Characterizing Interfacial Structures of Dye-Sensitized Solar Cell Working Electrodes

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ABSTRACT: In this feature article, we discuss the fundamental use of materials-characterization methods that directly determine structural information on the dye-\(\text{TiO}_2\) interface in dye-sensitized solar cells (DSCs). This interface is usually buried within the DSC and submerged in solvent and electrolyte, which renders such metrological work nontrivial. We will show how \textit{ex-situ} X-ray reflectometry (XRR), atomic-force microscopy (AFM), grazing-incidence X-ray scattering (GIXS), pair-distribution-function analysis of X-ray diffraction data (gaPDF), and \textit{in-situ} neutron reflectometry (NR) can be used to deliver specific structural information on the dye-\(\text{TiO}_2\) interface regarding dye anchoring, dye aggregation, molecular dye orientation, intermolecular spacing between dye molecules, interactions between the dye molecules and the \(\text{TiO}_2\) surface, and interactions between the dye molecules and the electrolyte components and precursors. Some of these materials-characterization techniques have been developed specifically for this purpose. We will demonstrate how the direct acquisition of such information from materials-characterization experiments is crucial for assembling a holistic structural picture of this interface, which in turn can be used to develop DSC design guidelines. Moreover, we will show how these methodologies can be used in the experimental-validation process of “design-to-device” pipelines for big-data- and machine-learning-based materials discovery. We conclude with an outlook on further developments of this design-to-device approach as well as the materials characterization of more dye-\(\text{TiO}_2\) interfacial structures that involve known DSC dyes using the methods described herein. In addition, we propose to combine these formally disparate metrologies so that their complementary merits can be exploited simultaneously. New metrologies of this kind could serve as a “one-stop-shop” for the materials characterization of surfaces, interfaces, and bulk structures in DSCs and other devices with layered architectures.

INTRODUCTION

Solar energy may become a promising prospective renewable alternative to fossil fuels that could potentially be able to satisfy the ever-increasing global demand for energy. Among several photovoltaic technologies that have been developed thus far, dye-sensitized solar cells (DSCs) exhibit a variety of particular advantages that may afford DSCs niche commercial applications in solar-powered windows and interior design for energy-sustainable buildings.\(^1\)-\(^4\) Specifically, DSCs are highly efficient under ambient conditions and indoor environments. They are also naturally transparent, produced cost-effectively, environmentally benign, and flexible. Their transparency and flexibility also render it feasible to deposit DSCs on flexible substrates or fibers in order to create passive energy harvesters in wearable devices and textiles.\(^5\)-\(^6\)

The design of conventional DSCs based on liquid electrolytes has not changed significantly since their introduction by Grätzel and O’Reagan in 1991 (Figure 1).\(^6\) In principle, a DSC is a two-electrode electrochemical cell with the following setup. The counter electrode usually consists of fluorine-doped tin oxide (FTO) glass with a thin layer of the platinum catalyst. The working electrode normally consists of a layer of mesoporous \(\text{TiO}_2\) nanoparticles deposited onto the FTO glass, which is then adsorbed with a monolayer of the dye molecules. The two electrodes are then sealed, and a liquid electrolyte is deposited in the space between the electrodes. Incoming visible light is absorbed by the dye molecules, which move from the ground to the excited state, before the excited dye molecules inject electrons into the conduction band (CB) of the semiconductor. The oxidized dye molecule is regenerated by the transfer of an electron from the redox mediator. Electrons in the semiconductor and positive charges (“holes”) in the electrolyte diffuse to the FTO back contact and counter electrode, respectively. The difference between the Fermi levels of the working and counter electrodes under illumination results in the electric potential difference between the electrodes.\(^7\)

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It should be noted here that the photoactive dye fulfills two crucial purposes in such DSCs: (i) it serves as the principal light-harvesting component and (ii) it initiates the injection of electrons from its excited state into the CB of the semiconductor. It is thus easy to see how the dye—semiconductor interface and our understanding thereof are of pivotal importance in developing systematic molecular design guidelines for improved DSCs.

