, BornAgain fittings were also performed for all dye particles that are assumed to be located on the surface of the dye layer (*cf.* Figures A11-A16). The results shown in Table 3.3 suggest that, unlike fitting for particles at the bottom of the dye layer, there is no clear or uniform trend of correlation between the dye-layer density and the particle-distribution density (constant size) or the particle size (constant distribution density) for all three dyes. These results suggest that the dye layer is 'bottom heavy', which stands to reason given that at least a monolayer of dye molecules was observed in our experimental studies, with some lateral dye aggregation. Overall, this observation indicates that the positions of dye particles as shown in Figure 3.11 play an essential role in determining the GISAXS patterns, and that the fitting results are likely to be affected significantly by the occurrence of aggregation. This is especially true for **N3** layers of lower density, which was seen to be significantly affected by Yoneda peak stretching due to aggregation at an **N3** sensitization concentration of 1 mM; the fitting for particles at the surface suggests a

higher particle distribution density (constant size) as well as particle size (constant distribution density), in contrast to the fitting for particles at the bottom of the dye layer, which suggests a lower particle-distribution density (constant size) as well as particle size (constant distribution density). In comparison, for **MK-2**, the fitting for particles that sit on the surface or at the bottom of the dye layer both yield the same trend, i.e., that a higher dye-layer density is pertinent to a larger particle-distribution density (constant size) and particle size (constant distribution density).

Table 3.2 BornAgain-fitted parameters of GISAXS ($\alpha_i = 0.4^\circ$) patterns for dyes on amorphous TiO₂. All dye particles are assumed to be located at the bottom and slightly above the dye layer.

BornAgain fittted GISAXS	с _{мк-2} (mM)		с _{№3} (mM)		с _{N749} (mM)	
parameters	0.50	1.00	0.50	1.00	0.50	1.00
Particle-distribution density (a.u.) (radius:1 nm)	0.0394	0.0021	0.0041	0.0009	0.0015	0.0112
χ ²	27.99	15.89	41.29	49.98	32.56	35.39
Particle size (nm) (density: 0.01 a.u.)	1.148	0.747	0.859	0.627	0.758	1.026
χ ²	28.17	15.60	41.32	49.44	45.60	35.35
Dye layer density from XRR (\times 10 ⁻⁴ unit/Å ³)	6.85	4.24	12.05	4.87	3.70	5.95



Figure 3.10 Correlation between the BornAgain-fitted dye-layer density and the particle-distribution density or the particle size (radius); these three parameters are near-coincident for **MK-2**, **N3**, and **N749**. Dye particles are assumed to be located at the bottom and slightly above the dye layer.



Figure 3.11 Schematic illustration of the particle positioning in the three-layer sample system: a semi-finite air layer, a middle layer including the dye layer and a TiO_2 layer, and a semi-finite silicon substrate layer. The *z*-axis is pointing up for each of these 3 layers. For a middle layer such as the dye layer, *z* = 0 corresponds to the top interface; thus, negative *z* values should be used for particles within the dye layer.

Table 3.3 BornAgain-fitted parameters of GISAXS ($\alpha_i = 0.4^\circ$) patterns for dyes on amorphous TiO₂. All dye particles are assumed to be located on the surface of the dye layer.

BornAgain fittted GISAXS	с _{мк-2} (mM)		с _{№3} (mM)		с _{N749} (mM)	
parameters	0.50	1.00	0.50	1.00	0.50	1.00
Particle density (a.u.)distribution(radius:1 nm)	0.0006	0.0004	0.0003	0.0004	0.0005	0.0005
χ ²	28.03	15.92	41.40	49.98	32.57	35.61
Particle size (nm) (density: 0.01 a.u.)	0.603	0.580	0.540	0.549	0.604	0.588
χ ²	27.36	15.34	40.57	49.30	45.25	34.96
Dye layer density from XRR (\times 10 ⁻⁴ unit/Å ³)	6.85	4.24	12.05	4.87	3.70	5.95

3.4 Conclusions

Dye^{...}TiO₂ interfacial structures featuring the organic metal-free dye **MK-2**, or one of the ruthenium-based organometallic dyes **N3** and **N749**, adsorbed onto thin films of amorphous TiO₂, were studied herein using XRR and GISAXS methods. This structural investigation was motivated by the fact that these interfaces represent working electrodes for DSSCs, and their structures are known to affect the photovoltaic properties of DSSCs. XRR data were used to determine the thickness and density of dye layers on these dye^{...}TiO₂ interfacial structures. GISAXS data determined the size and separation of the dye nanoaggregates that form in their self-assembled structures. GISAXS data also reveal the extent of short-range order in these dye self-assemblies, which manifests as dye nanoaggregation in both lateral and longitudinal directions, i.e., perpendicular and parallel to the TiO₂ surface. The interfacial structures were also studied as a function of the fabrication conditions using different sensitization concentrations.

The results show that the thickness and density of **MK-2** and **N3** layers on TiO_2 are strongly correlated with the dye-sensitization concentration. A high dye-layer thickness, caused by use of a high dye-sensitization concentration (e.g. 1.00 mM), is

accompanied by a low dye-layer density and vice versa. The result is a less efficient, more disordered, packing of dyes on its self-assembly that exhibits a wider vertical span on TiO₂, to the extent that extensive lateral dye aggregation occurs. This affords a low-density dye layer with large XRR-fitted thickness. Unlike **MK-2** and **N3**, **N749** exhibits a higher dye-layer density at 1.00 mM. This could be attributed to the extraordinarily large intermolecular spacing of **N749** (*cf.* APM for **N749** in Tables A1-A3) that allows a higher degree of dye adsorption at higher sensitization concentration. The lack of a trend in variation of thickness upon increasing the sensitization concentration from 0.05 mM to 1.00 mM also indicates that the self-assembly of **N749** on TiO₂ in the lateral direction is different from that of **MK-2** and **N3**. This could be due to a variety of reasons, although a buffering effect from the counterion in **N749** is an interesting proposition, especially since the other two subject dyes do not contain a counterion.

Dye nanoaggregates form along the dye self-assemblies with largest inter-particle separations of 203 nm, 158 nm and 199 nm for MK-2, N3 and N749, respectively, when sensitized at 1.00 mM (MK-2 and N3) or 0.5 mM (N749). When fabricated under these conditions, the nanoaggregate separations along the dye self-assembly are uniform for N3, while the other two dyes additionally feature smaller inter-particle separations of approximately 67 nm and 61 nm (MK-2) as well as 104 nm and 46 nm (N749). The particle size of N3 in longitudinal direction is similar to its inter-particle separation, and N3 also exhibited a monodisperse particulate structure. Data were more limited for the determination of their particle sizes, although an approximate range of 156-198 nm was estimated for the particle diameters of the three dyes. Naturally, MK-2 and N749 should feature smaller particle diameters as they exhibit the observed polydispersity in terms of their smaller inter-particle separations mentioned above. Indeed, their dye self-assemblies do not appear to be monodisperse in the Guinier region. N3 also presents the shortest-range order in longitudinal direction. Shorter-range order in dye self-assemblies is correlated with higher dye-sensitization concentrations for MK-2 and N3 in both longitudinal and lateral direction. N749 nanoaggregates appear to show contrary results, which are nonetheless in line with other results that have been reported recently¹¹¹.

These experimental findings were corroborated by GISAXS simulations based on the distorted-wave Born approximation. Results revealed that strong correlations exist between the dye-layer density and the particle-distribution density or the particle size, when particles are assumed to lie at the bottom of the dye layer. These results suggest that the dye layer is 'bottom heavy', particularly when there are expanses of dye molecules in lateral direction on TiO_2 owing to the occurrence of dye aggregation along this trajectory.

4. Insights into the influence of the fabrication process on the variation of the dye...TiO₂ interfacial structure through several case studies using X-ray reflectometry

4.1 Introduction

In Chapter 4, we show how X-ray reflectometry (XRR) can be employed to determine dye…TiO₂ interfacial structures for working electrodes fabricated under different sensitization conditions, i.e., varying dye concentrations sensitization time, based on several case studies. The results provide insights into the dye…TiO₂ interfacial structures for both amorphous and nanocrystalline TiO₂ in terms of dye molecule orientations, intermolecular spacing, dye aggregation, and the extent of dye adsorption, all of which laid the foundation for the subsequent systematic study using high-throughput XRR to obtain more intrinsic and generic characteristics of these dye…TiO₂ interfacial structures.

4.2 Methods and materials

This chapter examines several XRR case studies in order to gauge the influence of the fabrication process, i.e., sensitization concentration and time, on the $dye\cdots TiO_2$ interfacial structures **for MK-2**, **N3**, and **N749** adsorbed on thin films of TiO₂. The three DSSC dyes are shown in Scheme 3.1.



Scheme 3.1 Chemical structures of the organic dye MK-2 and the Ru-based dyes N3 and N749 ('black dye').

Preparation and sensitization of thin films of TiO₂. In order to prepare amorphous and nanocrystalline TiO₂ films with atomically flat surfaces, which is necessary for XRR

measurements, we employed an atomic layer deposition (ALD) technique. ALD is based on a reaction sequence of gaseous precursors to deposit thin films, the thickness of which can be controlled precisely on the Angstrom scale. All TiO₂ films were sensitized by immersion of the substrates into solutions of the dyes, followed by washing with pure solvent. TiO₂ films were sensitized with **MK-2** (95%, Sigma Aldrich) in MeCN:*t*-butanol:toluene (1:1:1, v/v), while sensitization with **N3** · 2H₂O (95%, Solaronix) and **N749** (95%, Solaronix) was carried out in MeCN:*t*-butanol (1:1, v/v) (Sigma Aldrich, ACS reagent grade). The resulting films were rinsed with neat acetonitrile and dried under a flow of N₂ prior to being subjected to XRR measurements.

X-ray reflectometry (XRR). XRR measurements were conducted using a Rigaku SmartLab reflectometer with a rotating anode (9 kW), a Cu-K α X- ray source (λ = 1.541 Å), and a Ge (220 × 2) monochromator. Reflectivity data were collected in increments of 0.01° for a detector range of 0.1° < 2 θ < 8°. The results were refined using GenX⁹³ to reveal associated structural parameters, whereby the X-ray reflectivity was plotted as a function of the momentum transfer vector (Q) perpendicular to the TiO₂ surface based on $Q = \frac{4\pi \sin \theta}{\lambda}$.

4.3 The dye…TiO₂ interfacial structure on thin films of TiO₂ as a function of the sensitization time and concentration

The structural change of the dye layers as a function of the sensitization time was investigated by an XRR model simulation. In this study, a constant dye sensitization concentration (0.5 mM) was used throughout.

4.3.1 A case study of the MK-2···TiO₂ interfacial structure on amorphous TiO₂ as a function of the dye sensitization time

The XRR plots are shown in Figure 4.1, while the fitted parameters of interest are shown in Figure 4.2. In this study, the adsorption mass index (AMI) is defined as the product of the density (unit/Å³) and the thickness (Å) according to:

$$AMI (unit/Å^2) = density (unit/Å^3) \times thickness (Å)$$
 (4.1)

Hence, for a given dye the APM is inversely proportional to the AMI:

$$APM = \frac{r_e Z}{d(SLD)} \propto \frac{1}{AMI}$$
(4.2)



Figure 4.1 Reflectivity profiles (offset for clarity) of **MK-2** dye layers on amorphous TiO₂ films as a function of the sensitization time ($d_{TiO2} = \sim 3.98 \text{ g/cm}^3$; $t_s = 10-1200 \text{ min}$; $c_{MK-2} = 0.50 \text{ mM}$).



Figure 4.2 Fitted XRR parameters: dye-layer thickness, surface roughness, as well as AMI and APM for **MK-2** on amorphous thin films of TiO₂ as a function of time ($d_{TiO2} = ~3.98 \text{ g/cm}^3$; $t_s = 10-1200 \text{ min}$; $c_{MK-2} = 0.50 \text{ mM}$). The fitting errors for the dye-thickness values are provided in Appendix B. Fitting error bars may not be visible when they are smaller than symbols.

During $t_s = 0.20$ minutes of sensitization, a significant increase in the thickness of the **MK-2** layer (~14 Å \rightarrow ~17 Å) can be observed. For $t_s = 20.60$ min, the thickness of the **MK-2** layer remains constant (~16.5 Å) (Figure 4.2). Figure 4.2 also illustrates the change of the **MK-2** adsorption mass as a function of sensitization time. The AMI generally varies in line with the change of thickness, and for $t_s > 20$ min of sensitization, the AMI reaches a plateau, indicating a fast **MK-2**...TiO₂ binding process, while the restructuring and/or reorientation of **MK-2** should occur subsequently.

A rapid increase of the thickness of **MK-2** is observed for $t_s = 1-15$ h of sensitization (Figure 4.2). The formation of a complete monolayer structure should be finished after $t_s \sim 10$ h of sensitization, although the thickness of the dye layer increases to 38.1 Å for $t_s > 15$ h, which suggests the formation of a double layer, considering the maximum

possible dye layer thickness for **MK-2** (27.58 Å)⁹⁹. It is noteworthy that molecules of **MK-2** adopt a monolayer structure before $t_s = 10$ h of sensitization, considering that the molecular geometry should become increasingly more upright especially for $t_s = 1$ -10 h, and that the adsorption mass increases concurrently. In the literature, the **MK-2** thickness values vary between 19 Å and 24 Å for samples sensitized at dye concentrations of 0.3 mM ($t_s = 20$ h). Therefore, **MK-2** probably starts to form a second layer structure for $t_s > 10$ h of sensitization. For $t_s > 20$ h of sensitization, the adsorption mass finally reaches a maximum that is comparable to approximately twice the value of the initial adsorption mass, i.e., when the first saturation is reached. This result further corroborates the hypothesis that a double layer is formed. The strong correlation between the rapid change of the dye orientation and the dye adsorption amount ($t_s = 5$ -10 h) suggests an increasingly upright geometry of the dyes, which probably allows a continued adsorption by creating more intermolecular space.

The start of the formation of the second layer of **MK-2** molecules at $t_s = 10$ h is also likely to induce higher surface roughness, which was corroborated by the fitted surface roughness values of **MK-2**. Even though the surface roughness gradually decreases after the formation of more complete multilayers ($t_s \sim 15$ h), it still retains relatively high levels thereafter.

4.3.2 A case study of the N3/N749····TiO₂ interfacial structure on amorphous TiO₂ as a function of the sensitization time

The corresponding XRR plots are shown in Figure 4.3, with the fitted parameters of interest shown in Figures 4.4 and 4.5.



Figure 4.3 Reflectivity profiles (offset for clarity) of dye layers of **N3 and N749** on thin films of amorphous TiO₂ as a function of sensitization time ($d_{TiO2} = \sim 3.98$ g/cm³; $t_s = 1-1200$ min; $c_{N3/N749} = 0.50$ mM).





Figure 4.4 Fitted XRR parameters: dye layer thickness and AMI for **N3** and **N749** on thin films of amorphous TiO₂ as a function of sensitization time ($d_{TiO2} = \sim 3.98$ g/cm³; $t_s = 1-1200$ min; $c_{N3/N749} = 0.50$ mM). Fitting error bars may not be visible if they are smaller than the symbols.



Figure 4.5 Fitted XRR parameter APM for **N3** and **N749** on thin films of amorphous TiO₂ as a function of sensitization time ($d_{TiO2} = \sim 3.98$ g/cm³; $t_s = 1-1200$ min; $c_{N3/N749} = 0.50$ mM). Fitting error bars may not be visible if they are smaller than the symbols.

Figure 4.4 shows that the layer thickness of **N3** generally increases with increasing sensitization time. During the first 5 minutes, the dye orientation should change before retaining a more stable orientation (5-30 min), then adopting a more upright position with a higher tilt angle, which enables higher dye loadings. This is matched by a corresponding variation of the AMI, which is feasible considering the previous assumption that the dye...TiO₂ binding should be fast relative to the subsequent reorientation of the dye molecules and additional adsorption. It is notable that the AMI for $t_s = 20$ h is close to that of $t_s = 60$ min ($c_{N3} = 0.50$ mM), indicating that the mass adsorption should be close to completion after the first hour of sensitization.

Figure 4.4 also displays the change of the layer thickness of **N749** during sensitization. The thickness of **N749** increases monotonously from 10.95 Å to 12.55 Å for $t_s = 1-10$ min, whereupon the thickness remains relatively constant (~12.6 Å) for $t_s = 10-60$ min. In contrast, the AMI of **N749** increases continuously for $t_s = 10-60$ min. This continued increase of the AMI despite the lack of growth of the layer thickness of **N749** stands in sharp contrast to the absorption behavior of **MK-2** and **N3**. Clearly, the APM of **N749** shown in Figure 4.5 is much larger than that of **MK-2** and **N3**. This is probably the main reason that the mass adsorption continues even without relying on gaining intermolecular space from the change of the molecular geometry.

4.3.3 A case study of the MK-2/N3/N749····TiO₂ interfacial structures on thin films of amorphous TiO₂ of varying density as a function of the sensitization concentration

The X-ray reflectometry plots and associated fitting results for **MK-2** layers that are fabricated on thick (high density) amorphous TiO_2 thin films using different sensitization concentrations are shown in Figures 4.6 and 4.7. Figure 4.7 illustrates the comparison of the **MK-2** layer thickness on both dense (high density) and sparse (comparatively lower density) amorphous TiO_2 thin films. The thickness values for sparse amorphous TiO_2 films were obtained from Chapter 3.



Figure 4.6 Reflectivity profiles of the **MK-2** layers on dense amorphous TiO₂ films (d_{TiO2} = ~3.98 g/cm³; t_s = 20 h; c_{dye} =0.05-1.00 mM).



Figure 4.7 Comparison of XRR-fitted thickness values of **MK-2** dye layers fabricated at different concentrations on amorphous TiO₂ thin films of varying density ($d_{sparse} = ~3.18 \text{ g/cm}^3$; $d_{dense} = ~3.98 \text{ g/cm}^3$; $t_s = 20 \text{ h}$; $c_{MK-2} = 0.05$ -1.00 mM). Fitting error bars may not be visible if they are smaller than the symbols. The values for sparse amorphous TiO₂ films were obtained from Chapter 3. Other structural information of **MK-2** on dense TiO₂ are shown in Table A1.

Figure 4.7 shows that the thickness of the **MK-2** layers on dense TiO₂ films rises substantially upon increasing the sensitization concentration from 0.05 mM to 0.50 mM, while a further increase of the sensitization concentration does not significantly increase the layer thickness. The thickness for $c_{MK-2} = 0.50$ mM (39.10 Å) suggests the formation of multilayer structures of **MK-2** on dense TiO₂ films after $t_s = 20$ h, implying that a lower concentration (0.25-0.50 mM) might be more suitable for the generation of dye monolayer structures, which should be more favorable in terms of charge-transfer kinetics and thus improve the overall DSSC performance.

The XRR plots and associated fitting results for **N3** layers that are fabricated on dense (high density) amorphous TiO_2 thin films using different sensitization concentrations are illustrated in Figures 4.8 and 4.9. Figure 4.9 shows a comparison of the **N3** layer thickness on both dense (high density) and sparse (low density) amorphous TiO_2 thin films. The thickness values for thin (low density) amorphous TiO_2 films were obtained from Chapter 3.



Figure 4.8 Reflectivity profiles of **N3** layers on dense amorphous TiO₂ films ($d_{TiO2} = \sim 3.98 \text{ g/cm}^3$; $t_s = 20 \text{ h}$; $c_{N3} = 0.05 \cdot 1.00 \text{ mM}$).



Figure 4.9 Comparison of the XRR-fitted thickness values of **N3** dye layers fabricated using different concentrations on amorphous TiO₂ thin films of varying density ($d_{sparse} = -3.18 \text{ g/cm}^3$; $d_{dense} = -3.98 \text{ g/cm}^3$; $t_s = 20 \text{ h}$; $c_{MK-2} = 0.05$ -1.00 mM). Fitting error bars may not be visible if they are smaller than the symbols. The values for sparse amorphous TiO₂ films were obtained from Chapter 3. Other structural information of **N3** on dense TiO₂ are shown in Table A2.

It is also worth noting in Figure 4.9 that the thickness values of **N3** on sparse amorphous TiO_2 films are all higher than their corresponding values on dense amorphous TiO_2 films. This could be tentatively explained by the fact that sparse amorphous TiO_2 contains: i) the relatively sparse TiO_2 , which would reduce the amount of dye molecules adsorbed, and hence decrease the intermolecular interactions between the dye molecules that forces them down, and ii) a lower TiO_2 density, which should reduce the **N3**...TiO₂ interactions, which potentially has an effect of dragging the molecules down.

Unlike on sparse amorphous TiO₂ films, where the formation of over stacking structure at 1.00 mM affords a significantly lower density value, the overstacking structure of **N3** on dense amorphous TiO₂ films at 1.00 mM does not lead to a significantly lower density value (*cf.* Tables A2 and B5), which indicates a different stacking mode of **N3** on the dense TiO₂ surface at 1.00 mM.

The X-ray reflectometry plots and associated fitting results for N749 layers that are

fabricated on dense (high density) amorphous TiO_2 thin films at different sensitization concentrations are illustrated in Figures 4.10 and 4.11. Figure 4.11 shows a comparison of the **N749** layer thickness on both dense (high density) and sparse (low density) amorphous TiO_2 thin films. The thickness values for thin (low density) amorphous TiO_2 films were obtained from Chapter 3.



Figure 4.10 Reflectivity profiles of **N749** layers on dense amorphous TiO₂ films (d_{TiO2} = ~3.98 g/cm³; t_s = 20 h; c_{N749} = 0.05-1.00 mM).



Figure 4.11 Comparison of XRR-fitted thickness values of **N749** layers fabricated at different concentrations on amorphous TiO₂ thin films of varying density ($d_{sparse} = \sim 3.18$ g/cm³; $d_{dense} = \sim 3.98$ g/cm³; $t_s = 20$ h; $c_{MK-2} = 0.05$ -1.00 mM). Fitting error bars may not be visible if they are smaller than the symbols. The values for sparse amorphous TiO₂

films were obtained from Chapter 3. Other structural information of **N749** on dense TiO₂ are shown in Table A3.

Apart from the thickness for **N749** on sparse amorphous TiO_2 at 0.25 mM, where the overstacking structure forms, the thickness of the **N749** layer is highest for the lowest concentration (0.05 mM) on both dense and sparse amorphous TiO_2 (Figure 4.11). Upon further increasing the concentration, the thickness of **N749** on both dense and sparse amorphous TiO_2 decreases before it steadily rises, probably due to closer interactions between the dye molecules at higher concentrations, which should force the dye molecules to anchor on the surface, before a further increase of the concentration results in a closer packing that forces the dye molecules to stand up.

It is moreover noteworthy that the thickness of **N749** on dense amorphous TiO_2 is generally lower than that on sparse amorphous TiO_2 , which is probably due to the increased intermolecular interactions of **N749** on dense amorphous TiO_2 that force the molecules down, similar to the case of **N3**. This is also supported by the fact that the density for **N749** layers on dense amorphous TiO_2 is obviously higher than that on sparse amorphous TiO_2 (*cf.* Tables A3 and B6), except at sensitization concentration of 1mM, where the aggregation effects dominate. This indicates that the substrate structural parameters, such as the density, exerts a profound influence on the orientation of **N749**.

4.3.4 A case study of the MK-2/N3/N749····TiO₂ interfacial structures on nanocrystalline TiO₂ thin films as a function of the sensitization time

XRR measurements were performed on **MK-2**, **N3**, and **N749** adsorbed on nanocrystalline TiO₂ thin films (density: ~ 3.84 g/cm^3 ; thickness: ~ 250 Å), using dye solution with a constant concentration (0.50 mM). Figure 4.14 shows the reflectivity profiles for **MK-2**, **N3**, and **N749** on nanocrystalline TiO₂ thin films ($t_s = 10 \text{ min} - 20 \text{ h}$).



Figure 4.14 Reflectivity profiles of **MK-2**, **N3**, and **N749** on nanocrystalline thin films of TiO₂ ($t_s = 10 \text{ min} - 20 \text{ h}$).

The thickness values of the dye molecules on nanocrystalline TiO_2 fluctuate around certain values without obvious trends (Figure 4.15). At present, we assume that the ordered structure of the nanocrystalline TiO_2 substrate probably confines the geometry restructuring of the dye molecules during sensitization.



Figure 4.15 XRR-fitted thickness of **MK-2**, **N3**, and **N749** on thin films of nanocrystalline TiO₂ as a function of time ($t_s = 10 \text{ min} - 20 \text{ h}$). Fitting error bars may not be visible if they are smaller than the symbols.

4.3.5 A case study of the MK-2/N3/N749····TiO₂ interfacial structures on nanocrystalline TiO₂ thin films as a function of the sensitization concentration

XRR measurements were performed on **MK-2**, **N3**, and **N749** adsorbed on thin films of nanocrystalline TiO₂ (density: ~ 3.84 g/cm^3 ; thickness: ~ 250 Å), using dye solutions with different concentrations but constant sensitization time ($t_s = 20 \text{ h}$). Figure 4.16 shows the concentration-dependent reflectivity profiles for **MK-2**, **N3**, and **N749** on thin films of nanocrystalline TiO₂ ($t_s = 20 \text{ h}$).



Figure 4.16 Reflectivity profiles of **MK-2**, **N3**, and **N749** on thin films of nanocrystalline TiO₂ as a function of the concentration ($t_s = 20$ h).



Figure 4.17 XRR-fitted thickness of **MK-2**, **N3**, and **N749** on thin films of nanocrystalline TiO₂ as a function of the concentration ($t_s = 20$ h). Fitting error bars may not be visible if they are smaller than the symbols.

Figure 4.17 shows that upon increasing the sensitization concentration of **MK-2** from $c_{MK-2} = 0.05$ mM to $c_{MK-2} = 0.50$ mM, the **MK-2** molecules adopt a more upright position on the surface of the thin films of nanocrystalline TiO₂, similar to the case of thin films of amorphous TiO₂. As the maximum dye layer thickness for a monolayer of **MK-2** is 27.58 Å, double or multilayers should be formed on the nanocrystalline TiO₂ surface at $c_{MK-2} = 1.00$ mM. A similar monotonous trend of the dye molecules adopting a more upright position upon increasing the concentration also applies to **N3** and **N749** on thin films of nanocrystalline TiO₂.

Compared with the potentially overstacking structure observed for N3 and N749 on amorphous TiO_2 thin films, the results shown in Figure 4.17 reveal that both N3 and N749 remain a consistent monolayer structure when the sensitization concentration varies between 0.05 mM to 1.00 mM. Therefore, we presume at present that the crystal structure of TiO_2 probably imposes a confinement on the formation of molecular overlaying, which is likely to be caused by the molecular entanglement.

4.4 Conclusions

The results in this chapter show the dye \cdots TiO₂ interfacial structures on thin film of TiO₂ in terms of dye molecule orientations, intermolecular spacing, dye aggregation, and extent of dye adsorption, as a function of sensitization concentration and time. It should be noticed that with the increase of the sensitization time, dye molecules tend to stand more upright on the TiO₂ surface until a stable state is reached, evident from the corresponding variation of dye-layer thickness values. Meanwhile, it was also observed that the increase of sensitization concentration leads to a general increase of thickness for dye layers on amorphous TiO₂. However, this trend is less distinct than the variation trend for the thickness as a function of sensitization time. This was demonstrated by larger dye-layer thickness values, even at much lower sensitization concentrations, presumably due to the dye self-assembly process, wherein dye molecules are closer packed on TiO₂ and forced down toward the TiO₂ surface when the sensitization concentration increases. It was also noticed that the morphology of the TiO₂ (amorphous or nanocrystalline) and density (high or low) appear to influence the dye...TiO₂ interfacial structures, such as the thickness and the density of the dye layer. In the subsequent chapter, the dye self-assembly mechanism on TiO₂ will be examined using a more systematic study, especially with regard to the relationship between the dye···TiO₂ interfacial structure and the fabrication parameters in order to potentially reveal more generic characteristics of the self-assembly mechanism of dyes on TiO₂.

5. Establishing relationships between the dye^{...}TiO₂ interfacial structure and DSSC fabrication parameters using high-throughput X-ray reflectometry

5.1 Introduction

Dye-sensitized solar-cells (DSSCs) are a contender for next-generation solar-powered window technologies and energy-sustainable wearables. Yet, a systematic means by which the fabrication of DSSC working electrodes can be tailored is distinctly lacking; consequently, DSSC device fabrication procedures are far from optimal. We show how high-throughput X-ray reflectometry (XRR) can be employed to establish relationships between dye…TiO₂ interfacial structures, which constitute these DSSC working electrodes, and their fabrication conditions. 360 XRR measurements enable the systematic determination of the lateral dye-layer thickness of the dye…TiO₂ interfacial structures for three dyes, **MK-2**, **N3**, and **N749** ('black dye'), as a function of 12 dye-sensitization times, 5 concentrations of the sensitizing solutions, with or without rinsing effects. 2-D and 3-D correlation mappings of these relationships afford a predictive screening method for tailoring optimal DSSC fabrication conditions for these dyes, elucidate the underlying dye self-assembly mechanisms, and rationalize dye…TiO₂ interfacial structures for given DSSC fabrication conditions in terms of dye aggregation, dye molecule orientations, and extent of dye adsorption.

DSSCs are promising for the development of electricity-generating windows in future energy-sustainable buildings due to their low cost, high efficiency, and low environmental impact¹¹². Moreover, their ability to be manufactured on flexible substrates, or as fibers, affords them prospects as passive energy harvesters in wearable devices and textiles^{69–72}. DSSC operation is initiated by charge separation at an interface that comprises self-assembled dye molecules on the surface of a semiconductor (usually TiO₂). This dye…TiO₂ interface represents the DSSC working electrode with the dye as the light harvester. Once the dye has been photo-excited by sunlight, it injects an electron into the conduction band (CB) of TiO₂, which triggers a current, thereby front-ending the DSSC photovoltaic response. It is therefore crucial to understand the interfacial properties and processes between dye molecules and the semiconductor surface in order to improve DSSC device design.

Previous studies have shown that the interfacial structure of the DSSC working electrode affects its photoelectric properties and processes^{78,79}, the interfacial surface potential¹¹³, and undesired recombination reactions⁷⁴. Various interfacial properties and processes at the dye \cdots TiO₂ interface that influence the charge-transfer kinetics in DSSC devices have been studied, including the dye structure^{73,74}, the chemical interactions between the anchoring groups on dye molecules and the oxide surface^{75,76}, and the electronic character of the oxide substrates⁷⁷.

The orientation of dye molecules on the TiO₂ surface is crucial for the dye-packing structure and for the availability of binding sites on the TiO₂ surface, both of which determine the dye surface coverage and thus the short-circuit current density, J_{sc} , as well as the power-conversion efficiency (PCE, η)^{81,114,115}. Moreover, the orientation and coverage of dye molecules on the TiO₂ surface define the exposure of this semiconducting surface to the redox electrolyte, whereby close proximity between the redox electrolyte and TiO₂ may accelerate the electron recombination can also be expedited by close contact between TiO₂ and the oxidized dye, which also depends on the dye orientation¹¹⁶.

Previous structural studies aimed at determining the orientation of organic dye molecules anchored onto TiO₂ surfaces via carboxylate ions within the dye, have focused on experiments that employ idealized conditions, e.g., single-crystal substrates under high-vacuum conditions. Such studies have employed experimental methods such as near-edge X-ray absorption fine structure (NEXAFS)⁸³, X-ray photoelectron spectroscopy (XPS)⁸⁴, and polarized Fourier-transform infrared (FTIR) spectroscopy⁸⁵. However, there is a dearth of studies that probe the dye…TiO₂ interfacial structure of DSSC working electrodes that feature more complex dye structures and powdered oxides. X-ray reflectometry (XRR) is a highly suitable technique for the examination of organic molecules adsorbed onto atomically flat surfaces. A few XRR studies have been conducted to examine the self-assembled structure of a zinc-porphyrin dye on a TiO₂ substrate.⁹⁰ Since then, the molecular orientation and packing density of a range of metal-containing and metal-free organic dyes on TiO₂ surfaces have been determined^{31,91}.

The influence that DSSC fabrication conditions have on dye ··· TiO₂ interfacial structures has received much less attention. Yet, it has been shown that fabrication conditions can profoundly alter the dye···TiO₂ interfacial structure. For example, Cole *et al.* showcased changes in dye···TiO₂ interfacial structure upon varying the sensitization solvent for the industrial standard DSSC dye **N3** (Scheme 5.1) and its doubly-deprotonated analogue **N719**¹⁰⁰. Although only a few variations of the DSSC fabrication conditions were explored in that study, it revealed the desperate need for a more systematic investigation into the influence of DSSC fabrication conditions on the dye···TiO₂ interfacial structure. The acquired knowledge base could then be used to develop structure–property relationships between the dye···TiO₂ interfacial structures and DSSC fabrication conditions to ultimately afford guidelines for the systematic optimization of DSSC device fabrication.

To this end, we present in this chapter a systematic XRR study that explores the variation of the thickness of dye layers on atomically flat TiO₂ surfaces as a function of different DSSC working-electrode fabrication conditions (dve-sensitization time and solution concentration as well as follow-up rinsing). Sufficient empirical data should allow determining structure-property relationships between dye...TiO₂ interfacial structures and DSSC fabrication conditions. In this study, we examined three dyes: **MK-2**, a high-profile organic dye, whose best recorded DSSC performance is 8.3%¹¹⁷, as well as N3 and N749 ('black dye'), which are arguably two of the most prominent Ru-based DSSC dyes with maximum PCE values of 10.0%⁸ and 10.4%¹¹⁸, respectively. Observed trends in the dye...TiO₂ interfacial structure may be specific to one, two, or all three dyes. In the latter event, those trends may have more generic applications. 2-D and 3-D correlation maps of the dye-layer thickness as a function of the dye-sensitization time and concentration, generated from the analyzed data of the 360 XRR measurements, produce the central resource to determine links between the dye...TiO₂ interfacial structure of the DSSC working electrode and its fabrication conditions. We will show that dye molecules tend to bind to TiO₂ surfaces via a multistep self-assembly mechanism. Once fully sensitized, dyes stand more upright on TiO₂ in DSSC working electrodes that have been fabricated with longer sensitization time and higher sensitization concentration, up to a point, particularly when not subjected to solvent rinsing. We will show that the commonly adopted fabrication process of

rinsing the substrate with neat acetonitrile after sensitization affects the molecular packing, molecular orientation, and aggregation behavior of the dyes on thin films of amorphous TiO₂. Dye····TiO₂ interfacial structure metrics such as the tilt angle of the dye molecule and the extent of dye adsorption on the TiO₂ surface are deduced from these data. A predictive screening method for optimizing DSSC fabrication conditions is also afforded by these correlation mappings. Overall, empirical guidance based on the results is gathered from this molecular engineering study to help find the optimal conditions for fabricating DSSCs.



Scheme 5.1 Chemical structures of the organic dye MK-2 and the Ru-based dyes N3 and N749 ('black dye').

5.2 Methods and materials

Preparation of thin films of amorphous TiO₂. The 10-nm thick batch 3 amorphous films of TiO₂ (*cf.* Chapter 2.5 for preparation method) with atomically flat surfaces were deposited on silicon wafer substrates by atomic layer deposition (ALD).

X-ray reflectometry (XRR). XRR measurements were conducted using a Rigaku SmartLab reflectometer with a rotating anode (9 kW), a Cu-K α X- ray source (λ = 1.541 Å), and a Ge (220 × 2) monochromator. Reflectivity data were collected in increments of 0.01° for a detector range of 0.1° < 2 θ < 8°.

5.3 Results and discussion

This section begins with a description of the data acquired for establishing structureproperty relationships that relate the nature of a dye...TiO₂ interfacial structure to certain DSSC fabrication conditions which are known to influence this structure. Data are then mapped in a fashion that enables such relationships to be deduced for each of the three case studies of MK-2, N3 and N749 dyes. Relationships that are specific to a dye or appear to have generic application are distinguished. The parent mappings correlate dye sensitization time and the corresponding concentration of dye-sensitizing solution with the dye-layer thickness on TiO₂ surfaces. Separate mappings are provided for DSSC working electrodes that have been rinsed or not during their fabrication process. The use of these mappings in identifying dye self-assembly mechanisms during DSSC fabrication, tendencies for dye aggregation, and preferred binding modes for anchoring dye molecules onto the TiO_2 surface, are all showcased. The manner by which these mappings provide a predictive screening option, toward optimizing DSSC fabrication conditions, is also demonstrated. Two proxies for dyelayer thickness that pertain to DSSC-relevant parameters are also detailed. The case study concerning **MK-2** is used to show how the preferred orientation of dye molecules on TiO₂ surfaces can be used as a proxy for the dye-layer thickness in these correlation mappings to predict the average tilt angle of dye molecule with respect to a TiO₂ surface, for a given sensitization time and sensitization concentration that has either been rinsed or not. This tilt angle helps to estimate the binding mode of the (carboxylate) anchoring group that connects the dye to the TiO₂ surface^{30,119} which, in turn, affects the efficiency of the electron injection process in the DSSC and hence the J_{sc} produced that governs its photovoltaic output. The area-per-molecule (APM) concept is then described as another proxy for the dye-layer thickness for a given density of the dye layer in order to evaluate the extent of dye adsorption as a function of the targeted DSSC fabrication conditions for all three case studies.

DSSC fabrication processes and parameters for data analysis. The generic details of the DSSC fabrication process are introduced here, even though full details are given in the experimental methods section, since the results sought are specific to variations in certain aspects of the DSSC fabrication. Figure 5.1 illustrates the key steps that were undertaken to produce the DSSC working electrodes. To this end, atomically flat (thickness: 10 nm) amorphous films of TiO₂ were initially prepared on silicon substrates using atomic layer deposition (ALD). Each TiO₂ film was then sensitized by immersing the substrates into a solution of the subject dyes; MeCN:*t*-butanol:toluene (1:1:1, v/v) was used for **MK-2** (95%, Sigma Aldrich); MeCN:*t*-butanol (1:1, v/v) (Sigma Aldrich,

ACS reagent grade) was used for $N3 \cdot 2H_2O$ (95%, Solaronix) and N749 (95%, Solaronix). Dye sensitization was followed by either no rinse or a rinse with neat acetonitrile (5 s) before drying the resulting DSSC working electrode under a flow of N₂ prior to the XRR measurements³¹. XRR was used to determine variations in the dye...TiO₂ interfacial structures fabricated using different dye concentrations, sensitization times, and rinsing conditions. The sensitization and XRR measurement were performed at ambient temperature and in the presence of atmospheric moisture.



Figure 5.1 Schematic illustration of the fabrication process of DSSC working electrodes employed in this study, whereby an amorphous thin film of TiO₂ was prepared on a silicon substrate using atomic layer deposition (ALD), which was then sensitized in a dye solution before being rinsed and dried, or simply dried.

Sourcing data on dye...**TiO**₂ **interfacial structures that relate to DSSC fabrication parameters.** A total of 360 XRR plots were acquired that cover exhaustive combinations of 5 dye solution concentrations (0.01 mM, 0.05 mM, 0.25 mM, 0.5 mM, 1 mM) versus 12 dye sensitization periods (1 min, 2 min, 5 min, 10 min, 30 min, 60 min, 5 h, 10 h, 15 h, 20 h, 30 h, 40 h) for each of the three dyes, with and without rinse (see Appendix C for all 360 XRR data and fits). This plentiful source of XRR data enabled the construction of detailed 3-D isosurface and 2-D contour plots that map the correlations between dye concentration and sensitization time against the dye-layer thickness for each dye, with or without rinse.

5.3.1 Correlation mappings of sensitization time and sensitization concentration against the dye-layer thickness

Figure 5.2 shows the 3-D isosurface plots that map smoothed fits of the XRR-refined dye-layer thickness of the dye \cdots TiO₂ interfacial structures of **MK-2**, **N3**, and **N749** dyes against the varying fabrication conditions: sensitization concentration and sensitization time. Three pairs of plots are presented since the 3-D isosurfaces for each dye \cdots TiO₂ structure have either been subjected to rinsing or not.



Figure 5.2 3-D isosurface maps of the dye-layer thicknesses for dye…TiO₂ interfacial structures on silicon substrates, fabricated using different dye sensitization times and concentrations. (a) **MK-2** thickness after sensitization, followed by no rinse. (b) **MK-2** thickness after sensitization, followed by a 5s rinse. (c) **N3** thickness after sensitization, followed by no rinse. (d) **N3** thickness after sensitization, followed by a 5s rinse. (e) **N749** after sensitization, followed by no rinse. (f) **N749** after sensitization, followed by a 5s rinse. The 3D isosurface maps were generated using a logarithmic fitting along the sensitization time and then smoothed using Renka and Cline gridding methods.¹²⁰
The color range is chosen such that the thickness above that of a maximum monolayer height is shown as red, i.e., ~28 Å for MK-2, and ~ 13 Å for both **N3** and **N749**.

5.3.2 Identifying dye self-assembly mechanisms in the DSSC fabrication process

One important characteristic of these 3-D isosurface mappings is that they can identify key aspects of the dye self-assembly mechanisms, while molecular chromophores adsorb on TiO₂ surfaces during the DSSC sensitization process. All three dyes show certain common features in this regard when DSSC working electrodes were not rinsed. To that end, Figures 5.2(a), (c), and (e) reveal that the dye-layer thickness initially grows rapidly while the sensitization time, t_s , precedes $t_s = 500$ min, whereafter the rate by which the dye-layer thickness increases diminishes drastically, although the thickness continues to augment monotonically as a function of increasing sensitization time. The sensitization time appears to control the self-assembly process of the dye for $t_s < 500$ min. Beyond this timeframe, the concentration of the dye sensitizing solution appears to dominate the growth mechanism of the dye...TiO₂ interfacial structure.

Thereby, the concentration of the dye solution used for the sensitization process exhibits common traits in dye-layer thickness above this threshold sensitization time of t_s > 500 min. The 3-D isosurfaces of all three dyes not subjected to rinsing effects (Figures 5.2(a), (c) and (e)) feature a ridge at low dye solution concentrations that falls into a valley in the 0.2-0.4 mM region, the exact concentration of the valley floor naturally depends on the precise nature of the dye; this valley rises with a further increase in dye concentration to form a plateau that remains stable at high dye concentrations. In stark contrast, the cognate isosurfaces, which feature DSSC working electrodes that have been rinsed, display only very subtle valleys/ridges (Figures 5.2(b), (d) and (f)). This trend suggests that the initially sparse provision of dye molecules on the TiO₂ surface will result in a somewhat random organization of self-assembled dyes which are inefficiently distributed. As more dye molecules reach the TiO₂ surface, the sparsely distributed dye molecules are forced to reorganize themselves in order to accommodate more dye molecules on the TiO₂ surface. This reorganization seems to lead initially to a decrease of the dye-layer thickness, one interpretation of which is that the dyes that had already been bound to the TiO2 surface

are pushed down on that surface by incoming dyes that try to fit between them, once no gaps are left to fully accommodate new ones. Increasing the dye concentration further results in a rejuvenation of the dye-layer thickness, as the dye self-assembly starts to adopt a more extended and thus ordered configuration, whereby its structure grows into a more homogeneous form. Further increases in dye concentration have diminishing effects as the dye-layer thickness moves towards a constant. Indeed, the concerted 3-D isosurface mappings of both sensitization time and concentration show that a plateau in dye-layer thickness is eventually reached as these parameters increase to a certain threshold value, beyond which the dye self-assembled structure remains constant in height, irrespective of further increases in sensitization time and concentration. Figure 5.3 provides an illustrative summary of this proposed mechanism for dye self-assembly on TiO₂ surfaces, based on these XRR findings.



Figure 5.3 Proposed mechanism for the formation of a self-assembled monolayer of dyes on TiO₂ surfaces during the DSSC sensitization process. The term $<d_0>$ denominates the average initial dye-layer thickness, which increases ($\Delta d = +ve$) or decreases ($\Delta d = -ve$) at each distinct step of the dye-sensitization process.

This second rise in dye-layer thickness as a function of increasing dye concentration is likewise observed in the 3-D isosurfaces that pertain to the rinsed DSSC working electrodes that contain **MK-2** or **N3** (Figure 5.2(b) and 5.2(d)), thus corroborating the

notion that the dye self-assembly rises until it reaches a stable dye-layer thickness. The rinsed DSSC working electrode that contains **N749** (Figure 5.2(f)) presents an exception that will be explained shortly. The dye-layer thickness of DSSC working electrodes that contain **MK-2** and **N3** nonetheless rise to a significantly higher stable value when they have been rinsed: *cf.* the maximum dye-layer thicknesses for **MK-2** (33 Å and 19 Å) and **N3** (18 Å and 16 Å) for rinsed and non-rinsed DSSC working electrodes, respectively. These dye-layer thickness differences with and without rinsing are indicative of dye aggregation, which has been reported to influence the photovoltaic properties of DSSC working electrodes⁹². These specific differences are in fact indicators of the *formation* of dye aggregation in **MK-2** and a *worsening* of dye aggregation in **N3** due to rinsing effects. This conclusion is reached by considering that the maximum molecular height of **MK-2** and **N3** on TiO₂ is 28 Å⁹⁹ and 10-13 Å (depending on the dye···TiO₂ binding mode)¹⁰⁰ and the average orientation of these dye molecules with respect to the TiO₂ surface affords a lateral dye-layer thickness of ~23 Å and ~10 Å.

In other words, a self-assembled monolayer of **MK-2** molecules forms as long as the DSSC working electrode is not rinsed; while more than one layer of **N3** molecules naturally self-assemble on TiO₂ surfaces even in the absence of rinsing effects, except at $t_s < 500$ min, where the dye-layer thicknesses are less than the maximum molecular height of **N3** (~13 Å for a bidentate bridging binding mode of two of its carboxylate ions from the same carboxylatobipyridyl ligand)¹⁰⁰.

As mentioned earlier, **N749** presents an exception to these trends in **MK-2** and **N3**. Rinsing a DSSC working electrode that contains **N749** actually *reduces* its dye-layer thickness and a distinct valley, centered at 0.5 mM, appears in the 3-D isosurface of the rinsed form (Figure 5.2(f)), which is markedly higher than the trend-carrying valley that manifests in the non-rinsed case (Figure 5.2(e)). Moreover, a dye-layer thickness plateau in the 3-D isosurface is not formed at higher dye concentrations for rinsed DSSC working electrodes that contain **N749**. The maximum molecular height of **N749** on TiO₂ will be similar to that of **N3** (13 Å) since these two dyes are chemically very similar. Given that the 3-D isosurface displays a maximum dye-layer thickness of ~13 Å for rinsed **N749** dye···TiO₂ interfacial structures, compared to ~15 Å in its non-rinsed counterpart, rinsing seems to afford the self-assembled monolayers of **N749** on TiO₂ surfaces while not rinsing results in a level of lateral dye aggregation.

A rationalization for this exception is not entirely clear, although **N749** does differ from **N3** in possessing only three carboxylic acid groups, all of which are oriented toward the TiO₂ surface, thus exposing its isothiocyanate ligands at the top surface of the self-assembled monolayer; these NCS ligands are likely to ward off dye aggregation once stray, unbound, dye molecules have been rinsed off the top surface of the self-assembled monolayer. In contrast, **N3** will self-assemble onto a TiO₂ surfaces with carboxylic acids exposed on the top surface of the self-assembled dye layer; as such, **N3** molecules can dimerize via hydrogen-bonds that readily form between carboxylic acid groups. This would explain why **N3** and **N749** behave so differently despite being chemically very similar.

Overall, all three dyes evidence the same generic multi-step self-assembly mechanism, notwithstanding this exception in rinsing effects for N749. Thereby, the dye-layer thickness increases rapidly for $t_s < 500$ min, while there remains sparse provision of dye molecules on the TiO₂ surface. During this DSSC fabrication period, the sensitization time appears to control the self-assembly process. Beyond this timeframe, the concentration of the sensitizing solution appears to govern how the dye... TiO_2 interfacial structure grows. High concentrations yield, as expected, the thickest dye layers, although low concentrations also produce dye layers of substantial thickness, to the extent that low and high concentrations can produce dye layers of similar thickness for certain dyes such as MK-2. Moderate concentrations (0.2-0.4 mM; the exact value depends on the specific dye) afford a depletion in dye-layer thickness, presumably because the sparsely distributed dyes are forced to reorganize to accommodate more dyes on the TiO₂ surface. The dye-layer thickness rejuvenates when the dye concentration reaches a sufficiently high concentration, up to a point where it eventually plateaus. A concerted mapping of dye sensitization time and concentration shows that a plateau in dye-layer thickness is reached when both of these parameters exceed certain threshold values, beyond which the dye selfassembled structure remains constant in height, irrespective of any further increase in sensitization time or concentration.

One thing to bear in mind is that the same dye-layer thickness may not imply the same dye...TiO₂ interfacial structure. For example, one may anticipate that high sensitization times and concentrations could yield highly ordered, homogeneous, and tightly packed structures; while another dye...TiO₂ interface with the same dye-layer thickness could result from a more speedy fabrication process that engenders more disordered, inhomogeneous, and inefficiently packed structures.

5.3.3 Enabling 'dial up' fabrication conditions of a dye...TiO₂ interfacial structure to suit a DSSC working electrode

Figure 5.4 illustrates 2-D contour plot representations of these correlation maps. These are essentially collapsed forms of the 3-D isosurfaces. The manner by which these mappings are visually represented affords a ready 'dial up' option for creating custom $dye\cdots$ TiO₂ interfacial structures, e.g. selecting the DSSC fabrication parameters (sensitization concentration and time as well as rinsing options) on the map, which refer to a particular dye-layer thickness that corresponds to a specific binding mode of the dye on TiO₂ surfaces.



Figure 5.4 2-D contour maps of the dye-layer thicknesses for dye...TiO₂ interfacial structures on silicon substrates, fabricated using different dye sensitization times and concentrations. (a) **MK-2** thickness after sensitization, followed by no rinse. (b) **MK-2** thickness after sensitization, followed by a 5s rinse. (c) **N3** thickness after sensitization,

followed by no rinse. (d) **N3** thickness after sensitization, followed by a 5s rinse. (e) **N749** after sensitization, followed by no rinse. (f) **N749** after sensitization, followed by a 5s rinse. These 2-D contour maps were generated using a logarithmic fitting along the sensitization time and then smoothed using Renka and Cline gridding methods¹²⁰.

The nature of these correlation maps also offers a means by which one can predict the optimal fabrication conditions for a DSSC working electrode, e.g. DSSC fabrication conditions may be optimized for photovoltaic device output by tailoring the dye-layer thickness of a dye...TiO₂ interfacial structure so that it averts deleterious dyeaggregation effects, by selecting a set of sensitization time and concentration parameters as well as rinsing conditions from this type of map that ensures that a selfassembled monolayer of dye molecules will form on the DSSC working electrode. More efficient DSSC fabrication conditions can also be targeted by exploiting sensitization time and concentration correlations against the dye-layer thickness. For example, Figure 5.4(c) shows that the N3 dye \cdots TiO₂ interfacial structures can be fabricated with similar dye-layer thickness values by employing either a high sensitization concentration (0.6 mM) with a short (400 min) sensitization time, or a moderate solution sensitization concentration (0.3 mM) with a long (2400 min) sensitization time. Such efficiency may be especially important when manufacturing DSSCs that contain very expensive dyes, where low sensitization concentrations and high sensitization times would be the preferable). Alternatively, short sensitization times may be required when a batch of DSSCs needs to be fabricated rapidly, e.g., considering the time-efficiency needs of an industrial DSSC-production factory setting.

The 3-D isosurfaces and 2-D contour maps presented in this study can also be used to determine physically important dye \cdots TiO₂ interfacial structural features that can be derived from the dye-layer thickness. Two structural features are particularly noteworthy given that they govern the DSSC photovoltaic output through the nature of the dye \cdots TiO₂ binding mode and the extent of dye adsorption: the preferred orientation of the dye molecules on the TiO₂ surfaces and the area-per-molecule (APM) footprint that dyes cast on the TiO₂ surface, respectively. These can each be presented as proxies for the dye-layer thickness in the ways showcased in the next two sections.

5.3.4 Mapping preferred orientations of dye molecules on a TiO₂ surface in dye…TiO₂ interfacial structures as a function of DSSC fabrication conditions

Owing to the relatively rigid and well understood anchoring of **MK-2** onto TiO₂ surfaces^{99,121}, the dye-layer thickness of **MK-2** was used as a case study to show how the orientation of a dye molecule on a TiO₂ surface can be determined and thence mapped as a function of the DSSC fabrication conditions. Specifically, the sensitization time and concentration under non-rinsing DSSC fabrication conditions is mapped. Non-rinsing conditions were chosen since a determination of the preferred molecular orientation of a dye on a TiO₂ surface presumes a dye monolayer; this presumption seems valid for non-rinsed **MK-2** molecules, judging from the XRR results which show that the **MK-2** dye...TiO₂ thickness values do not exceed the maximum molecular height of **MK-2** on TiO₂; this contrasts with rinsed **MK-2**...TiO₂ interfaces for which XRR results suggest **MK-2** aggregates.

Figure 5.5 describes this process through a sequence of images that begins with an illustration of how this preferred orientation of dye molecules is trigonometrically defined by a tilt angle of the maximum molecular height of the dye with respect to a TiO₂ surface, α . Figure 5.5(a) shows that this angle is determined by two parameters, d_{obs} and d_{max}. As we have seen already, the dye-layer thickness, d_{obs}, can be obtained from XRR measurements. The maximum molecular height of the dye on TiO₂, d_{max}, is determined by the sum of (i) the average COO⁻⁻⁻⁻TiO₂ bond length (2.05 Å)⁹⁹ that is associated with the **MK-2**·--TiO₂ separation, and (ii) the distance between the atom (O⁻) in the anchoring group of the dye that is closest to the TiO₂ surface, which was obtained from the crystal structure of **MK-2**¹²¹. Figure 5.5(b) illustrates this maximum molecular height (d_{max} = 27.58 Å) for a bidentate-bridging binding mode of **MK-2** on thin films of TiO₂⁹⁹.



Figure 5.5 Illustration of the preferred molecular orientation of **MK-2** on a TiO₂ surface under varying sensitization conditions, followed by no rinse. This is characterized by (a) the tilt angle of a dye on a TiO₂ surface, α , which is defined by the maximum molecular height of dye on TiO₂, d_{max} (obtained from the crystal structure of a dye) and the dye-layer thickness (d_{obs}), which is obtained from XRR measurements; (b) the maximum molecular height ($d_{max} = 27.58$ Å) and a bidentate-bridging mode of **MK-2** on thin films of TiO₂; (c,d) 2-D slices of a tilt angle proxy for the 3-D isosurface given in Figure 5.2(a), which track sensitization time at certain sensitization concentrations and vice versa, respectively; (e,f) 3-D isosurface mappings of the dye tilt angle as a function of sensitization time and concentration, annotated with elliptical representations of the dye molecules (green) at different tilt angles according to a variation of (e) the sensitization times at a fixed sensitization concentration (0.01 mM), and (f) sensitization concentration at a fixed sensitization time (1min).

Figures 5.5(c)-(f) refer to the use of this tilt angle as a proxy for the dye-layer thickness, in order to facilitate an understanding of how DSSC fabrication conditions influence the preferred molecular orientation of dyes on TiO₂ surfaces. Figure 5.5(c) presents a 2-D body-diagonal slice of the tilt-angle proxy form of the aforementioned 3-D isosurface for **MK-2**. This demonstrates that the tilt angle of **MK-2** molecules tends to an upper bound of ~45° as sensitization concentrations reach 0.5 - 1 mM for t_s > ~40 h (2400

min). Figure 5.5(d) presents a complementary 2-D slice that tracks sensitization concentrations for selected sensitization times. Its largest peak (purple profile) reveals how this maximum tilt angle of MK-2 can also be achieved at a much lower sensitization concentration (0.1 mM), using the same sensitization time. Moreover, Figure 5.5(d) tracks how this peak diminishes upon reducing dye sensitization time, such that maximum dye tilt angles for $t_s < 10$ h necessitate higher sensitization concentrations, and even then reach smaller maximum tilt angles than are possible for t_s = 40 h. Figure 5.5(d) also highlights a manifestation of the aforementioned observation that pertains to the dye self-assembly mechanism, in that the tilt angle of **MK-2** does not increase monotonously with increasing sensitization concentration. Instead, after an initial rise in dye tilt angle at low sensitization concentrations, the tilt angle tends to decrease with increasing sensitization concentrations until ~0.4 mM is reached, when it begins to rise again steadily. Overall, the MK-2 molecules tend to adopt a tilt angle between 23° and 45° under various dye sensitization conditions, when the DSSC working electrodes so formed are not subjected to rinsing. In general, these trends suggest that dye adsorption onto TiO₂ surfaces is an intermediate, rather than ultrafast, process and that it spans the time order of hours.

The tilt angle of the **MK-2** molecules was not tracked in the same way for the DSSC fabrication conditions that involved rinsing, since d_{max} for **MK-2** is exceeded at higher sensitization times and concentrations, i.e., some extent of lateral dye aggregation must occur under such DSSC fabrication conditions. The concept of a dye tilt angle is rendered moot where dye aggregation is significant, given its definition presumes only one dye molecule stems upwards from the TiO₂ surface.

5.3.5 Mapping the projected area per molecule that a dye casts on a TiO₂ surface in dye…TiO₂ interfacial structures as a function of the DSSC fabrication conditions

The second structural feature of a dye \cdots TiO₂ interface that can be useful as a proxy for the dye-layer thickness is the projected area per molecule (APM) that a dye casts onto a TiO₂ surface. This dye "footprint" on a TiO₂ surface effectively affords a measure of the extent of dye adsorption at the dye \cdots TiO₂ interface. This structural feature is important since higher levels of dye adsorption result in increased generation of electron charges, which is beneficial for the photovoltaic output.

The average projected APM on TiO₂ surface can be expressed as:

$$APM = \frac{r_e Z}{d_{obs}(SLD)}$$
(5.1)

where r_e refers to the classical electron radius (2.82×10^{-15} m), Z is the sum of atomic number, d_{obs} is the dye-layer thickness obtained from XRR model refinements, and SLD is the scattering-length density of the dye layer, which is another refinable model parameter in the analysis of XRR data. Lower APM values indicate a higher extent of dye adsorption mass and vice versa.

Figure 5.6 (a) shows an APM-proxy form of the 3-D isosurface plot for **MK-2** with no rinsing. The APM of **MK-2** exhibits minima for sensitization concentrations of 0.1 mM, pending that $t_s > 500$ s. Such minima indicate maxima for the extent of dye adsorption. As the sensitization concentration increases to ~0.3 mM, the aforementioned valley in dye-layer thickness manifests as an APM ridge, whose maximum indicates the lowest amount of dye adsorption, i.e., DSSC fabrication conditions associated with this APM-ridge region are highly unfavorable.





Figure 5.6 APM-proxy forms of the 3-D isosurface and 2-D contour plots that map the variation in dye…TiO₂ interfacial structures as a function of dye sensitization times and concentrations for (a,b) **MK-2**, (c,d) **N3**, (e,f) **N749**, whereby DSSC fabrication conditions did not include rinsing in comparison to (g,h) **MK-2**, (i,j) **N3**, (k,l) **N749**, whereby DSSC fabrication conditions include 5s rinsing.

Figures 5.6(c), (d), (i), and (j) demonstrate that the largest amount of dye adsorption (lowest APM) for **N3** is achieved at the highest sensitization time (t_s = 2400 min/40 hr) and the highest concentration (1 mM), i.e., these DSSC fabrication conditions can be regarded as the optimal for the sensitization of TiO₂ with **N3**. The APM-proxy form of the 2-D contour map for **N3** (Figure 5.6(d) and (j)) demonstrates that a similar APM can be achieved via a trade-off between the sensitization concentration and time under most fabrication conditions, i.e., lower sensitization concentrations with higher sensitization times yield results similar to those obtained from higher sensitization concentrations with lower sensitization times.

Figures 5.6(e) and 5.6(f) show that the highest amount of dye adsorption (lowest APM) is achieved for **N749** at the highest sensitization concentration (1 mM) when subjected to no rinse; its APM values are relatively insensitive to the sensitization time. The similar trend of variation for APM is also observed for **MK-2** when subjected to 5s rinse as shown in Figure 5.6(g) and 6(h). In stark contrast, Figures 5.6(e), (f), (k), and (I) show that the lowest amount of dye adsorption (highest APM) is achieved at a

sensitization concentration of ~0.1 mM, and that this variation is equally independent of the sensitization time. This sensitization concentration should thus be avoided during the DSSC fabrication process of **N749**.

5.4 Conclusions

High-throughput X-ray reflectometry has been used to determine the dye-layer thickness of **MK-2**, **N3**, and **N749** on thin films of amorphous TiO₂ obtained from systematically varying DSSC fabrication conditions (sensitization time and concentration as well as rinsing effects). The results revealed that the self-assembly of the dyes is a multi-step process, whose characteristics may be generic given that they are common to the three dyes studied, which include organic and organometallic chromophores, have different numbers of anchoring groups, and present disparate tendencies towards dye aggregation. Results also demonstrate that rinsing DSSC working electrodes as part of the fabrication process seems to promote dye aggregation in the case of **MK-2** and **N3**, while **N749** presents an exception.

2-D and 3-D correlation mappings of these fabrication conditions against the dye-layer thickness provide a means by which a DSSC device manufacturer can 'dial up' the DSSC fabrication conditions that are needed to produce a working electrode with a specific dye-layer thickness. Alternatively, the DSSC manufacturer may use these correlation mappings to produce DSSC devices that possess a given dye-layer thickness in the most time- or cost-efficient means. One caveat worth noting is that two DSSC devices with the same dye-layer thickness do not necessarily exhibit the same dye···TiO₂ interfacial structure; higher sensitization times and concentrations may well yield more ordered, homogeneous, and tightly-packed structures compared to those forged from a speedy fabrication process, which may afford a dye...TiO₂ interface that features a more disordered, inhomogeneous and inefficiently packed structure. Several proxy forms of the dye-layer thickness have also been derived in order to evaluate tilt angles associated with the molecular orientation of dyes on a TiO₂ surface or deduce the extent of dye adsorption on a TiO₂ surface as fashioned by an area-permolecule metric. Overall, these mappings provide a predictive screening of DSSC fabrication conditions for these three dyes, which may be extendable given that certain characteristics of these mappings appear somewhat generic. The associated

relationships between the dye…TiO₂ interfacial structure and DSSC fabrication conditions established through this study begin to overcome the stark lack of a systematic means by which DSSC device optimization can be tailored. Once armed with a sufficiently wide knowledge base of dye…TiO₂ interfacial structure-fabrication relationships, the molecular engineering of DSSC devices may become possible, whereby fabrication conditions can be optimized to suit a given solar-cell application.

6. Examining the structure and solvent ingression effect at the dye…TiO₂ Interface in an emulation DSSC for MK-2, N3, and N749 using a combination of *in-situ* neutron reflectometry and *ex-situ* X-ray reflectometry

6.1 Introduction

As the working electrode of dye-sensitized solar cells (DSSCs) consists of dye molecules adsorbed onto semiconducting nanoparticles (usually TiO₂), a reliable prediction of the DSSC performance of a given dye requires in-depth knowledge about the precise structure of the dye \cdots TiO₂ interface, as well as of the correlation between the dye structure and the photovoltaic properties. In particular, the electron-injection and -recombination kinetics that affect the function of a DSSC device depend on the dye...TiO₂ interfacial structure, especially the preferred molecular orientation and the binding modes of the dye on the TiO₂ substrate. Recently, the structure of the buried dye--TiO₂ interface in the DSSC, where it serves as the working electrode, has been determined using *in-situ* neutron reflectometry (NR)⁹⁹. In this case study, *in-situ* NR was employed to probe the dye...TiO₂ interface once buried in an emulation DSSC device, and the results were complemented with structural information from ex-situ Xray reflectometry (XRR) and roughness metrology measurements. The thus obtained data allowed determining the dye-layer thickness and molecular binding modes of the high-performance metal-free organic sensitizer **MK-2** as well as the Ru-based dyes **N3** and **N749** ('black dye') relative to the TiO₂ surface. Moreover, the results provided an initial insight into the solvent ingression behavior within an emulation DSSC device under dark conditions and illumination with white light.

6.2 Methods and materials

Given that the working electrode of the DSSC is a buried interface within the DSSC device, neutron reflectometry (NR) should be particularly useful in this context due to its penetrative characteristics. Moreover, NR is able to discriminate signals that arise from the dye or the TiO₂ surface, due to sufficient contrast in scattering length density (SLD) of the individual DSSC layers.

Herein, we report the results obtained from *in-situ* NR measurements on the highperformance DSSC dye **MK-2**, molecules of which were adsorbed onto atomically flat, amorphous TiO₂ that were fabricated by atomic layer deposition (ALD). In particular, refinements of the NR data yielded the dye-layer thickness, the tilt angle of **MK-2** relative to the TiO₂ surface, and initial insights into the solvent ingress behavior within an emulation DSSC device under dark conditions and under illumination with white LED light. The chemical structures of **MK-2**, **N3**, and **N749** are shown in Scheme 6.1.



Scheme 6.1 Chemical structures of the organic dye MK-2 and the Ru-based dyes N749 ('black dye') and N3.

Preparation and sensitization of thin films of TiO₂. The 11-nm thick batch 2 TiO₂ films (*cf.* Chapter 2.5 for preparation method) were sensitized by immersion of the substrates into dye solutions, followed by washing with pure solvent. Prior to dye sensitization, the substrates were dried in a stoving cabinet for a minimum of 30 minutes in order to remove any residual surface water. The TiO₂ films were sensitized for 20 h with 0.3 mM solutions of **MK-2** (95%, Sigma Aldrich) in MeCN:*t*-butanol:toluene (1:1:1, v/v) (Sigma-Aldrich, 99.5% ACS reagent grade), **N3**·2H₂O (95%, Solaronix) in MeCN:*t*-butanol (1:1, v/v), or **N749** (95%, Solaronix) in MeCN:*t*-butanol (1:1, v/v). The resulting films were rinsed with neat MeCN and dried under a flow of N₂ prior to being subjected to NR measurements³¹.

Preparation of counter-electrodes. FTO glass counter-electrodes were prepared by drop-casting a 5 mM solution of chloroplatinic acid hydrate (99.995%, Sigma-Aldrich) in isopropanol (ACS reagent grade, Sigma-Aldrich) onto clean FTO glass slides (TEC 8, Sigma-Aldrich, $60 \times 60 \times 3.2$ mm³) prior to heating to 390 °C for 15 minutes.

X-ray Reflectometry (XRR). XRR measurements were conducted using a Rigaku SmartLab reflectometer with a 9 kW rotating anode with a Cu-K α X- ray source (λ =

1.541 Å) and a Ge (220 × 2) monochromator. Reflectivity data were collected in increments of 0.01° for a detector range of 0.1° < 2 θ < 8°.

Neutron reflectometry (NR). *In-situ* NR measurements were conducted using the OFFSpec reflectometer at the ISIS neutron facility, UK. With a primary flight path of 23.7 m from the grooved solid methane moderator, the instrument is equipped with a linear, position-sensitive detector (sample-detector distance: 3.6 m) and a single, well shielded ³He gas detector (sample-detector distance: 3.2m), which affords a constant angular and wavelength resolution of dQ/Q = 2%. Beam profiles were collected at the sample angle $\varphi = 0.3^{\circ}$, 0.75°, and 2°.

Measurements in the dark were conducted on thin films of amorphous TiO₂ thin film sensitized with **MK-2**, **N3**, or **N749**. Other measurements were carried out on **MK-2**-sensitized thin films of TiO₂ under illumination with white light. Emulation solar cells under open-circuit conditions were illuminated using THORLABS LEDD1B high power LEDs operating at a current of 1200 mA. The reduced data were refined in GenX⁹³, which uses the differential evolutional algorithm to perform robust optimization and avoid local minima. The reflectivity was plotted as a function of the momentum transfer vector (*Q*) perpendicular to the TiO₂ surface.

$$Q = \frac{4\pi \sin \theta}{\lambda} \tag{6.1}$$

wherein θ is the incident angle and λ is the wavelength of the neutrons. The schematic diagram of the sample measurement geometry is shown in the Appendix D. The substrates are two-inch *n*-type silicon (100) wafers with a thickness \geq 5 mm, which ensures an uninterrupted beam transmission and avoids excessive attenuation of the neutron beam. Deuterated acetonitrile (d₃-MeCN) was used to enhance contrast at the dye--electrolyte interface.

6.3 Results and discussion

6.3.1 Dye-..TiO₂ interfacial structure and dye volume fraction revealed by *ex-situ* XRR

Ex-situ reflectivity measurements on silicon wafers in an air-solid environment under X-ray irradiation with ambient light were conducted, and the corresponding reflectivity SLD profiles are shown in Figure 6.2. Data were collected in increments of 0.01° for a detector range of $0.1^{\circ} < 2\theta < 8^{\circ}$. Nominal values for the X-ray SLD of each layer were used to construct initial structural models using a three-layer approach. For the substrates, SLD values of 20.1×10^{-6} , 18.9×10^{-6} , and 31.2×10^{-6} Å⁻² were set for the silicon wafer, the native oxide layer, and the TiO₂ layer, respectively, while the SLD and thickness values of the dye layers were free to vary in the fits. The thickness of the native oxide layer was set to 5 Å^{31,94–96}, and the thickness of TiO₂ was refined to ~110 Å for all three dyes. The roughness values of the silicon and native oxide layer were set to 1 Å, while those of the dye and TiO₂ layers were free to vary in the fits. The fits. The reflectivity data and fitting profiles are shown in Figure 6.1.



Figure 6.1 *Ex-situ* XRR data and corresponding SLD profiles (inset) for **MK-2**, **N3**, and **N749** on thin films of amorphous TiO₂.

Table 6.1 Structural data with errors for **MK-2**, **N3**, and **N749** on thin films of amorphous TiO₂, determined by XRR reflectometry model simulations using GenX.

Dyes	Thickness (Å)	Density (10 ⁻⁴ unit/Å ³)	Surface roughness (Å)	Dye volume fraction $\varphi(\%)$	FOM logR1
MK-2	18.9	5.74	4.8	73.4	0.01755
Errors	(-0.5,0.6)	(-0.17, 0.16)	(-0.51,0.55)	(-2.2,2.0)	NA
N3	25.9	8.58	12.0	54.6	0.01808
Errors	(-0.8,1.3)	(-0.80, 0.75)	(-0.93,1.15)	(-5.1,4.8)	NA
N749	16.8	4.76	3.7	85.3%	0.01699
Errors	(-0.3,0.3)	(-0.27, 0.19)	(-0.42,0.47)	(-4.8,3.4)	NA

The errors are calculated based on a (default) 5% increase in the optimal figure of merit (FOM) (total logarithmic difference between the simulation and measurement).

The 'unit' in the table is defined as a dye molecule. The X-ray scattering length density (SLD) of each dye layer can be derived by multiplying the fitted density of each dye layer with the total X-ray scattering length of a dye molecule (**MK-2**: 1450 fm; **N3**: 1003 fm; **N749**: 2075 fm).

6.3.2 Dye-..TiO₂ interfacial structure, dye volume fraction and solvent ingression revealed by *in-situ* NR supported by *ex-situ* XRR results

Nominal values for the neutron SLD of each layer were used to construct initial structural models using a three-layer approach. For the substrates, values of 2.07 × 10^{-6} , 3.48×10^{-6} , and 2.39×10^{-6} Å⁻² were used for the silicon wafer, the native oxide layer, and the TiO₂ layer, respectively. The SLD values of the native oxide and the TiO₂ layers were free to vary in the fits but the fitting results suggest they are close to the initially set nominal values. The thickness of the native oxide layer was set to 5 Å. The SLD of subphase solvent (d₃-MeCN) was set to 4.92×10^{-6} Å⁻². The SLD and thickness values of dyes were free to vary in the fits, and all the interfacial roughness values were free to vary and they tend to be small (1-2 Å) except those for the dye...solvent interfaces. The *in-situ* reflectivity data and fitting profiles for **MK-2** in the dark and under illumination are shown in Figure 6.2, while the fitting results are summarized in Table 6.2.



Figure 6.2 *In-situ* NR profile with simulation error bars and corresponding SLD profile (inset) for **MK-2** on thin films of amorphous TiO₂ under dark and LED illumination conditions.

Table 6.2 Structural data for **MK-2** on amorphous thin films of TiO₂ in the dark and under illumination with white light (LED), determined by an NR reflectometry model simulation using GenX.

MK-2	Thickness (Å)	Fitting error (Å)	Density (10 ⁻⁴ unit/Å ³)	Fitting error (10 ⁻⁵ unit/Å ³)	SLD (10 ⁻⁶ Å ⁻²)	Roughness (Å) (TiO ₂ MK-2 interface)	Roughness (Å) (solvent··· MK-2 interface)	FOM (logbars)
Dark	25.2	(-1.1, 1.0)	7.50	(-7.0, 14.8)	1.24	1.00	9.8	1.92
LED illumination	27.5	(-0.9, 1.2)	8.77	(-6.6, 10.2)	1.45	1.00	9.5	2.34

The 'unit' in the table is defined as a dye molecule. The neutron SLD of each dye layer can be derived by multiplying the fitted density of each dye layer with the total neutron scattering length of a dye molecule (**MK-2**: 165.5 fm; **N3**: 228.3 fm; **N749**: 155.6 fm; TiO₂: 8.2 fm).

The simulation of the NR measurements afforded relatively small roughness values (~1 Å) for TiO₂ (Table 6.2). These results are consistent with those of roughness metrology measurements (D3 in Appendix D), which showed a relatively homogenous surface structure of TiO₂ and the native silicon oxide (roughness < 2 Å). However, it should also be noted that the surface area used for the roughness metrology measurements ($0.12 \times 0.1 \text{ mm}^2$) is relatively small compared to that of the neutron-illuminated area ($25 \times 31.2 \text{ mm}^2$). Therefore, the results of the roughness metrology measurements should reflect the microstructure of the surface, while the simulated NR roughness depicts the roughness on a larger scale. Moreover, it is noticed that although the dye/solvent interfacial roughness is smaller than half of the dye layer thickness, it is still much larger that of TiO₂/dye interface, indicating the dye/solvent interfacial structure is quite rough.

Figure 6.3 illustrates the preferred bidentate-bridging coordination mode of **MK-2** on the TiO₂ surface. The associated dye···TiO₂ separation is considered as the average COO⁻···TiO₂ bond length (2.05 Å)⁹⁹. Given the dimension of **MK-2** (*vide infra*), the maximum possible dye-layer thickness d_{max} for a monolayer of **MK-2** is 28.28 Å (NR) and 27.58 Å (XRR).



Figure 6.3 Schematic illustration of the dimension and the preferred binding mode of **MK-2** on thin films of TiO₂. Values in parentheses are those used for XRR studies as the explicit position and bond lengths of hydrogen atoms are excluded⁹⁹.

Thickness values for monolayers of **MK-2** on thin films of amorphous TiO₂ of 25.2 Å (in the dark), 27.5 Å (under illumination with white LED light), and 18.9 Å (air-solid environment; ambient light) were obtained. The corresponding calculated tilt angles for each condition were calculated as shown in Figure 6.4. Since neutrons are able to detect the top hydrogen atoms in the **MK-2** layer, it is worth noting that the NR equivalent of the XRR thickness of the **MK-2** layer would be counted as d = 28.28*sin (43.4°) = 19.43 Å, based on the tilt angle of 43.4° relative to the TiO₂ surface and the *d_{max}* of **MK-2** for NR studies.



Figure 6.4 Calculated **MK-2** tilt angles in an emulation DSSC cell (red, NR) and at the air-solid environment (black, XRR).

As neutrons are able to detect hydrogen atoms with much higher precision than X-rays, the slightly higher d_{max} value obtained from the *in-situ* NR analysis was used, which incorporates the explicit position and bond lengths of hydrogen atoms, whose presence may be discounted during the *ex-situ* XRR analysis.