The commercialization of DSCs has already begun, although their photovoltaic output remains inferior to that of other types of solar cells, despite the fact that the maximum attainable power conversion efficiency (PCE) for liquid DSCs has been estimated to be ~20% with an open-circuit voltage ($V_{OC}$) of ~920 mV and a short-circuit current density ($J_{SC}$) of ~30 mA cm$^{-2}$. In this context, it is important to note that the mechanism by which electricity is generated in DSCs is fundamentally different from that of other photovoltaic cells, which are usually based on p–n junctions. In DSCs, the tasks of absorbing light and transporting charge carriers are separated, whereby the former is accomplished by the dye and the latter by the semiconductor. Indeed, this separation of tasks is what gives rise to their ability to excel under only ambient-light conditions. Nevertheless, our understanding of the operational mechanisms that underpin the generation of energy in DSCs is incomplete and still fragmented. This applies in particular to the structural nature of the dye—semiconductor interface, which represents the DSC working electrode. To render industrial applications more feasible and commercialization potential more appealing, it is imperative to develop new analytical tools to improve PCE values of DSCs and establish systematic molecular design guidelines for advancements in DSC technology. DSC working electrodes have already been probed experimentally and by computational methods. However, DSC-oriented metrologies have so far focused on experiments and characterization techniques that describe the dye--TiO$_2$ interface more or less indirectly.

For example, Pazoki et al. have recently reviewed various metrological techniques that help to indirectly characterize DSC components. These include the Brunauer--Emmett--Teller (BET) method, Raman, UV--vis, and FTIR spectroscopy, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), valence electron and molecular orbital analysis, and conductivity, electrochemical, isoelectric point, and zeta potential measurements. Beyond individual DSC components, these authors have also discussed how current—voltage ($I$--$V$) and incident photon-to-current conversion efficiency (IPCE) measurements can be used to quantify the ensemble performance of the photovoltaic device. In addition, photoinduced spectroscopy techniques can be used to gauge the optical response upon perturbation by light. Such techniques may use short laser pulses for excitation (pulsed laser spectroscopy), such as transient absorption spectroscopy (TAS), time-resolved fluorescence spectroscopy, or an on/off modulated source (photinduced absorption spectroscopy).

This feature article focuses on the fundamental use of materials-characterization methods that directly determine structural information on the dye--TiO$_2$ interface. Such metrological work is nontrivial given that this interface is buried within the DSC and submerged in solvent and electrolyte. In the following sections, we will show how ex-situ X-ray reflectometry (XRR), atomic-force microscopy (AFM), grazing-incidence X-ray scattering (GIXS), pair-distribution function analysis of X-ray diffraction data (X-PDF), and in-situ neutron reflectometry (NR) can be used to deliver specific structural information about one or more aspects of the dye--TiO$_2$ interface. We will also demonstrate how the acquisition of such information from materials-characterization experiments is crucial for assembling a holistic structural picture of this interface, which in turn can be used to guide DSC design.

### APPLICATION OF MATERIALS CHARACTERIZATION TECHNIQUES TO DIRECTLY DETERMINE THE DYE--TiO$_2$ INTERFACIAL STRUCTURE IN DSCS

Before delving into specific materials-characterization techniques, it is worth noting that the complexity and the delicate interplay between various structural aspects of the dye--semiconductor interface must always be taken into consideration. In other words, when one examines a single layer of dye adsorbed onto the mesoporous semiconductor ex situ (vide infra), i.e., in the absence of solvent/electrolyte/additives/light, the results will most likely differ from those obtained from materials-characterization experiments on the dye--semiconductor interface when it has been buried under the electrolyte (in situ) or buried under the electrolyte upon exposure to irradiation (in operando).

Because the semiconductor is in most cases TiO$_2$, the expression “dye--TiO$_2$ interface” will in this feature article henceforth be interchangeable with “dye--semiconductor interface.”

#### Ex-Situ X-ray Reflectometry (XRR) Studies on the Dye--TiO$_2$ Interfacial Structure

Ex-Situ DSC-Specific XRR Methodology. Ex-situ XRR can be used to determine the preferred structural orientation and molecular packing of the dye adsorbed on the semiconductor, which is most frequently TiO$_2$. For that purpose, data are acquired on TiO$_2$ substrates before and after sensitization with the photoactive dye. It should be noted here that for a good signal in XRR measurements, atomically flat amorphous TiO$_2$ films are usually necessary. However, the surface of a DSC working electrode tends to consist of mesoporous TiO$_2$ nanocrystals (50–100 nm). Fortunately, it is suitable to approximate the mesoporous TiO$_2$ surface of a DSC working electrode to that of an atomically flat TiO$_2$ surface in XRR measurements on account of the scale of the dye--TiO$_2$ interfacial structure; in other words, the dye molecules are very small (a few nanometers) so that the radius of curvature of a typical TiO$_2$ nanoparticle (50–100 nm) will appear flat at the molecular scale.