The simulated dye-layer thickness for **MK-2** at the air-solid interface is significantly smaller than that measured in the emulation DSSC, which indicates that the solvent has a strong influence on the tilt angle and the molecular packing mode of **MK-2** on TiO₂. The *in-situ* NR analysis also revealed a likely change of the tilt angle and an increase of solvent ingression at the **MK-2**...TiO₂ interface under illumination. The factors that hypothetically cause the change in dye thickness include the interaction of light-induced charges, the perturbation of the electronic-structure configuration of the

dye, and the modulation of the binding mode of the dye molecules. The possibility of illumination-induced heat effects should be further assessed, if they caused the solvent to simply evaporate, which would most likely lead to an increase of the solvent ingress at the dye...TiO₂ interface. As

$$SLD_{obs} = SLD_{dye} \cdot \varphi_{dye} + SLD_{svt} \cdot \varphi_{svt},$$
 (6.2)

the solvent volume fraction at the dye...TiO₂ interface, φ_{svt} , was assessed, wherein φ_{dye} refers to the dye volume fraction, which was obtained from the XRR and NR results, while SLD_{obs} is the NR-simulated SLD of the dye, SLD_{dye} the theoretical SLD of dye layer of nominal density, and SLD_{svt} the calculated SLD of d₃-MeCN. It should be noted here that we might have to consider an inaccuracy of the theoretical SLD itself, or an inaccuracy of using theoretical SLD values of the dyes to describe the SLD of a fully surface-covered dye layer, as the solvent ingression at the dye...TiO₂ interface might stop at the full dye coverage when the packing density of dye molecules is different from the nominal dye density value depending on the self-assembled dye layer structure. This equation is therefore not confined to $\varphi_{dye} + \varphi_{svt} = 1$ here, as φ_{dye} might deviate from its real value; however, φ_{svt} is calculated based on the known SLD_{svt} and therefore accurate. It is also important to note that the φ_{dye} in the solvent is calculated based on the results from XRR and NR, assuming the dye only changes its orientation upon submerging in the solvent, thus ignoring any desorption of dye molecules in the solvent environment.

The change of the dye-layer thickness, which results from the change of the dye orientation, should also lead to a change of the density and SLD values of the layer, according to

$$SLD \propto density = \frac{m_{layer}}{v_{layer}} = \frac{m_{layer}}{d \cdot S},$$
 (6.3)

wherein *d* and *S* are the thickness and surface area values of the dye layer, respectively.

Based on the XRR-fitted density values, the surface coverage of the **MK-2** dye layer is calculated as $\varphi_{MK-2,xrr}$ = 73.4%. The change of the orientation does not lead to a change of the layer mass and the surface area, i.e., the product SLD·d should remain constant, while the tilt angle changes. Hence, changes of the solvent volume fraction,

 φ_{svt} , at the dye...TiO₂ interface as a function of the tilt angle between dark and LEDillumination conditions (Table 6.1) were determined based on eqs. 6.3 and 6.2, in which the thickness value obtained from XRR is converted into its NR equivalent. The results show that the solvent ingression increases at the dye...TiO₂ interface, when the **MK-2** molecules stand more upright on TiO₂. Apparently, the increase of the dye-layer thickness induces a reduction of the φ_{dye} , which is likely to increase the vacant space for solvent ingression on TiO₂ and thus increases φ_{svt} at the dye...TiO₂ interface. However, if the fitted change of the dye orientation is an artifact, it is still possible that the increase of φ_{svt} at the dye...TiO₂ interface is caused by the light-induced heat, which may enhance the solubility of solvent.

Moreover, when assuming that φ_{svt} is accurate, and that the TiO₂ surface is either covered with dye or solvent molecules, i.e., $\varphi_{dye} + \varphi_{svt} = 1$, then φ_{dye} in the dark and under LED illumination should be calculated as 89.7% and 84.1%, respectively. The lower-than-expected fitted φ_{dye} means the real SLD_{dye}, assuming 100% surface coverage of **MK-2** in acetonitrile, should be lower than the theoretical SLD of a dye layer of nominal density.

Table 6.1 NR-fitted φ_{dye} and φ_{svt} at the dye...TiO₂ interface for **MK-2** in the dark and under LED illumination in acetonitrile.

МК-2	Dye volume fraction φ_{dye} derived from equation 6.3 (%)	Error (%)	Solvent volume fraction φ_{svt} derived from equation 6.2 (%)	Error (%)
In the dark	56.7	(-1.6,1.4)	10.3	(-0.4,0.4)
Under LED illumination	51.8	(-1.7,1.5)	15.9	(-0.4,0.4)



Figure 6.5 *In-situ* NR profile with simulation error bars and corresponding SLD profile (inset) for **N3** and **N749** on thin films of amorphous TiO₂ in the dark.

Table 6.2 Structural data for N3 and N749 on thin films of amorphous TiO_2 in the dark, determined by an NR reflectometry model simulation using GenX.

	Thickness	Fitting error	Density	Fitting error	SLD	Roughness (Å)	Roughness (Å)	FOM
Dye	(Å)	(Å)	(10 ⁻³ unit/Å ³)	(10 ⁻⁴ unit/Å ³)	(10 ⁻⁶ Å ⁻²)	(TiO₂⊷dye interface)	(solventdye interface)	(logbars)
N3	26.9	(-1.2, 1.2)	1.79	(-1.06, 1.65)	4.09	1.5	11.0	1.12
N749	12.9	(-1.2, 1.3)	0.82	(-1.27, 0.36)	1.27	1.7	5.2	1.04

Figure 6.5 shows the *in-situ* NR data and fitting profiles for **N3** and **N749** in the dark, while the fitting results are summarized in Table 6.2. A comparison of the ex-situ and *in-situ* structural data for **N3** and **N749** on thin films of amorphous TiO₂ (Table 6.3) shows an obvious difference of dye-layer thickness for N749 while the thickness of N3 exhibits little variation, which suggests that the orientation of molecules of N749 on TiO_2 is more vulnerable to the influence of the solvent than that of molecules of N3, probably because N3 contains more carboxylate anchors that could potentially adopt more than one stable (bidentate or tridentate) coordination modes and prevent itself from thickness change. Both the ex-situ and in-situ fitted thickness values of N3 suggest the formation of stacked structures on the TiO₂, given the monolayer thickness of N3 on the TiO₂ surface is 10-13 Å, depending on the dye...TiO₂ binding mode¹⁰⁰. The dye/solvent interfacial roughness for N3 is 11.0 Å while the dye/solvent interfacial roughness for N749 is 5.2 Å. This indicates the dye/solvent interface of N3 is rougher than that of N749, probably due to the higher extent of stacking of dye molecules. It is also worth noting that the thickness of N749 revealed by ex-situ XRR is slightly higher than the maximum height of the N749 molecule⁶⁴, indicating that N749 dye molecules also form some sort of stacked structures on TiO₂. However, the lower thickness of N749 obtained from *in-situ* NR suggests this stacked structure may reorganize itself by promoting its anchoring on TiO₂ in the solvent environment to an extent that its thickness is less than that of a monolayer.

Table 6.3 Comparison of the structural parameters for **N3** and **N749** on thin films of amorphous TiO₂ determined by *in-situ* NR and *ex-situ* XRR model simulations using GenX.

	Dye	Thickness (Å)	Error (Å)	Density (10 ⁻⁴ unit/ų)	Error (10 ⁻⁴ unit/Å ³)
<i>In-situ</i> NR	N3	26.9	(-1.2,1.2)	17.93	(-1.06,1.65)
	N749	12.9	(-1.2,1.3)	8.18	(-1.27,0.36)
<i>Ex-situ</i> XRR	N3	25.9	(-0.8,1.3)	8.58	(-0.80,0.75)
	N749	16.8	(-0.3,0.3)	4.76	(-0.27,0.19)

Table 6.4 shows the calculated dye and solvent volume fractions for **N3** and **N749** in acetonitrile based on the structural parameters shown in Table 6.3, using eqs. 6.2 and

6.3. The dye volume fractions revealed by XRR are $\varphi_{N3,xrr}$ = 54.6% and $\varphi_{N749,xrr}$ = 85.3%. Due to the geometry of **N3** and **N749** on TiO₂^{64,100}, the NR equivalent of the XRR-fitted thickness are considered identical to the XRR-fitted thickness, as the top atoms in the dye layer are not hydrogens atoms and would thus cause little discrepancy in thickness obtained from NR or XRR. However, as the tetrabutylammonium cation (TBA⁺) in **N749** are likely to be dissociated from the dye layer in the acetonitrile, the calculation of the dye coverage in solvent environment using equation 6.3 would not be appropriate considering that counterintuitively, the φ_{dye} would be larger than 1, as the product of SLD·d would not remain constant when TBA⁺ cations are removed from the dye layer.

Table 6.4 NR-fitted dye and solvent volume fractions at the dye...TiO₂ interface for **N3** in the dark in acetonitrile.

Dye	Dye volume fraction $\varphi_{dye}(\%)$	Error (%)	Solvent volume fraction φ_{svt} (%)	Error (%)
N3	52.5	(-4.9,4.6)	44.9	(-3.3,3.6)
N749	111.34	(-6.3,4.4)	1.9	(-1.0,1.5)

Table 6.4 shows that **N3** exhibits a much higher solvent volume fraction than **MK-2** and **N749**, which suggests that molecules of **N3** are loosely packed on TiO₂ so that numerous vacant sites are available for solvent ingression. Although the formation of such stacked structures of **N3** on TiO₂ has not yet been confirmed experimentally, one of the reasons for why we suspect such stacking is the fact that each molecule of **N3** contains two molecules of crystal water, which may prohibit its adsorption on TiO₂ during the sensitization. Conversely, the much lower φ_{svt} in the **N749** layer in acetonitrile compared to those of **MK-2** and **N3** indicates a more compact molecular packing that is relatively resistant to solvent ingression. It is also worth noting here that the sum of φ_{dye} and φ_{svt} is close to 1 for **N3**, which means the true SLD_{dye} assuming 100% surface coverage of the stacked structures for the **N3** dye layer in acetonitrile is close to the theoretical SLD of the dye layer of nominal density.

Moreover, the area per molecule (APM) for each dye was calculated using eq 2.44. Table 6.5 shows the structural parameters for all three dyes by fitting the *ex-situ* XRR data. The calculated APM of **N749** is much higher than that of **N3** (Table 6.5). As the

molecular structure of **N749** is similar to that of **N3**, this difference in APM may arise from the large intermolecular area occupied by the TBA⁺ cations in the **N749** dye layers. Given the high APM of **N749** and the potential mobility of the TBA⁺ cation in the solvent environment, we assume that the solvent ingression would be significant when TBA⁺ cations are mobilized and removed from the **N749** dye layer. However, the stacked structures of **N749** in this study exhibit very low levels of solvent ingression, suggesting that either the number of TBA⁺ cations leaving the layer is low or that the stacked structures block the mobilization of the TBA⁺ cations.

Dyes	Thickness (Å)	Error (Å)	SLD (10 ⁻⁶ Å ⁻²) Error (10 ⁻⁶ Å ⁻²)	APM (Å ²)
MK-2	18.9	(-0.5,0.6)	8.32	(-0.25,0.23)	91.58
N3	25.9	(-0.8,1.3)	8.60	(-0.80,0.75)	44.83
N749	16.8	(-0.3,0.3)	9.88	(-0.56,0.39)	101.52

 Table 6.5 X-ray SLD and APM of MK-2, N3, and N749 at air-solid interface.

6.4 Conclusions

In-situ NR measurements indicated a change of the orientation of **MK-2** and the solvent volume fraction at the dye \cdots TiO₂ interface in an emulation DSSC device in the dark and under illumination with white LED light. Although the thickness change of **MK-2** in the dark and under illumination is not significant and may be an artifact, the results suggest a correlation between the change of dye orientation and the solvent ingression at the solid-liquid interface. In addition, a combined *in-situ* NR and *ex-situ* XRR analysis suggested a different orientation for **MK-2** and **N749** on TiO₂ at the air-solid environment from that in the emulation DSSC device. This result indicates that the solvent may potentially influence the anchoring mode and hence the orientation of the dyes on TiO₂. This study also demonstrates a method for the evaluation of the dye and solvent volume fractions of the dye layer by combining *in-situ* NR and *ex-situ* XRR data. Overall, the results suggest that the presence of solvent may affect the dye orientation on TiO₂. The results also imply that the LED illumination potentially affects the dye orientation and solvent volume fraction at the dye \cdots TiO₂ interface.

7. Examining the structure of the dye···TiO₂ interface in the presence of solvent and electrolyte components in dye-sensitized solar cells by high-flux *in-situ* neutron reflectometry

Dye-sensitized solar-cells (DSSCs) offer a basis for next-generation solar-powered window technologies and energy-sustainable wearables. Yet, detailed information on how the electrolyte in a DSSC device affects the working electrode is distinctly lacking. Herein, we show how *in-situ* neutron reflectometry (NR) can be employed to determine the dye…TiO₂ interface structures of **MK-2**, **N3**, and **N749**, which constitutes the DSSC working electrode, in the presence of the electrolyte components. The NR studies are supported by infrared (IR) and photoelectron spectroscopy. Results afford plausible self-assembled dye structures of **MK-2**, **N3**, and **N749** on TiO₂ in the presence of the electrolyte components. The presence of the electrolyte components. The presence of the electrolyte solvent(s), LiI, and I₂ ingress into the dye layer. A higher propensity for the dye layer to desorb in R-OH solvents is observed in the case studies of the three subject dyes owing to the potential formation of hydrogen (deuterium) bonds.

7.1 Introduction

DSSCs have the potential to serve in solar-powered windows of energy-sustainable buildings^{1,67,68}, and as passive energy harvesters in wearable devices and textiles^{69–} ⁷². Yet, their innovation is hampered by a lack of understanding of how the dye molecules interact with their device environment. A typical DSSC consists of a photoanode where the dye is adsorbed onto the surface of a semiconductor (usually TiO₂) and injects photo-induced electrons into the conduction band (CB) of the semiconductor; the electrical current passes to the counter-electrode, which is classically coated with platinum in order to catalyze the redox reaction of the electrolyte (often I^{-}/I_{3}^{-}) that is sandwiched between the two electrodes. The adsorption geometry and packing of the dye molecules on the surface of TiO₂ play a pivotal role in determining various properties of the DSSC working electrode and thus the associated device, e.g., the open-circuit voltage (V_{oc}), the short-circuit current density (J_{SC}), and the power-conversion efficiency (PCE, η)^{31,81,82,114,115}. Moreover, the key loss mechanism from electron recombination is affected by the distance between TiO₂ and the oxidized dye, which also depends on the dye orientation¹¹⁶. Charge transfers from the dye to the CB of TiO₂, onto the counter-electrode, and thence to the electrolyte, which acts to replenish the original charge on the dye. Charge recombination between

CB electrons in TiO_2 and the redox electrolyte can occur around the dye... TiO_2 interface.

The chemical aspects of an electrolyte will also contribute to the efficiency of DSSCs^{122,123}. For example, previous work has shown that chemical constituents of electrolyte solutions featuring the most common redox couple, I⁻/I₃⁻, play an important role for the photon-to-electron conversion efficiency^{124–126}. The redox couple is typically Li⁺, balanced in solution by Na+, tetrabutylammonium (TBA+) or dimethylhexylimidazolium (DMHI⁺) cations that were part of the iodide salt used to chemically generate the redox couple. Interactions solely between these cations and a TiO₂ surface within a solvent have been well studied¹²⁷⁻¹³⁰. Amongst other things, such studies revealed that the amount of photocharge generated by light follows the trend, DMSI⁺ < TBA⁺ < Na⁺ < Li⁺. Moreover, Na⁺ and Li⁺ were found to influence the potential charge¹²⁷. The nature by which a dye... TiO_2 interface is influenced by electrolyte solutions that contain these cations, as well as other chemical constituents, therefore needs to be investigated. In particular, the structural impact of an electrolyte solution on the dye orientation, self-assembled dye packing structure, and dye adsorption modes on TiO_2 needs to be determined.

Structure-property relationships that unfold from such investigations in these functional devices are sought since they will help to furnish advanced molecular design guidelines for the next generation of DSSCs. However, to the best of our knowledge, only very few structural studies have investigated how the dye…TiO₂ interface is affected by both cations and anions, that together comprise the electrolyte. Previous studies by Cole *et al.* have uncovered how Li⁺ cations from the electrolyte influence the dye…TiO₂ binding configuration of the organic sensitizer **MK-44** via complexation of Li⁺ to the cyanoacrylate anchoring group of the dye⁹⁹. Specific interactions of the l⁻/l₃⁻ redox mediators with the dye **N3** have been studied computationally using density functional theory (DFT); the results revealed distinctive S-I bonding, which suggests interactions between l⁻ and **N3** via the SCN⁻ ligands¹³¹. Moreover, infrared (IR) spectroscopy measurements revealed the probable formation of l₂SCN⁻ ligands¹³², albeit with calculated weak binding energies which suggests that this ligand should be relatively unstable. Overall, it is clear that the dye…TiO₂ interfacial structure within the electrolyte environment strongly influences the performance of the photovoltaic

devices. Accordingly, detailed information is sought about the molecular behavior of the solvent and electrolyte on this fundamentally important dye...TiO₂ interface.

The majority of dye…TiO₂ structural influences on the photovoltaic device performance, which stem from the dye orientation and molecular packing in DSSCs, have been postulated on the basis of spectroscopic^{81,133,134}, diffraction⁸⁶, imaging^{87,88}, and computational tools^{4,89}. Recently, X-ray reflectometry (XRR) has been employed to determine the molecular orientation and packing density of a range of metal-containing and purely organic dyes^{31,91}. More recently, the structure of the buried dye…TiO₂ interface in the DSSC working electrode was determined using *in-situ* neutron reflectometry (NR)⁹⁹.

In the present study, we use *in-situ* NR to determine the dye…TiO₂ interfacial structure of three high-performance DSSC dyes buried within a device, with the electrolyte solution present or absent. IR and X-ray photoelectron spectroscopy (XPS) were also applied to provide insights into the change in adsorption modes of the dyes on TiO₂ once the solvent and electrolyte had been introduced. The results demonstrate how the solvent and electrolyte influence the dye…TiO₂ interfacial structure, and potentially affect the charge-transfer dynamics and photovoltaic performance of DSSC working electrodes within a sample environment that emulates that of a DSSC device.

7.2 Materials and methods

7.2.1 Materials

7.2.1.1 Selection of chemical dyes for this study

Given that the working electrode of the DSSC device is a buried interface within its device architecture, NR should be particularly useful for probing its structure, given the characteristic ease by which neutrons can penetrate deep into materials. Moreover, NR is able to discriminate signals that arise from the dye or the TiO₂ surface, since the scattering length density (SLD) of various DSSC layers exhibit sufficient contrast.

Ruthenium-based organometallic dyes are commonly employed in DSSCs^{4,5} owing to their good power conversion efficiency. This is despite their high costs, significant environmental impact, modest molar extinction coefficients, and the finite supply of transition-metal precursors. However, metal-free organic sensitizers have recently

attracted attention on account of their superior performance with respect to costefficiency, environmental impact, and molar extinction coefficients, as well as with regard to the established flexibility of their molecular tailoring and the diversity of organic molecular structures^{12,13,17}.

In this study, three high-performance DSSC dyes (Scheme 7.1) were investigated, i.e., the metal-free organic sensitizer **MK-2**, and the archetypal ruthenium-based sensitizers **N749** ('black dye') and **N3**. The best recorded DSSC performance for **MK-2** is $8.3\%^{117}$. As such, **MK-2** represents one of the highest-performing organic DSSC dyes under traditional device manufacturing conditions, e.g. using an I_3 -/I⁻ redox electrolyte. **N3** is known as the industry standard DSSC dye with a maximum PCE value of $10.0\%^8$, while **N749** exhibits better photovoltaic performance with the maximum PCE value of $10.4\%^{118}$.



Scheme 7.1 Chemical structures of the organic dye MK-2 as well as the rutheniumbased dyes N749 ('black dye') and N3.

7.2.1.2 Materials for reflectometry experiments

A full DSSC device assembly was constructed for the *in-situ* NR experiments. This section details the preparation of its constituent parts. The working electrodes fabricated for these *in-situ* NR experiments were also used for the *ex-situ* XRR measurements. Atomically flat, amorphous TiO₂ films were considered necessary for affording good signal in both types of reflectometry measurements. It was deemed suitable to approximate a TiO₂ surface in a DSSC to that of a flat TiO₂ surface in these measurements, owing to the scale of the dye…TiO₂ interfacial structure: dye molecules are very small (a few nm) relative to a typical DSSC TiO₂ nanoparticle (50-100 nm)

such that the radius of curvature of a TiO_2 nanoparticle will appear flat at the molecular scale.

7.2.1.2.1 Preparation of thin films of amorphous TiO2

The batch 3 atomically flat amorphous TiO_2 thin films (*cf.* Chapter 2.5 for preparation method) were prepared using atomic layer deposition (ALD) at Argonne National Laboratory (ANL), USA. The 12-nm TiO_2 film thicknesses showed high uniformity across all samples, as confirmed by reflectometry (*cf.* Table E4).

7.2.1.2.2 Fabrication of dye... TiO₂ working electrodes

Thin-films of TiO₂ on silicon wafer substrates were sensitized with each dye. This involved immersing the wafers into a 0.3 mM solution of each dye for 20 h; acetonitrile:*t*-butanol:toluene (1:1:1, v/v) was used for **MK-2** (95%, Sigma Aldrich), while acetonitrile:*t*-butanol (1:1, v/v) was used for **N3** (95%, Dyesol), **N3**·2H₂O (95%, Solaronix), and **N749** (95%, Solaronix); all solvents (ACS reagent grade) were purchased from Sigma Aldrich. Sensitized wafers were subsequently rinsed with neat acetonitrile (10 s) and dried under a flow of N₂ prior to the *in-situ* and *ex-situ* measurements.

7.2.1.2.3 Preparation of the counter-electrode

Fluorine-doped tin oxide (FTO) glass counter-electrodes with platinum as the electrontransfer catalyst were prepared by drop-casting a 5 mM solution of chloroplatinic acid hydrate (99.995%, Sigma-Aldrich) in isopropanol (ACS reagent grade, Sigma-Aldrich) onto clean FTO glass slides (TEC 8, Sigma-Aldrich, $90 \times 90 \times 3.2 \text{ mm}^3$), which were subsequently heated for 15 minutes at 390 °C.

7.2.1.2.4 Electrolyte solutions

Solutions of 0.7 M lithium iodide (LiI) (99.9%, Sigma Aldrich) and 0.05 M iodine (I_2 ; 99.99%, Sigma Aldrich) were mixed in a solvent to form the active I^-/I_3^- redox electrolyte. d_3 -acetonitrile (99.8%, Sigma Aldrich) or d_4 -methanol (99.8%, Sigma Aldrich) were the solvents employed in the NR studies; their deuterated nature enables sufficient neutron scattering contrast of the buried interface within each sample under investigation.

Hydrogenated acetonitrile (MeCN) or methanol (MeOH) (ACS reagent grade, Sigma Aldrich) provided the solvent media for the active I^{-}/I_{3}^{-} redox electrolytes in the IR and XPS studies. Both MeCN and MeOH are commonly used solvents for dissolving the I^{-}/I_{3}^{-} redox electrolyte in battery research^{99,135–138}.

7.2.1.3 Materials for XPS and IR Measurements

Neither XPS nor IR measurements mandated atomically flat, amorphous TiO₂ films. Moreover, XPS and IR signal would benefit from a sample that contains a much thicker (μ m) TiO₂ film. Therefore, nanocrystalline TiO₂ thin films were prepared for these measurements, using the doctor-blade method. This is the most commonly used fabrication method to create TiO₂ thin films for DSSC devices. The mixture of TiO₂ nanoparticles, dye solution and electrolyte was also used for IR measurement.

7.2.1.3.1 Preparation and sensitization of nanoparticulate TiO₂ films

Films of nanocrystalline TiO₂ were fabricated by initially depositing one layer of nanoparticulate TiO₂ paste (Dyesol, DSL 18NR-T) onto a clean ITO coated glass substrate (1 × 1 cm², Sigma Aldrich) using the doctor-blade technique. Sintering this paste at 500 °C for 30 min yielded mesoporous films of TiO₂. These films were then submersed in a 0.5 mM solution of **MK-2** (95%, Sigma Aldrich) in MeCN:*t*-butanol:toluene (1:1:1, v/v), or in 0.5 mM solutions of **N3**·2H₂O (95%, Solaronix), or **N749** (95%, Solaronix) in MeCN:*t*-butanol (1:1, v/v) for 20 h; all solvents (ACS reagent grade) were purchased from Sigma Aldrich. Thereafter, the substrates were rinsed with neat MeCN and dried under a flow of nitrogen. An active dye…TiO₂ working-electrode surface area of ~1 cm² was created via removal of excess TiO₂ from the periphery of the parent film.

7.2.2 Methods

7.2.2.1 Contrast-matched in-situ NR

In-situ NR measurements were conducted using the high-intensity INTER reflectometer at the ISIS neutron facility (UK). The instrument was equipped with a low-background ³He gas detector (adjustable sample-detector distance: 2-8 m), and beam profiles were collected at the sample angle $\varphi = 0.5^{\circ}$ and 2°. Measurements in

the dark were conducted on thin films of amorphous TiO_2 sensitized with **MK-2**, **N3**, or **N749**. Other measurements were carried out on sensitized thin films of TiO_2 under illumination using THORLABS LEDD1B high power LEDs operating at a current of 1200mA, under open-circuit conditions. The reduced data were refined using GenX⁹³, which employs a differential evolutional algorithm to perform robust optimization and avoid local minima. The *in-situ* NR data were plotted as a function of the momentum transfer vector (*Q*) perpendicular to the TiO₂ surface based on eq 7.1.

$$Q = \frac{4\pi \sin \theta}{\lambda} \tag{7.1}$$

wherein θ is the incident angle and λ is the wavelength of the neutrons. A schematic diagram of the sample measurement geometry is shown in the Figure E17, while the beam size and profile are shown in Figure E18. The substrates are three-inch *n*-type silicon (100) wafers (thickness ≥ 5 mm), which ensures an uninterrupted beam transmission and avoids excessive attenuation of the neutron beam. Deuterated acetonitrile (d₃-MeCN) and deuterated methanol (d₄-MeOH) were used to enhance the contrast between the dye and the electrolyte. Nominal values for the neutron SLD of each layer were used to construct initial structural models using a three-layer approach. For the substrates, values of 2.07 × 10⁻⁶ Å⁻², 3.48 × 10⁻⁶ Å⁻², and 2.39 × 10⁻⁶ Å⁻² were used for the silicon wafer, the native oxide layer, and the TiO₂ layer, respectively. The SLD of the subphase solvents d₃-MeCN and d₄-MeOH was set to 4.92 × 10⁻⁶ Å⁻² and 5.80 × 10⁻⁶ Å⁻², respectively. All TiO₂ film thicknesses were refined to 12 nm (*cf.* Table E4).

Contrast matching represents an effective way of using the power of neutron reflection. Figure 7.1 shows a schematic illustration of the *in-situ* NR experimental geometry with different solvent contrasts. Mixing CH₃CN with CD₃CN (d₃-MeCN) afforded acetonitrile with different H/D ratios, which eventually furnished solvent contrasts similar to that of silicon (d₃-MeCN volume ratio: 20.8%) and TiO₂ (d₃-MeCN volume ratio: 29.7%). Contrast-matching silicon allows examining exclusively the dye…TiO₂ interface and the native oxide layer, while contrast-matching TiO₂ allows examining exclusively the dye layer and the silicon substrate with the native oxide layer.





7.2.2.2 Ex-situ NR

Ex-situ air-solid NR measurements were carried out using the single-frame (2.0 Å < λ < 7 Å) mode of a time-of-flight neutron reflectometer, i.e., the Multipurpose Reflectometer (MR) at the China Spallation Neutron Source (CSNS)¹³⁹. Reflected neutron beam spectra were acquired on a 2D position-sensitive ³He area detector with an active area of 20 × 20 cm² and a spatial resolution of 1.5 mm. Incident neutron angles of 0.3°, 0.6°, or 1.2°, were used to cover the *q* range required for these data. Direct beam measurements were collected under the same collimation conditions. NR data were fitted using the default layer model in GenX. The neutron SLD profiles along the normal direction of the films were extracted. These NR experiments at CSNS used the same samples as those employed for the NR work on the INTER reflectometer at the ISIS Neutron and Muon Facility, with two exceptions: the electrolyte constituents from the samples for the INTER experiments were all removed prior to the CSNS experiments by rinsing the dye-sensitized substrates with the same solvent that had been used in the INTER experiments. Further details about this procedure and its influence are provided in the Appendix E3.

7.2.2.3 X-ray reflectometry (XRR)

XRR measurements were conducted using a Rigaku SmartLab reflectometer (9 kW rotating anode; Cu-K α X-ray source; $\lambda = 1.541$ Å) equipped with a Ge (220 × 2) monochromator. X-ray reflectivity data were collected in increments of 0.01° for a detector range of 0.1° < 2 θ < 8°. Nominal values for the X-ray SLD of each layer were used to construct initial structural models based on a three-layer approach. For the substrates, SLD values of 20.1 × 10⁻⁶ Å⁻², 18.9 × 10⁻⁶ Å⁻², and 31.2 × 10⁻⁶ Å⁻² were used for the silicon wafer, the native oxide layer, and the TiO₂ layer, respectively. By fitting the X-ray reflectivity data, the thickness of the **MK-2**, **N3**, and **N749** dye layers on 12
nm thick films of amorphous TiO₂ (*cf.* Table E4) were determined for different sensitization concentrations and periods.

7.2.2.4 X-ray photoelectron spectroscopy (XPS)

XPS measurements were performed on a Thermo Fisher Scientific NEXSA spectrometer under high vacuum (P ~ 10^{-8} millibar) with thin-film samples of nanoparticulate TiO₂ on silicon substrates sensitized with each DSSC dye, prepared as detailed in section 7.2.1.3. Samples were analyzed using a micro-focused monochromatic AI X-ray source (72 W) over an area of approximately 400 µm. Data were recorded at pass energies of 200 eV for survey scans and 50 eV for high-resolution scans in increments of 1 eV and 0.1 eV, respectively. Charge neutralization of the sample was achieved using a combination of both low-energy electrons and argon ions.

7.2.2.5 Attenuated total reflection (ATR)-Fourier-transform IR spectroscopy (FTIR)

ATR-FTIR measurements were performed on thin films of nanoparticulate TiO₂ on silicon substrates sensitized with each DSSC dyes, prepared as detailed in section 7.2.1.3. The experimental setup is schematically illustrated in Figure 7.2. The substrates were clamped on top of the crystal through which the evanescent wave of IR light is transmitted and incident onto the dye…TiO₂ layers, before it is reflected internally multiple times and finally exits the sample. There is a very small gap in between the substrate and the crystal that serves to trap the solvent or electrolyte in order to emulate the sandwich cell structure of the DSSCs. In this study, air-solid ATR-FTIR indicates air is trapped in the gap while liquid-solid ATR-FTIR indicates solvent or electrolyte are trapped in the gap during the measurement.



Figure 7.2 Schematic illustration of the interaction of IR light with the sample in the ATR-FTIR measurements.

7.2.3 Models

The analysis for the solvent and dye coverage on TiO_2 adopts a triple co-refinement with d₃-MeCN, Si-contrast-matched, and TiO_2 -contrast-matched as the solvents. The analysis for the electrolyte additions adopts a double co-refinment with d₃-MeCN, Sicontrast-matched as the solvents.

The dye \cdots TiO₂ interface structures were examined using the dye/solvent coverage model, in which the dye and solvent volume fractions in the dye layer were calculated using eq 7.2:

$$SLD_{obs} = SLD_{dye} \cdot \varphi_{dye} + SLD_{svt} \cdot (1 - \varphi_{dye}), \tag{7.2}$$

wherein SLD_{dye} is the SLD of the dye under the assumption that the TiO₂ surface is 100% covered. SLD_{svt} is the SLD of the solvent (d₃-MeCN, Si-contrast-matched d₃-MeCN/MeCN, or TiO₂-contrast-matched d₃-MeCN/MeCN). φ_{dye} is the dye volume fraction and $1 - \varphi_{dye}$ is the solvent volume fraction. The TiO₂ surface is assumed to be covered with either dye or solvent molecules.

Figure 7.3 shows the three-layer structural model and four-layer structural model with the corresponding representative SLD profiles for the fitting of neutron reflectivity. In particular, the four-layer model adopts an extra top layer in the presence of all electrolyte components. For the substrates, SLD values of 2.07×10^{-6} Å⁻² were set for the silicon wafer, while the SLD values of native oxide and the TiO₂ layers were free to vary in the fits. The fitted SLD values of TiO₂ layers were close to the nominal value while the fitting results suggest the SLD values of the native oxide layers were lower than the nominal value for silicon dioxide, indicating potential void structures or lower extent of oxidation within the native oxide layers. The thickness values were set at 2 Å on the basis of the measurements made on blank TiO₂ substrates, except that for the dye…TiO₂ interface which was allow to vary slightly considering the solvent ingression effect.



Figure 7.3 The representative SLD profiles and the corresponding three-layer structural model and four-layer structural model for the fitting of neutron reflectivity.

7.3 Results and discussion

7.3.1 Dye…TiO₂ interfacial structures sensitized by MK-2, N3, or N749 dyes in d₃acetonitrile solution

7.3.1.1 Examining the dye \cdots TiO₂ interface structure and ingression of solvent molecules in the dye layers in the presence of d₃-MeCN/MeCN by in-situ NR measurements

In order to examine the extent of dye adsorption and solvent ingression more accurately, three sets of *in-situ* NR meaurements, differing with respect to their neutron-scattering-contrast conditions (fully deuterated; Si-contrast-matched; TiO₂-contrast-matched), were collected by submerging the thin films of dye-sensitized TiO₂ on silicon wafers in different solvent environments. The *in-situ* NR and fitted SLD profiles are shown in Figure 7.4, with Table 7.1 showing the fitted structural parameters of dye layers and dye volume fractions.



Figure 7.4 *In-situ* NR profiles and fittings (offset for clarity), as well as the SLD values obtained from the co-refinement of the data collected for thin films of dye-sensitized TiO₂ on silicon wafers submerged in Si-contrast-matched or TiO₂-contrast-matched d₃-MeCN, MeCN, or d₃-MeCN, taking into account the solvent ingression in the dye layer.

Table 7.1 Fitted structural parameters of dye layers and dye volume fractions for **MK-2**, **N3**, and **N749** by co-refinement of *in-situ* NR data collected for three contrast-matching scenarios (d₃-MeCN, Si-contrast-matched d₃-MeCN/MeCN, and TiO₂-contrast-matched d₃-MeCN/MeCN).

Dye	Dye layer thickness (Å)	Fitting error (Å)	ρ _{dye} (unit/ų)	Fitting error (10 ⁻⁵ unit/ų)	$arphi_{dye}$	$oldsymbol{arphi}_{solvent}$	FOM logbars
MK-2	20.6	(-0.7, 0.8)	0.000584	(-3.1, 3.5)	91.35%	8.65%	1.363
N3	11.5	(-0.5, 0.5)	0.000995	(-5.8, 7.3)	92.13%	7.87%	2.231
N749	10.3	(-0.5, 0.3)	0.000763	(-6.1, 5.5)	55.68%	44.32%	2.101

The 'unit' in the table is defined as one dye molecule. The neutron SLD of each dye layer can be obtained from multiplying the fitted density of each dye layer with the total neutron scattering length of a dye molecule (**MK-2**: 165.5 fm; **N3**: 228.3 fm; **N749**: 155.6 fm; TiO₂: 8.2 fm).

One of the reasons that the fitted dye volume fraction for **N749** is significantly lower than that of **MK-2** and **N3** (Table 7.1) might be the dissociation of tetrabutylammonium

cations (TBA⁺). ATR-FTIR spectra of dye···TiO₂ films on ITO coated glass substrates before and after rinsing with MeCN or MeOH (Figure E19) indirectly support this assumption given the disappearance of the C-O stretching vibration for **N749** after rinsing. This result suggests that the binding of TBA⁺ cations in **N749** may change in these solvents and consequently influence the surface coverage of **N749** on TiO₂, e.g. by dissociation, and therefore reduce the amount of adsorbed dye molecules and thus increase the intermolecular space available for solvent ingression.

7.3.1.2 Determining anchoring group configurations for **MK-2**, **N3** or **N749** dyes on TiO_2 via dye-layer thicknesses

Table 7.2 shows the NR and XRR measured dy

Table 7.2 shows the NR and XRR measured dye layer thickness for **MK-2**, **N3**, and **N749** in this work. The results were shown with consistency when related to the previous work performed on the same dyes at the same sensitization concentration (0.3 mM), time (20 h), and solvents. Considering the lateral height of the **MK-2**, **N3**, and **N749** dye molecules (Figure 7.5), these dye molecules likely form monolayer structures given the measured thickness values from the NR and XRR.

Table 7.2 The NR and XRR measured dye layer thickness for **MK-2**, **N3**, and **N749** in this work and the previous work done on the same dyes at the same sensitization concentration (0.3 mM), time (20 h), and solvents.

Dye layer thickness (Å)	N3	N749	MK-2
This work			
<i>In-situ</i> NR (Table 7.1, INTER, triple co- refinement)	11.5 (+0.5/-0.5)	10.3 (+0.3/-0.5)	20.6 (+0.8/-0.8)
Ex-situ XRR (Table E2-(1))	10.7 (+0.3/-0.3)	11.2 (+0.3/-0.1)	19.4 (+0.7/-0.4)
<i>Ex-situ</i> NR/XRR co- refinement (Table E1)	10.4 (+0.2/-0.5)	10.5 (+0.3/-0.2)	19.5 (+1.0/-1.3)
Other work ^{99,100,140}	N3	N749	MK-2
In-situ NR	11.8+/-1.2	-	23.6+/-1.9
<i>Ex-situ</i> XRR	10.2+/- 0.3 A	-	23.2+/- 0.2 A

Figure 7.5 illustrates the 3-D molecule structures of **MK-2**, **N3**, and **N749** on a TiO₂ surface with annotated lateral height for the maximal height of one molecule (from anchor point to opposite tip of the dye molecule) for various anchoring group configurations based on the density function theory calculations¹⁰¹.



Figure 7.5 The lateral height of (a) N3, (b) N749, (c) MK-2 dye molecules on TiO₂ surfaces for various group configurations. The blue triangle indicates the anchoring position on TiO₂¹⁰¹. Adapted from Chen, H. *et al*, 2019.

7.3.2 Dye···TiO₂ interfacial structures sensitized by MK-2, N3 or N749 dyes in d_3 -acetonitrile solution in the presence of electrolyte precursor or fully active electrolyte

7.3.2.1 Dye...TiO₂ interfacial structures determined by neutron reflectometry

Lil is the most commonly used DSSC electrolyte precursor and that Li⁺ ions can potentially influence the photovoltaic performance, while I^{-}/I_{3}^{-} is by far the most commonly used DSSC electrolyte. In order to establish the influence that the electrolyte precursor, Lil, and the fully active electrolyte (I^{-}/I_{3}^{-} redox couple) have on the dye…TiO₂ interfacial structures that were presented 7.3.1.1, the dye…TiO₂ interfacial structures during the progressive addition of electrolyte components (Lil/I₂) were probed by neutron reflectometry.

Specifically, *in-situ* NR data were recorded for two different scattering-contrast scenarios (d₃-MeCN and Si-contrast-matched d₃-MeCN/MeCN) by submerging thin films of dye-sensitized TiO₂ on silicon wafers in MeCN and/or d₃-MeCN in the presence of Lil or Lil/l₂. Figure 7.6 shows fits of reflectivity and SLD profiles to the sample models assuming a uniform dye-layer density regardless the solvent ingression, and with no extra layer on top of the dye layer in the presence of Lil and l₂. Apparently, it is observed from the SLD profile that the dye…solvent interfacial roughness for **MK-2** in the presence of Lil and l₂ is too large to render this model effective in describing the sample.



Figure 7.6 Fits of reflectivity and SLD profiles to the **MK-2** sample models with no extra layer on top of the dye in the presence of Lil and I₂, and assuming uniform dye-layer density in the two solvents of different contrasts.

To accurately describe the sample system, the dye/solvent coverage model based on eq 7.2 was used for the fitting of the NR data, as the extent of solvent ingression should be considered particularly when co-refining data collected in different solvent environments. Nevertheless, since the full electrolyte (Lil/l₂) likely induces the formation of an extra layer on top of the dye layer in MeCN as further suggested by the substantial fitted **MK-2**...solvent interfacial roughness value shown in Table E4, the Lil/l₂-electrolyte-induced top layer as well as the solvent ingression in the top layer are included in the fitting model, i.e., the four-layer structural model. The *in-situ* NR data and the fitted SLD profiles are shown in Figure 7.7. The fittings exhibit refined interfacial roughness values (~ 2 Å). The results (Table 7.3) show solvent ingression for all dyes in MeCN, even though the extent of solvent ingression in the **MK-2** and **N3** dye layers is much lower than that in **N749**.

It should be noted that the backgrounds for the d₃-MeCN are apparently higher than those for the silicon-matched solvent. This difference may be arise from the fact that

the background is sample related, and the compositions of d_3 -MeCN and siliconmatched solvent are in fact different. Besides, the slightly different sample alignment may also cause the sampling of the different background, and the background subtraction for the silicon-matched solvent also contributes its background being lower than that for d_3 -MeCN.





Figure 7.7 *In-situ* NR profiles and fittings as well as SLDs obtained from fitting the corefinement for data collected for thin films of dye-sensitized TiO₂ on silicon wafers

submerged in d₃-MeCN and Si-contrast-matched d₃-MeCN/MeCN under consideration of the solvent ingression in the dye layer.

7.3.2.1.1 Modulation of dye \cdots TiO₂ interfacial structure from adding the electrolyte precursor, Lil

Table 7.3 contains a summary of the numerical information for each fit, i.e., the thickness, density, and coverage values for the dye layers. The fitted structural parameters of the dye layers, including the surface coverage of the dyes on TiO₂, show that the addition of Lil to the solvent results in a decrease of the dye coverage, and therefore, a change of the overall SLD of the dye layer for all three dyes. The reason for this is because the dye/solvent coverage model is designed to accurately describe the fractions of dye and solvent in the layer, however, when other components ingress into the dye layer and for instance increase the overall SLD, the fitted dye coverage will decrease (solvent coverage increases) to reflect this, given the SLD of the solvent is much larger than that of the dye. This result suggests that Lil may potentially ingress into the dye layers, which might be due to the interaction between Li⁺ and the COO⁻ group as well as the CN⁻ groups of the cyanoacrylic anchor^{99,141} to form a special coordination mode. It is worth noting that for both MK-2 and N749, the SLD_{dve} is much lower than either the SLD of Si-contrast matched d₃-MeCN/MeCN or d₃-MeCN. Therefore, the lower values for the fitted dye coverage after the addition of Lil (higher solvent ingression rate) indicates a higher fitted overall SLD of dye layers for both Sicontrast matched d₃-MeCN/MeCN or d₃-MeCN. As the SLD_{dve} for N3 is very similar to the SLD of Si-contrast-matched d₃-MeCN/MeCN, the fitting of the Si-contrast-matched d₃-MeCN/MeCN data is insensitive to the variation of the dye coverage. Therefore, the fitted dye coverage in the co-refinement of the data was determined by fitting only the data for d₃-MeCN. As the SLD_{dye} of **N3** is much lower than the SLD of d₃-MeCN, the decreased fitted dye coverage after the addition of Lil also indicates a higher fitted overall SLD of the dye layer.

7.3.2.1.2 Modulation of dye····TiO₂ interfacial structure from adding the full active electrolyte Γ/I_3^- redox couple

For **MK-2**, the further addition of I_2 leads to an even higher solvent ingression rate, suggesting that I_2 also ingresses into the dye layer. It should be noted here that the

further addition of I_2 leads to a full surface coverage of the TiO₂ surface for **N3** and **N749**, which means the dye molecules and electrolyte cover the TiO₂ surface, i.e., there is almost no solvent ingression in the presence of Lil/I₂, indicating a more pronounced I_2 ingression for the **N3** and **N749** layers than for those of **MK-2**. This may either be due to a blocking of the solvent ingression in the dye layer upon further addition of I_2 on top of the dye layer, or due to the circumstance that the I_2 molecules occupy most of the intermolecular space within the dye layer.

Table 7.3 Co-refined structural parameters of the dye layers (or top layer where specified) for two contrast-matching scenarios (d_3 -MeCN and Si-contrast-matched d_3 -MeCN/MeCN) in the presence of Lil or Lil/l₂ under consideration of the solvent ingression in the dye layer as well as the top layer (where specified).

	Solution	Dye layer (or top layer where specified)					
Dye		Thickness (Å)	Fitting error (Å)	ρ _{dye} (10 ⁻⁴ unit/Å ³) or ρ _{top} (unit(l ₂) /Å ³)	Fitting error (10 ⁻⁵ unit/ų)	Coverage	FOM logbars
	MeCN	20.6	(-0.7, 0.8)	5.84	(-3.1, 3.5)	91.4%	1.363
	MeCN+Lil	20.6	(-0.6, 0.8)	5.86	(-3.5, 2.6)	87.8%	2.667
MK-2	MeCN+Lil+l ₂	20.8	(-1.0, 0.9)	5.97	(-5.1, 6.5)	62.7%	1.556
	MeCN+Lil+l ₂ (top layer)	30.3	(-1.0, 1.5)	0.01025	(-8.0, 6.9)	11.8%	1.556
	MeCN	11.5	(-0.5, 0.5)	9.95	(-5.8, 7.3)	92.1%	2.231
	MeCN+Lil	11.6	(-0.4, 0.5)	9.75	(-5.4, 8.2)	78.8%	1.985
N3	MeCN+Lil+l ₂	13.3	(-0.3, 0.3)	9.90	(-2.3, 2.1)	99.7%	1.243
	MeCN+Lil+l ₂ (top layer)	22.2	(-0.4, 0.4)	0.01054	(-5.4, 8.2)	4.5%	1.243
	MeCN	10.3	(-0.5, 0.3)	7.63	(-6.1, 5.5)	55.7%	2.101
N749	MeCN+Lil	10.9	(-0.6, 0.8)	7.74	(-7.7, 8.0)	36.3%	1.069
	MeCN+LiI+I ₂	12.5	(-0.7, 0.7)	12.81	(-8.2, 3.6)	99.9%	0.986
	MeCN+Lil+l ₂ (top layer)	35.4	(-1.2, 1.4)	0.01066	(-7.6, 4.1)	5.5%	0.986

Table 7.3 also shows the fitted structural parameters for the top layer on **MK-2**, **N3**, and **N749** when the electrode is buried in the presence of all electrolyte components. Once the extra top layer, which is currently assumed to be I_2 , is added to the fitting model, the fitting of the NR data for **MK-2** affords reasonable interfacial roughness values, especially considering the roughness of the dye…solvent interface (~2 Å) in contrast to the considerably high value of 19.8 Å when no extra top layer was added (*cf.* Table E4), suggesting the top layer is a better representation of the true sample model. Table 7.3 also demonstrates that the fitted surface coverage of the top layer is relatively low (4-12%), which suggests that the top layer is sparsely packed on top of the dye layer. In order to better understand the composition of the top layer, *ex-situ* XRR results in Table E2-(2) were combined with the fitted structural parameters from the NR measurements to reveal the percentile composition of I_2 and Lil in the top layer, based on the following equations:

$$SLD_{x-ray,top} = SLD_{x-ray,I2} \cdot \varphi_{I2} + SLD_{x-ray,LiI} \cdot \varphi_{LiI}, \qquad (4)$$

$$SLD_{neutron,top} = SLD_{neutron,I2} \cdot \varphi_{I2} + SLD_{neutron,LiI} \cdot \varphi_{LiI}, \qquad (5)$$

These equations are based on the assumption that the top layer is composed of either Lil or l₂. $SLD_{x-ray,top}$ is the fitted SLD value of the top layer obtained from XRR, $SLD_{neutron,top}$ is the fitted SLD value of the top layer obtained from NR, $SLD_{x-ray,L2}$ and $SLD_{neutron,I2}$ are the nominal X-ray and neutron SLD values of l₂, while $SLD_{x-ray,LiI}$ and $SLD_{neutron,LiI}$ are the nominal X-ray and neutron SLD values of Lil. φ_{l_2} is the volume fraction of l₂ in the top layer, while φ_{LiI} is the volume fraction of Lil in the top layer. The calculated volume-fraction percentages of l₂ in the top layer ($\frac{\varphi_{l_2}}{\varphi_{LiI}+\varphi_{l_2}}$) are 94.61%, 96.37%, and 94.69% for layers of **MK-2**, **N3**, and **N749**, respectively, suggesting that the top layer consists almost exclusively of l₂ and validate the aforementioned extra layer model assumption. Based on the structural parameters of the l₂ layer, as well as the electrolyte ingression behavior within and on top of the **MK-2** layer in the presence of Lil/l₂, an electrolyte ingression mechanism is proposed in Figure 7.8. At this point, we assume that the electrolyte ingression in the **N3** and **N749** dye layers follows a similar mechanism but has a lower surface coverage on top of the dye layer.



Figure 7.8 Schematic illustration of the proposed electrolyte ingression within and on top of the **MK-2** dye layer in the solvent environment. The thickness of the top iodine layer is approximately ~30 Å with a surface coverage of 11.8%. The chemical compound triiodides are expected to exist as separate iodine and iodide ions. The lithium and iodide ions would be detached from the top layer more easily than the iodine once removed from the solvent environment, leaving the majority composition of the top layer as iodine. The lithium cations that are left within the dye layer in the solvent environment are expected to from complexation with the anchoring groups of dye molecules.

In order to examine the effect of electrolyte ingression across the **MK-2** layer, in which the most significant Lil/l₂ ingression effect was observed according to the reflectivity profiles, the density variation model was adopted for the **MK-2** layer on TiO₂, which assumes that the dye layer consists of an upper and a lower sub-layer with different coverage values due to different levels of electrolyte ingression in lateral direction. Figure 7.9 shows the *in-situ* NR profiles and fittings as well as the SLD values obtained from the fitting co-refinement for thin films of **MK-2**-sensitzied TiO₂ on silicon wafers submerged in d_3 -MeCN or Si-contrast-matched d_3 -MeCN/MeCN, using the dye density variation model.



Figure 7.9 *In-situ* NR profiles and fittings as well as SLD values obtained from fitting the co-refinement for data collected for thin films of **MK-2**...sensitized TiO₂ on silicon wafers submerged in d_3 -MeCN and Si-contrast-matched d_3 -MeCN/MeCN under consideration of iodine and solvent ingression in the dye layer, as well as the solvent ingression in the top layer (iodine).

Table 7.4 shows the structural parameters of the dye layer divided into upper and lower sub-layers of different density using the two-layer density-variation model. The surface coverage is used to indicate the SLD of dye layer, based on the dye/solvent coverage model. The upper sub-layer exhibits lower surface coverage and hence higher solvent ingression and overall SLD, as a result of higher extent of electrolyte ingression. The lower sub-layer exhibits higher surface coverage and therefore lower solvent ingression and overall SLD, as a result of lower degree of electrolyte ingression. Figure 7.10 schematically illustrates the two-layer density variation in direction perpendicular to substrate plane relative to the geometry of the dye molecules. The carbazole moiety in **MK-2** acts as an amine based and would mostly likely be transformed into a carbazolium moiety when the COOH group is deprotonated. The carbazolium moiety attracts the negatively charged $1^{-}/l_{3}^{-}$ to the dye layer. At this point we speculate that the density variation is caused by the long alkyl chains of **MK-2**, which may block the build-up of the iodine complexation in lateral direction. Table 7.5 shows the fitted structural parameters for the top l_2 layer using the density-variation model. Both the fitted

thickness and coverage values of **MK-2** dye layer as well as the top iodine layer are consistent with those obtained from the sample model with no dye density variation in lateral direction (Table 7.3).

Table 7.4 The fitted co-refined structural parameters of the **MK-2** layer in the presence of Lil/I₂ (d₃-MeCN and Si-contrast-matched d₃-MeCN/MeCN) under consideration of solvent ingression in the dye layer as well as the top layer (iodine), and assuming a density variation in the **MK-2** layer due to different level of iodine ingression.

Density variation model	Solution	Dye layer					
		Thickness (Å)	Fitting error (Å)	<i>ρ_{dye}</i> (10 ⁻⁴ unit/Å ³)	Fitting error (10 ⁻⁵ unit/Å ³)	Coverage	
MK-2 upper	MeCN+Lil+l ₂	7.9	(-0.3, 0.4)	5.02	(-3.6, 4.2)	49.5%	1 097
MK-2 lower	MeCN+Lil+I ₂	12.5	(-0.3, 0.5)	5.95	(-4.7, 5.2)	69.3%	1.007

Table 7.5 The fitted co-refined structural parameters of the top I_2 layer in the presence of Lil/I₂ (d₃-MeCN and Si-contrast-matched d₃-MeCN/MeCN) under consideration of solvent ingression in the dye layer as well as the top layer (iodine), and assuming a density variation in the **MK-2** layer due to different level of iodine ingression.

	lodine layer					
Solution	Thickness (Å)	Fitting error (Å)	ρ _{ι2} (unit/ų)	Fitting error (10 ⁻⁴ unit/Å ³)	Coverage	
MeCN+LiI+I ₂	29.3	(-0.7, 0.5)	0.01058	(-3.9, 5.5)	11.5%	1.087



Figure 7.10 Schematic illustration of the **MK-2** layer using the two-layer densityvariation model due to different level of electrolyte ingression in the dye layer in the presence of Lil/l₂. It is worth noting the carbazole moiety in **MK-2** dye molecule is probably converted into a carbazolium moiety upon deprotonation of the COOH group during adsorption, as the resulting proton would likely be scavenged by the amine group.

7.3.2.2 Influence of electrolyte constituents on $dye \cdots TiO_2$ adsorption determined via C=O vibrational signatures of ATR-FTIR

Figure 7.11 shows the C=O absorption wavenumber of layers of MK-2, N3, and N749 on nanoparticulate TiO₂ films in MeCN or MeOH. For MK-2, the C=O stretching vibration is slightly intensified at the same absorption wavenumber in MeCN or MeOH (~1714 cm⁻¹). However, the corresponding C=O absorption wavenumbers in layers of N3 and N749, particularly those of N3, are significantly higher in MeCN (~1732 cm⁻¹) than in MeOH (~1720 cm⁻¹). This may tentatively be attributed to (a) interactions between MeCN and uncoordinated carboxyl/carboxylate groups that are present in N3 (four COOH groups) and N749 (one COO⁻ and two COOH groups), or (b) interactions between MeCN and bidentately or tridentately coordinated carboxylate groups rather than monodentately coordinated carboxylate groups. In contrast, MK-2 only contains one carboxylate group per molecule, which is used for anchoring, and therefore, interactions between MeCN and the uncoordinated COOH groups are intrinsically limited. It is also worth noting that the Ru-based dyes N3 and N749 should be considered 'globular', i.e., the central Ru atom exhibits an octahedral coordination geometry in which uncoordinated COOH groups are located on the outside of the coordination polyeder. In contrast, the metal-free dye MK-2 exhibits a pronounced rodlike aspect ratio and its hydrocarbon-based surface should be characterized by significant hydrophobicity with the exception of the positively charged terminal carbazolium moiety. In case of the ingression of the Lil/l₂ equilibrium, there might be a higher ingression of nonpolar I_2 in the middle layer and accumulation of I^-/I_3^- on the top of the **MK-2** layer. A TiO₂ surface covered with **N3** and **N749** can thus be feasibly expected to be able to interact well with polar solvent molecules. Moreover, the dielectric constant of MeCN (37.5) and MeOH (32.7) is similar, and they are both able to engage in hydrogen bonds. The proton of MeOH can be expected to engage in hydrogen bonding with COOH/COO⁻ groups and consequently, the interaction

between MeOH and the Ru-based dyes should be higher than those with the metalfree dye, given that **MK-2** potentially exhibits one carbazolium group, while **N749** and **N3** exhibit two and three COOH groups respectively, apart from one COO⁻ group after adsorption. In fact, the protons of COOH in uncoordinated carboxyl groups existing in **N3** and **N749** are also able to engage in hydrogen bonding with MeCN, which likely results in the distortion of the C=O adsorption wavenumber.



Figure 7.11 FTIR-ATR spectra showing the C=O absorption wavenumber of dyesensitized nanoparticulate TiO₂ films in air, MeCN or MeOH.

Figure 7.12 shows that the presence of the electrolyte shifts the absorption wavenumber of the SCN⁻ ligands in **N3** and **N749** to ~2100 cm⁻¹, which corroborates the formation of I_2 SCN⁻¹³², which in turn could influence the molecular orientation of these dyes on TiO₂. A previous computational study has shown the low free binding energy of I_2^{132} , which is consistent with the experimental findings that the peak shifts of the IR spectra of **N3** and **N749** are caused by the formation of I_2 SCN⁻ (Figure 7.12), and that they are easily reversible upon rinsing the substrates with neat MeCN.

Figure 7.12 also shows that the presence of Li⁺ cations affects the C=O stretching vibration of the dye molecules, which is reflected in the substantially increased C=O absorbance in the dye layer as evident from the air-solid ATR-FTIR measurements on substrates after rinsing with electrolyte dissolved in MeCN and drying under a flow of N₂. The C=O absorbance even remains slightly increased after further rinsing of the

substrates with neat MeCN and drying under a flow of N₂. This result stands in contrast to those obtained for substrates rinsed with MeCN and dried under a flow of N₂ (Figure E19), where the ATR-FTIR absorbance peaks for C=O remains almost identical before and after rinsing with MeCN and MeOH, which suggests that the C=O stretching vibration is shifted due to the interactions with the electrolyte components rather than the solvent. It seems that the interactions between the Li⁺ cations and the carboxylate groups leads to the formation of a 'special' coordination mode to strengthen the absorbance intensity of the C=O stretching vibration. At this point, we assume that the Li⁺ cation could engage in binding with the negatively charged oxygen atom of the carboxylate (e.g. in the solid state) as they are both second-row elements, and a hard acid and base, respectively. This would significantly affect the binding mode of the carboxylate (monodentate) and change the C=O absorption. The strengthened C=O stretching mode would appear at a wavenumber that is slightly lower than that of the characteristic C=O stretching vibration (1670-1820 cm⁻¹), indicating potential conjugation (lower energy) of the carboxylate groups, probably due to the enhanced intermolecular dye...dye interaction in the presence of solvent. Since the IR spectra also showed a significant reduction of the C=O absorbance once the dye layer had been washed with neat MeCN, these results suggest that the monodentate bridging mode is weaker than the bidentate bridging mode, which would explain the detachment of Li⁺ from the dye layer. This would also mean replacing Ti⁴⁺ with Li⁺, which would potentially lead to desorption of the dye. In this respect, it might be worth modifying the cation of the electrolyte, using a cation that is less hard (low charge, high volume, maybe even sterically hindered; e.g. [nBu₄N]⁺, i.e., [nBu₄N]I/I₂), which could feasibly be expected to increase the propensity of the COO⁻ group to remain coordinated to Ti⁴⁺.



Figure 7.12 Air-solid ATR-FTIR spectra (offset for clarity) showing the reversible complexation of electrolyte components (Li^+) on the C=O moieties of the dyes, and of electrolyte components (I_2) on SCN⁻.

Figure 7.13 illustrates an intensification of the liquid-solid ATR-FTIR absorbance of the C=O group at 1600 cm⁻¹ for **MK-2** and at 1625 cm⁻¹ for **N3** and **N749**, once the dyesensitized substrate is in contact with Lil dissolved in MeCN. This further suggests that the Li⁺ cations potentially interact with the C=O moiety of the carboxylate groups of dyes on TiO₂. In fact, Li⁺ has been shown to strongly interact with the carboxylate group of some organic dyes^{99,141}. As the COO⁻ group would probably chelate the Li⁺ cation if possible, it seems likely that an equilibrium between bidentate and monodentate bridging is present for Li⁺ and COO⁻ in solution.



Figure 7.13 Liquid-solid ATR-FTIR spectral area (offset for clarity) for the absorption of C=O in the presence of solvent and electrolyte.

Furthermore, ATR-FTIR measurements were carried out on dye-sensitized thin films of nanoparticulate TiO₂, as this enables a better observation of the interactions between the dyes and TiO₂, specifically the changes of the C=O stretching vibrations in the carboxylate group, due to much larger effective surface area of the nanoparticulate TiO₂. The results in Figure 7.14 show that the C=O absorption wavenumber of a mixture of TiO₂ nanoparticles and dye solution does not change upon adding the electrolyte in MeCN. However, the intensified absorbance of C=O stretching vibration during the addition of electrolyte justifies the aforementioned assumption that Li⁺ cation could engage in binding with the negatively charged oxygen atom of the carboxylate. Moreover, when the mixture of dye solution and nanoparticles are dried by exposure to air, a discrepancy is observed between the C=O absorption wavenumber of the mixture with or without electrolyte. This could be interpreted in terms of a competition for the carboxylate groups by two Lewis acids Li⁺ and Ti⁴⁺, whereby the former has the advantage that it can move relatively freely in the presence of solvent, while the latter is spatially constrained. Overall, we concluded that the addition of electrolyte affects the binding of the carboxylate group onto TiO₂, which we tentatively ascribed to $Li^+\cdots COO^-$ interactions. These undesired interactions could be suppressed by using a cation for the electrolyte that is less similar to Ti^{4+} and/or less mobile in order to suppress these undesired interactions. The electrolyte function is carried out by I⁻ and I₂ and should hence not be affected.







7.3.2.3 Interactions between electrolyte constituents and isothiocyanate ligands determined via XPS

XPS S 2p spectra (Figure 7.15) potentially support the interaction between I_2 and the SCN⁻ ligands by showing an obvious shift of peaks when **N3** and **N749** are in contact with the electrolyte in MeCN, while no apparent peak shift was observed for **MK-2**. This might also be an interaction between Li⁺ and SCN⁻, given that S is the second-row homologue of O. When the electrolyte interacts with **N3** and **N749** on TiO₂ nanoparticles, a higher positive oxidation state is observed for the S atom, as the S 2p3/2 binding energy increases from 168.3 eV to 169 eV. This result suggests that I_2 might have oxidized the sulphur atom in an SCN⁻ group of **N3** and **N749** to approach the sulfate state (SO₄²⁻). On the other hand, the XPS spectra for **MK-2** show relatively stable S 2p3/2 peaks at approximately 164 eV, which is mostly likely due to the higher stability of sulphur in the thiophene moieties.



Figure 7.15 XPS spectra showing the influence of the electrolyte on the S 2p spectra of **MK-2**, **N3**, and **N749** adsorbed on nanoparticulate TiO₂ sintered on ITO coated glass.

Moreover, the XPS Ti 2p spectra (Figure 7.16) for MK-2, N3, and N749 after exposure to the electrolyte in MeCN exhibit apparent peaks at binding energies of ~459 eV (Ti 2p3/2) and 464.5 eV (Ti 2p1/2). Moreover, N3 exhibits pronounced peak splitting at 461.7 eV and 464.2 eV in the absence of the electrolyte. Since S is a higher homologue of O, the coordination via the S atom from the Ru-based dyes (and their SCN⁻) ligands to the TiO₂ Lewis acids should be possible. Therefore, we assumed that due to the different anchoring geometry of N3 relative to N749 and the influence of the TBA⁺ in **N749**, the particularly strong interaction between SCN⁻ group in N3 and the TiO₂ surface causes the peak splitting, which is likely to be weakened when I^{-}/I_{3}^{-} are added to block the interaction between SCN⁻ and the TiO₂ surface (the addition of I⁻ or $I_3^$ would lead to competitive coordination at the Ti sites, or the formation of I₂SCN⁻), thus showing no such peak splitting after the electrolyte interaction with the N3...TiO₂ interface. This is supported with previous findings of S...TiO₂ interactions between the SCN⁻ ligands in **N719** and the nanoporous TiO₂ surface, by using near-edge X-ray absorption fine structure (NEXAFS) spectroscopy¹⁴². Nevertheless, in order to anchor with one COO⁻ group onto the TiO₂ surface, N3 requires a deprotonation of at least one of the COOH groups, while MK-2 has a CN-COOH group with higher tendency of coordination, and **N749** contains one COO⁻ group ready for coordination. This may tentatively explain the low intensity of the Ti 2p peaks of N3 on TiO₂ as the deprotonation may generate H⁺ that passivates the Ti sites.



Figure 7.16 XPS spectra showing the effect of the electrolyte on the Ti 2p spectra of **MK-2**, **N3**, and **N749** adsorbed on nanoparticulate TiO₂ sintered on ITO coated glass.

7.3.3 Dye···TiO₂ interfacial structures sensitized by MK-2, N3 or N749 dyes in d_4 -methanol solution

MeOH is a commonly used solvent for dissolving the I^{-}/I_{3}^{-} redox electrolyte in battery research. *In-situ* NR data were also collected for thin films of dye-sensitized TiO₂ on silicon wafers upon submerging in d₄-MeOH and in the presence of Lil/I₂. The *in-situ* NR and fitted SLD profiles, under consideration of the solvent ingression in the dye layer, are shown in Figure 7.17.







Figure 7.17 *In-situ* NR profiles and fittings as well as SLD values obtained from a single-fitting refinement of the NR data collected for thin films of dye-sensitized TiO_2 on silicon wafers submerged in d₄-MeOH, under consideration of solvent ingression in the dye layer.

Table 7.6 shows the fitted structural parameters obtained from the single-fitting refinement of the NR data collected for TiO₂ sensitized with **MK-2**, **N3**, or **N749** in d₄-MeOH. The surface coverage of **MK-2** on TiO₂ in d₄-MeOH is significantly lower than that in d₃-MeCN, indicating large solvent ingression as a result of the plausible self-assembled stacking structure of **MK-2** that contains voids on TiO₂. The addition of Lil leads to a significant decrease in the fitted surface coverage, i.e., to a higher solvent ingression rate, suggesting a higher SLD of the dye layer, which is expected as a consequence of the Lil ingression in the dye layer. However, further addition of I₂ does not induce obvious changes of the solvent ingression rate for any of the dyes, indicating that the effect of the ingression of I₂ is relatively small in d₄-MeOH in the presence of I₁⁻ anions leads to the formation of complexation within and on top of the dye layers.

Each molecule of N3 dye that we purchased from Solaronix contains two crystal water molecules that were incorporated upon crystallization of dye molecules from water or moist solvents in the process of production. We observed that N3 layers, fabricated in the presence of crystal-structure-derived water molecules, show an even lower surface coverage on TiO₂ than **MK-2**, which is consistent with the suspected stacking structure of N3 molecules on TiO₂, which would result in a higher thickness but lower density (cf. Table E2-(1)) and thus allows a significant solvent ingression within and across the stacked dye layers. Therefore, we believe that R-OH solvents such as water (R = H) and methanol (R = Me), are able to engage in hydrogen bonding with COOH/COO⁻ groups and can thus promote the desorption of the dye molecules better than the R-CN solvents such as acetonitrile (R = Me). Moreover, the addition of Lil results in an increase of the solvent ingression rate, suggesting a higher SLD of the dye layer as a consequence of the Lil ingression. Even though the addition of I₂ does not significantly change the fitted solvent ingression rate, the thickness of N3 increases substantially, which was tentatively ascribed to the interaction between the SCN⁻ ligands with I₂, which forces the loosely packed N3 molecules in a more upright position on TiO₂. Nevertheless, the fitting results also suggest that the illumination with LED light has little impact on the dye \cdots TiO₂ interface structures under open-circuit conditions.

It should be noted that the nucleophilic substitution reaction between Lil and d₄-MeOH slowly causes the formation of LiOD. Therefore, it is understandable that certain dyes

will be affected more than others, as this nucleophilic substitution reaction is likely affected by the acidic level of the solution, e.g., **N749** and **N3** once deprotonated have more ions than **MK-2** (which only has one COO⁻). Although MeOH is commonly used to dissolve I^{-}/I_{3}^{-} redox electrolyte in battering research, this study shows its influence on the dye…TiO₂ interface structures, i.e., its adverse effect on the dye adsorption, which potentially renders its large scale application in DSSCs limited.

Table 7.6 Structural parameters obtained from a single-fitting refinement of NR data collected for TiO₂ sensitized with **MK-2**, **N3**, or **N749** in d₄-MeOH, under consideration of solvent ingression in the dye layer.

	Solution	Dye layer					
Dye		Thickness (Å)	Fitting error (Å)	ρ _{dye} (10 ⁻⁴ unit/Å ³)	Fitting error (10 ⁻⁵ unit/Å ³)	Coverage	logbars
	d₄-MeOH	29.4	(-0.5, 0.5)	5.78	(-4.8, 3.3)	37.5%	2.074
	d₄-MeOH+Lil	33.5	(-0.6, 0.6)	5.89	(-2.5, 3.1)	23.3%	1.620
MK-2	d ₄ -MeOH+LiI+I ₂	35.7	(-0.7, 0.6)	6.04	(-4.7, 4.2)	23.1%	2.355
	d ₄ -MeOH+Lil+l ₂ (light on)	35.4	(-0.8, 0.5)	5.82	(-3.6, 4.8)	22.8%	1.438
	d₄-MeOH	28.5	(-0.6, 0.4)	10.67	(-10.9, 7.2)	17.1%	1.865
	d₄-MeOH+Lil	29.0	(-0.4, 0.6)	11.08	(-7.1, 5.9)	9.5%	2.604
N3 ·2H ₂ O	d ₄ -MeOH+LiI+I ₂	35.2	(-0.8, 0.5)	10.52	(-9.5, 6.3)	8.8%	2.191
	d ₄ -MeOH+Lil+l ₂ (light on)	35.9	(-0.8, 0.4)	11.07	(-6.2, 5.3)	8.7%	2.698
N749	d ₄ -MeOH	8.9	(-0.4, 0.4)	7.53	(-3.9, 4.5)	50.3%	2.012
	d₄-MeOH+Lil	8.8	(-0.3, 0.3)	7.79	(-6.1, 3.3)	38.2%	1.595
	d ₄ -MeOH+LiI+I ₂	10.3	(-0.3, 0.3)	7.39	(-4.4, 5.8)	36.2%	1.476
	d ₄ -MeOH+LiI+I ₂ (light on)	10.6	(-0.4, 0.3)	7.62	(-7.0, 4.6)	37.8%	1.223

7.3.4 Examining the effect of the electrolyte on the interface structure by changes of the reflectivity profiles

The effects of electrolyte on the dye…TiO₂ interface structure were examined by progressive addition of the electrolyte components and recording the corresponding reflectivity profiles (Figure 7.18). An obvious change in the *in-situ* NR profile of **MK-2** was observed upon addition of I₂ in MeCN, indicating that I₂ changes the **MK-2**…solvent interface structure in MeCN. However, the systematic change in the *in-situ* NR profile of **MK-2** is in comparison relatively small upon addition of LiI, indicating that

the **MK-2** \cdots TiO₂ interface structure in MeCN may change more in response to the addition of I₂ than the addition of LiI.



Figure 7.18 *In-situ* NR profiles of **MK-2**, **N3**, and **N749** adsorbed on thin films of atomically flat TiO_2 on silicon wafers submerged in deuterated solvent, deuterated solvent and Lil, as well as deuterated solvent and Lil and I_2 .

The steepness of the fitted SLD profile for the **MK-2**...solvent interface (Figure E20(a)) suggests that the addition of Lil also slightly reduces the roughness of the **MK-2**...solvent interface. This could potentially be interpreted in terms of Li⁺ filling the space between molecules of **MK-2**, which would level the undulation at the interface. However, further addition of I₂ leads to a substantial increase of the roughness of the **MK-2**...solvent interface, as seen from the drastic reduction of SLD variation steepness at the dye...solvent interface and the distortion of the SLD profile at the **MK-2**...TiO₂ interface (Figure E20(a)). This interpretation would also be consistent with the considerably high fitted **MK-2**...solvent interfacial roughness value (19.8 Å) shown in Table E4. Even though the fitting sample model assumes no extra layer on top of the dye, it has the limitation as the **MK-2**...solvent interfacial roughness value is almost comparable to the thickness of a dye layer, and the **MK-2**...solvent interfacial roughness value is almost between the dye and the solvent, presumably following the reaction of I₂ + I⁻ → I₃⁻ to

first form I_{3} anions and subsequently form coordination polymers on the **MK-2** molecules, which contain large intermolecular spaces due to the long alkyl chains.

Furthermore, an apparent change in the NR profile for **MK-2** and thus of the **MK-2**…solvent interface structure was observed during the addition of Lil in MeOH. In comparison, the change in the NR profile for **MK-2** is relatively modest upon addition of I₂, suggesting that the **MK-2**…TiO₂ interface structure in MeOH is more sensitive to the effect of Lil (particularly Li⁺) than to that of I₂. At this point, we suspect that Li⁺ may affect the coordination mode of the COO⁻ group and thus lead to desorption, which could result in the formation of e.g. bi-layers (lamellae). In comparison, the addition of Lil to **N3** and **N749** introduces more subtle changes in the *in-situ* NR profiles, which requires more scrutinous fittings to reveal the actual structural variation.

In general, a different behavior of the dye···TiO₂ interface structure was observed during the addition of the electrolyte components in MeCN or MeOH. One of the reasons could be that molecules of **MK-2** on TiO₂ may adopt a weaker coordination mode in MeOH than in MeCN, which would hence be more susceptible to the influence of the electrolyte components. This is supported by the observation that MeOH is better than MeCN in mobilizing the dye molecules based on the parameter to evaluate the adsorption extent while investigating the solvent rinsing effect (*cf.* Appendix E3), which we tentatively attributed to the influence of the ability to form hydrogen (deuterium) bonds in MeOH. Moreover, the electrolyte constituents react with MeOH in contrast to MeCN. This is due to the nucleophilic substitution reaction between Lil and d₄-methanol, which slowly causes the formation of LiOD and the depletion of I⁻ due to the formation of CD₃I. Ultimately, the supply of I₃⁻ to gather on the **MK-2** dye molecules may become insufficient to form coordination polymers and roughen the dye···solvent interface during the addition of I₂.

7.3.5 Plausible self-assembly structures of MK-2, N3, and N749 on TiO₂ in the presence of solvent and electrolyte

Tables 7.3 and 7.6 show that the thickness of the dye layer remains relatively stable throughout the addition of LiI in either MeCN or MeOH, except for **MK-2** in MeOH, where the thickness increases significantly upon addition of LiI and slightly upon further addition of I_2 . The thickness of **MK-2** remains constant (~ 20 Å) throughout the addition of LiI and I_2 in MeCN. However, the thickness of **MK-2** in MeOH (~ 29 Å) is higher than

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the maximum molecular length of **MK-2** (Scheme 7.2) and increases upon addition of LiI and I₂ (particularly upon addition of LiI). This result suggests that in MeOH, molecules of **MK-2** may adopt a structure on TiO_2 that is different from a uniformly packed monolayer, probably due to the fact that the propensity of MeOH to mobilize the dye molecules is higher than that of MeCN (see the SI for the 'rinsing effect'). Accordingly, the addition of Li⁺ in MeOH may modulate the orientation of **MK-2** more easily by interacting with the carboxylate and nitrile molecules of the cyanoacrylic groups of the dye molecules^{99,141}.



Scheme 7.2 (a) Crystal structure of **MK-2**. The distance between O2 and the hydrogen atom on C1 is 26.09 Å; the distance between O2 and the hydrogen atom on C22 is 26.32 Å, which is similar to the calculated maximum molecule length (26.23 Å) given a bidentate-bridging binding mode. (b) Chemical structure used to derive the calculated maximum molecular height ($d_{max} = 28.28$ Å, with the hydrogen atom included particularly for NR study) including the average COO⁻...TiO₂ bond length (2.05 Å) and a bidentate-bridging mode of **MK-2** on thin films of TiO₂⁹⁹.

At this point, we assume that molecules of **MK-2** intertwine and form a stacking structure on TiO_2 in MeOH, which would explain why the thickness of the dye layer is higher than the maximum molecular height of **MK-2** on TiO_2 according to the *in-situ* NR results. Nevertheless, if the coordination modes of the **MK-2** molecules on TiO_2 are in equilibrium between e.g. monodentate and bidentate bridging, it might be possible for the solvent molecules to dissolve the COO⁻ group, especially in the monodentate mode, which would desorb the **MK-2** molecules. Once detached, these

should either form micelles or inverted double layers to minimize the exposure of the long lipophilic core of **MK-2** dye to the polar solvent. Moreover, the carbazole moiety in MK-2 acts as an amine base and would most likely be transformed into a carbazolium moiety when the COOH group in the cyanoacrylic anchor is deprotonated during the adsorption of MK-2 on TiO₂. Such a carbazolium moiety would in all likelihood endow **MK-2** with a hydrophilic end group, which would, given the presence of several long alkyl chains, turn MK-2 into a surfactant. In addition, as d₄-MeOH contains an OD group that is able to engage in deuterium bonding, which is similar to hydrogen bonding, the ability of d₄-MeOH to form deuterium bonds may lead to the detachment of the adsorbed dye molecules and subsequent rearrangement. This may be particularly obvious for **MK-2** as it contains only one carboxylate anchor group per molecule. In addition, the hollow space in the dye layer presumably accommodates the Li⁺ and I⁻/I₃⁻ during the addition of the electrolyte components, thus slightly pushing the MK-2 molecules in a more upright position compared to the stable structure of MK-2 observed in acetonitrile. This assumption of a hollow space in the **MK-2** layer on TiO₂ in MeOH would also explain the significantly higher solvent ingression (>60%) compared to that in MeCN (<10%).