A representative illustration of the experimental setup of a reflectivity experiment is shown in the Supporting Information (Figure S1). The thin film of TiO$_2$ is supported by a silicon wafer substrate that comprises silicon in the bulk that is topped with a natural oxide layer. A model is fitted to the X-ray reflectivity data by a
Figure 2. Chemical schematics of Ru-bipyridyl-based dye N719 and the three Zn-porphyrin-based dyes P199, P10, and P18.

The results can be plotted as a function of the momentum transfer vector ($Q$) perpendicular to the TiO$_2$ surface (eq 1), wherein $\theta$ denotes the incident angle and $\lambda$ denotes the wavelength of the X-rays, respectively.

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

Initial structural models can be prepared with a three-layer approach that uses nominal literature values for the scattering-length density (SLD) of the silicon wafer, the native oxide layer, and the TiO$_2$ layer. It is possible to calculate the SLD for the dye (eq 2), considering the classical electron radius ($r_e = 2.81 \times 10^{-13}$ m), which is the scattering length of the electron, the total number of electrons in the dye ($Z$), the molar mass (M) of a molecular dye, and the Avogadro constant ($N_A$), as well as the molecular volume of the dye ($V$) and the density ($\rho$), which can be obtained from the crystal structure of the molecular dye.

$$\text{SLD} = \frac{r_e Z}{V} = \frac{r_e N_A Z}{M}$$

Comparing the experimentally observed SLD value for the dye on TiO$_2$ with its theoretically calculated value for the pure dye allows one to draw conclusions about the dye-layer thickness ($d$); see eq 3 and ref 33. It is also possible to measure the average projected area per (dye) molecule (APM) that is subtended on the TiO$_2$ surface (eq 3), which in turn affords the surface concentration, $[\text{dye}]_{\text{surf}}$ (eq 4).

$$\text{APM} = \frac{r_e Z}{d \times \text{SLD}}$$

$$[\text{dye}]_{\text{surf}} = \frac{1}{N_A \times \text{APM}}$$

Taking into account trigonometric considerations and the two-dimensional length and width of the dye molecule, the dye-layer thickness can be translated into pertinent information about the tilt angle of the dye molecule relative to the semiconductor surface and the intermolecular distance between individual dye molecules; both of these are of paramount importance to device performance. These results can be used in combination with DSC-device-performance measurements to assess various practical requirements that involve the dye--TiO$_2$ structure of a DSC, for example, determining whether a coadsorbent that hampers electron recombination is required to prevent the electrolyte from interacting directly with the semiconductor.

Application of XRR to Examine Dye--TiO$_2$ Interfaces. We now exemplify the use of XRR in studying the dye--TiO$_2$ interface for specific DSC dyes.

Molecular Orientation and Packing of the Ru-Bipyridyl Dye N719 and Zn-Porphyrin Dyes on TiO$_2$. In 2011, Griffith et al. reported the first application of XRR to determine the orientation and packing density of four organometallic dyes while they were adsorbed on TiO$_2$ surfaces. The subject dyes involved three zinc-porphyrin dyes (P10, P18, and P199; Figure 2) and the ruthenium-bipyridyl-based dye ditetrabutylammonium cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) (N719; Figure 2). These dyes vary significantly in molecular size and shape and display different interfacial geometries once adsorbed onto TiO$_2$ surfaces. Extracting such structural information is highly desirable because the orientation and packing of the dye molecules on the semiconductor surface affect the barrier width for through-space charge tunneling, the alignment of the molecular dipole moments of the dyes, the local interfacial electric field, and electron/hole recombination reactions.

The XRR data obtained by Griffith et al. revealed that these dyes adsorb in monolayers. Under the applied conditions and provided high SLD contrast between the semiconductor and dye layers in these systems, Griffith et al. demonstrated that the XRR measurements can resolve film thicknesses with a maximum error of 0.2 Å. The structures of their sensitized films were fitted by a two-layer approach, which was constrained by the experimentally measured dye-layer thickness. This provided low surface roughness values, clear Kiessig fringes, and low background reflectivity, which suggested a narrow distribution, i.e., a relatively uniform alignment of all dye molecules on the TiO$_2$ surface. Moreover, given that these dyes were found to self-assemble in monolayers, the molecular size of each subject dye manifests systematically in the dye-layer thickness, i.e., larger dyes generate thicker dye layers.