It is also noteworthy that for N3 and N749, the thickness of the dye monolayers remains relatively stable upon addition of Lil, regardless of the solvent. Dye molecules such as N3 and N749, which contain SCN⁻ ligands, tend to be pushed more upright on TiO₂ when I_2 is added to the electrolyte under formation of I_2 SCN⁻. This might be rationalized in terms of an interaction between I_2 and on thiocyanate group (SCN⁻) in N3 and N749, which is supported by the increased thickness upon addition of I₂ in either MeCN or MeOH based on the *in-situ* NR results. Particularly, the thickness increases significantly upon addition of I₂ for N3 (with crystal water) in MeOH, which we tentatively attributed to interactions between the I₂SCN⁻ ligands that forces the loosely packed N3 dye molecules upright on TiO₂. In addition, the interdye spacing would be filled with Li⁺, which could influence the carboxylate groups of the dyes and potentially affect the dye orientation. However, the thickness variation for N3/N749 upon addition of Li⁺ is indiscernible in either MeCN or MeOH, probably due to their octahedral coordination geometries via different dcbpy ligands, which would be expected to induce negligible thickness variation even in the event of orientational change due to the Li⁺···COO⁻ interaction.
7.4 Conclusions

In-situ NR has been used to determine the thickness and density of layers of MK-2, N3, and N749 on thin films of amorphous TiO₂ in the presence of Lil and/or I₂. The results suggest different self-assembly structures for these dyes in different solvents and in the presence of Lil and/or I_2 . The fitting results demonstrate a significantly different self-assembly structure for the **MK-2** layer in d₄-methanol relative to that in d₃-acetonitrile, which is likely due to a weaker binding between the carboxylate anchors and the TiO₂ surface in d_4 -methanol compared to that in d_3 -acetonitrile. The thickness of the MK-2 layer and hence the orientation of the MK-2 molecules on TiO₂ in d₄methanol is more susceptible to the effect of the presence of Lil and/or I2, which is reflected in a change of the thickness values, particularly when Lil is added. However, the organometallic dyes N3 and N749 are not vulnerable to the intervention of Lil in either d₃-acetonitrile or d₄-methanol, probably due to their lower aspect ratio (width to height) compared to **MK-2** that allows less anisotropic orientation on the TiO₂ surface. However, even though I₂ has been reported to interact with the SCN⁻ ligands in N3 and N749 dyes, its influence on the thickness variation of N3 and N749 layers is relatively low, except for N3 (fabricated in the presence of crystal-structure-derived water molecules) in d₄-methanol, which possibly results in desorption-induced stacking.

In comparison to **MK-2** and **N3**, **N749** exhibits a much lower surface coverage in d₃-MeCN, probably due to the weakly coordinating tetrabutylammonium cations (TBA⁺) of **N749**, which easily dissociate in the presence of solvent and thus result in the formation of large intermolecular space available for solvent ingression. Further refinement of the applied model under consideration of the solvent ingression allowed extracting the information of the dye coverage and solvent ingression rate, which suggest that both Lil and l₂ exhibit some sort of ingression in the dye layer in d₃-MeCN. Particularly for **N3** and **N749**, the l₂ ingression is more pronounced than that for **MK-2**, as the fitted results suggest no solvent coverage on the TiO₂ surface in the presence of Lil/l₂. Nevertheless, the fitting results also suggest that the formation of an extra top layer is induced for **MK-2**, **N3**, and **N749** in the presence of Lil/l₂, which consists mostly of l₂ and exhibits a thickness of 20-40 Å as well as a coverage of 4-12%. However, even though the fitting results suggest Lil ingression in the dye layers for **MK-2**, **N3**, and **N749** in d₄-methanol, the l₂ ingression within and on top of the dye layers are almost negligible, probably due to the formation of LiOD and the depletion of l⁻ due to

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the formation of CD₃I when LiI is added to d_4 -methanol, which affords less I_3^- available for polymerizations within and on top of the dye layers.

Furthermore, the fitted low dye coverage values in d₄-methanol for **MK-2** (<40%) corroborate the proposed self-assembly mechanism of **MK-2** on TiO₂ in d₄-methanol. We suspect that **MK-2** plausibly forms a stacked structure with a void in d₄-methanol, which results in a lower density that allows significant solvent ingression. It is also worth noting that the **N3** layer fabricated from the dye starting materials that contains crystal water exhibit a significantly lower dye coverage, which agrees with the suspected stacking structure of the **N3** layer on TiO₂, i.e., higher thickness but lower density. The crystal water molecules are similar to d₄-methanol as far as they are able to engage in hydrogen bonding. Such R-OH (water: R = H; methanol: R = Me) solvents thus seem to be able to promote the desorption of dye molecules better than the R-CN solvents such as acetonitrile (R = Me).

8. Concluding remarks and future work

8.1 Concluding remarks

The dye…TiO₂ interface structure of the DSSC working electrode is crucial to the charge transfer kinetics and hence the photovoltaic performance of DSSC devices, as it is where the initial charge separation happens. This project aims to better understand how the dye…TiO₂ interface of the DSSC working electrode operates at the molecular level. X-ray and neutron techniques were mainly used to study the dye…TiO₂ interface structure, while other techniques such as IR spectroscopy, XPS as well as imaging techniques (AFM & STM) were also used to complement results and analysis.

In summary, the major work in this thesis includes determining the dye nanoaggregate structures of **MK-2**, **N3**, and **N749** at the dye \cdots TiO₂ interface, which represent the working electrode of dye-sensitized solar cells; establishing relationships between the dye \cdots TiO₂ interfacial structure and DSSC fabrication parameters using high-throughput X-ray reflectometry; and examining the structure of the dye \cdots TiO₂ interface in the presence of solvent and electrolyte components in dye-sensitized solar cells.

In Chapter 3, we find that nanoaggregates of the **MK-2**, **N3** and **N749** are separated by several hundred nanometers (158-203 nm) at dye…TiO₂ interfaces that had been fabricated using concentrated dye solutions (0.5 mM or 1.0 mM). **MK-2** and **N749** dyes also display smaller inter-particle separations. The observed dye nanoparticle diameters (156-198 nm) using Guinier analysis are comparable to the largest hitherto reported inter-particle separations. Self-assemblies of all three dyes exhibit both lateral and longitudinal short-range order, and **N3** displays a particularly short coherence length along the TiO₂ surface, with extensively structured disorder in longitudinal direction.

In Chapter 5, we find that self-assembly of the dyes is a multi-step process, and it is an intermediate rather than ultrafast process and spans the time order of hours. The molecular consequences of rinsing DSSC working electrodes after dye sensitization on the dye self-assembly are revealed for the first time, i.e., rinsing DSSC working electrodes as part of the fabrication process seems to promote dye aggregation in the case of **MK-2** and **N3**, while **N749** presents an exception. 2-D and 3-D correlation mappings of these fabrication conditions against the dye-layer thickness and density

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provide a means to guide the DSSC device manufacturer to produce a working electrode with a specific dye-layer thickness.

In Chapter 6, a combined *in-situ* NR and *ex-situ* XRR analysis suggests a different orientation (dye-layer thickness) for **MK-2** and **N749** on TiO₂ at the air-solid environment from that in the emulation DSSC device (solvent environment). It also demonstrates a method for the evaluation of the dye and solvent volume fractions of the dye layer by combining *in-situ* NR and *ex-situ* XRR data. Regarding the potential change of orientation for **MK-2** under LED illumination, the results also suggest a corresponding well change of solvent ingression at the solid-liquid interface. The change of solvent ingression (5.6%) may support that the minor thickness change (4.8%) may not be an artifact (given SLD_{d3-MeCN}>>SLD_{MK-2}), but a light induced heat effect that simply causes enhanced solubility of solvent .

In Chapter 7, we find different self-assembly structures for MK-2, N3 and N749 dyes in different solvents and in the presence of Lil and/or I₂. We also observe a significantly different self-assembly structure for the **MK-2** layer in d₄-methanol relative to that in d_3 -acetonitrile, which is likely due to a weaker binding between the carboxylate anchors and the TiO_2 surface in d₄-methanol compared to that in d₃-acetonitrile. The thickness of the MK-2 layer and hence the orientation of the MK-2 molecules on TiO₂ in d₄methanol is more susceptible to the effect of the presence of Lil and/or l₂, which is reflected in a change of the thickness values, particularly when Lil is added. The organometallic dyes N3 and N749 are not vulnerable to the intervention of Lil in either d_3 -acetonitrile or d_4 -methanol, probably due to their lower aspect ratio (width to height) compared to **MK-2** that allows less anisotropic orientation on the TiO₂ surface. **N749** exhibits a much lower surface coverage in d₃-MeCN, probably due to the weakly coordinating tetrabutylammonium cations (TBA⁺) of **N749**, which easily dissociate in the presence of solvent and thus result in the formation of large intermolecular space available for solvent ingression. The formation of an extra top layer is induced for MK-2, N3, and N749 in the presence of Lil/I₂ in d₃-MeCN, which consists mostly of I₂ and exhibits a thickness of 20-40 Å as well as a coverage of 4-12%; However, even though the fitting results suggest Lil ingression in the dye layers for MK-2, N3, and N749 in d4methanol, the l₂ ingression within and on top of the dye layers is almost negligible, probably due to the formation of LiOD and the depletion of I⁻ due to the formation of CD₃I when Lil is added to d_4 -methanol, which affords less I_3^- available for

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polymerizations within and on top of the dye layers. A higher propensity for the dye layer to desorb in R-OH solvents is observed in the case studies of the three subject dyes owing to the potential formation of hydrogen (deuterium) bonds.

In view of the investigation of the adsorption behaviors of dye on TiO₂, other experimental techniques such as quartz crystal microbalance (QCM) could be used to directly measure the mass uptake of dye on TiO₂ surface. A quartz crystal sensor can be coated with TiO₂ using ALD that is used for coating the silicon substrates for reflectometry measurements. The sensor can then be exposed to dye solution to measure mass change *in-situ*²². Besides, given the collection time for an analyzable neutron reflectivity data of our sample is approximately 1 hour on the high-flux neutron reflectometer, *in-situ* NR experiments can also be performed to measure the reflectivity change from the dye \cdots TiO₂ on silicon wafer during its submersion in the dye solution, which emulates the sensitization process (20 h) during which the dye adsorbs onto TiO₂. This tentatively helps to quantify the dye adsorption during the sensitization process in real time. Moreover, to further improve the analyzability of the reflectivity signal from the sample, the thickness of the TiO_2 thin film could be increased to bring about more Kiessig fringes in low Q with more resolvable features. Nevertheless, it could be advanced to study the anchoring mechanism of monolayer dye on TiO₂ using reflection FTIR which appeared promising as suggested with more details by section 8.2. Also, the effect of light on the dye...TiO₂ interface structure under open-circuit conditions could be examined as suggested with more details by section 8.3. Further investigation under short-circuit conditions may provide more insights regarding the effect of light on the dye \cdots TiO₂ interface structure.

8.2 Testing the feasibility of using reflection FTIR to examine the anchoring mechanism of the dyes on TiO₂

Specular reflectance sampling using FTIR spectroscopy was performed on dyesensitized thin films of TiO₂ that were deposited on silicon substrate by atomic layer deposition (ALD). To facilitate the measurement, a variable angle VeeMAX II accessory was used, given its sensitivity toward dye monolayers on the atomically flat thin films of TiO₂. It has traditionally been challenging to use FTIR and other spectroscopic techniques to examine the monolayer due to the relatively low signal obtained from the monolayer sample. In our experiment, we adopted a grazing angle reflection mode to measure the specular reflectance at a higher angle (~80° normal to the surface), as this has been recognized as one of the best ways to enhance the IR signal obtained from a monolayer on a surface. Moreover, in order to improve the intensity of the signal, we used a sample mask with a 2-inch instead of a 3/8-inch aperture to expand the area of illumination at this grazing angle of reflection. The results shown in Figures 8.1 and 8.2 clearly show the spectral differences (peak splitting) at around 1100 cm⁻¹ (C-O stretching) for monolayers of two different dyes, i.e., **D131** and **N749** (Scheme 8.1) adsorbed on atomically flat thin films of TiO₂. The observed spectral differences were tentatively ascribed to the influence of the cyano group in **D131**. Overall, these experimental findings demonstrate the feasibility of using reflection FTIR to examine dye monolayers on atomically flat thin films of TiO₂, which is not possible using the traditional attenuated total reflection-Fourier-transform IR spectroscopy (ATR-FTIR).



Scheme 8.1 Chemical structures of the organic dye D131 and the Ru-based dye N749 ('black dye').



Figure 8.1 FTIR spectra for dye layers of **D131** and **N749** recorded using a grazing angle of IR incidence (log reflectance offset for clarity).





8.3 The effect of light on the dye…TiO₂ interfacial structure

The effect of light on the dye...TiO₂ interface structure was investigated under opencircuit conditions. Some differences in the *in-situ* neutron reflectivity profiles were observed for **N749** submerged in Si-contrast-matched solvent (Figure 8.3 (a) and Figure 8.4 (a)) or in d₄-MeOH (Figure 8.3 (b) and Figure 8.4 (b)) in the presence of all electrolyte components, in the dark or under illumination with white light (LED). However, apart from the fact that some deviated data singularities appeared upon exposure to light, the low number of data points in this measurement makes it difficult to conclude a systematic real change in the **N749**…TiO₂ interfacial structure upon exposure to light. Therefore, we suggest that more data points are collected at Q = 0.03 - 0.05 (for Si-contrast-matched solvents), and at Q = 0.05 - 0.15 (for d₄-MeOH) in order to improve the statistical reliability. Overall, given the current measurement resolution, it can only be concluded that the systematic differences are negligible between the *in-situ* NR profiles measured under illumination with white light (LED) and those measured in the dark, indicating a negligible effect of light on the dye…TiO₂ interfacial structure under open-circuit conditions.



Figure 8.3. Comparison of *in-situ* NR profiles (in dark or under illumination) for $dye\cdots TiO_2$ on silicon wafers submerged in (a) Si-contrast-matched d_3 -MeCN/MeCN; (b) d_4 -MeOH; c) d_3 -MeCN (measurements for **MK-2** and **N3** in d_3 -MeCN were performed only at the angle of 0.5°).

(a)













Figure 8.4. Comparison of *in-situ* NR profiles (in dark or under illumination) plotted as RQ⁴ versus Q for dye…TiO₂ on silicon wafers submerged in (a) Si-contrast-matched d₃-MeCN/MeCN; (b) d₄-MeOH.

9. Appendices

Appendix A – Supporting information for Chapter 3

A1. XRR-derived structures of MK-2, N3, and N749 on thin films of amorphous TiO₂ for different sensitization concentrations

Table A1. XRR-fitted structural parameters of **MK-2** layers on thin films of amorphous TiO₂ fabricated using different sensitization concentrations ($d_{TiO2} = \sim 3.18 \text{ g/cm}^3$; $t_s = 20$ h; $c_{MK-2} = 0.05$ -1.00 mM).

	с _{мк-2} [mM]				
MK-2 on thin films of amorphous TiO ₂	0.05	0.25	0.50	1.00	
Thickness (Å)	18.3	23.0	24.2	38.1	
Error (+)	0.3	0.2	0.4	0.5	
Error (-)	0.3	0.3	0.3	0.4	
Density (unit/Å ³)	0.000724	0.000630	0.000685	0.000424	
Error (+)	0.000023	0.000024	0.000021	0.000017	
Error (-)	0.000030	0.000025	0.000026	0.000024	
APM (Ų)	75.31	68.83	60.16	61.60	
Roughness (Å)	6.8	6.2	8.8	5.7	
FOM logR1	0.01691	0.01098	0.01248	0.01280	

The 'unit' in the table is defined as a unit of the dye molecule. The X-ray scattering length density (SLD) of each dye layer can be derived by multiplying the fitted density of each dye layer with the total X-ray scattering length of a dye molecule, i.e., 1450 fm for **MK-2**, 1003 fm for **N3**, and 2075 fm for **N749**.

Table A2. XRR-fitted structural parameters for the **N3** layers on thin films of amorphous TiO₂ fabricated using different sensitization concentrations ($d_{TiO2} = \sim 3.18$ g/cm³; $t_s = 20$ h; $c_{N3} = 0.05$ -1.00 mM).

	С _{№3} [mM]				
N3 on thin films of amorphous TiO ₂	0.05	0.25	0.50	1.00	

Thickness (Å)	16.2	16.5	16.1	20.1
Error (+)	0.5	0.3	0.3	0.3
Error (-)	0.2	0.3	0.3	0.5
Density (unit/Å ³)	0.001089	0.001129	0.001205	0.000487
Error (+)	0.000220	0.000106	0.000060	0.000053
Error (-)	0.000301	0.000090	0.000084	0.000038
APM (Ų)	56.32	53.54	51.34	101.70
Roughness (Å)	6.5	7.0	7.0	2.3
FOM logR1	0.02535	0.02433	0.01978	0.01536

Table A3. XRR-fitted structural parameters for the **N749** layers on thin films of amorphous TiO₂ fabricated using different sensitization concentrations ($d_{TiO2} = \sim 3.18$ g/cm³; $t_s = 20$ h; $c_{N749} = 0.05$ -1.00 mM).

		С _{N749} [mM]					
N749 on thin films of amorphous TiO ₂	0.05	0.25	0.50	1.00			
Thickness (Å)	16.4	20.1	15.2	16.0			
Error (+)	0.3	0.8	0.3	0.4			
Error (-)	0.2	0.2	0.3	0.3			
Density (unit/Å ³)	0.000462	0.000384	0.000370	0.000595			
Error (+)	0.000036	0.000021	0.000032	0.000065			
Error (-)	0.000029	0.000083	0.000048	0.000050			
APM (Å ²)	131.25	128.75	176.23	104.25			
Roughness (Å)	5.7	4.5	6.3	6.4			
FOM logR1	0.01715	0.01700	0.01324	0.01744			

A2. Q_z positions of the Yoneda peak for the horizontal cut analysis of the experimental GISAXS data

Table A4. Calculated Q_z positions for the Yoneda peaks obtained from different incident angles (α_i) of the X-ray beam. The Q_z positions were confirmed to be highly consistent with the experimental observations.

α i [°]	Q _z position of the predominant Yoneda peak (Å ⁻¹)
0.15	0.035
0.20	0.041
0.25	0.046
0.30	0.052
0.35	0.057
0.40	0.063

The Q_z position of the predominant Yoneda peak was calculated based on the critical edge. The critical edge $k_c = \sqrt{4\pi \cdot SLD_s}$ is determined by the substrate if the SLD of the film is smaller than that of the substrate. However, if the SLD of the film is larger than that of the substrate, the critical edge is jointly determined by the SLD of the film and the substrate, i.e., $\sqrt{4\pi \cdot SLD_s} < k_c < \sqrt{4\pi \cdot SLD_f}$. The exact position of the critical edge depends on the thickness and the SLD of the film. In general, if the film is thin and the SLD is small, the critical edge k_c is closer to the critical edge of the substrate. Conversely, if the film is thick, the critical edge k_c is closer to the critical edge of the film⁴⁷. In our case, our sample system could be regarded as the dye...TiO₂ and TiO₂...substrate systems in tandem. For the dye...TiO₂ systems, the SLD of TiO₂ is larger than that of the dye (cf. A4), then the k_c of the dye...TiO₂ system is determined by the SLD of TiO₂. In the meantime, the SLD of TiO₂ is also larger than that of the substrate which could be viewed as SiO₂...Si system that has a k_c close to that of silicon (cf. A4), and given that the TiO₂ is relatively thick, the k_c of the whole system is determined by the SLD of the TiO₂ film. The above Q_z positions were therefore calculated based on the critical edge of the TiO_2 film.

A3. XRR-fitted structural parameters used for the GISAXS simulations of the dye…TiO₂ thin films fabricated using different sensitization concentrations

Table A5. XRR-derived structural and X-ray optical parameters of layers used for the

 GISAXS simulations.

Dye	Concentration	Molecular formula	Density (g/cm³)	Thickness (Å)	Refractive index δ (10 ⁻⁶)	Refractive index β (10 ⁻⁸)
		$C_{58}H_{70}N_2O_2S_4$	1.09	24.2	1.556	0.377
	0.50 mM	TiO ₂	3.19	164.7	4.079	9.309
	0.50 1110	SiO ₂	3.09	5.0	4.125	2.267
MK-2		Si	2.33		3.111	1.709
WITY-2		$C_{58}H_{70}N_2O_2S_4$	0.67	38.1	0.957	0.232
	1.00 mM	TiO ₂	3.18	151.2	4.066	9.280
	1.00 1110	SiO ₂	3.00	5.0	4.005	2.201
-		Si	2.33		3.111	1.709
		$C_{26}H_{16}O_8N_6S_2Ru$	1.41	16.1	1.881	1.195
	0.50 mM	TiO ₂	3.23	209.1	4.130	9.426
		SiO ₂	2.77	5.0	3.698	2.032
N3		Si	2.33		3.111	1.709
NJ	1.00 mM	$C_{26}H_{16}O_8N_6S_2Ru$	0.57	20.1	0.761	0.483
		TiO ₂	3.13	154.7	4.002	9.134
	1.00 1110	SiO ₂	2.89	5.0	3.858	2.120
		Si	2.33		3.111	1.709
		$C_{53}H_{82}O_6N_8S_3Ru$	0.68	15.2	0.960	0.417
	0.50 mM	TiO ₂	3.19	202.4	4.079	9.309
	0.00 1110	SiO ₂	2.78	5.0	3.711	2.040
N749		Si	2.33		3.111	1.709
117 45		$C_{53}H_{82}O_6N_8S_3Ru$	1.10	16.0	1.552	0.674
	1.00 mM	TiO ₂	3.24	213.3	4.143	9.455
	1.00 mixi	SiO ₂	3.06	5.0	4.085	2.245
		Si	2.33		3.111	1.709

Table A6. Structural data for 100% surface coverage of **MK-2**, **N3**, and **N749** on thin films of TiO₂.

Dye	Mass density	Molecular	Density
	(g/cm ³)	Volume (Å ³)	(unit/ų)
MK2	1.24	1284.34	0.00078156

N3	1.84	636.51	0.00157031
N749	1.28	1462.75	0.00068398

A4. GISAXS simulation parameters for layers of MK-2, N3, and N749 on silicon substrates

 Table A7. Critical angles of the X-ray beam for layers and substrates of samples.

Duo	Sensitization concentration					
Dye	0.5	mM		1 י	тM	
MK-2	Molecular formula	Refractive index (δ)	Critical angle $(\frac{180\sqrt{2\delta}}{\pi})$	Molecular formula	Refractive index (δ)	Critical angle $(\frac{180\sqrt{2\delta}}{\pi})$
	$C_{58}H_{70}N_2O_2S_4$	1.56E-06	0.101°	$C_{58}H_{70}N_2O_2S_4$	9.57E-07	0.079°
WII X-2	TiO ₂	4.08E-06	0.164°	TiO ₂	4.07E-06	0.163°
	SiO ₂	4.13E-06	0.165°	SiO ₂	4.01E-06	0.162°
	Si	3.11E-06	0.143°	Si	3.11E-06	0.143°
	Molecular formula	Refractive index (δ)	Critical angle $(\frac{180\sqrt{2\delta}}{\pi})$	Molecular formula	Refractive index (δ)	Critical angle $(\frac{180\sqrt{2\delta}}{\pi})$
N3	$C_{26}H_{16}O_8N_6S_2Ru$	1.88E-06	0.111°	$C_{26}H_{16}O_8N_6S_2Ru$	7.61E-07	0.071°
110	TiO ₂	4.13E-06	0.165°	TiO ₂	4.00E-06	0.162°
	SiO ₂	3.70E-06	0.156°	SiO ₂	3.86E-06	0.159°
	Si	3.11E-06	0.143°	Si	3.11E-06	0.143°
	Molecular formula	Refractive index (δ)	Critical angle $(\frac{180\sqrt{2\delta}}{\pi})$	Molecular formula	Refractive index (δ)	Critical angle $(\frac{180\sqrt{2\delta}}{\pi})$
N749	$C_{53}H_{82}O_6N_8S_3Ru$	9.60E-07	0.079°	$C_{53}H_{82}O_6N_8S_3Ru$	1.55E-06	0.101°
	TiO ₂	4.08E-06	0.164°	TiO ₂	4.14E-06	0.165°
	SiO ₂	3.71E-06	0.156°	SiO ₂	4.09E-06	0.164°
	Si	3.11E-06	0.143°	Si	3.11E-06	0.143°

Since the incident angle of the synchrotron X-ray beam (0.15°) is above the critical angle of the dye layer, but below that of the thin film of TiO₂ (Table A7), total reflection occurs at the TiO₂ surface after the X-ray beam penetrates the dye layer. The following GISAXS simulations shown at $\alpha_i = 0.15^\circ$ mostly excluded the effect of the TiO₂ thin film, allowing the extraction of the influence of the dye layer density on the GISAXS pattern. This is especially effective when comparing substrates with inhomogeneous thin films of TiO₂ underneath the dye layers. In summary, the general variation trends of the GISAXS patterns match both the simulation and experimental GISAXS results at $\alpha_i = 0.4^\circ$.



Figure A1. Simulated GISAXS patterns ($\alpha_i = 0.15^\circ$) for **MK-2**, **N3**, and **N749** on TiO₂covered Si substrates with dye layer density and thickness values equal to those of the experimental sample: a) $c_{MK-2} = 0.50$ mM; b) $c_{MK-2} = 1.00$ mM; c) $c_{N3} = 0.50$ mM; d) c_{N3} = 1.00 mM; e) $c_{N749} = 0.50$ mM; f) $c_{N749} = 1.00$ mM; $d_{TiO2} = \sim 3.18$ g/cm³; $t_s = 20$ h; all GISAXS patterns are plotted on a logarithmic intensity scale.

When α_i (0.15°) is above the critical angle of the dye layer but below that of the thin film of TiO₂, the geometric model of the sample system used in the BornAgain simulation could be simplified, as the dye layer on top of the thin film of TiO₂ is considered a subphase (Figure A2). The GISAXS simulations using either the full or

simplified sample models were carried out and are shown in Figure A2. The subtle differences in the GISAXS patterns between the full and simplified models as the result of evanescent waves further support the validity of the previous use of GISAXS simulation at $\alpha_i = 0.15^\circ$ in order to reveal only the dye layer information.



Figure A2. Full and simplified geometric models of the sample system.



Figure A3. Simulated GISAXS patterns ($\alpha_i = 0.15^\circ$) for a) **MK-2**...TiO₂ on silicon; full sample model; b) simplified **MK-2** on TiO₂; subphase sample model; c) **N3**...TiO₂ on silicon; full sample model; d) simplified **N3** on TiO₂; subphase sample model; e) **N749**...TiO₂ on silicon, full sample model; f) simplified **N749** on TiO₂, subphase sample model; dye density and thickness values equal to those of experimental samples

fabricated using a sensitization concentration of 0.50 mM ($d_{TiO2} = \sim 3.18$ g/cm³; $t_s = 20$ h) were used; all GISAXS patterns are plotted on a logarithmic intensity scale.



Figure A4. Simulated GISAXS pattern ($\alpha_i = 0.15^\circ$) for a) **MK-2**···TiO₂ on silicon; full sample model; b) simplified **MK-2** on TiO₂; subphase sample model; c) **N3**···TiO₂ on silicon; full sample model; d) simplified **N3** on TiO₂; subphase sample model; e) **N749**····TiO₂ on silicon; full sample model; f) simplified **N749** on TiO₂; subphase sample model; using dye layer density and thickness values equal to those of experimental samples fabricated using a sensitization concentration of 1.00 mM ($d_{TiO2} = \sim 3.18$ g/cm³; $t_s = 20$ h); all GISAXS patterns are plotted on a logarithmic intensity scale.

The GISAXS patterns are comparable for the full sample models and the simplified dye on TiO₂ subphase sample models. The slight differences are due to the total external reflection being nearly, but not completely loss-less, as the absorption coefficient, β , of TiO₂ and the layers underneath used for simulations is not zero.

A5. BornAgain fitting of the distribution density and particle size for the experimental GISAXS data using Python scripts for layers of MK-2, N3, and N749 on silicon substrates

In the previous simulation, we used $\alpha_i = 0.15^\circ$ (data collection time = 4s), i.e., an incident angle well below the critical angle of layers underneath the dye, in order to study the GISAXS patterns that emanate from the dye layers. In addition, we also

examined the GISAXS patterns upon increasing α_i to 0.4°, when the dye…TiO₂ layer and the silicon substrate were completely penetrated by the X-ray beam. For this system, Python scripts were used to obtain the BornAgain fitting results of the distribution density and size of particles. In summary, the trend of particle density / particle size variation upon increasing the sensitization concentration from 0.5 mM to 1 mM is consistent with the trend of dye layer density variation obtained from the experimental XRR measurements. All particles are assumed to be located at the bottom of the dye layer.

 $\alpha_i = 0.4^\circ$; particle distribution density = 0.0394 a.u.; $\chi^2 = 27.99$.





 $\alpha_i = 0.4^\circ$; particle distribution density = 0.0021 a.u.; $\chi^2 = 15.89$.



Figure A5. GISAXS fitting of the particle distribution density for **MK-2**...TiO₂ on silicon substrates with dye layer density and thickness values equal to those for the experimental samples fabricated using: a) $c_{MK-2} = 0.50$ mM, and b) $c_{MK-2} = 1.00$ mM

 $(d_{TiO2} = \sim 3.18 \text{ g/cm}^3, t_s = 20 \text{ h})$; all GISAXS patterns are plotted on a logarithmic intensity scale; spherical particle shape (radius: 1 nm).

 $\alpha_i = 0.4^\circ$; particle distribution density = 0.0041 a.u.; $\chi^2 = 41.29$.



 $\alpha_i = 0.4^\circ$; particle distribution density = 0.0009 a.u.; $\chi^2 = 49.98$.



Figure A6. GISAXS fitting of the particle distribution density for **N3**...TiO₂ on silicon substrates with dye layer density and thickness values equal to those of experimental samples fabricated using: a) $c_{N3} = 0.50$ mM, and b) $c_{N3} = 1.00$ mM ($d_{TiO2} = ~3.18$ g/cm³; $t_s = 20$ h); all GISAXS patterns are plotted on a logarithmic intensity scale; spherical particle shape (radius: 1 nm).

 $\alpha_i = 0.4^\circ$; particle distribution density=0.0015 a.u.; $\chi^2 = 32.56$.



 $\alpha_i = 0.4^\circ$; particle distribution density = 0.0112 a.u.; $\chi^2 = 35.39$.





Figure A7. GISAXS fitting of the particle distribution density for **N749**...TiO₂ on silicon substrates with dye layer density and thickness values equal to those of the experimental samples fabricated using: a) $c_{N749} = 0.50$ mM, and b) $c_{N749} = 1.00$ mM ($d_{TiO2} = \sim 3.18$ g/cm³, $t_s = 20$ h); all GISAXS patterns are plotted on a logarithmic intensity scale; spherical particle shape (radius: 1 nm).



 $\alpha_i = 0.4^\circ$; particle size (radius) = 1.148 nm; $\chi^2 = 28.17$.



(a)

 $\alpha_i = 0.4^\circ$; particle density = 0.747 nm; $\chi^2 = 15.60$.

Figure A8. GISAXS fitting of the particle size for **MK-2**···TiO₂ on silicon substrates with dye layer density and thickness values equal to those of the experimental samples fabricated using: a) $c_{MK-2} = 0.50$ mM, and b) $c_{MK-2} = 1.00$ mM ($d_{TiO2} = \sim 3.18$ g/cm³, $t_s = 20$ h); all GISAXS patterns are plotted on a logarithmic intensity scale; spherical particle shape; particle distribution density: 0.01 a.u.

 $\alpha_i = 0.4^\circ$; particle size (radius) = 0.859 nm; $\chi^2 = 41.32$.



 $\alpha_i = 0.4^\circ$; particle size (radius) = 0.627 nm; $\chi^2 = 49.44$.



Figure A9. GISAXS fitting of the particle size for N3····TiO₂ on silicon substrates with dye layer density and thickness values equal to those of the experimental samples fabricated using: a) $c_{N3} = 0.50$ mM, and b) $c_{N3} = 1.00$ mM ($d_{TiO2} = \sim 3.18$ g/cm³, $t_s = 20$ h); all GISAXS patterns are plotted on a logarithmic intensity scale; spherical particle shape: particle distribution density: 0.01 a.u.

 $\alpha_i = 0.4^\circ$; particle size (radius) = 0.758 nm; $\chi^2 = 45.60$.



 $\alpha_i = 0.4^\circ$; particle size (radius) = 1.026 nm; $\chi^2 = 35.35$.



Figure A10. GISAXS fitting of the particle size for **N749**...TiO₂ on silicon substrates with dye layer density and thickness values equal to those of the experimental samples fabricated using: a) $c_{N749} = 0.50$ mM, and b) $c_{N749} = 1.00$ mM ($d_{TiO2} = \sim 3.18$ g/cm³, $t_s = 20$ h); all GISAXS patterns are plotted on a logarithmic intensity scale; spherical particle shape; particle distribution density: 0.01 a.u.

BornAgain fittings were also performed for all dye particles that were assumed to be located on the surface of the dye layer.



 $\alpha_i = 0.4^\circ$; particle distribution density = 0.0006 a.u.; $\chi^2 = 28.03$.

 $\alpha_i = 0.4^\circ$; particle distribution density = 0.0394 a.u.; $\chi^2 = 15.92$.





Figure A11. GISAXS fitting of the particle distribution density for **MK-2**···TiO₂ on silicon substrates with dye layer density and thickness values equal to those of experimental samples fabricated using: a) $c_{MK-2} = 0.50$ mM, and b) $c_{MK-2} = 1.00$ mM ($d_{TiO2} = \sim 3.18$ g/cm³; $t_s = 20$ h); all GISAXS patterns are plotted on a logarithmic intensity scale; spherical particle shape (radius: 1 nm).

 $\alpha_i = 0.4^\circ$; particle distribution density = 0.0003 a.u.; $\chi^2 = 41.40$.



 $\alpha_i = 0.4^\circ$; particle distribution density = 0.0004 a.u.; $\chi^2 = 49.98$.



Figure A12. GISAXS fitting of the particle distribution density for **N3**...TiO₂ on silicon substrates with dye layer density and thickness values equal to those of the experimental sample fabricated using: a) $c_{N3} = 0.50$ mM, and b) $c_{N3} = 1.00$ mM ($d_{TiO2} = ~3.18$ g/cm³; $t_s = 20$ h); all GISAXS patterns are plotted on a logarithmic intensity scale; spherical particle shape (radius: 1 nm).

 $\alpha_i = 0.4^\circ$; particle distribution density = 0.0005 a.u.; $\chi^2 = 32.57$.



 $\alpha_i = 0.4^\circ$; particle distribution density = 0.0005 a.u.; $\chi^2 = 35.61$.



Figure A13. GISAXS fitting of the particle distribution density for **N749**...TiO₂ on silicon substrates with dye layer density and thickness values equal to those of the experimental samples fabricated using a) $c_{N749} = 0.50$ mM, and b) $c_{N749} = 1.00$ mM ($d_{TiO2} = \sim 3.18$ g/cm³, $t_s = 20$ h); all GISAXS patterns are plotted on a logarithmic intensity scale; spherical particle shape (radius: 1 nm).

 α_i = 0.4°; particle size (radius) = 0.603 nm; χ^2 = 27.36.



 $\alpha_i = 0.4^\circ$; particle size (radius) = 0.580 nm; $\chi^2 = 15.34$.





Figure A14. GISAXS fitting of the particle size for **MK-2**···TiO₂ on silicon substrates with the dye layer density and thickness values equal to those of the experimental samples fabricated using: a) $c_{MK-2} = 0.50$ mM, and b) $c_{MK-2} = 1.00$ mM ($d_{TiO2} = \sim 3.18$ g/cm³; $t_s = 20$ h); all GISAXS patterns are plotted on a logarithmic intensity scale; spherical particle shape; particle distribution density: 0.01 a.u.

 $\alpha_i = 0.4^\circ$; particle size (radius) = 0.540 nm; $\chi^2 = 40.57$.



 $\alpha_i = 0.4^\circ$; particle size (radius) = 0.549 nm; $\chi^2 = 49.30$.



Figure A15. GISAXS fitting of the particle size for **N3**...TiO₂ on silicon substrates with dye layer density and thickness values equal to those of the experimental samples fabricated using: a) $c_{N3} = 0.50$ mM, and b) $c_{N3} = 1.00$ mM ($d_{TiO2} = \sim 3.18$ g/cm³; $t_s = 20$ h); all GISAXS patterns are plotted on a logarithmic intensity scale; spherical particle shape; particle distribution density: 0.01 a.u.

 $\alpha_i = 0.4^\circ$; particle size (radius) = 0.604 nm; $\chi^2 = 45.25$.



"Experimental" data Simulated data 10¹ Relative difference Parameters 10-1 10-2 10-3

(a)

 α_i = 0.4°; particle size (radius) = 0.588 nm; χ^2 = 34.96.

(b)

Figure A16. GISAXS fitting of the particle size for **N749**...TiO₂ on silicon substrates with the dye layer density and thickness values equal to those of the experimental samples fabricated using: a) $c_{N749} = 0.50$ mM, and b) $c_{N749} = 1.00$ mM ($d_{TiO2} = \sim 3.18$ g/cm³; $t_s = 20$ h); all GISAXS patterns are plotted on a logarithmic intensity scale; spherical particle shape; particle distribution density: 0.01 a.u.

A6. Surface structure of dye layers fabricated at high sensitization concentration and solution aggregation effects at high dye solution concentration

GIXRD measurements (incident angle = 0.7° ; detector angle = $50-60^{\circ}$) shed lights on the surface structure of the dye molecules on thin films of amorphous TiO₂ (d_{sparse} = ~3.18 g/cm³). Figure A17 demonstrates that the surface structures of both **MK-2** and **N749** samples fabricated at 0.50 mM and 1.00 mM produce similar GIXRD patterns. However, the **N3** layer fabricated at c_{N3} = 1.00 mM exhibits a quite different structure from that fabricated at 0.50 mM, i.e., no diffraction peaks were recorded within the detector angle range, indicating an absence of structural periodicity. This further supports the hypothesis that the **N3** layer exhibits a distinctive structure on the surface of amorphous TiO₂ when fabricated at relatively high concentration (e.g. 1.00 mM). Moreover, FTIR-ATR measurements were performed on **MK-2**, **N3**, and **N749** solutions with different concentrations. The advantage of ATR-FTIR over transmission-FTIR is its limited path length into the sample, which avoids the problem of strong attenuation of the IR signal in aqueous solutions, which usually exhibit high absorbing power. Figure A18 shows that an apparent absorbance peak appears when the concentration of the solution of **N3** reaches exceptionally high values (e.g. 5.00 mM), which suggests a potentially distinctive aggregation of **N3** molecules at such very high concentrations.



Figure A17. GIXRD patterns for **MK-2**, **N3**, and **N749** dye…TiO₂ on silicon substrates fabricated using dye concentrations of 0.50 mM and 1.00 mM ($d_{TiO2} = \sim 3.18$ g/cm³; $t_s = 20$ h).





A7. Sample-detector set-ups for the GISAXS experiments

A Pilatus 2M detector was used for the GISAXS measurements with a sample-detector distance of 3017mm, and an X-ray energy of 12.5 keV. The central pixel was at the N_{bin} position (739, 1554), which translates to a mm position (u_0 , v_0) of (127.1, 21.5). The detailed GISAXS sample-detector geometry with respect to the incident X-ray beam is shown in Figure A19.



Figure A19. Schematic illustration of the geometry of the GISAXS detector perpendicular to the direct beam with detector local coordinates of $(u_0, v_0) = (127.1 \text{ mm}, 21.5 \text{ mm})$, which represents the point where the direct X-ray beam hits the detector

plane. The size of the detector area was 254 × 289 mm² with a total number of 1475 × 1679 pixels. The pixel coordinates for (u_0, v_0) are (739, 125). The length of the normal vector *n* denotes the sample-detector distance.





Figure A20. Guinier plots and linear approximation (slope of the linear fit = $1/3R_g^2$) for low-*q* intensity profile along Q_y (obtained from a horizontal cut at the Yoneda peak position) at $\alpha_i = 0.20^\circ$ (both the dye and TiO₂ layers are probed), for (a) **MK-2**, (b) **N3**, and (c) **N749** layers fabricated using different sensitization concentrations.



Figure A21. Calculated R_g values at $\alpha_i = 0.20^\circ$ (both the dye and TiO₂ layers are probed by X-ray) for **MK-2**, **N3**, and **N749** layers as a function of the sensitization concentration.



Figure A22. The Guinier plots and linear approximation for **MK-2**, **N3**, and **N749** dye layers fabricated using the sensitization concentration that produced the most obvious peaks along Q_y , i.e., 1.00 mM for **MK-2** and **N3**, and 0.50 mM for **N749**, at (a) $\alpha_i = 0.20^\circ$, (b) $\alpha_i = 0.30^\circ$, (c) $\alpha_i = 0.40^\circ$.

A9. Python scripts for the BornAgain fittings

The BornAgain fitting for each measurement data requires two Python files, i.e., the fit_data.py and sample_builder.py files. The fit_data.py file contains the parts related to initiating the detector, setting up the simulation, loading the experimental data from a tif file, and finally setting up the fit engine. The sample_builder.py file contains the sample description, wherein our sample represents a five-layer system (silicon substrate, native oxide, TiO₂, dye and air) with dye particles placed inside or on top of the dye layer.

In this section, we show examples of the fit_data.py and sample_builder.py files for fitting the particle size (radius) of **MK-2**···TiO₂ on a silicon substrate with the structural parameters equal to those of the experimental sample fabricated using $c_{MK-2} = 0.50$ mM. All particles (spherical particle shape) are assumed to be located on the surface of the dye layer with a distribution density of 0.01 a.u. and $\alpha_i = 0.4^\circ$. The registered parameter is task-specific, and the structural parameters of each individual sample were built based on its structural and X-ray optical parameters (Table A5).
fit_data.py

""" Real life example: experiment at 107 """ import matplotlib from matplotlib import pyplot as plt import numpy import bornagain as ba from bornagain import deg, angstrom, nm from SampleBuilderMK205 import MySampleBuilder

def create_detector():

"""
Returns a model of the I07 detector
"""
detector = ba.RectangularDetector(1475, 254.0, 1679, 289.0)

detector.setPerpendicularToDirectBeam(3017.0, 127.108, 21.5) **return** detector

def create_simulation():

.....

.....

Creates and returns GISAS simulation with beam and detector defined

simulation = ba.GISASSimulation()
simulation.setDetector(create_detector())
simulation.setBeamParameters(0.0992*nm, 0.4*deg, 0.0*deg)
simulation.setBeamIntensity(7.0e+14)
simulation.setRegionOfInterest(0, 0, 254.0, 289.0)
return simulation

def load_real_data(filename="mk2 0.5mm 0.4.tif"):

Fill histogram representing our detector with intensity data from tif file. Returns cropped version of it, which represent the area we are interested in. """ hist = ba.IHistogram.createFrom(filename) return hist

def run_fitting():
 simulation = create_simulation()
 sample_builder = MySampleBuilder()
 simulation.setSampleBuilder(sample_builder)

real_data = load_real_data()

fit_suite = ba.FitSuite()
draw_observer = ba.DefaultFitObserver(draw_every_nth=10)
fit_suite.attachObserver(draw_observer)
fit_suite.initPrint(10)
fit_suite.addSimulationAndRealData(simulation, real_data)

setting fitting parameters with starting values

fit_suite.addFitParameter("*size", 1, ba.AttLimits.limited(0.0, 10), 0.01)

use_two_minimizers_strategy = False
if use_two_minimizers_strategy:
 strategy1 = ba.AdjustMinimizerStrategy("Genetic")
 fit_suite.addFitStrategy(strategy1)

Second fit strategy will use another algorithm. # It will use best parameters found from previous minimization round. strategy2 = ba.AdjustMinimizerStrategy("Minuit2", "Migrad") fit_suite.addFitStrategy(strategy2)

running fit
fit_suite.runFit()

plt.show()

if __name__ == '__main__':

run_fitting()

sample_builder.py

5 layers system (substrate, SiO2, TiO2, dye and air).

import numpy
import bornagain as ba
from bornagain import deg, angstrom, nm, kvector_t
import ctypes

class MySampleBuilder(ba.IMultiLayerBuilder):

```
.....
```

.....

.....

.....

def __init__(self):
 ba.IMultiLayerBuilder.__init__(self)
 self.sample = None

parameters describing the sample
self.size = ctypes.c_double(0.01)

register parameters

self.registerParameter("size", ctypes.addressof(self.size))

constructs the sample for current values of parameters

def buildSample(self):

defining materials

material_1 = ba.HomogeneousMaterial("Air", 0.0, 0.0)

material_2 = ba.HomogeneousMaterial("MK2", 1.55599999996e-06, 3.77e-09)

material_3 = ba.HomogeneousMaterial("MK2 particle", 1.77026000003e-06, 4.28907e-09)

material_4 = ba.HomogeneousMaterial("TiO2", 4.07899999999e-06, 9.309e-08)

material_5 = ba.HomogeneousMaterial("SiO2", 4.1250000002e-06, 2.267e-08)

material_6 = ba.HomogeneousMaterial("Substrate", 3.11099999994e-06, 1.709e-08)

```
# Defining Layers
```

```
layer_1 = ba.Layer(material_1)
```

layer_2 = ba.Layer(material_2, 2.416)

layer_3 = ba.Layer(material_4, 16.465)

- layer_4 = ba.Layer(material_5, 0.5)
- layer_5 = ba.Layer(material_6)

Defining Form Factors

formFactor_1 = ba.FormFactorFullSphere(self.size.value*nm)

Defining Particles

particle_1 = ba.Particle(material_3, formFactor_1)
particle_1_position = kvector_t(0.0*nm, 0.0*nm, 0.0*nm)
particle_1.setPosition(particle_1_position)

Defining Particle Layouts and adding Particles
layout_1 = ba.ParticleLayout()
layout_1.addParticle(particle_1, 1)
layout_1.setTotalParticleSurfaceDensity(0.01)

Defining Roughness Parameters

layerRoughness_1 = ba.LayerRoughness(1.0, 0.3, 5.0*nm)
layerRoughness_2 = ba.LayerRoughness(1.0, 0.3, 5.0*nm)
layerRoughness_3 = ba.LayerRoughness(1.0, 0.3, 5.0*nm)
layerRoughness_4 = ba.LayerRoughness(1.0, 0.3, 5.0*nm)

Adding layouts to layers

layer_2.addLayout(layout_1)

Defining Multilayers

multiLayer_1 = ba.MultiLayer()
multiLayer_1.setCrossCorrLength(10)
multiLayer_1.addLayer(layer_1)
multiLayer_1.addLayerWithTopRoughness(layer_2, layerRoughness_1)
multiLayer_1.addLayerWithTopRoughness(layer_3, layerRoughness_2)
multiLayer_1.addLayerWithTopRoughness(layer_4, layerRoughness_3)
multiLayer_1.addLayerWithTopRoughness(layer_5, layerRoughness_4)
return multiLayer_1

Appendix B – Supporting information for Chapter 4

B1. XRR-fitted structural parameters for MK-2, N3, and N749 on amorphous thin films of TiO_2 as a function of the sensitization time

Table B1. Structural parameters for **MK-2** on thin films of amorphous TiO₂ ($d_{TiO2} = ~3.98 \text{ g/cm}^3$) as a function of the sensitization time, determined by XRR model simulations using GenX⁹³.

	Sensitization time [min]								
MK-2	10	20	30	40	50				
Thickness (Å)	14.0	17.0	16.1	16.5	16.8				
Error (+)	0.5	0.2	0.4	0.1	0.1				
Error (-)	0.1	0.2	0.1	0.2	0.2				
Density (unit/Å ³)	0.000720	0.000643	0.000678	0.000659	0.000672				
Roughness (Å)	4.6	4.0	4.6	4.1	4.5				
AMI (unit/Å ²)	0.010102	0.010905	0.010902	0.010890	0.011308				
APM (Å ²)	98.56	91.30	91.32	91.43	88.04				
FOM logR1	0.01424	0.01384	0.01255	0.01346	0.01322				
MK-2	60	300	600	900	1200				
Thickness (Å)	16.4	19.6	25.8	38.1	39.1				
Error (+)	0.2	0.2	1.3	0.4	0.8				
Error (-)	0.1	0.3	1.6	0.7	1.3				
Density (unit/Å ³)	0.000643	0.000570	0.000573	0.000593	0.000546				
Roughness (Å)	3.9	4.8	9.2	8.4	7.6				
AMI (unit/Ų)	0.010568	0.011189	0.014755	0.022604	0.021349				
APM (Å ²)	94.21	88.98	67.48	44.05	46.64				
FOM logR1	0.01152	0.01290	0.01589	0.01372	0.01438				

The 'unit' in the table is defined as one dye molecule. The X-ray scattering length density (SLD) of each dye layer can be derived by multiplying the fitted density of each dye layer with the total X-ray scattering length of one dye molecule, i.e., 1450 fm for **MK-2**; 1003 fm for **N3**; and 2075 fm for **N749**.

		t₅ (min)							
N3	1	5	10	30	60	1200			
Thickness (Å)	12.1	13.4	13.5	13.2	14.9	15.5			
Error (+)	0.2	0.2	0.2	0.6	0.2	0.2			
Error (-)	0.1	0.2	0.2	0.3	0.2	0.1			
Density (unit/Å ³)	0.001213	0.001155	0.001191	0.001157	0.001130	0.001128			
Roughness (Å)	4.7	4.5	4.8	3.6	3.8	4.0			
AMI (unit/Ų)	0.014726	0.015512	0.016019	0.015249	0.016848	0.017507			
APM (Å ²)	67.60	64.18	62.14	65.28	59.09	56.86			
FOM logR1	0.01586	0.01683	0.01626	0.01601	0.01608	0.01468			

Table B2. Structural parameters for **N3** on thin films of amorphous TiO₂ ($d_{TiO2} = \sim 3.98$ g/cm³) as a function of the sensitization time, determined by XRR model simulation using GenX.

Table B3. Structural parameters for **N749** on thin films of amorphous TiO₂ ($d_{TiO2} =$ ~3.98 g/cm³) as a function of the sensitization time, determined by XRR model simulations using GenX.

	t₅ (min)								
N749	1	5	10	30	60	1200			
Thickness (Å)	11.0	11.6	12.6	12.6	12.6	11.7			
Error (+)	0.19	0.07	0.05	0.06	0.09	0.08			
Error (-)	0.16	0.02	0.18	0.40	0.14	0.23			
Density (unit/ų)	0.000502	0.000500	0.000465	0.000478	0.000540	0.000581			
Roughness (Å)	3.6	3.5	3.3	3.5	3.6	3.8			
AMI (unit/Ų)	0.005492	0.005824	0.005833	0.006036	0.006820	0.006812			
APM (Ų)	181.18	170.86	170.60	164.86	145.90	146.06			
FOM logR1	0.01260	0.01299	0.01179	0.01221	0.01204	0.01388			

Table B4. XRR-fitted structural parameters of **MK-2** layers fabricated at different concentrations on thin films of amorphous TiO₂ ($d_{TiO2} = \sim 3.98$ g/cm³; $t_s = 20$ h; $c_{MK-2} = 0.05-1.00$ mM).

MK-2 on thin films of amorphous TiO ₂	0.05	0.25	0.50	1.00
Thickness (Å)	18.3	23.4	39.1	39.0
Error (+)	0.2	1.0	0.8	0.8
Error (-)	0.2	0.9	1.3	1.2
Density (unit/Å ³)	0.000648	0.000658	0.000546	0.000447
Roughness (Å)	3.7	8.5	7.6	8.1
AMI (unit/Ų)	0.011839	0.015391	0.021349	0.017424
FOM logR1	0.01331	0.01656	0.01438	0.01235

Table B5. XRR-fitted structural parameters for the **N3** layers fabricated at different concentrations on thin films of amorphous TiO₂ ($d_{TiO2} = \sim 3.98$ g/cm³; $t_s = 20$ h; $c_{N3} = 0.05-1.00$ mM).

		С _{№3} [mM]						
N3 on thin films of amorphous TiO ₂	0.05	0.25	0.50	1.00				
Thickness (Å)	13.3	14.4	15.5	18.1				
Error (+)	0.3	0.2	0.2	0.2				
Error (-)	0.3	0.1	0.1	0.2				
Density (unit/ų)	0.000963	0.001056	0.001128	0.000948				
Roughness (Å)	3.9	4.0	4.0	4.0				
AMI (unit/Ų)	0.012760	0.015206	0.017507	0.017140				
FOM logR1	0.01677	0.01430	0.01468	0.01557				

Table B6. XRR-fitted structural parameters for the **N749** layers fabricated at different concentrations on thin films of amorphous TiO₂ ($d_{TiO2} = \sim 3.98$ g/cm³; $t_s = 20$ h; $c_{N749} = 0.05-1.00$ mM).

	C _{N749} [mM]						
N749 on thin films of amorphous TiO ₂	0.05	0.25	0.50	1.00			
Thickness (Å)	13.8	11.2	11.7	12.6			
Error (+)	0.2	0.1	0.1	0.1			
Error (-)	0.2	0.6	0.2	0.2			
Density (unit/Å ³)	0.000621	0.000543	0.000581	0.000516			

Roughness (Å)	3.9	3.9	3.8	3.5
AMI (unit/Ų)	0.008545	0.006065	0.006809	0.006507
FOM logR1	0.01468	0.01426	0.01388	0.01433

Table B7. Materials constants used to simplify the XRR simulations.

	MK-2	N3	N749	TiO ₂	SiOx	Silicon
SLD (10 ⁻⁶ /Å ²)	10.15	13.70	12.45	31.28	/	20.07
Density (unit/Å ³)	0.0007	0.0013	0.0006	0.02895	/	0.0499
Thickness (Å)	/	/	/	/	5	/
Assumed coverage [™]	89.6%	82.8%	87.7%	/	/	/

B2. Statistical trend of variation for the recorded XRR-fitted dye layer thickness values of dye molecules on amorphous TiO₂ films as a function of the sensitization time

Figure B1 illustrates both the linear and logarithmic regression model summary and parameter estimates for **MK-2** dye layer thickness values recorded on thin films of amorphous TiO₂ ($d_{TiO2} = \sim 3.98 \text{ g/cm}^3$) as a function of the sensitization time for sensitization concentrations < 0.25 mM, whereby a clear correlation of dye layer thickness variation against time was observed upon fitting the XRR results. The solvent rinsing time was not controlled after the sensitization during these experiments. Overall, the much higher R² value shows that logarithmic fitting of the thickness value against the sensitization time affords a significantly higher correlation than linear fitting, indicating that a logarithmic relationship might be more generic to represent the dye geometry variation trend versus the sensitization time for the dye-self-assembly process on TiO₂ during sensitization. Therefore, a logarithmic fitting of the thickness –

^{iv} The assumed coverage is defined as $\varphi = \frac{SLD_{obs}}{SLD_{cal}}$, where SLD_{obs} is the observed scattering length density for the dye layer, and SLD_{cal} is the scattering length density calculated assuming 100% surface coverage.

time variation trend will be adopted in the subsequent systematic study for the three dyes of interest.



Figure B1. Regression analysis of the thickness values for the **MK-2** layer as a function of the sensitization time for different sensitization concentrations, whereby a clear correlation of thickness variation against time is observed.

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Figure C1. Reflectivity data and fitting for **MK-2** \cdots TiO₂ interfaces on silicon substrates fabricated using different sensitization times and concentrations, followed by 5 s rinsing in neat acetonitrile and drying under a flow of N₂.



Figure C2. Reflectivity data and fitting for **MK-2** \cdots TiO₂ interfaces on silicon substrates fabricated using different sensitization times and concentrations, followed by no rinsing in neat acetonitrile and drying under a flow of N₂.



Figure C3. Reflectivity data and fitting for N3····TiO₂ interfaces on silicon substrates fabricated using different sensitization times and concentrations, followed by 5 s rinsing in neat acetonitrile and drying under a flow of N₂.



Figure C4. Reflectivity data and fitting for N3····TiO₂ interfaces on silicon substrates fabricated using different sensitization times and concentrations, followed by no rinsing in neat acetonitrile and drying under a flow of N₂.



Figure C5. Reflectivity data and fitting for N749····TiO₂ interfaces on silicon substrates fabricated using different sensitization times and concentrations followed by 5 s rinsing in neat acetonitrile and drying under a flow of N₂.



Figure C6. Reflectivity data and fitting for N749····TiO₂ interfaces on silicon substrates fabricated using different dye sensitization times and concentrations, followed by no rinsing in neat acetonitrile and drying under a flow of N₂.

C2. Standard tabular information for XRR fittings

Tables C1-C6 show the standard tabular information for each fit: dye-layer thickness, density, and roughness with errors that are generated by GenX, which uses the differential-evolution algorithm for fitting.

The 'unit' in the table is defined as one dye molecule. The X-ray scattering length density (SLD) of each dye layer can be derived by multiplying the fitted density of each dye layer with the total X-ray scattering length of a dye molecule, i.e., 1450 fm for **MK-2**; 1003 fm for **N3**; and 2075 fm for **N749**.

Table C1. Fitting results of the thickness, density, and roughness for **MK-2** layers fabricated using different sensitization times and concentrations, followed by 5 s rinsing in neat acetonitrile and drying under a flow of N_2 .

Concentration (mM)	Time (min)	Dye layer thickness (Å)	Error (Å)	Density (unit/ų)	Error (10 ⁻⁵ unit/ų)	Roughness (Å)	Error (Å)	FOM logR1
	1	14.0	(-0.19, 0.18)	0.000652	(-3.2, 1.0)	3.6	(-0.19, 0.14)	0.01387
	2	14.4	(-0.24, 0.13)	0.000712	(-3.1, 0.5)	4.2	(-0.21, 0.20)	0.01437
	5	14.5	(-0.16, 0.77)	0.000767	(-16.1, 2.9)	5.3	(-1.36, 0.29)	0.01849
	10	13.7	(-0.59, 0.21)	0.000705	(-5.9, 18.8)	4.0	(-0.39, 1.23)	0.01446
	30	13.5	(-0.12, 0.23)	0.000745	(-7.4, 0.9)	4.1	(-0.37, 0.04)	0.01597
0.04	60	11.7	(-0.67, 0.40)	0.000985	(-8.1, 9.1)	5.5	(-0.46, 0.45)	0.01700
0.01	300	16.4	(-0.16, 0.17)	0.000638	(-3.5, 1.4)	3.3	(-0.16, 0.14)	0.01534
	600	16.3	(-0.17, 0.14)	0.000687	(-1.9, 2.2)	3.6	(-0.21, 0.28)	0.01558
	900	15.3	(-0.29, 0.14)	0.000658	(-4.3, 4.0)	3.9	(-0.33, 0.20)	0.01565
	1200	16.7	(-0.17, 0.19)	0.000695	(-2.8, 1.2)	3.4	(-0.19,0.07)	0.01406
	1800	21.0	(-0.13, 0.21)	0.000650	(-2.4, 2.1)	3.7	(-0.39, 0.31)	0.01746
	2400	20.2	(-0.43, 0.14)	0.000613	(-1.5, 3.9)	3.8	(-0.19, 0.57)	0.01761
	1	14.2	(-0.09, 0.39)	0.000659	(-7.2, 2.4)	3.8	(-0.59, 0.17)	0.01637
	2	14.3	(-0.20, 0.16)	0.000665	(-3.2, 2.9)	3.9	(-0.23, 0.36)	0.01553
	5	15.6	(-0.22, 0.21)	0.000530	(-2.9,3.0)	2.1	(-0.35, 0.47)	0.01562
	10	16.2	(-0.24, 0.17)	0.000521	(-1.3, 2.1)	2.4	(-0.19, 0.28)	0.01645
	30	14.7	(-0.18, 0.28)	0.000654	(-6.7, 1.4)	3.5	(-0.71, 0.10)	0.01621
0.05	60	16.8	(-0.23, 0.15)	0.000656	(-3.1, 2.1)	3.7	(-0.41, 0.25)	0.01705
0.05	300	18.0	(-0.08, 0.16)	0.000667	(-3.2, 1.7)	3.0	(-0.36, 0.16)	0.01570
	600	19.0	(-0.16, 0.31)	0.000601	(-2.5, 2.8)	2.5	(-0.29, 0.14)	0.01758
	900	18.9	(-0.05, 0.11)	0.000765	(-2.6, 0.9)	3.6	(-0.18, 0.04)	0.01427
	1200	17.4	(-0.26, 0.03)	0.000678	(-0.4, 7.5)	3.4	(-0.07, 0.05)	0.01427
	1800	19.8	(-0.13, 0.18)	0.000659	(-3.1, 1.3)	3.3	(-0.21, 0.17)	0.01526
	2400	20.6	(-0.21, 0.12)	0.000647	(-1.5, 4.4)	3.4	(-0.09, 0.43)	0.01579
	1	15.1	(-0.19, 0.27)	0.000719	(-6.2, 1.8)	4.4	(-0.39, 0.13)	0.01763
	2	15.8	(-0.27, 0.32)	0.000678	(-7.1, 3.5)	4.2	(-0.49, 0.29)	0.01872
	5	16.4	(-0.16, 0.67)	0.000693	(-9.8, 2.7)	4.8	(-0.98, 0.23)	0.02091
	10	15.0	(-0.10, 0.15)	0.000693	(-2.6, 2.4)	3.8	(-0.14, 0.38)	0.01536
	30	16.1	(-0.20, 0.11)	0.000518	(-3.4, 3.8)	2.2	(-0.32, 0.32)	0.01518
0.05	60	17.1	(-0.32, 0.12)	0.000706	(-1.9, 4.8)	3.5	(-0.21, 0.69)	0.01482
0.25	300	14.5	(-0.13, 0.38)	0.000730	(-7.3, 3.0)	4.1	(-0.33, 0.30)	0.01482
	600	19.4	(-0.17, 0.15)	0.000861	(-7.0, 7.5)	3.9	(-0.22, 0.17)	0.01864
	900	19.0	(-0.17, 0.27)	0.000631	(-4.3, 2.2)	3.4	(-0.27, 0.14)	0.02071
	1200	18.2	(-0.14, 0.18)	0.000629	(-2.0, 0.5)	3.3	(-0.20, 0.19)	0.01857
	1800	20.3	(-0.12, 0.38)	0.000572	(-3.7, 3.5)	3.4	(-0.29, 0.47)	0.01935
	2400	20.1	(-0.09, 0.16)	0.000644	(-1.7, 2.7)	3.8	(-0.31, 0.16)	0.01619
0.50	1	15.8	(-0.19, 0.30)	0.000520	(-5.7, 3.2)	3.0	(-0.62, 0.35)	0.02023

Concentration (mM)	Time (min)	Dye layer thickness (Å)	Error (Å)	Density (unit/ų)	Error (10⁻⁵ unit/ų)	Roughness (Å)	Error (Å)	FOM logR1
	2	16.2	(-0.24, 0.21)	0.000557	(-3.7, 4.0)	2.8	(-0.48, 0.19)	0.02094
	5	16.1	(-0.07, 0.17)	0.000656	(-5.3, 1.3)	3.6	(-0.53, 0.10)	0.01922
	10	15.9	(-0.23, 0.09)	0.000565	(-3.0, 4.2)	2.8	(-0.51, 0.11)	0.02069
	30	17.0	(-0.35, 0.22)	0.000594	(-3.1, 5.3)	3.2	(-0.30, 0.61)	0.01528
	60	17.8	(-0.16, 0.21)	0.000638	(-2.7, 1.7)	3.8	(-0.20, 0.23)	0.01546
	300	19.2	(-0.14, 0.17)	0.000704	(-5.0, 2.6)	3.9	(-0.37, 0.24)	0.01573
	600	21.1	(-0.83, 0.22)	0.000574	(-2.8, 7.2)	4.1	(-0.34, 0.95)	0.01878
	900	20.0	(-0.06, 0.10)	0.000658	(-1.3, 2.2)	3.2	(-0.18, 0.22)	0.01647
	1200	18.2	(-0.06, 0.23)	0.000647	(-2.8, 2.3)	3.3	(-0.28, 0.33)	0.01475
	1800	21.5	(-0.52, 0.25)	0.000667	(-8.3, 2.5)	5.2	(-0.71, 0.26)	0.01742
	2400	19.9	(-0.26, 0.22)	0.000629	(-2.9, 4.2)	3.7	(-0.19, 0.44)	0.01663
	1	15.4	(-0.89, 0.80)	0.001957	(-4.6, 3.3)	3.6	(-0.17, 0.12)	0.02778
	2	11.7	(-1.36, 1.13)	0.001628	(-5.8, 12.5)	3.7	(-0.15, 0.12)	0.02248
	5	11.5	(-0.89, 0.79)	0.001588	(-7.0, 8.7)	3.7	(-0.24, 0.23)	0.02828
	10	15.3	(-1.42, 0.70)	0.001609	(-5.4, 4.3)	3.4	(-0.08, 0.26)	0.02533
	30	17.3	(-0.82, 0.61)	0.001626	(-6.6, 6.5)	3.9	(-0.17, 0.14)	0.02310
1.00	60	19.6	(-0.90, 1.41)	0.001999	(-3.9, 3.7)	3.9	(-0.19, 0.13)	0.02558
1.00	300	17.1	(-0.94, 1.36)	0.001475	(-3.3, 5.3)	3.7	(-0.15, 0.08)	0.02655
	600	29.1	(-1.43, 0.72)	0.001638	(-4.8, 8.0)	3.6	(-0.12, 0.08)	0.02340
	900	26.9	(-1.42, 1.98)	0.001966	(-4.7, 2.7)	3.5	(-0.10, 0.10)	0.02549
	1200	22.1	(-0.17, 0.74)	0.001764	(-2.3, 8.3)	3.4	(-0.10, 0.14)	0.02636
	1800	36.7	(-1.54, 1.71)	0.001940	(-12.8, 4.6)	3.5	(-0.08, 0.17)	0.02346
	2400	36.7	(-1.02, 0.79)	0.001946	(-4.6, 12.6)	3.4	(-0.11, 0.26)	0.02593

Table C2. Fitting results of the thickness, density, and roughness of **MK-2** layers fabricated using different sensitization times and concentrations, followed by no rinsing in neat acetonitrile and drying under a flow of N_2 .

Concentration (mM)	Time (min)	Dye layer thickness (Å)	Error (Å)	Density (unit/ų)	Error (10⁻⁵ unit/ų)	Roughness (Å)	Error (Å)	FOM logR1
	1	11.8	(-0.32, 0.49)	0.000359	(-3.4, 2.0)	2.7	(-1.06, 0.29)	0.01992
	2	12.7	(-0.38, 0.45)	0.000416	(-9.5, 8.5)	3.0	(-1.79, 0.70)	0.01972
	5	13.0	(-0.70, 0.22)	0.000473	(-1.7, 7.8)	2.9	(-0.17, 0.77)	0.01992
	10	10.0	(-0.01, 0.88)	0.000820	(-30.9, 11.1)	4.9	(-1.15, 0.28)	0.02028
	30	12.1	(-0.13, 0.50)	0.000858	(-1.2, 3.7)	5.4	(-0.26, 0.37)	0.02085
0.01	60	14.2	(-0.39, 0.23)	0.000708	(-3.8, 11.9)	4.1	(-0.56, 0.75)	0.01750
0.01	300	14.5	(-0.07, 0.39)	0.000532	(-6.5, 4.5)	3.0	(-0.66, 0.31)	0.01807
	600	16.4	(-0.16, 0.30)	0.000571	(-7.0, 2.7)	3.4	(-0.56, 0.23)	0.01775
	900	15.1	(-0.49, 0.33)	0.000504	(-9.5, 11.0)	5.1	(-0.93, 0.37)	0.02460
	1200	14.7	(-0.29, 0.77)	0.000587	(-8.0, 3.5)	5.3	(-0.83, 0.09)	0.02654
	1800	14.2	(-0.31, 0.33)	0.000557	(-11.7, 8.4)	5.3	(-0.59, 0.68)	0.02308
	2400	18.3	(-0.32, 0.09)	0.000730	(-2.5, 6.6)	3.5	(-0.23, 0.66)	0.01707
	1	12.8	(-0.76, 0.27)	0.000554	(-5.7, 18.0)	3.5	(-0.31, 1.17)	0.01923
	2	11.5	(-0.22, 0.99)	0.000689	(-21.4, 5.4)	4.2	(-1.25, 0.27)	0.01999
	5	13.5	(-0.38, 0.36)	0.000391	(-5.9, 7.1)	1.9	(-0.73, 0.85)	0.01995
	10	12.3	(-0.69, 0.31)	0.000554	(-8.9, 18.6)	3.2	(-0.39, 0.86)	0.01947
	30	13.6	(-0.78, 0.26)	0.000678	(-7.7, 18.8)	3.9	(-0.25, 1.33)	0.01806
	60	14.2	(-0.39, 0.24)	0.000688	(-6.2, 6.8)	3.9	(-0.38, 0.59)	0.01873
0.05	300	16.4	(-0.58, 0.22)	0.000622	(-3.7, 14.0)	3.2	(-0.31, 1.24)	0.01629
	600	17.6	(-0.21, 0.18)	0.000667	(-4.0, 2.0)	3.5	(-0.31, 0.20)	0.01526
	900	18.7	(-0.24, 0.11)	0.000617	(-2.2, 4.7)	3.2	(-0.15, 0.55)	0.01576
	1200	16.5	(-0.30, 0.23)	0.000649	(-3.2, 4.8)	3.6	(-0.24, 0.40)	0.01638
	1800	17.5	(-0.18, 0.23)	0.000655	(-4.9, 1.9)	3.7	(-0.46, 0.23)	0.01599
	2400	18.9	(-0.06, 0.33)	0.000763	(-7.9, 1.4)	3.8	(-0.64, 0.22)	0.01790
	1	13.0	(-0.31, 0.30)	0.000691	(-2.2, 3.6)	4.2	(-0.18, 0.39)	0.01895
	2	13.1	(-0.46, 0.21)	0.000712	(-5.9, 5.3)	4.5	(-0.33, 0.19)	0.01838
	5	13.4	(-0.28, 0.48)	0.000658	(-11.1, 4.5)	3.9	(-0.63, 0.46)	0.01947
	10	14.5	(-0.03, 0.47)	0.000644	(-8.7, 0.9)	4.2	(-0.85, 0.09)	0.01828
	30	14.4	(-0.30, 0.11)	0.000492	(-1.7, 4.3)	2.8	(-0.38, 0.57)	0.01865
0.05	60	16.2	(-0.43, 0.14)	0.000500	(-1.8, 3.8)	2.1	(-0.23, 0.67)	0.01857
0.25	300	15.3	(-0.01, 0.02)	0.000730	(-0.3, 0.2)	4.4	(-0.02, 0.02)	0.01905
	600	17.7	(-0.17, 0.10)	0.000607	(-2.9, 2.9)	2.9	(-0.38, 0.22)	0.01583
	900	17.8	(-0.35, 0.25)	0.000606	(-2.8, 2.7)	3.5	(-0.22, 0.46)	0.01720
	1200	16.9	(-0.27, 0.18)	0.000589	(-1.7, 5.0)	3.2	(-0.09, 0.40)	0.01604
	1800	17.8	(-0.30, 0.08)	0.000572	(-1.5, 5.3)	2.5	(-0.16, 0.59)	0.01763
	2400	18.5	(-0.19, 0.15)	0.000577	(-3.8, 1.1)	2.1	(-0.53, 0.35)	0.01648
0.50	1	15.9	(-0.59, 0.33)	0.000417	(-5.0, 7.7)	2.2	(-0.89, 0.98)	0.02030

Concentration (mM)	Time (min)	Dye layer thickness (Å)	Error (Å)	Density (unit/ų)	Error (10⁻⁵ unit/ų)	Roughness (Å)	Error (Å)	FOM logR1
	2	15.0	(-0.53, 0.24)	0.000419	(-2.5, 5.5)	2.2	(-0.32, 0.82)	0.01940
	5	16.3	(-0.58, 0.14)	0.000531	(-2.2, 5.7)	3.0	(-0.25, 0.62)	0.01869
	10	15.4	(-0.43, 0.36)	0.000491	(-6.6, 6.9)	3.2	(-0.63, 0.69)	0.01790
	30	14.5	(-1.11, 0.60)	0.000452	(-6.2, 12.4)	3.0	(-0.63, 1.01)	0.01840
	60	16.5	(-0.23, 0.43)	0.000487	(-4.1, 2.6)	2.8	(-0.48, 0.29)	0.01820
	300	17.1	(-0.11, 0.24)	0.000561	(-5.0, 1.6)	2.8	(-0.71, 0.13)	0.01769
	600	18.4	(-0.32, 0.11)	0.000572	(-1.4, 2.9)	2.9	(-0.21, 0.53)	0.01761
	900	19.8	(-0.24, 0.25)	0.000556	(-5.0, 2.0)	2.9	(-0.66, 0.50)	0.01775
	1200	17.3	(-0.36, 0.16)	0.000522	(-1.5, 4.3)	3.1	(-0.22, 0.57)	0.01686
	1800	18.0	(-0.17, 0.21)	0.000553	(-2.4, 1.8)	2.7	(-0.40, 0.14)	0.01632
	2400	19.5	(-0.30, 0.19)	0.000635	(-5.6, 4.1)	3.6	(-0.42, 0.55)	0.01745
	1	15.9	(-0.17, 0.58)	0.000581	(-11.3, 3.2)	4.7	(-1.23, 0.29)	0.01547
	2	16.8	(-0.31, 0.09)	0.000544	(-2.4, 2.0)	4.1	(-0.22, 0.33)	0.01366
	5	15.7	(-0.04, 0.60)	0.000601	(-9.9, 1.0)	4.2	(-0.98, 0.12)	0.01495
	10	16.9	(-0.04, 0.15)	0.000496	(-3.3, 1.6)	2.7	(-0.45, 0.16)	0.01528
	30	17.8	(-0.29, 0.51)	0.000499	(-7.9, 3.6)	4.3	(-0.58, 0.30)	0.01437
1.00	60	17.9	(-0.15, 0.32)	0.000551	(-4.3, 1.5)	3.5	(-0.38, 0.16)	0.01536
1.00	300	19.1	(-0.40, 0.25)	0.000493	(-4.6, 2.7)	3.9	(-0.74, 0.23)	0.01720
	600	18.4	(-0.29, 0.14)	0.000541	(-3.3, 2.8)	3.4	(-0.24, 0.31)	0.01368
	900	21.7	(-0.36, 0.62)	0.000545	(-7.8, 2.2)	5.3	(-0.81, 0.28)	0.01709
	1200	18.4	(-0.18, 0.15)	0.000511	(-5.9, 1.4)	3.2	(-0.73, 0.25)	0.01592
	1800	19.4	(-0.19, 1.08)	0.000544	(-1.3, 4.3)	7.5	(-2.11, 0.33)	0.01634
	2400	19.2	(-0.14, 0.13)	0.000615	(-5.2, 3.0)	3.3	(-0.36, 0.10)	0.01520

Table C3. Fitting results of the thickness, density, and roughness of **N3** layers fabricated using different sensitization times and concentrations, followed by 5 s rinsing in neat acetonitrile and drying under a flow of N_2 .