N719 was found to differ from the Zn-porphyrin dyes inasmuch as its overarching pseudosotropic shape can be considered to be spherical rather than characterized by an anisotropic aspect ratio. N719 also contains two carboxylate groups rather than the one cyanoacrylic anchor group that is featured in each of the three Zn-based dyes. The monolayer of N719 on TiO$_2$ was thus modeled by a two-layer approach, which was constrained by the experimentally measured dye-layer thickness. This provided low surface roughness values, clear Kiessig fringes, and low background reflectivity, which suggested a narrow distribution, i.e., a relatively uniform alignment of all dye molecules on the TiO$_2$ surface. Moreover, given that these dyes were found to self-assemble in monolayers, the molecular size of each subject dye manifests systematically in the dye-layer thickness, i.e., larger dyes generate thicker dye layers.
consistent with a computational study conducted by De Angelis et al.\textsuperscript{31}

The area per molecule (APM) for N719 on the TiO\textsubscript{2} surface, as determined from XRR measurements, was 194 Å\textsuperscript{2}. Considering the smallest molecular length of N719 (~7 Å),\textsuperscript{32} the measured dye-layer thickness confirms that the dye adsorbs as a monolayer on the surface.

These experimentally derived XRR values were supported by calculated values (thickness: 9.0 Å; APM: 170 Å\textsuperscript{2}; and SLD\textsubscript{calc}: 9.3 \times 10\textsuperscript{−6} Å\textsuperscript{−2}; Figure 3a). These results suggested a surface-packing arrangement of one molecule per modeled molecular volume, which is consistent with the spherical model of N719; this renders spatial packing isotropic. In contrast, the XRR results for all of the porphyrin-dye-sensitized TiO\textsubscript{2} surfaces suggested that their end-to-end molecular length from their anchoring group to their furthest molecular extremity adopts an angle of 35−40° relative to the surface plane on densely packed TiO\textsubscript{2} surfaces; thereby, their spatial separation is characterized by π···π stacking interactions with an intermolecular spacing of 3−4 Å.

The experimentally determined XRR parameters of the P199 dye layer (thickness: 13.0 Å; SLD: 10.6 \times 10\textsuperscript{−6} Å\textsuperscript{−2}; APM: 101 Å\textsuperscript{2}; and surface coverage: 1.6 \times 10\textsuperscript{−10} mol/cm\textsuperscript{2}) are also consistent with those of a monolayer, considering the molecular dimensions of P199, whose longest molecular length excluding or including the binding ligand is 16 or 22 Å, respectively. An orientational visualization of a molecule of P199 constrained to a height of 13 Å (Figure 3b) revealed that one can expect the molecule to adopt a tilt angle (35−40°) between the plane of the macrocycle and the TiO\textsubscript{2} surface plane, which would result in an APM of 270 Å\textsuperscript{2} on the surface. Because this area is substantially larger than the experimentally determined one (APM: 101 Å\textsuperscript{2}), this difference provides direct evidence for a close packing of the P199 molecules on the TiO\textsubscript{2} surface. Given the high level of planarity and lateral width (16 Å) observed in the porphyrin moiety, multiple porphyrin molecules can potentially pack into the projected volume occupied by neighboring dye molecules. In fact, the calculated P199 orientation suggests that approximately three molecules of P199 overlap into the volume of another dye molecule with an intermolecular spacing of 3−4 Å, which results in an APM of 113 Å\textsuperscript{2} and reproduces the experimentally observed dye-film thickness (13.0 Å) and SLD (10.1 \times 10\textsuperscript{−6} Å\textsuperscript{−2}) of P199.

For TiO\textsubscript{2} films that were sensitized with the Zn-porphyrin dimers P10 and P18, which contain the same anchor group as P199, dye···TiO\textsubscript{2} interfacial interactions and orientations can be expected to be similar. Nevertheless, the molecular dimensions of P10 and P18 are significantly different from those of P199, and thus the thickness of their adsorbed dye layers can also be expected to vary significantly. For P10 and P18, the refined SLD (P10: 9.5(1) \times 10\textsuperscript{−6} Å\textsuperscript{−2}; P18: 9.2(2) \times 10\textsuperscript{−6} Å\textsuperscript{−2}) and surface roughness values (P10: 4.1(1) Å; P18: 5.0(1) Å) were similar to those of P199, indicating dye monolayers of similar mass and packing density. However, their
calculated dye-layer thicknesses differ significantly from that of the P199 layer: P10 (24.1 Å; Figure 3c) and P18 (18.1 Å; Figure 3d) dye layers are thicker by ~75 and ~30%, respectively.