Concentration (mM)	Time (min)	Dye layer thickness (Å)	Error (Å)	Density (unit/ų)	Error (unit/ų)	Roughness (Å)	Error (Å)	FOM logR1
	1	13.7	(-0.53, 0.13)	0.000727	(-1.8, 10.5)	2.6	(-0.09, 0.76)	0.01867
	2	11.7	(-0.42, 0.93)	0.001037	(-3.5, 14.5)	4.1	(-1.31, 0.48)	0.01913
	5	10.8	(-1.66, 0.36)	0.001256	(-9.3, 4.4)	5.3	(-0.33, 1.51)	0.01953
	10	12.5	(-0.52, 0.29)	0.001067	(-3.0, 12.4)	4.7	(-0.11, 0.70)	0.01924
	30	13.9	(-0.91, 0.56)	0.000641	(15.1, 14.3)	4.2	(-0.69, 1.00)	0.02484
Concentration (mM) 0.01 0.05 0.25	60	13.3	(-0.42, 0.66)	0.000577	(-8.5, 7.4)	3.4	(-0.86, 0.67)	0.02035
	300	11.6	(-1.55, 0.54)	0.001028	(-14.6, 42.2)	4.7	(-0.53, 1.62)	0.01942
	600	12.6	(-0.10, 0.60)	0.000865	(-12.3, 2.0)	3.8	(-0.64, 0.14)	0.01919
	900	12.5	(-0.61, 0.13)	0.000918	(-3.9, 16.4)	3.8	(-0.37, 0.72)	0.01984
	1200	13.2	(-0.30, 1.05)	0.000727	(-11.0, 4.9)	5.5	(-1.01, 0.34)	0.02037
	1800	13.2	(-0.27, 0.61)	0.000846	(-8.5, 5.0)	4.1	(-0.46, 0.40)	0.02037
	2400	13.4	(-0.28, 0.44)	0.000886	(-14.0, 4.9)	4.1	(-0.80, 0.20)	0.01750
	1	11.8	(-0.47, 1.08)	0.001034	(-28.6, 16.3)	4.4	(-1.39, 0.56)	0.01877
	2	12.2	(-0.25, 1.37)	0.001001	(-30.5, 5.0)	4.8	(-0.88, 0.24)	0.02183
	5	11.5	(-0.30, 0.26)	0.000930	(-6.1, 6.9)	3.7	(-0.27, 0.28)	0.01543
	10	11.5	(-0.75, 0.49)	0.000845	(-5.8, 23.4)	3.9	(-0.20, 0.83)	0.01819
	30	11.8	(-0.13, 0.55)	0.000956	(-19.4, 2.4)	4.1	(-0.84, 0.11)	0.01577
0.05	60	12.1	(-0.14, 0.53)	0.000884	(-12.9, 4.7)	3.6	(-0.58, 0.16)	0.01463
0.05	300	12.5	(-0.14, 0.73)	0.000931	(-19.9, 3.3)	4.2	(-0.86, 0.16)	0.01596
	600	13.5	(-0.35, 0.31)	0.000888	(-11.5, 12.5)	3.5	(-0.63, 0.60)	0.01555
	900	13.4	(-0.52, 0.13)	0.000970	(-3.6, 13.0)	4.0	(-0.19, 0.59)	0.01580
	1200	13.3	(-0.30, 0.14)	0.001132	(-6.1, 9.9)	3.9	(-0.34, 0.38)	0.01710
	1800	14.4	(-0.26, 0.23)	0.000764	(-7.0, 6.3)	3.4	(-0.40, 0.39)	0.01560
0.01	2400	13.9	(-0.28, 0.21)	0.000968	(-11.1, 9.2)	3.8	(-0.43, 0.40)	0.01672
	1	14.0	(-0.36, 0.60)	0.000989	(-14.6, 8.5)	4.1	(-0.69, 0.47)	0.01999
	2	14.5	(-0.61, 0.54)	0.000669	(-12.9, 25.2)	4.0	(-0.61, 1.20)	0.02203
	5	11.6	(-0.64, 0.55)	0.001079	(-7.5, 2.2)	4.7	(-0.42, 0.13)	0.01868
	10	14.5	(-0.16, 0.50)	0.000854	(-7.4, 3.3)	3.4	(-0.23, 0.18)	0.01791
	30	14.0	(-0.27, 0.50)	0.000766	(-5.2, 3.0)	4.3	(-0.47, 0.32)	0.02030
0.05	60	14.6	(-0.15, 0.57)	0.000837	(-11.2, 5.3)	3.7	(-0.76, 0.42)	0.01903
0.25	300	16.8	(-0.69, 0.58)	0.000634	(-4.3, 11.3)	3.9	(-0.42, 0.75)	0.02039
	600	14.6	(-0.47, 0.15)	0.001037	(-5.0, 13.3)	3.6	(-0.31, 0.67)	0.01657
	900	15.0	(-0.06, 0.36)	0.000949	(-9.0, 6.2)	4.2	(-0.43, 0.13)	0.01657
	1200	17.6	(-1.06, 1.02)	0.000614	(-6.2, 4.8)	4.8	(-0.54, 0.44)	0.02208
	1800	20.0	(-0.67, 0.48)	0.000756	(-7.5, 22.2)	3.7	(-0.38, 1.52)	0.01976
0.01	2400	15.6	(-0.07, 0.44)	0.001052	(-12.6, 1.7)	3.6	(-0.34, 0.45)	0.02036
0.50	1	14.8	(-0.14, 0.53)	0.000785	(-12.3, 2.9)	3.3	(-0.95, 0.26)	0.01927

Concentration (mM)	Time (min)	Dye layer thickness (Å)	Error (Å)	Density (unit/ų)	Error (unit/ų)	Roughness (Å)	Error (Å)	FOM logR1
	2	14.1	(-0.22, 0.23)	0.000793	(-3.4, 11.0)	4.3	(-0.37, 0.48)	0.02047
	5	14.0	(-0.08, 0.60)	0.000568	(-7.4, 2.1)	2.9	(-0.77, 0.20)	0.01807
	10	15.0	(-0.91, 0.94)	0.000588	(-16.3, 4.7)	3.2	(-1.28, 0.85)	0.01937
	30	14.4	(-1.15, 0.22)	0.000753	(-8.8, 26.9)	3.5	(-0.47, 1.44)	0.01991
	60	13.7	(-0.07, 0.65)	0.001016	(-11.9, 2.4)	4.1	(-0.57, 0.12)	0.01745
	300	16.2	(-0.40, 0.22)	0.000920	(-3.6, 10.1)	3.9	(-0.11, 0.54)	0.01741
	600	17.2	(-0.65, 0.45)	0.000819	(-8.1, 23.1)	5.1	(-0.48, 1.82)	0.01951
	900	17.4	(-0.72, 0.14)	0.000809	(-4.3, 17.5)	3.7	(-0.38, 1.33)	0.01811
	1200	15.6	(-0.30, 0.43)	0.000964	(-10.8, 2.6)	3.9	(-0.62, 0.33)	0.01937
	1800	16.6	(-0.69, 0.30)	0.000883	(-8.7, 24.2)	4.4	(-0.54, 1.61)	0.01904
	2400	18.7	(-0.55, 0.61)	0.000752	(-16.4, 3.3)	4.1	(-1.01, 0.22)	0.01789
	1	13.0	(-0.06, 0.43)	0.000995	(-15.0, 2.2)	4.1	(-0.73, 0.11)	0.01789
	2	12.9	(-0.23, 0.35)	0.000961	(-18.5, 5.9)	4.6	(-0.56, 0.27)	0.01969
	5	13.6	(-0.16, 0.45)	0.000767	(-7.9, 2.5)	3.2	(-0.46, 0.17)	0.01623
	10	14.2	(-0.26, 0.46)	0.000753	(-8.6, 6.3)	3.7	(-0.60, 0.28)	0.01548
	30	15.3	(-0.26, 0.21)	0.000950	(-5.8, 23.6)	3.9	(-0.34, 0.69)	0.01756
1.00	60	14.3	(-0.49, 0.07)	0.000921	(-2.9, 16.8)	3.9	(-0.11, 0.70)	0.01753
1.00	300	14.8	(-0.13, 0.37)	0.000916	(-6.5, 1.1)	4.1	(-0.43, 0.08)	0.01574
	600	16.3	(-0.37, 0.18)	0.000864	(-3.9, 10.7)	3.6	(-0.28, 0.66)	0.01562
	900	15.4	(-0.28, 0.29)	0.000987	(-6.9, 7.7)	3.9	(-0.27, 0.34)	0.01759
	1200	16.3	(-0.33, 0.25)	0.000871	(-2.4, 6.3)	4.1	(-0.13, 0.30)	0.01851
	1800	16.9	(-0.21, 0.18)	0.001029	(-6.9, 8.4)	3.8	(-0.26, 0.25)	0.01773
	2400	18.0	(-0.33, 0.22)	0.001177	(-6.0, 4.0)	4.4	(-0.24, 0.21)	0.01869

Table C4. Fitting results of the thickness, density and roughness of N3 layers fabricated using different sensitization times and concentrations, followed by no rinsing in neat acetonitrile and drying under a flow of N_2 .

Concentration (mM)	Time (min)	Dye layer thickness (Å)	Error (Å)	Density (unit/ų)	Error (unit/ų)	Roughness (Å)	Error (Å)	FOM logR1
	1	11.9	(-0.11, 0.66)	0.000960	(-18.5, 3.6)	Error (unit/A3)Roughness (A)Error (A)From (A)(-18.5, 3.6)4.0(-0.82, 0.12)0.0(-19.6, 2.2)4.5(-0.70, 0.12)0.0(-8.9, 11.6)3.9(-0.40, 0.69)0.0(-10.2, 31.3)4.1(-0.31, 0.90)0.0(-5.5, 1.1)3.2(-0.39, 0.15)0.0(-15.6, 9.1)3.7(-0.89, 0.39)0.0(-15.6, 9.1)3.7(-0.89, 0.39)0.0(-20.9, 4.2)4.2(-0.99, 0.19)0.0(-21.1, 8.4)4.2(-1.11, 0.43)0.0(-2.8, 10.3)3.2(-0.23, 0.60)0.0(-3.1, 11.3)3.4(-0.43, 0.51)0.0(-3.1, 11.3)3.4(-0.40, 1.83)0.0(-3.1, 11.3)3.4(-0.40, 1.83)0.0(-3.1, 11.3)3.4(-0.40, 1.83)0.0(-5.1, 11.3)3.4(-0.40, 1.83)0.0(-5.2, 25.4)3.7(-0.29, 1.10)0.0(-7.4, 4.1)4.0(-0.40, 1.83)0.0(-7.4, 4.1)4.0(-0.41, 0.71)0.0(-7.4, 4.1)4.0(-0.41, 0.71)0.0(-7.4, 4.1)4.0(-0.24, 0.51)0.0(-5.7, 6.0)4.1(-0.31, 0.51)0.0(-5.7, 6.0)4.1(-0.53, 0.47)0.0(-5.7, 6.0)3.3(-0.25, 0.95)0.0(-5.6, 20.0)3.3(-0.25, 0.95)0.0(-5.6, 20.0)3.3(-0.21, 0.70)0.0(-1.5, 16.5)4.1(-	0.01588	
	2	10.8	(-0.17, 0.59)	0.001139	(-19.6, 2.2)	4.5	(-0.70, 0.12)	0.01701
Concentration (mM)	5	11.8	(-0.34, 0.22)	0.000875	(-8.9, 11.6)	3.9	(-0.40, 0.69)	0.01574
	10	10.8	(-0.80, 0.27)	0.001048	(-10.2, 31.3)	4.1	(-0.31, 0.90)	0.01788
	30	12.7	(-0.12, 0.36)	0.000759	(-5.5, 1.1)	3.2	(-0.39, 0.15)	0.01531
	60	11.8	(-0.33, 0.37)	0.000870	(-12.5, 13.2)	3.6	(-0.51, 0.50)	0.01682
	300	12.7	(-0.28, 0.52)	0.000852	(-15.6, 9.1)	3.7	(-0.89, 0.39)	0.01613
	600	14.1	(-0.11, 0.32)	0.000793	(-6.1, 2.5)	3.6	(-0.41, 0.12)	0.01412
	900	12.5	(-0.18, 0.69)	0.000948	(-20.9, 4.2)	4.2	(-0.99, 0.19)	0.01668
	1200	13.2	(-0.19, 0.67)	0.000900	(-21.1, 8.4)	4.2	(-1.11, 0.43)	0.01656
	1800	14.2	(-0.47, 0.21)	0.000710	(-2.8, 10.3)	3.2	(-0.23, 0.60)	0.01635
	2400	13.8	Error (Å)Christy (unit/Å3)Chrosty (Å)Fror (Å)(-0.11, 0.66)0.000960(-18.5, 3.6)4.0(-0.82, 0.12)(-0.17, 0.59)0.001139(-19.6, 2.2)4.5(-0.70, 0.12)(-0.34, 0.22)0.000875(-8.9, 11.6)3.9(-0.40, 0.69)(-0.34, 0.22)0.000759(-5.5, 1.1)3.2(-0.39, 0.15)(-0.33, 0.37)0.000793(-5.5, 1.1)3.2(-0.39, 0.31)(-0.12, 0.36)0.000793(-6.1, 2.5)3.6(-0.41, 0.12)(-0.18, 0.69)0.000900(-21.1, 8.4)4.2(-1.11, 0.43)(-0.47, 0.21)0.000710(-2.8, 10.3)3.2(-0.23, 0.60)(-0.27, 0.31)0.000845(-8.1, 11.3)3.4(-0.43, 0.51)(-0.68, 0.39)0.000844(-13.2, 66.8)3.6(-0.40, 1.83)(-0.77, 0.31)0.000804(-13.2, 66.8)3.6(-0.40, 1.83)(-0.78, 0.20)0.000894(-7.9, 2.1)3.6(-0.38, 0.18)(-0.29, 0.30)0.000978(-7.4, 4.1)4.0(-0.48, 0.21)(-0.61, 0.11)0.000774(-2.4, 7.9)3.3(-0.15, 0.60)(-0.47, 0.21)0.000863(-5.7, 6.0)4.11(-0.31, 0.51)(-0.58, 0.68)0.001077(-3.4, 7.7)3.4(-0.24, 0.51)(-0.64, 0.15)0.000754(-3.0, 14.0)3.8(-0.17, 0.99)(-0.47, 0.15)0.000754(-3.0, 14.0)3.8(-0.17, 0.99)(-0.47, 0.15)0.000754(-3.0, 14.0)3.8(-0.25, 0.5	0.01693				
	1	11.9	(-0.68, 0.39)	0.000926	(-9.1, 17.0)	3.9	(-0.32, 0.53)	0.01689
	2	11.2	(-1.77, 0.38)	0.000894	(-13.2, 66.8)	3.6	(-0.40, 1.83)	0.01718
	5	12.2	(-0.78, 0.20)	0.000891	(-6.2, 25.4)	3.7	(-0.29, 1.10)	0.01772
0.01	10	12.5	(-0.11, 0.37)	0.000863	(-7.9, 2.1)	3.6	(-0.38, 0.18)	0.01739
	30	11.9	(-0.29, 0.30)	0.000978	(-7.4, 4.1)	4.0	(-0.48, 0.21)	0.01789
	60	14.0	(-0.61, 0.11)	0.000724	(-2.5, 7.9)	3.3	(-0.15, 0.60)	0.01722
	300	14.2	(-0.34, 0.15)	0.000787	(-3.4, 7.7)	3.4	(-0.24, 0.51)	0.01573
	600	12.7	(-0.58, 0.08)	0.001007	(-4.9, 21.6)	3.8	(-0.12, 0.70)	0.01776
	900	15.4	(-0.42, 0.22)	0.000884	(-5.7, 6.0)	4.1	(-0.31, 0.51)	0.01709
	1200	13.6	(-0.10, 0.42)	0.000960	(-10.8, 3.7)	4.2	(-0.41, 0.07)	0.01687
	1800	13.1	(-0.19, 0.21)	0.000970	(-12.1, 8.2)	4.1	(-0.53, 0.47)	0.01656
	2400	15.1	(-0.78, 0.16)	0.000754	(-3.0, 14.0)	3.8	(-0.17, 0.99)	0.01582
	1	12.6	(-0.21, 0.47)	0.000742	(-8.2, 8.3)	3.7	(-0.61, 0.16)	0.01673
	2	11.5	(-0.47, 0.15)	0.000772	(-5.6, 20.0)	3.3	(-0.25, 0.95)	0.01743
	5	11.9	(-0.81, 0.28)	0.000853	(-6.8, 18.5)	3.7	(-0.21, 0.70)	0.01670
	10	12.4	(-0.15, 0.58)	0.000837	(-14.3, 3.4)	3.6	(-0.63, 0.16)	0.01785
	30	12.4	(-0.33, 0.61)	0.001010	(-15.8, 10.9)	4.2	(-0.73, 0.66)	0.01578
0.05	60	13.0	(-0.36, 0.25)	0.001101	(-1.5, 16.5)	4.1	(-0.05, 0.59)	0.01785
0.25	300	14.1	(-0.31, 0.39)	0.000734	(-5.0, 6.3)	4.0	(-0.62, 0.44)	0.01647
	600	14.0	(-0.28, 0.12)	0.000952	(-6.6, 10.1)	4.2	(-0.28, 0.33)	0.01591
0.01	900	13.0	(-0.21, 0.31)	0.001136	(-13.8, 9.8)	4.3	(-0.42, 0.31)	0.01802
	1200	14.5	(-0.26, 0.24)	0.001099	(-9.5, 6.5)	4.0	(-0.53, 0.33)	0.01798
	1800	14.9	(-0.32, 0.19)	0.001177	(-5.5, 14.0)	4.1	(-0.24, 0.66)	0.01706
	2400	13.7	(-0.31, 0.19)	0.001139	(-11.4, 8.7)	3.8	(-0.66, 0.43)	0.01933
0.50	1	11.3	(-0.35, 0.36)	0.001146	(-9.5, 4.5)	4.5	(-0.33, 0.28)	0.01804

Concentration (mM)	Time (min)	Dye layer thickness (Å)	Error (Å)	Density (unit/ų)	Error (unit/ų)	Roughness (Å)	Error (Å)	FOM logR1
	2	11.4	(-0.25, 0.41)	0.000818	(-1.7, 5.2)	3.7	(-0.07, 0.45)	0.01614
	5	11.8	(-0.14, 0.31)	0.001016	(-14.8, 5.6)	4.1	(-0.60, 0.25)	0.02463
	10	11.6	(-0.60, 0.19)	0.001111	(-7.9, 20.9)	4.2	(-0.32, 0.62)	0.02701
	30	12.1	(-0.16, 0.22)	0.001032	(-9.3, 4.4)	4.0	(-0.33, 0.07)	0.02654
	60	13.0	(-0.46, 0.10)	0.001122	(-4.9, 18.0)	4.2	(-0.36, 0.43)	0.02724
	300	13.6	(-0.19, 0.26)	0.000941	(-15.4, 3.4)	3.9	(-0.53, 0.13)	0.02086
	600	14.4	(-0.24, 0.10)	0.001183	(-3.7, 10.0)	4.2	(-0.17, 0.41)	0.02185
	900	14.3	(-0.31, 0.20)	0.001097	(-11.1, 12.7)	4.2	(-0.17, 0.33)	0.02528
	1200	14.0	(-0.28, 0.10)	0.001203	(-9.9, 9.5)	4.1	(-0.33, 0.37)	0.02252
	1800	14.5	(-0.27, 0.27)	0.001150	(-12.4, 5.0)	4.3	(-0.31, 0.11)	0.02701
	2400	17.6	(-0.21, 0.14)	0.001303	(-3.7, 9.1)	4.8	(-0.13, 0.43)	0.02668
	1	13.0	(-0.34, 0.27)	0.000841	(-7.0, 7.2)	3.9	(-0.44, 0.61)	0.01640
	2	13.5	(-0.21, 0.33)	0.000792	(-7.4, 1.6)	3.5	(-0.33, 0.09)	0.01593
	5	12.1	(-0.17, 0.07)	0.001035	(-18.1, 5.1)	4.5	(-0.87, 0.22)	0.01682
	10	12.3	(-1.03, 0.13)	0.000793	(-5.3, 15.9)	3.8	(-0.22, 0.83)	0.01796
	30	14.0	(-0.40, 0.37)	0.000909	(-4.6, 7.0)	4.1	(-0.25, 0.35)	0.01714
1.00	60	13.1	(-0.08, 0.39)	0.001115	(-14.9, 2.9)	4.0	(-0.56, 0.20)	0.01758
1.00	300	13.3	(-0.48, 0.27)	0.001021	(-2.9, 9.1)	4.5	(-0.16, 0.59)	0.01897
	600	14.7	(-0.37, 0.23)	0.001122	(-6.7, 12.2)	3.9	(-0.29, 0.50)	0.01766
	900	15.0	(-0.21, 0.26)	0.001208	(-9.7, 7.1)	4.3	(-0.45, 0.28)	0.01890
	1200	15.5	(-0.33, 0.16)	0.001154	(-4.9, 15.5)	4.3	(-0.21, 0.60)	0.01810
	1800	17.1	(-0.29, 0.30)	0.000977	(-7.4, 1.9)	3.9	(-0.44, 0.11)	0.01854
	2400	16.5	(-0.27, 0.22)	0.001238	(-8.3, 9.5)	4.6	(-0.27, 0.54)	0.01879

Table C5. Fitting results of the thickness, density, and roughness of **N749** layers fabricated using different sensitization times and concentrations, followed by 5 s rinsing in neat acetonitrile and drying under a flow of N_2 .

Concentration (mM)	Time (min)	Dye layer thickness (Å)	Error (Å)	Density (unit/ų)	Error (unit/ų)	Roughness (Å)	Error (Å)	FOM logR1
	1	13.4	(-0.14, 0.47)	0.000419	(-7.4, 2.3)	Roughness (Å) Error (Å) From (Å) 3.4 (-0.92, 0.27) 0.00 2.5 (-0.46, 0.59) 0.00 3.0 (-0.38, 0.42) 0.00 4.2 (-0.69, 0.23) 0.00 3.7 (-0.81, 0.13) 0.00 3.3 (-0.29, 0.36) 0.00 3.3 (-0.78, 0.75) 0.00 3.4 (-0.78, 0.63) 0.00 3.1 (-0.57, 0.41) 0.00 4.3 (-1.08, 0.37) 0.00 4.6 (-0.95, 0.21) 0.00 4.7 (-0.62, 0.10) 0.00 4.7 (-0.62, 0.10) 0.00 4.6 (-0.72, 0.61) 0.00 3.6 (-0.72, 0.61) 0.00 4.5 (-0.48, 0.56) 0.00 3.6 (-0.23, 0.24) 0.00 3.4 (-0.38, 0.40) 0.00 3.4 (-0.17, 0.14) 0.00 3.6 (-0.23, 0.24) 0.00 3.7 (-0.60, 0.53) 0.00 <td>0.01914</td>	0.01914	
	2	12.4	(-0.32, 0.43)	0.000341	(-2.5, 4.7)	2.5	(-0.46, 0.59)	0.02011
Concentration (mM) 0.01 0.05 0.25	5	13.2	(-0.32, 0.36)	0.000368	(-3.7, 3.1)	3.0	(-0.38, 0.42)	0.01948
	10	12.8	(-0.43, 0.67)	0.000419	(-8.1, 2.6)	4.2	(-0.69, 0.23)	0.02203
	30	12.8	(-0.46, 0.45)	0.000403	(-5.6, 1.5)	3.7	(-0.81, 0.13)	0.02155
	60	11.8	(-0.18, 0.79)	0.000410	(-4.3, 1.8)	3.3	(-0.29, 0.36)	0.02047
	300	11.7	(-0.37, 0.92)	0.000384	(-8.9, 4.6)	3.4	(-0.78, 0.75)	0.01935
	600	14.5	(-0.43, 0.34)	0.000273	(-3.2, 3.0)	2.5	(-0.78, 0.63)	0.01820
	900	12.7	(-0.30, 0.36)	0.000370	(-3.5, 1.9)	3.1	(-0.57, 0.41)	0.02040
	1200	11.1	(-0.36, 0.86)	0.000493	(-13.3, 5.6)	4.3	(-1.08,0.37)	0.01915
	1800	10.6	(-0.22, 0.84)	0.000531	(-13.1, 3.6)	4.6	(-0.95, 0.21)	0.01849
	2400	10.2	(-0.21, 0.63)	0.000594	(-10.3, 2.1)	4.7	(-0.62, 0.10)	0.01767
	1	11.2	(-0.34, 0.25)	0.000539	(-4.6, 3.9)	4.2	(-0.22, 0.21)	0.01969
	2	11.9	(-0.49, 0.34)	0.000292	(-2.7, 3.5)	2.2	(-0.48, 0.70)	0.02177
	5	11.5	(-0.36, 0.32)	0.000432	(-6.1, 4.9)	3.6	(-0.72, 0.61)	0.01924
	10	11.1	(-0.33, 0.41)	0.000552	(-7.0, 8.2)	4.5	(-0.48, 0.56)	0.01993
0.01	30	10.8	(-0.28, 0.67)	0.000556	(-11.1, 5.5)	4.4	(-0.51, 0.49)	0.02050
	60	10.4	(-0.60, 0.33)	0.000575	(-5.9, 13.9)	4.6	(-0.44, 0.86)	0.02050
	300	11.0	(-0.31, 0.34)	0.000354	(-3.5, 2.9)	3.4	(-0.38, 0.40)	0.02147
	600	11.2	(-0.23, 0.82)	0.000355	(-9.8, 3.5)	3.4	(-0.81, 0.28)	0.01822
	900	11.7	(-0.27, 0.20)	0.000470	(-2.8, 3.2)	4.1	(-0.17, 0.14)	0.01832
	1200	12.9	(-0.29, 0.33)	0.000361	(-2.6, 2.5)	3.6	(-0.23, 0.24)	0.01922
	1800	13.0	(-0.46, 0.08)	0.000361	(-2.5, 5.5)	3.0	(-0.43, 0.65)	0.01900
	2400	10.7	Inc. (A)(unit/Å)(unit/Å)(A)13.4(-0.14, 0.47)0.000419(-7.4, 2.3)3.412.4(-0.32, 0.43)0.000368(-3.7, 3.1)3.012.8(-0.43, 0.67)0.000419(-8.1, 2.6)4.212.8(-0.46, 0.45)0.000403(-5.6, 1.5)3.711.8(-0.18, 0.79)0.000410(-4.3, 1.8)3.311.7(-0.37, 0.92)0.000384(-8.9, 4.6)3.414.5(-0.43, 0.34)0.000273(-3.2, 3.0)2.512.7(-0.30, 0.36)0.000370(-3.5, 1.9)3.111.1(-0.36, 0.86)0.000433(-10.3, 2.1)4.711.2(-0.21, 0.63)0.000531(-13.1, 3.6)4.610.2(-0.21, 0.63)0.000532(-4.6, 3.9)4.211.9(-0.49, 0.34)0.000292(-2.7, 3.5)2.211.5(-0.36, 0.32)0.000432(-6.1, 4.9)3.611.1(-0.33, 0.41)0.000552(-7.0, 8.2)4.511.2(-0.23, 0.82)0.000354(-3.5, 2.9)3.411.4(-0.60, 0.33)0.000575(-5.9, 13.9)4.611.0(-0.31, 0.34)0.000354(-3.5, 2.9)3.411.2(-0.23, 0.82)0.000355(-9.8, 3.5)3.611.4(-1.01, 0.23)0.000361(-2.5, 5.5)3.011.7(-0.27, 0.20)0.000470(-2.8, 3.2)4.112.9(-0.29, 0.33)0.000361(-2.6, 2.5, 5.5)3.6<	4.2	(-0.60, 0.53)	0.01964		
	1	11.4	(-1.01, 0.23)	0.000502	(-3.6, 14.6)	4.3	(-0.19, 1.15)	0.01893
	2	12.0	(-0.32, 0.26)	0.000439	(-4.6, 6.2)	3.6	(-0.41, 0.67)	0.01977
	5	10.4	(-1.71, 0.33)	0.000566	(-10.2, 33.7)	4.3	(-0.70, 1.70)	0.01943
	10	12.2	(-0.52, 0.21)	0.000420	(-2.8, 3.7)	3.7	(-0.31, 0.44)	0.01951
	30	11.2	(-0.37, 0.29)	0.000393	(-3.0, 3.2)	3.3	(-0.09, 0.07)	0.01890
0.05	60	10.8	(-1.13, 0.27)	0.000419	(-4.1, 19.1)	3.6	(-0.26, 1.31)	0.01609
0.25	300	11.8	(-0.09, 0.31)	0.000367	(-2.5, 2.8)	3.5	(-0.18, 0.32)	0.01343
	600	12.6	(-0.24, 0.13)	0.000427	(-1.4, 5.0)	3.9	(-0.17, 0.54)	0.01392
0.01	900	11.4	(-0.20, 0.21)	0.000421	(-3.7, 3.1)	3.7	(-0.42, 0.30)	0.01586
	1200	10.8	(-0.26, 0.17)	0.000412	(-2.6, 7.7)	3.6	(-0.08, 0.49)	0.01560
	1800	11.4	(-0.13, 0.27)	0.000491	(-6.6, 3.6)	4.2	(-0.50, 0.18)	0.01538
	2400	10.4	(-0.37, 0.70)	0.000526	(-13.0, 5.7)	4.2	(-0.87, 0.26)	0.01536
0.50	1	12.3	(-0.25, 0.27)	0.000506	(-3.6, 5.3)	4.5	(-0.45, 0.44)	0.01657

Concentration (mM)	Time (min)	Dye layer thickness (Å)	Error (Å)	Density (unit/ų)	Error (unit/ų)	Roughness (Å)	Error (Å)	FOM logR1
	2	9.8	(-0.10, 0.54)	0.000533	(-12.7, 4.4)	4.1	(-0.60, 1.18)	0.01679
	5	10.0	(-0.36, 0.94)	0.000450	(-19.2, 8.4)	3.9	(-1.15, 0.53)	0.01664
	10	11.7	(-0.61, 0.16)	0.000390	(-3.3, 12.6)	3.2	(-0.25, 0.98)	0.01916
	30	13.0	(-0.31, 0.31)	0.000344	(-2.3, 2.2)	2.9	(-0.42, 0.27)	0.01912
	60	11.3	(-0.50, 0.80)	0.000528	(-8.0, 1.8)	5.2	(-1.05, 0.24)	0.02126
	300	11.1	(-0.22, 0.19)	0.000538	(-2.6, 3.9)	4.0	(-0.28, 0.18)	0.01835
	600	11.5	(-0.22, 0.49)	0.000493	(-7.7, 5.3)	4.2	(-0.56, 0.50)	0.02083
	900	10.4	(-0.29, 0.36)	0.000492	(-3.0, 2.3)	4.2	(-0.30, 0.21)	0.01800
	1200	10.4	(-0.30, 0.26)	0.000618	(-3.7, 3.2)	5.0	(-0.38, 0.25)	0.01862
	1800	10.7	(-0.25, 0.21)	0.000481	(-3.1, 3.5)	4.2	(-0.47, 0.36)	0.01756
	2400	11.1	(-0.54, 0.30)	0.000473	(-3.0, 11.2)	4.1	(-0.22, 0.85)	0.01577
	1	11.7	(-0.26, 0.21)	0.000448	(-2.5, 2.9)	3.6	(-0.16, 0.19)	0.01638
	2	10.9	(-0.57, 0.39)	0.000544	(-5.4, 5.5)	4.5	(-0.42, 0.46)	0.02028
	5	10.6	(-0.23, 0.46)	0.000610	(-9.5, 4.4)	5.4	(-0.63, 0.31)	0.01949
	10	11.9	(-0.45, 0.16)	0.000520	(-4.3, 9.6)	4.4	(-0.39, 0.70)	0.02036
	30	10.0	(-0.27, 0.60)	0.000673	(-12.5, 5.8)	4.9	(-0.49, 0.12)	0.01985
1.00	60	11.3	(-0.62, 0.68)	0.000427	(-13.2, 10.4)	3.8	(-1.12, 0.61)	0.02116
1.00	300	13.0	(-0.30, 0.12)	0.000387	(-1.2, 4.1)	3.9	(-0.08, 0.21)	0.01351
	600	11.7	(-0.21, 0.30)	0.000432	(-2.9, 2.4)	3.7	(-0.20, 0.19)	0.01495
	900	12.4	(-0.42, 0.24)	0.000428	(-4.3, 5.5)	3.6	(-0.38, 0.58)	0.01542
	1200	11.9	(-0.09, 0.41)	0.000432	(-8.8, 4.0)	3.7	(-0.66, 0.41)	0.01641
	1800	11.0	(-0.21, 0.65)	0.000580	(-13.4, 3.8)	4.5	(-0.98, 0.24)	0.01619
	2400	12.0	(-0.27, 0.18)	0.000457	(-2.6, 3.5)	4.0	(-0.19, 0.23)	0.01464

Table C6. Fitting results of the thickness, density, and roughness of **N749** layers fabricated using different sensitization times and concentrations, followed by no rinsing in neat acetonitrile and drying under a flow of N_2 .

Concentration (mM)	Time (min)	Dye layer thickness (Å)	Error (Å)	Density (unit/ų)	Error (unit/ų)	Roughness (Å)	Error (Å)	FOM logR1
	1	10.4	(-0.13, 0.55)	0.000631	(-11.9, 3.2)	4.5	Pess Error (Å) Perss (-0.71, 0.18) 0 (-0.92, 0.27) 0 (-1.01, 0.28) 0 (-0.47, 0.53) 0 (-0.51, 1.09) 0 (-0.51, 1.09) 0 (-0.51, 1.09) 0 (-0.57, 0.42) 0 (-0.78, 0.36) 0 (-0.78, 0.36) 0 (-0.78, 0.36) 0 (-0.78, 0.36) 0 (-0.78, 0.36) 0 (-0.78, 0.32) 0 (-0.78, 0.36) 0 (-0.79, 0.79) 0 (-0.43, 0.53) 0 (-0.79, 0.79) 0 (-0.70, 0.79) 0 (-0.70, 0.79) 0 (-0.70, 0.79) 0 (-0.70, 0.79) 0 (-0.70, 0.79) 0 (-0.712, 0.63) 0 (-0.74, 0.43) 0 (-0.45, 0.43) 0 (-0.45, 0.46) 0 (-0.712, 0.09) 0 <t< td=""><td>0.01546</td></t<>	0.01546
Concentration (mM) Time (min) I 1 2 5 10 30 60 300 60 300 600 900 1 0.01 300 60 900 1 2 100 300 60 900 1 200 1200 1 2 1200 1 2 100 30 60 300 600 300 600 300 60 900 1 2 5 10 30 600 300 60 900 1 2 1200 1 30 600 300 60 100 30 60 100 30 60 100 300 60 100 300 60 100 300 60 100<	2	10.3	(-0.19, 0.47)	0.000707	(-13.9, 4.9)	5.2	(-0.92, 0.27)	0.01686
	5	12.9	(-0.09, 0.49)	0.000386	(-8.4, 1.4)	3.5	(-1.01, 0.28)	0.01913
	10	13.8	(-0.37, 0.37)	0.000327	(-2.1, 1.9)	2.7	(-0.47, 0.53)	0.01942
	30	12.8	(-0.94, 0.53)	0.000352	(-6.7, 12.5)	3.1	(-0.51, 1.09)	0.02071
	60	12.8	(-0.41, 0.28)	0.000398	(-3.6, 5.7)	3.6	(-0.44, 0.70)	0.01908
	300	13.7	(-0.36, 0.41)	0.000373	(-5.6, 1.4)	3.2	(-0.95, 0.42)	0.01849
	600	14.2	(-0.21, 0.23)	0.000435	(-3.2, 4.3)	3.7	(-0.27, 0.44)	0.01937
	12.5	(-0.34, 0.35)	0.000455	(-4.1, 3.9)	3.8	(-0.57, 0.46)	0.01992	
	1200	13.0	(-0.37, 0.56)	0.000407	(-6.1, 3.1)	3.7	(-0.78, 0.36)	0.02007
	1800	13.6	(-0.48, 0.31)	0.000380	(-2.1, 2.6)	4.1	(-0.38, 0.40)	0.02038
	2400	13.9	(-0.04, 0.03)	0.000470	(-0.3, 0.6)	3.6	(-0.02, 0.03)	0.01908
	1	11.7	(-0.24, 0.19)	0.000525	(-4.6, 5.0)	4.3	(-0.50, 0.54)	0.01973
	2	11.7	(-0.32, 0.35)	0.000416	(-3.9, 3.9)	3.4	(-0.49, 0.32)	0.01929
	5	10.0	(-0.38, 0.36)	0.000589	(-4.7, 4.8)	5.5	(-0.38, 0.49)	0.01923
	10	14.8	(-0.59, 0.76)	0.000166	(-3.8, 2.8)	3.2	(-0.43, 0.53)	0.01788
0.05	30	11.3	(-0.34, 0.20)	0.000473	(-4.5, 4.7)	4.5	(-0.39, 0.53)	0.01848
	60	13.7	(-0.59, 0.81)	0.000240	(-5.3, 3.2)	4.1	(-0.50, 0.60)	0.02730
	300	13.5	(-0.62, 0.74)	0.000223	(-4.9, 3.9)	4.2	(-0.70, 0.79)	0.02063
	600	12.9	(-0.25, 0.29)	0.000371	(-2.8, 2.1)	3.0	(-0.28, 0.33)	0.02068
	900	11.0	(-0.31, 0.43)	0.000577	(-5.5, 5.9)	4.7	(-0.24, 0.63)	0.01823
	1200	13.4	(-0.58, 1.16)	0.000218	(-4.8, 2.4)	3.5	(-0.81, 0.43)	0.02396
0.01	1800	14.2	(-0.31, 0.38)	0.000296	(-2.5, 2.1)	3.6	(-0.45, 0.43)	0.01467
	Image Image <th< td=""><td>13.6</td><td>(-0.98, 0.62)</td><td>0.000243</td><td>(-5.0, 4.1)</td><td>5.1</td><td>(-0.44, 0.41)</td><td>0.01967</td></th<>	13.6	(-0.98, 0.62)	0.000243	(-5.0, 4.1)	5.1	(-0.44, 0.41)	0.01967
	1	10.9	(-0.43, 0.91)	0.000645	(-1.3, 9.1)	5.0	(-0.82, 0.59)	0.01696
	2	11.0	(-0.66, 0.30)	0.000555	(-5.8, 12.1)	4.2	(-0.37, 0.69)	0.01647
	5	12.1	(-0.69, 0.23)	0.000325	(-3.9, 6.3)	3.5	(-0.38, 0.73)	0.01403
	10	11.6	(-0.32, 0.15)	0.000382	(-2.7, 3.2)	3.8	(-0.45, 0.36)	0.01458
	30	12.8	(-0.41, 0.32)	0.000353	(-2.2, 2.3)	4.4	(-0.12, 0.09)	0.01450
0.05	60	12.2	(-0.65, 0.15)	0.000355	(-1.4, 4.8)	3.9	(-0.26, 0.46)	0.01243
0.05	300	12.4	(-0.37, 0.39)	0.000304	(-5.0, 4.3)	4.0	(-0.32, 0.49)	0.01738
	600	12.8	(-0.17, 0.20)	0.000587	(-7.4, 6.1)	4.0	(-0.57, 0.39)	0.01682
0.01	900	15.9	(-0.36, 0.81)	0.000283	(-7.9, 8.1)	4.2	(-0.64, 1.61)	0.02536
	1200	13.7	(-0.51, 0.66)	0.000295	(-7.4, 3.0)	5.4	(-0.82, 0.30)	0.01921
0.01	1800	16.3	(-0.45, 0.35)	0.000290	(-2.8, 2.6)	4.0	(-0.39, 0.42)	0.01963
	2400	17.8	(-1.52, 2.29)	0.000159	(-4.3, 3.9)	5.4	(-0.74, 0.23)	0.02302
0.50	1	14.9	(-0.44, 0.15)	0.000367	(-3.0, 6.7)	3.2	(0.65, 0.95)	0.02004

Concentration (mM)	Time (min)	Dye layer thickness (Å)	Error (Å)	Density (unit/ų)	Error (unit/ų)	Roughness (Å)	Error (Å)	FOM logR1
	2	14.7	(-0.40, 0.35)	0.000358	(-4.8, 2.1)	3.4	(-0.80, 0.37)	0.02065
	5	14.1	(-0.31, 0.20)	0.000342	(-2.6, 2.2)	3.5	(-0.22, 0.23)	0.01647
	10	13.9	(-0.23, 0.08)	0.000456	(-3.0, 3.6)	4.2	(-0.41, 0.49)	0.01682
	30	15.2	(-0.58, 0.60)	0.000220	(-2.6, 2.3)	4.8	(-0.86, 0.24)	0.01538
	60	14.4	(-0.39, 0.12)	0.000405	(-1.2, 5.9)	3.4	(-0.11, 0.52)	0.01774
	300	13.6	(-0.20, 0.23)	0.000405	(-4.9, 1.4)	3.5	(-0.44, 0.16)	0.01960
	600	13.3	(-0.14, 0.27)	0.000530	(-8.6, 3.7)	4.0	(-0.53, 0.24)	0.01834
	900	15.8	(-0.77, 0.17)	0.000333	(-1.4, 5.4)	4.3	(-0.19, 0.68)	0.01901
	1200	16.1	(-0.67, 0.76)	0.000186	(-4.5, 3.1)	4.9	(-1.77, 0.14)	0.01954
	1800	15.9	(-0.47, 0.40)	0.000341	(-4.4, 1.7)	4.0	(-0.59, 0.55)	0.02002
	2400	15.9	(-0.62, 0.64)	0.000249	(-1.8, 2.4)	4.3	(-0.28, 0.25)	0.01645
	1	13.5	(-0.19, 0.70)	0.000435	(-8.8, 2.6)	4.6	(-0.76, 0.28)	0.02008
	2	13.0	(-0.35, 0.19)	0.000429	(-4.1, 6.3)	4.4	(-0.38, 0.58)	0.01665
	5	14.3	(-0.14, 0.42)	0.000387	(-6.9, 1.7)	4.1	(-0.76, 0.19)	0.01924
	10	13.2	(-0.46, 0.25)	0.000472	(-4.1, 5.9)	4.3	(-0.28, 0.72)	0.01835
	30	14.6	(-0.37, 0.26)	0.000415	(-4.2, 5.0)	4.2	(-0.52, 0.49)	0.01901
1.00	60	13.9	(-0.37, 0.43)	0.000343	(-1.9, 2.3)	3.6	(-0.15, 0.18)	0.02013
1.00	300	14.5	(-0.72, 0.28)	0.000375	(-3.2, 8.5)	3.4	(-0.19, 0.97)	0.02002
	600	13.0	(-0.42, 0.47)	0.000459	(-3.2, 6.9)	4.1	(-0.34, 0.40)	0.01869
	900	15.0	(-0.46, 0.09)	0.000396	(-1.5, 3.5)	4.1	(-0.17, 0.47)	0.01398
	1200	14.8	(-0.41, 0.23)	0.000380	(-2.4, 3.0)	3.6	(-0.31, 0.53)	0.01536
	1800	14.8	(-0.41, 0.27)	0.000377	(-4.1, 4.4)	4.2	(-0.54, 0.51)	0.01390
	2400	15.4	(-0.64, 0.12)	0.000361	(-2.3, 5.1)	4.3	(-0.21, 0.67)	0.01542

Appendix D – Supporting information for Chapter 6

D1. Sample environment for the *in-situ* NR measurements



d

Figure D1. (a) Model showing the OffSpec DSSC sample assembly clamped into a position of the bespoke sample holder. (b) Bespoke sample stage with multiple sample holders. (c) View from below the sample holder after filling the gap between the electrodes with d₃-MeCN. (d) Side view of the sample assembly.

С

b

D2. Geometries of the NR measurements



Figure D2. OffSpec reflectometer with the sample stage in position. The neutrons arrive from the beamline (left), are projected onto the samples (middle), and reflected into the detector (right).



Figure D3. Schematic diagram showing the geometry of the sample position and the alignment with respect to the neutron beam.



Figure D4. (a) Measurement geometry of the NR measurements. (b) Diagram showing the path of the neutron beam (red) through a substrate (blue) of suitable thickness. The substrate needs to be sufficiently thick (\geq 5 mm) to allow an uninterrupted beam transmission. (c) Diagram showing unwanted reflection at the air-substrate interface, which degrades the beam flux incident upon the interface of interest when a thinner substrate is used.

The neutron intensity along the x (beam width) and y (beam length) axes are shown in Figure D5. The gradient of illumination along the y axis results in the constant and varying illumination areas shown in Figure D6.



Figure D5. Neutron intensity along the x and y axes. (a) side view; (b) top view.

The neutron beam size and profile for measurements with regards to the LED illuminated area (ϕ = 40 mm) are shown in Figure D6.



Figure D6. Neutron beam size and profile. The neutron illumination area needs to be within the area of the gasket, so that the scattering arises only from the sample. The slits are movable, and when measuring at 0.3° , they were used to define the beam footprint on the sample. When the sample angle and the detector angle were changed to 2° , the slits were opened by a factor of 20/3 to keep the same footprint on the sample.

D3. Characterization of the surface roughness of the native silicon-oxide layer and the TiO₂ on the silicon wafer

The surface roughness values of the native silicon oxide layer and the TiO_2 on the silicon wafer are important parameters when fitting the reflectometry data. The roughness values of the native silicon-oxide layer and the thin films of TiO_2 were characterized by optical roughness metrology on a Bruker GT-X 3D optical profiler.



Figure D7. Representative surface morphology of the native silicon-oxide layer.



Figure D8. Representative surface roughness profile of the native silicon-oxide layer.

Three measurements were performed on the roughness of the native oxide-layer on bare silicon wafers, which resulted in an average root-mean-square roughness of R_q = 1.94 Å.



Figure D9. Representative surface morphology of the thin film of TiO₂.



Figure D10. Representative surface roughness profile of the thin film of TiO₂.

Three measurements were performed in order to obtain average roughness values (R_q = 1.57 Å) of the thin films of TiO₂.

The surface area used for roughness metrology was $0.12 \times 0.1 \text{ mm}^2$, while the neutron illuminated area was $25 \times 31.2 \text{ mm}^2$. Although the roughness metrology tends to reflect the relative micro-structural information of the surface, it can still be considered a good representation of the neutron-beam-illuminated area, given that the thin films of TiO₂ fabricated by ALD exhibit high homogeneity on the mm scale. In the subsequent NR profiles fitting, the surface roughness of TiO₂ and the native silicon oxide layers were initially constrained to < 2 Å.

In the case where there is not significant roughness on the surface (usually < 100 Å), it is normally possible to model well the interfacial roughness as a thin film with the SLD in between that two adjacent layers. This is beneficial as we do not wish to measure the roughness¹⁴³. Under this assumption, smaller roughness values (regarded as the modelled thickness of the thin film) normally indicates a higher gradient of the SLD variation across the adjacent layers and vice versa.

D4. Light arrangements for the illumination of the samples.

Illumination was provided using THORLABS LEDD1B high-power LEDs with currents up to 1200 mA. The output current can be limited continuously from 200 mA to 1.2 A using the adjuster on the front of the unit when necessary. The four sample holders were simultaneously illuminated using four optical fibers directing light from the LED light source. Tin foils were used to seal the entire sample environment to shield light when dark conditions were required.



Figure D11. Illumination using optical fibres directing light from the LED light source.

Appendix E – Supporting information for Chapter 7

E1. *Ex-situ* air-solid NR experiments to examine the potentially different solvent effects on the adsorption behavior of MK-2, N3, and N749 on TiO₂

The structures **MK-2**, **N3**, and **N749** on the TiO₂ surface after their interaction with acetonitrile (exposed to d₃-acetonitrile and Lil/I₂, followed by rinsing with acetonitrile) and methanol (exposure to d₄-methanol and Lil/I₂, followed by rinsing with methanol) were examined by *ex-situ* neutron reflectometry (NR) measurements, which were carried out at the China Spallation Neutron Source (CSNS). The different dye layer structures, especially the fitted SLD profiles from NR shown in Figure E3 indicate potentially different solvent effects on the adsorption behavior of **MK-2**, **N3**, and **N749** on TiO₂.



Figure E1. Schematic illustration of the configuration of the air-solid reflectometry measurements used to probe the dye \cdots TiO₂ interface on silicon wafers.



Figure E2. *Ex-situ* air-solid NR profiles and fittings for the dye \cdots TiO₂ interface on silicon wafers after exposure to d₃-MeCN or d₄-MeOH and Lil/I₂ followed by rinsing with the corresponding hydrogenated solvent.



Figure E3. NR-derived SLD for thin films of dye-sensitized TiO₂ on silicon wafers after exposure to d₃-MeCN or d₄-MeOH and Lil/I₂ followed by rinsing with the corresponding hydrogenated solvent.

E2. *Ex-situ* air-solid NR profiles co-refined with the XRR profiles in order to examine the potentially different solvent effects on the adsorption behavior of MK-2, N3, and N749 on TiO₂

The structures of **MK-2**, **N3**, and **N749** on the TiO₂ surface after their interaction with acetonitrile and methanol were examined by co-refining the *ex-situ* NR data and the X-ray reflectometry (XRR) data. Compared to the fitting of the XRR data alone, the co-refining of the XRR data with the NR data provide results that are closer to the "true" values, as the NR data can be used as another set of constraints to find the optimal fitting results. The different dye-layer structures, especially the fitted SLD profiles of the dye layers (Figures E4-E9) indicate different solvent effects on the adsorption behavior of the dyes on TiO₂. Table E1 contains a summary of the GenX-derived numerical information for each co-refinement fitting, i.e., thickness, density and roughness values for the dye layers.


Figure E4. *Ex-situ* air-solid NR profiles (inset: magnification) co-refined with XRR data for **MK-2** \cdots TiO₂ on silicon wafers after exposure to d₃-MeCN and Lil/I₂ and rinsing with MeCN.



Figure E5. *Ex-situ* air-solid NR profiles (inset: magnification) co-refined with XRR data for **MK-2**…TiO₂ on silicon wafers after exposure to d₄-MeOH and Lil/I₂ and rinsing with MeOH.



Figure E6. *Ex-situ* air-solid NR profiles (inset: magnification) co-refined with XRR data for N3···TiO₂ on silicon wafers after exposure to d₃-MeCN and Lil/I₂ and rinsing with MeCN.



Figure E7. *Ex-situ* air-solid NR profiles (inset: magnification) co-refined with XRR data for **N3**...TiO₂ on silicon wafers after exposure to MeOH and Lil/I₂ and rinsing with MeOH.



Figure E8. *Ex-situ* air-solid NR profiles (inset: magnification) co-refined with XRR data for **N749**...TiO₂ on silicon wafers after exposure to MeCN and Lil/I₂ and rinsing with MeCN.



Figure E9. *Ex-situ* air-solid NR profiles (inset: magnification) co-refined with XRR for N749...TiO₂ on silicon wafers after exposure to MeOH and Lil/I₂ and rinsing with MeOH.

Table E1. Structural parameters obtained from co-refining *ex-situ* NR and XRR data for dye layers after exposure to MeCN or MeOH Lil/ I_2 followed by rinsing with the corresponding solvent. The I_2 top layers, which are due to I_2 ingression in the presence of Lil/ I_2 , are assumed to be negligible after rinsing with the corresponding solvent, and were therefore not included in the fittings of the sample models.

	Dye layer							
Dye and exposed solvent	Thickness (Å)	Fitting error (Å)	Density (10 ⁻⁴ unit/Å ³)	Fitting error (10 ⁻⁵ unit/Å ³)	Roughness (Å)	FOM logR1		
MK-2 (MeCN)	19.5	(-1.3, 1.0)	5.85	(-3.4, 8.4)	6.0	0.03396		
MK-2 (MeOH)	23.8	(-1.3, 1.1)	5.22	(-6.6, 9.7)	3.9	0.03420		
N3 (MeCN)	10.4	(-0.5, 0.2)	13.25	(-7.3, 5.0)	4.6	0.02708		
N3 (MeOH)	9.8	(-0.6, 0.5)	8.91	(-6.8, 11.3)	4.6	0.01970		
N749 (MeCN)	10.5	(-0.2, 0.3)	5.40	(-3.4, 1.9)	4.7	0.02964		
N749 (MeOH)	8.4	(-1.1, 0.3)	2.59	(-2.4, 11.4)	4.1	0.02061		

The 'unit' in the table is defined as one dye molecule. The neutron or X-ray scattering length density (SLD) of each dye layer can be derived by multiplying the fitted density of each dye layer with the total neutron or X-ray scattering length of one dye molecule.

A higher extent of fitted dye-layer density is observed for all dyes after interaction with acetonitrile, compared to that after interaction with methanol. The reasons for this behavior might be that the carboxylate anchors adsorb weaker to TiO_2 in methanol than in acetonitrile. This hypothesis is consistent with the results obtained for the degree of dye adsorption before and after solvent rinsing (*cf.* section E3), which

suggests that methanol exhibits a higher potential to detach the dyes from the TiO₂ surface. This could lead to a higher propensity toward dye-orientation change when adding electrolyte components in methanol.

E3. Solvent-rinsing effects on the dye layers

The solvent rinsing effects on the **MK-2**, **N3**, and **N749** layers regarding the adsorption mass were examined by fitting the XRR data collected for thin films of dye-sensitized TiO_2 before and after rinsing with the solvents. The thin films of dye-sensitized TiO_2 were previously used for the *in-situ* NR study in the presence of Lil/I₂.



Figure E10. *Ex-situ* XRR profiles of thin films of dye-sensitized TiO_2 on silicon wafers in the presence of Lil/I₂, measured before and after rinsing with the indicated solvent.

Table E2. (1) *Ex-situ* XRR-fitted structural parameters for the dye layers before and after rinsing with the indicated solvent (10 s), after exposure to Lil and I_2 ; (2) *ex-situ* XRR-fitted structural parameters for the I_2 top layer before rinsing with the indicated solvent after exposure to Lil/ I_2 in acetonitrile.

(1)

		Dye layer						
Rinse condition	Dye and exposed solvent	Thickness (Å)	Fitting error (Å)	Density (10 ⁻⁴ unit/Å ³)	Fitting error (10 ⁻⁵ unit/Å ³)	Roughness (Å)	Adsorption (AMI) of dye layer (unit/Å ²)	FOM logR1
	MK-2 (MeCN)	19.6	(-0.7, 1.1)	5.89	(-7.9, 1.7)	5.5	0.01157	0.01404
Before rinse	MK-2 (MeOH)	22.0	(-0.4, 0.4)	6.34	(-2.9, 2.1)	5.4	0.01397	0.01367
	N3 (MeCN)	11.3	(-0.4, 0.5)	14.43	(-3.3, 6.0)	5.5	0.01629	0.01611

	N3 (MeOH)	21.5	(-0.5, 0.5)	9.13	(-5.3, 2.5)	5.2	0.01963	0.01556
	N749 (MeCN)	13.0	(-0.3, 0.2)	6.27	(-5.7, 1.6)	4.9	0.00813	0.01508
	N749 (MeOH)	13.0	(-0.1, 0.2)	4.55	(-1.4, 5.0)	4.4	0.00579	0.01335
After	MK-2 (MeCN)	19.4	(-0.4, 0.7)	5.69	(-5.4, 13.5)	6.0	0.01102	0.02695
	MK-2 (MeOH)	21.5	(-1.6, 1.3)	5.20	(-3.6, 4.1)	8.0	0.01118	0.02813
	N3 (MeCN)	10.7	(-0.3, 0.3)	14.20	(-6.2, 5.9)	5.0	0.01521	0.01644
rinse	N3 (MeOH)	8.2	(-0.6, 0.4)	8.65	(-10.2, 8.8)	4.6	0.00711	0.02872
-	N749 (MeCN)	11.2	(-0.1, 0.3)	5.65	(-4.5, 2.2)	4.1	0.00634	0.01530
	N749 (MeOH)	8.4	(-0.5, 0.3)	2.26	(-3.3, 6.2)	3.3	0.00190	0.01732

(2)

		E				
Rinse condition	Dye and exposed solvent	Thickness (Å)	Fitting error (Å)	Density (10 ⁻³ unit (Si) /Å ³)	Fitting error (10 ⁻⁴ unit/Å ³)	FOM logR1
Before rinse	MK-2 (MeCN)	29.6	(-1.4, 1.7)	9.10	(-5.8, 6.2)	0.0141
	N3 (MeCN)	21.2	(-1.4, 1.5)	3.55	(-7.1, 5.7)	0.0189
	N749 (MeCN)	34.5	(-1.3, 1.3)	4.41	(-6.7, 7.3)	0.0158

The adsorption mass index (AMI), which represents the extent of average dye adsorption mass per surface area, can be defined as the product of the density (directly proportional to the SLD) and the thickness:

$$AMI (unit/Å^2) = density (unit/Å^3) \times thickness (Å)$$
(E1)

According to the fitting results, the relative variation of the calculated AMI regarding the rinsing effect for each sample is shown in Table E3.

Table E3. AMI for dye layers (after exposure to Lil/I₂ in MeCN or MeOH) before and after rinsing with the corresponding solvent for 10 s.

AMI (unit/Ų)	Before rinse	After rinse	Relative variation of AMI due to the rinsing effect
MK-2 in MeCN	0.01157	0.01102	-4.8%
MK-2 in MeOH	0.01397	0.01118	-20.0%
N3 in MeCN	0.01629	0.01521	-6.6%
N3 in MeOH	0.01963	0.00711	-63.8%
N749 in MeCN	0.00813	0.00634	-22.0%
N749 in MeOH	0.00579	0.00190	-67.2%
		243	

Rinsing in the corresponding solvent induced a reduction of the dye layer adsorption mass on TiO_2 , which may be due to the removal of some dye molecules on TiO_2 , and the removal of electrolyte constituents left in the dye layer. Particularly, the relatively larger reduction of AMI when rinsing the dyes with MeOH compared to that with MeCN indicates that MeOH may facilitate the desorption of the dyes from TiO_2 more easily than MeCN.

E4. Technical implementation of the background subtraction for the *in-situ* NR data

In-situ NR data were collected using an Si-contrast-matched subphase solvent. However, some abnormality manifested in the form of obvious dips in the reflectivity (at small Q values), where the intensity dropped below the background (Figures E13-15). This was tentatively ascribed to a background effect arising from instrument and sample. To eliminate this background effect, the background was measured directly on the sample (bare TiO₂ on silicon) using the Si-contrast-matched subphase solvent.

Figure E11 shows the detector with the measurement data loaded. The reflection manifests as a horizontal line across the detector, while the background appears across the whole detector. The background looks fairly homogeneous across this range, and the corrected background was obtained by adding a certain offset angle to the detector angle. The offset angle was chosen to be sufficiently large so that the reflection was not caught, but simultaneously sufficiently small that a potentially sampling of a different part of the background was avoided. In this case, we chose 0.2° , which corresponds to ca. 50 pixels (one pixel = 0.0042°). For each background subtraction, the actual subtracted background was obtained by scaling the measured background with a factor that is derived from matching the measured background with the measured NR data at high-Q range.



Figure E11. The spectrum of the detected neutrons (x-axis: time-of-flight (TOF) of the neutrons, i.e., proportional to the neutron wavelength.; y-axis: detector position in pixels).



Figure E12. Background measured by offsetting the detector angle by 0.2° on a sample wafer submerged in Si-matched-subphase solvent.

The following figures compare the *in-situ* NR data before and after background subtraction. The data quality is improved after background subtraction, i.e., fringe features are revealed at higher Q and the abnormal dips at Q = 0.05, which are

particularly pronounced for N3 and N749, were eliminated; new dips appear only at higher Q (~0.1), i.e., after the first-order fringes.



Figure E13. Background subtraction for thin films of **MK-2**-sensitized TiO_2 on silicon wafers submerged in Si-contrast-matched solvent.



Figure E14. Background subtraction for thin films of **N3**-sensitized TiO₂ on silicon wafers submerged in Si-contrast-matched solvent.



Figure E15. Background subtraction for thin films of **N749**-sensitized TiO₂ on silicon wafers submerged in Si-contrast-matched solvent.

E5. Errors in background subtraction for the in-situ NR data

The background subtraction with regards to error bar calculations is based on the principle that for any non-linear differentiable function f(x, y) of two variables, x and y can be expanded by a Taylor series according to:

$$f \approx f^0 + \frac{\partial f}{\partial x}x + \frac{\partial f}{\partial y}y$$
 (E2)

and hence:

$$\sigma_f^2 \approx \left|\frac{\partial_f}{\partial_x}\right|^2 \sigma_x^2 + \left|\frac{\partial_f}{\partial_y}\right|^2 \sigma_y^2 + 2\frac{\partial_f}{\partial_x}\frac{\partial_f}{\partial_y}\sigma_{xy} \tag{E3}$$

where σ_f is the standard deviation of the function f, σ_x is the standard deviation of x, which could be regarded as the *in-situ* NR data, σ_y is the standard deviation of y, which could be regarded as the background data, and σ_{xy} is the covariance between x and y, while f^0 is a constant and does not contribute to the error on f. When the variables x and y are uncorrelated, and specifically for the application of subtracting background counts from total counts, f = x - y, $\frac{\partial f}{\partial x} = 1$, $\frac{\partial f}{\partial y} = -1$, then

$$\sigma_f^2 \approx (1)^2 \sigma_x^2 + (-1)^2 \sigma_y^2$$
 (E4)

$$\sigma_f = \sqrt{\sigma_x^2 + \sigma_y^2} \tag{E5}$$

which is commonly known as 'taking the quadrature sum' and was used in the calculation of errors for the background subtracted data.

E6. Determination of the thickness of the native SiO₂ layer on the silicon wafers using the Strohmeier equation

The silicon wafers (ITME, SEMI Prime) used for ALD are normally covered with a thin layer of native SiO₂, the thickness of which is usually 5-25 Å^{31,94–96,144–147}. However, in order to construct a model that more accurately represents the structure of this native SiO₂ layer in our NR and XRR refinement, XPS measurements were carried out on these silicon wafers using a Thermo Fisher Scientific NEXSA spectrometer in order to reveal the true thickness of the native oxide layer. Samples were analyzed using a micro-focused monochromatic AI X-ray source (72 W) over an area of approximately 400 microns. Data were recorded at pass energies of 200 eV for survey scans and 50 eV for high-resolution scans in increments of 1 eV and 0.1 eV, respectively. Charge neutralization of the samples was achieved using a combination of both low energy electrons and argon ions. The actual thickness of the native oxide was determined using the Strohmeier equation (eq E6), based on the revealed percentage areas of the oxide and silicon peaks fitted from the high-resolution XPS spectrum¹⁴⁸. This calculation is straightforwardly based on a uniform overlayer model, and is achieved by only a single measurement per sample, whereby the oxidic and silicon peak intensities are recorded.

$$d = \lambda_{ox} \sin \theta \ln \left[\left(\frac{N_{si} \lambda_{si} I_{ox}}{N_{ox} \lambda_{ox} I_{si}} \right) + 1 \right]$$
(E6)

where *d* is the oxide thickness, θ the photoelectron take-off angle, which is kept at 90°, I_{ox} and I_{si} are the percentage areas of the oxide and silicon peaks fitted from the high-resolution spectrum, λ_{si} and λ_{ox} are the inelastic mean free paths of the photoelectron for the silicon and oxide, and N_{si} and N_{ox} are the volume densities of the silicon atoms in the silicon and oxide.



Figure E16. Percentage areas of the oxide and silicon peaks fitted from the highresolution XPS spectrum.

We measured $\lambda_{si} = 30.91$ Å and $\lambda_{ox} = 37.46 - 39.11$ Å, assuming a density of SiO₂ of 2.2-2.65 g/cm³, while $N_{si} = 0.05$ unit/Å³ and $N_{ox} = 0.0221-0.0266$ unit/Å³, where a unit is one molecule of Si or SiO₂, respectively. Therefore, $d = \lambda_{ox} \ln \left[\left(\frac{0.05 + 30.91 + 20.5}{N_{ox} \lambda_{ox} + 79.5} \right) + 1 \right]$ which affords values in the range of 12.6-14.8 Å. Accordingly, for this study, a thickness of ~15 Å was used for the silicon oxide in the X-ray and neutron reflectivity fittings.

E7. In-situ NR measurements and sample alignment geometries



Figure E17. (a) Measurement geometry of the *in-situ* NR measurements. (b) Diagram showing the path of the neutron beam (red) through a substrate (blue) of suitable thickness. The substrate needs to be sufficiently thick (\geq 5 mm) to allow an uninterrupted beam transmission. (c) Diagram showing an unwanted reflection at the air-substrate interface, which degrades the beam flux incident upon the interface of interest when a thinner substrate is used.

The alignment of the samples is achieved by changing the sample angle, φ , and the detector angle, θ . The sample is aligned so that the incident beam, which comes in at a fixed angle, is reflected by the sample to the θ where the detector is. The slits are movable, and the beam footprint on the sample was defined when measured at $\varphi = 0.5^{\circ}$. When the sample angle φ was changed to 2°, the slits were opened by a factor of 4 to keep the same footprint on the sample.



Figure E18. (a) Side view of the INTER NR neutron intensity along the beam length direction (y axis). (b) Top view of the neutron intensity along the beam width direction

(x axis). (c) Neutron beam size and profile. The area of illumination needs to be fitted inside the area of the gasket (ϕ = 65 mm) so that the scattering arises only from the sample.

E8. The influence of the solvent on the C-O stretching vibration in the carboxylate group of the dye

Figure E19 shows that both acetonitrile and methanol change the C-O stretching vibration (~1160 cm⁻¹) of the dyes to some extent, especially that of **N749**, where the C-O stretching vibration vanishes once it comes in contact with either solvent. This might be the result of the dissociation of the tetrabutylammonium (TBA⁺) cations in **N749** that influences the C-O stretch, which may consequently influence the adsorption mode of the carboxylate group.



Figure E19. FTIR-ATR spectra of dye \cdots TiO₂ films on ITO coated glass substrates before and after rinsing with acetonitrile or methanol and drying under a flow of nitrogen.

E9. Dye···TiO₂ interfacial structures in the presence of solvents and electrolyte components revealed by *in-situ* NR measurements (assuming a uniform dye-layer density regardless of the solvent, and no extra top layer (i.e. three-layer model) in the presence of Lil/I₂)

The data obtained from *in-situ* NR measurements, simulations, and fitted SLD profiles for **MK-2**, **N3**, and **N749** on TiO₂ in the presence of the solvents and electrolyte components are shown in Figures E20 and E21, whereby the fitting model assume a uniform dye-layer density regardless of the solvent, and no extra layer in the presence of Lil/l₂. Table E4 contains a summary of the numerical information for each fit, i.e., the thickness, density, and roughness values for the dye and TiO₂ layers in the presence of different solvents and electrolyte components. The roughness values for the dye…solvent interfaces were free to vary in the fits. The fitting results intuitively show the overall SLD of each dye and TiO₂ layer, but the assumption of a uniform dye layer density is limited, especially when used in co-refining data collected from two different scattering-contrast scenarios (fully deuterated and Si-contrast-matched). This is due to the fact that there is some solvent ingression in the dye layer, and therefore the overall dye layer SLD should be different in different scattering-contrast scenarios, given that eq E7 governs the dye/solvent coverage model:

$$SLD_{obs} = SLD_{dye} \cdot \varphi_{dye} + SLD_{svt} \cdot (1 - \varphi_{dye}), \tag{E7}$$

wherein the overall SLD of the dye layer (SLD_{obs}) is a function of the SLD of the solvent SLD_{svt} . The sample model represents a five-layer system (silicon substrate, native oxide, TiO₂, dye, and subphase solvent/electrolyte).







Figure E20. *In-situ* NR profiles, fittings, and SLD revealed by a fitting co-refinement for a) **MK-2**...TiO₂, b) **N3**...TiO₂, and c) **N749**...TiO₂ on silicon substrates submerged in silicon-contrast-matched d₃-MeCN/MeCN or d₃-MeCN. In the case of contrast

matching, the subphase solvent with silicon, the SLD contrast between the subphase solvent and the superphase silicon is very small, and hence the critical angle, which is proportional to the square root of the SLD contrast, is also very small. This can be directly observed by the y-axis intercept of the Si-contrast-matched reflectivity, which is orders of magnitude lower than 1.







Figure E21. *In-situ* NR profiles, fittings, and SLD obtained from fitting NR data of (a) **MK-2**···TiO₂, (b) **N3**···TiO₂, and (c) **N749**···TiO₂ on silicon substrates submerged in d₄-MeOH.

Table E4. Structural parameters determined by co-refinement of NR data for TiO_2 sensitized with **MK-2**, **N3**, and **N749**, collected in d₃-MeCN and Si-contrasted-matched d₃-MeCN/MeCN, and single refinement of NR data for TiO_2 sensitized with **MK-2**, **N3**, and **N749** collected in d₄-MeOH.

Co-refinement			Dye	ayer		TiO ₂ I	ayer	Solvent…dye	
deuterated / contrast matched MeCN)	Solution	Thickness (Å)	Fitting error (Å)	Density (unit/Å ³)	Fitting error (10 ⁻⁵ unit/Å ³)	Thickness (Å)	Density (unit/ų)	Roughness (Å)	FOM logbars
	d/h-MeCN	20.5	(-0.3, 0.3)	0.000672	(-3.4, 4.2)	120.61	0.0284	8.2	1.486
MK-2 (set 1)	d/h-MeCN+Lil	20.7	(-0.5, 0.4)	0.000696	(-4.8, 4.9)	120.97	0.0288	4.8	1.278
	d/h-MeCN+LiI+l2	20.0	(-0.5, 0.3)	0.000697	(-5.5, 3.8)	119.56	0.0290	19.8	1.371
	d/h-MeCN	11.3	(-0.3, 0.3)	0.001039	(-4.8, 5.3)	119.48	0.0288	5.2	1.312
N3 (set 1)	d/h-MeCN+Lil	11.9	(-0.4, 0.3)	0.001018	(-5.8, 7.3)	118.97	0.0290	5.3	1.488
	d/h-MeCN+Lil+l2	13.0	(-0.3, 0.2)	0.001025	(-7.3, 7.2)	119.09	0.0289	4.3	1.296
	d/h-MeCN	10.4	(-0.3, 0.4)	0.001208	(-3.8, 8.2)	119.30	0.0289	5.3	1.283
N749 (set 1)	d/h-MeCN+Lil	10.3	(-0.3, 0.3)	0.001281	(-4.9, 7.1)	119.57	0.0288	5.6	1.234
	d/h-MeCN+Lil+l ₂	12.6	(-0.4, 0.4)	0.001390	(-3.9, 6.2)	119.20	0.0287	5.1	1.123
Single refinement (fully deuterated MeOH)	Solution	Thickness (Å)	Fitting error (Å)	Density (unit/ų)	Fitting error (10 ⁻⁵ unit/Å ³)	Thickness (Å)	Density (unit/ų)	Roughness (Å)	FOM logbars
	d₄-MeOH	29.4	(-0.4, 0.5)	0.002351	(-8.2, 7.3)	123.08	0.0284	4.6	1.583
	d4-MeOH+Lil	33.5	(-0.4, 0.5)	0.002713	(-7.7, 10.1)	124.55	0.0281	5.0	1.311
MK-2 (set 2)	d4-MeOH+LiI+I2	35.7	(-0.5, 0.4)	0.002769	(-6.9, 11.3)	124.70	0.0281	5.8	1.209
	d₄-MeOH+LiI+I₂ (light on)	35.4	(-0.5, 0.5)	0.002767	(-9.2, 8.9)	123.61	0.0282	6.0	1.502
	d₄-MeOH	28.5	(-0.6, 0.5)	0.002202	(-5.7, 7.8)	118.78	0.0289	4.1	1.482
N3 (set 2)	d₄-MeOH+Lil	29.0	(-0.5, 0.5)	0.002307	(-5.7, 4.3)	119.69	0.0285	4.3	1.605
(with 2 crystal water)	d ₄ -MeOH+LiI+I ₂	35.2	(-0.8, 0.4)	0.002327	(-5.1, 4.8)	118.72	0.0286	6.4	2.254
water	d₄-MeOH+LiI+I₂ (light on)	35.9	(-0.4, 0.7)	0.002331	(-7.9, 6.2)	118.43	0.0285	6.9	2.056
	d₄-MeOH	8.9	(-0.5, 0.3)	0.002182	(-5.3, 3.9)	118.94	0.0285	4.8	2.544
	d₄-MeOH+Lil	8.8	(-0.3, 0.6)	0.002512	(-4.6, 6.8)	118.93	0.0285	4.6	2.791
N749 (set 2)	d ₄ -MeOH+LiI+I ₂	10.3	(-0.4, 0.5)	0.002575	(-5.2, 6.7)	120.04	0.0281	5.7	1.408
	d₄-MeOH+Lil+l₂ (light on)	10.6	(-0.4, 0.4)	0.002532	(-4.3, 4.9)	119.21	0.0283	6.2	1.584

Appendix F – Surface imaging using AFM and STM

The dye...TiO₂ silicon substrate surface was examined using DualScope atomic force microscopy (AFM) in tapping mode in air, with a lateral scan size of 5 µm x 5 µm, a lateral resolution of 1 nm, a vertical accuracy of 0.01 nm. The microscope was operated in tapping mode, in which the frequency and amplitude of the driving signal are kept constant, resulting a constant amplitude of the cantilever oscillation. When the tip comes close to the surface, the interaction of forces acting on the cantilever include Van der Waals forces, dipole-dipole interactions, and electrostatic forces. They cause the amplitude of the oscillation of the cantilever to change with regard to the distance between the tip and the sample. Thence, the amplitude is used as the parameter that is fed into the servo to control the height of the cantilever above the sample. As the cantilever is used to scan the sample, the servo adjusts the height of the cantilever to maintain a constant cantilever oscillation amplitude. Figure F1 shows the AFM images of bare amorphous TiO₂ and an MK-2 dye-sensitized amorphous TiO₂ surface. It is apparent that the sensitization of the thin film of TiO₂ with **MK-2** (20 h; 0.5 mM) induces the formation of some aggregates on the nanometer scale on the TiO₂ surface. The size of the most obvious nanoaggregates observed was around 200-300 nm, which agrees well with the GISAXS results (150-200 nm) in Chapter 3, considering the size was calculated based on a form factor for 2-D circular disks which may be slightly different from the actual shape of the nanoaggregates.





а

b

Figure F1. AFM images of a) a bare thin film of amorphous TiO_2 deposited on a silicon substrate using ALD; b) **MK-2** ($c_{MK-2} = 0.5$ mM; t_s : 20h) on a thin film of amorphous TiO_2 on a silicon substrate.

Scanning tunnelling microscopy (STM) experiments were conducted on an Omicron ultra-high-vacuum (UHV) chamber operated at room temperature with a near ultra-high vacuum ($1 \times 10^{-8} - 1 \times 10^{-9}$ mbar) in either constant-current or constant-height mode. To modify surfaces with extreme precision, a voltage pulse was applied to the tip at a certain point during the scan. Such voltage pulsing was used to desorb contaminants by applying a voltage pulse for a time up to 1 s. The lateral scan size was 200 nm x 200 nm, with a resolution of 1-5 nm, which allows visualizing atomic structure on the surface of the sample.



Figure F2. STM images (current) of a bare thin film of amorphous TiO₂ on a silicon substrate. Measured in constant-height mode to map the current variation across the surface.



Figure F3. STM images of an **MK-2** sensitized ($c_{MK-2} = 0.5$ mM; $t_s = 20$ h) thin film of amorphous TiO₂ on a silicon substrate. Measured in constant-height mode to map the current variation across the surface.

STM is based on the concept of the electron tunneling, i.e., when the voltage bias causes electrons to tunnel between the tip and sample, creating a current that can be measured. There are modes of operation that are called constant-height mode and constant-current mode, respectively. In constant-current mode, feedback electronics adjust the height between the tip and the surface by a piezoelectric height-control mechanism, and the height variation and the images are mapped with the aid of the tip topography, which ultimately shows a constant charge-density surface. In constant-height mode, when the tip moves across the sample, the current changes while the voltage and height are kept constant. The current variation across the surface, which is related to the charge density is thence mapped. Overall, scanning in constant-height mode is faster than the constant-current mode, as the piezoelectric movements require more time to register the height change in constant-current mode than registering the current change in constant-height mode¹⁴⁹. Figures F2 and F3 show the apparent coarse morphology of the amorphous TiO₂ surface and once it is sensitized by **MK-2** using STM in constant-height mode.

Appendix G – Experimental set-ups

G1. Diamond Light Source (UK) I07 synchrotron grazing-incidence small-angle X-ray scattering experiment





(b)

Figure G1. The configuration of the GISAXS to probe the dye…TiO₂ interface on silicon substrates on I07 at the Diamond Light Source, UK. (a) GISAXS flight tube; (b) Pilatus 2M detector.

Figure G1 (a) shows the GISAXS flight tube, which exhibit the following characteristics:

- Helium-filled to prevent air scattering.
- Mica entrance and kapton exit windows.
- Two internal beamstops, for the direct and reflected beam, which can be moved remotely.
- The entire tube can be easily swung out of the way to allow the diffractometer arm to be lowered for reflectivity or other measurements, if required.

A Pilatus 2M detector was used for the GISAXS measurements. The sample-detector distance was 3017 mm in our experiment, and the energy of X-ray was equal to 12.5 keV.

G2. ISIS (UK) OffSpec reflectometry experiment



Figure G2. (a) OffSpec reflectometry configuration; (b) OffSpec *in-situ* solar cell.



G3. ISIS (UK) INTER reflectometry experiment



Figure G3. Sample environment used for INTER reflectometry experiment.

G4. China Spallation Neutron Source (CSNS) Multipurpose Reflectometry experiment





Figure G4. The configuration of the ex-situ reflectometry to probe the dye···TiO₂ interface on a silicon substrate on the Multipurpose Reflectometer at the CSNS, China.

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