Molecular Orientation and Packing of the Organic Dye Coumarin 343 on TiO2 Surfaces. XRR has also been used to determine the preferred structural orientation and molecular packing of organic dyes such as Coumarin 343 (C343) on amorphous TiO2. In one of our previous studies, TiO2 substrates were sensitized by submersion in a 0.3 mM dye solution of C343 (97%, Sigma-Aldrich) in a binary solvent consisting of acetonitrile (MeCN) and t-butanol (MeCN/t-BuOH = 1:1 v/v) for 20 h. The structural parameters for the dye-sensitized TiO2 substrates were obtained from model refinements using a three-layer approach (dye layer, TiO2 film, and native oxide layer on the silicon substrates), from which the data for the untreated substrate (two-layer model) were subtracted. The thus-obtained results revealed a film thickness of 10.0 ± 2 Å for the monolayer of C343 (SLD: 8.6 ± 0.3 × 10⁻⁶ Å⁻²; surface roughness: 3.0 ± 0.4 Å). Given the molecular dimensions of C343 (Figure 4a), the experimentally obtained low mass density (0.96 g cm⁻³), and the measured average projected molecular footprint on the TiO2 surface (APM: 49.3 Å²/molecule), it could be deduced that molecules of C343 adopt an average tilt angle of ~61° relative to the TiO2 surface with an intermolecular distance of 8.2 Å (Figure 4b).

This substantial intermolecular separation is significantly wider than the longest molecular dimension of the solvent molecules and the redox electrolyte (MeCN: 2.59 Å; I⁻: ~5.27 Å),[34] these small molecules and ions can thus be expected to find facile access to the TiO2 surface through this monolayer (Figure 4c). It therefore seems that C343 does not fully passivate the TiO2 surface. Indeed, C343-based DSCs were found to display relatively low overall solar-cell performance owing to unwanted electron-decay pathways via electrolyte-based recombination reactions.[35] This notion would offer a reasonable rationalization for the low voltage (~0.41 V) of a C343-sensitized DSC[36] relative to that of other high-performance dyes such as (cis-bis(isothiocyanato)bis(2,2’-bipyridyl-4,4’-dicarboxylato ruthenium(II)) (N3),[37] which afford dye films with higher surface density.[38]

The unwanted electrolyte-based recombination reactions that are allowed by this thermodynamically controlled interfacial structure of C343 on TiO2 can be prevented by cosensitizing the DSC. Thereby, a suitably sized coadsorbate, such as deoxycholic acid (DCA; Figure 4a), is used to occupy the space between the adsorbed C343 chromophores to protect the TiO2 surface from electrolyte attack (Figure 4c).[39]

The specific adsorption behavior of C343 on TiO2 was tentatively attributed to the adsorption of H-type dimers. Thereby, only one of the two molecules of C343 per dimer adopts an orientation that is favorable to anchoring interactions with the TiO2 surface, while the other is bound via π···π interactions. This dimerization further deters the performance of C343-based DSCs because fewer anchoring groups are available per dye molecule. That said, the monomers that do not actively bind to the TiO2 surface are washed away during the fabrication process.

Investigating the Dye-Sensitization Process via XRR for N3 and N719 Dyes. XRR has also been used to directly examine how dye-sensitization conditions can affect the structure of a dye···TiO2 working electrode and thus the photovoltaic performance of the corresponding DSC. In 2018, our group presented a study on how steric and electronic factors associated with dye counterions, dye deprotonation levels, and the choice of sensitizing solvent impact the self-assembly behavior of the ruthenium-based dye N3 and its doubly deprotonated derivative N719 (Figure 5).[38]

The N719···TiO2 interfacial structure, characterized by a preferred anchoring mode that engages three of the four carboxylate groups in N719, was already discussed in the context of the XRR study by Griffith et al. (vide supra).[25]

In our study, XRR was used to examine the structural properties of the dye···TiO2 interfaces as a function of sensitization conditions. Initially, thin films of TiO2 were immersed for 20 h in a 0.3 mM solution of N3 or N719 in MeCN/t-BuOH (1:1 v/v). After the thin films were sensitized, removed from the solution, washed, and dried, we determined the preferred orientation of these dye anions from their anchoring group to their opposing molecular extremity with respect to the TiO2 surface. The associated dye load on this surface was also studied. Given that N3 and N719 differ purely by two protons and tetraethylammonium (TBA) cations, a comparison of the adsorption behavior should offer insight into the effect of the different deprotonation levels of N3 and N719 on the nature of dye···TiO2 binding. Thus, the N3···TiO2 interfacial structure was additionally investigated for sensitizing solvents with different dielectric constants, steric demands, and acidities.

Model refinements of the experimental XRR data based on the aforementioned three-layer approach (dye layer, thin film of TiO2, and native oxide layer on the silicon subphase) revealed comparable values for the SLD (N719: 13.7 ± 1.3 × 10⁻⁶ Å⁻²; N3: 11.6 ± 1.5 × 10⁻⁶ Å⁻²), surface roughness (N719: 4.0 ± 0.2 Å; N3: 3.3 ± 0.5 Å), mass density (N719: 1.52 g cm⁻³; N3: 1.36 g cm⁻³), and APM (N719: 128.2 Å²; N3: 85.0 Å²) for the thin films of TiO2 sensitized in MeCN/t-BuOH (1:1 v/v). However, it should also be noted here that although identical sensitization conditions were used for N719 in our study and that by Griffith et al.,[35] the mass density of the N719 film in our work was found to be 0.32 g cm⁻³ higher than that reported by Griffith et al., i.e., we obtained a more densely packed film.[25] Moreover, all of the parametric values were found to be lower for N3 than for N719, except for the surface concentration, which is higher for N3 [(2.0 ± 0.2) × 10⁻¹⁰ mol cm⁻²] than for N719 [(1.3 ± 0.1) × 10⁻¹⁰ mol cm⁻²].
despite the higher mass density of N719 relative to that of N3. This result would be expected if the molecular size of N719 was higher than that of N3, which would be feasible if at least some of the TBA⁺ counterions are incorporated within the N719···TiO₂ interface during the dye-sensitization process. This rationalization would, in turn, be commensurate with fewer dye molecules per unit area on the TiO₂ surface despite the higher mass density. Our results thus indicated that surface-adsorbed TBA⁺ cations must occupy an area that is approximately equal to the difference in measured APM between the N719 and N3 layers (43.2 Å²).

Moreover, the XRR results of our study suggest that N3 and N719 exhibit a minor variation in their dye···TiO₂ structures. The concentration of N3 molecules on the TiO₂ surface per unit area is higher than that of N719, which is consistent with the higher $j_{SC}$ values of devices sensitized with the former relative to those of the latter. However, the anions of N719 cover a TiO₂ surface with higher mass density due to the coadsorption of the TBA⁺ cations, which would at least partially explain the higher $V_{OC}$ and overall superior performance of N719 relative to that of N3.37,39 Subsequently, N3 was adsorbed on TiO₂ using MeCN/t-BuOH (1:1 v/v; $\varepsilon = 20.0$), ethanol (EtOH; $\varepsilon = 24.6$), EtOH/t-BuOH (1:1 v/v; $\varepsilon = 28.0$), or dimethyl sulfoxide (DMSO; $\varepsilon = 47.2$). The XRR results of these N3-sensitized TiO₂ surfaces are summarized in the Supporting Information (Table S1).

The corresponding results show that the trends in dye adsorption do not depend so much on the dielectric constant of the solvent (Figure 6a) but rather on the acidity of the dye solutions and the steric nature of the sensitizing solvent (Figure 6b). The thickest N3 dye layers were generated when they were sensitized in EtOH, albeit the dye anions pack less efficiently on the surface per unit area is higher than that of N719, which is consistent with the higher $j_{SC}$ values of devices sensitized with the former relative to those of the latter. However, the anions of N719 cover a TiO₂ surface with higher mass density due to the coadsorption of the TBA⁺ cations, which would at least partially explain the higher $V_{OC}$ and overall superior performance of N719 relative to that of N3.37,39

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TiO₂ surface than when other solvents are used. This suggests that N3 may adopt one of several bidentate conformations in the dye−TiO₂ interfacial structures that were fabricated from EtOH. Significantly thinner N3 layers were produced in EtOH/t-BuOH (1:1 v/v); these results were comparable to those obtained from MeCN/t-BuOH (1:1 v/v), where doubly deprotonated N3 coordinates to TiO₂ predominantly via a bidentate-bridging mode that includes two carboxylic groups. The corresponding results indicated that even a 4-fold measured for toluene, (1:1 v/v/v) of were sensitized for 20 h in a dye solution (0.3 mM; MeCN/DMSO, it is the acidity of coordinates to TiO₂ interface for those of other organic high-performance DSC dyes, and led to an average measured APM of 61.6 ± 1.0 Å on the TiO₂ surface. These values, in combination with the fact that the theoretically predicted SLD measured for MK-2 (10.1 × 10⁻⁶ Å⁻²) corresponds to a dye layer with a mass density of 1.11 g cm⁻³, which is comparable to those of other organic high-performance DSC dyes, and its smaller molecular structure, which is characterized by very thin layers that suggest tridentate or quaternary anchoring modes.

The experimental results of this study were corroborated by theoretical DFT calculations. Thereby, thermodynamic treatment of various Gibbs free energies afforded pKₐ values of N3 in various solvents at successive levels of deprotonation. The corresponding results indicated that even a 4-fold deprotonation of N3 in DMSO yields a pKₐ that is lower than that of singly deprotonated (pKₐ) N3 in EtOH or MeCN solution (Figure 6c). These results are consistent with the low pH values that were measured for N3 in DMSO solution and would explain the ease by which N3 can adsorb onto TiO₂ via tridentate or tetradsotentate coordination modes in this solvent.

Orientation of the Organic Dyes MK-2 and MK-44 with Respect to the TiO₂ Surface and Intermolecular Dye−Dye Spacing. In another ex-situ XRR study from our group, McCree-Grey et al. determined baseline details of the interfacial dye−TiO₂ structure for the high-performance organic dye 2-cyano-3-[5′′-[(9-ethyl-9H-carbazol-3-yl)]-3′,3′,3′′,4′′-tetra-n-hexyl-[2′,2′,5′,2′,5′,2′′]quater-thiophen-5-yl]acyric acid (MK-2) and its smaller molecular congener 2-cyano-3-[5-(9-ethyl-9H-carbazol-3-yl) thiophen-2-yl] acrylic acid (MK-44) (Figure 7). The molecular dimensions shown in Figure 7 refer to the crystal structure derived from X-ray diffraction data, where values in parentheses refer to neutron diffraction measurements (vide infra).

Thin films of amorphous TiO₂ held on silicon−water substrates, were sensitized for 20 h in a dye solution (0.3 mM; MeCN/t-BuOH/2H₂O in MeCN/t-BuOH (1:1 v/v), N3-2H₂O in MeCN/t-BuOH (1:1 v/v), or N749 in MeCN/t-BuOH (1:1 v/v)). The thus-obtained films were rinsed with neat MeCN and dried under a flow of N₂ prior to the XRR measurements.

Structural parameters (SLD, thickness, surface roughness, and mass density) for both the dye layers and the TiO₂ substrates were obtained from refinements of a three-layer model (a dye layer, TiO₂ film, and native oxide layer on the silicon subphase whose thickness was 5 nm). The SLDs of the native oxide layer (18.9 × 10⁻⁶ Å⁻²) and silicon substrate (20.1 × 10⁻⁶ Å⁻²) remained constant. The numerical values obtained from these XRR measurements are shown in Table S2.

These measurements indicate that MK-2 can adsorb onto a TiO₂ surface as a monolayer (dₘol = 23.2 ± 0.2 Å). The long axis of individual molecules of the MK-2 dye, which extends from the anchoring group to the furthest opposing molecular extremity, adopts a tilt angle (α) of 65.1 ± 1.1° with respect to the TiO₂ surface plane. The SLD measured for MK-2 (10.1 × 10⁻⁶ Å⁻²) corresponds to a dye layer with a mass density of 1.11 g cm⁻³, which is comparable to those of other organic high-performance DSC dyes, and its smaller molecular structure, which is characterized by very thin layers that suggest tridentate or quaternary anchoring modes.

In their entirety, the XRR experiments suggest a similar level of dye coverage for MK-2- and MK-44-sensitized TiO₂ samples. In contrast to MK-2, MK-44 showed minimal intermolecular facial overlap, which means that TiO₂ surfaces covered with MK-2 are effectively passivated against electron recombination.

Characterizing Nanoaggregates of DSC Dyes on TiO₂ Surfaces Using XRR. We have recently used XRR to examine the structure of nanoaggregates of three DSC dyes in dye−TiO₂ interfaces, namely, the organic dye MK-2 and the Ru-bipyridine-based dyes N3 and tris[tertbutylammonium] [tris(isothiocyanato)[2′,2′,2′′-terpyridine-4,4′′,4″-tricarboxylato]hydrogen ruthenium(II)] (N749; Figure 8). The employed dye-sensitization solutions were of significantly higher concentration (0.05−1.0 mM) than those in the studies discussed so far. Atomically flat TiO₂ films were sensitized for 20 h by immersion in a solution of MK-2 in MeCN/t-BuOH/toluene (1:1 v/v/v), N3-2H₂O in MeCN/t-BuOH (1:1 v/v), or N749 in MeCN/t-BuOH (1:1 v/v). The thus-obtained films were rinsed with neat MeCN and dried under a flow of N₂ before being used in the XRR measurements.

The XRR results showed that the dye-layer thickness of the dye−TiO₂ interface for N3 remains relatively constant for films created
using dye-sensitization concentrations that range from 0.05 mM to 0.5 mM. In contrast, the thickness of the MK-2 layer increases linearly with increasing concentration, while the thickness of the N749 layer reaches a maximum when the films were formed from 0.25 mM sensitization solution. The XRR results are summarized in Table S3.

Interestingly, the thickness of the MK-2 and N3 dye layers increases substantially when a dye-sensitization concentration of 1.0 mM was used, which was interpreted in terms of a sensitization saturation of the TiO2 surface. It is feasible to expect that beyond this point, dye molecules will start to stack on top of each other. This notion was corroborated by the fact that the dye-layer thickness of MK-2 on TiO2 obtained from a 0.5 mM dye solution (d_{obs} = 24.16 Å) was significantly lower than that obtained from a 1.0 mM dye solution (d_{obs} = 38.12 Å), which suggests the formation of MK-2 aggregates or multilayers in the lateral direction, i.e., in a direction perpendicular to the TiO2 surface, especially considering the maximum possible dye-layer thickness of an MK-2 monolayer (~28 Å).40

The dye-layer thickness of N3 on TiO2 remained relatively constant (d_{obs} ≈ 16 Å) for 0.05–0.5 mM dye-sensitization concentrations. Considering the maximum possible dye-layer thickness for a monolayer of N3 (~16 Å),38 these results suggested the formation of monolayers of molecules of N3 that adopt an almost upright orientation. However, upon increasing the concentration of the dye-sensitization solution to 1.00 mM, the dye-layer thickness increases to 20.10 Å; this result suggested that the N3–TiO2 interface must exhibit dye aggregation in the lateral direction relative to the TiO2 surface.

In the case of N749, increasing the concentration of the sensitization solution from 0.05 to 1.00 mM did not lead to a clear trend in the variation of the resulting layer of N749. Considering the maximum possible thickness of a monolayer of N749 (~16 Å),38 the obtained results were interpreted in terms of the formation of monolayers of N749 on TiO2. Thus, the thickness and density of layers of MK-2 and N3 on TiO2 strongly depend on the dye-sensitization concentration, whereby high concentrations (1.00 mM) afford thick dye layers of low density and low concentrations (e.g., 0.25 mM) furnish relatively thin dye layers of high concentration. In other words, the packing of MK-2 and N3 is less efficient and more disordered during self-assembly, which results in extensive lateral dye aggregation. For N749, a high density of the dye layer is observed at 1.00 mM, which is tentatively rationalized in terms of the substantial spacing between molecules of N749 on TiO2 under these sensitization conditions. This would allow a higher degree of dye adsorption at a higher sensitization concentration.

After our group had established that dye aggregation is a phenomenon that often occurs upon sensitization of TiO2 substrates, particularly when higher dye-sensitization concentrations are used, we became interested in how to more quantitatively examine such potentially forming dye aggregates. Such quantification would allow us to establish design guidelines for the molecular engineering of DSC dyes.

**AFM Studies of Dye Aggregates as a Function of the Dye-Sensitization Concentration and Sensitization Time.** AFM is a suitable materials-characterization technique for examining the formation of superficial aggregates, especially on account of its nanoscopic resolution.

As we have already mentioned in the Introduction, the resolution of AFM in the lateral direction, i.e., in the direction perpendicular to the TiO2 surface, is up to 0.1 nm; this is sufficient to quantify molecular dye aggregation. Conversely, in the horizontal direction, the maximum resolution of AFM is lower (~10 nm) on account of tip convolution effects, which prevents the quantification of individual dye molecules (diameter ≈ 1 nm)46 but still allows the examination of aggregates (vide supra).

**Ex-Situ DSC-Specific AFM Methodology.** AFM is an imaging method that complements X-ray scattering methods, such as XRR, in as far as it provides images of the surface directly. In contrast to XRR, AFM is a local rather than a bulk probe: AFM delivers a quantitative image of the dye– TiO2 interface from above its surface. Thus, AFM can be used to directly image dye aggregation and the spatial distribution of such aggregates on semiconductor surfaces. AFM is able to survey both lateral and longitudinal directions of a surface up to a certain depth and surface coverage, respectively. The tractable depth is usually defined by the range of the vertical profile of the surface that is under scrutiny. The longitudinal range of surface coverage is usually governed by the instrumental range of the horizontal movement of the AFM tip, the time, or resolution restraints of a given experimental study. These AFM studies are ultimately expected to help improve our understanding of the sensitization process and its governing factors, including the dye structure.

Various parameters that influence the charge-transfer kinetics in DSC devices have been extensively studied, using multiple types of methodologies. These parameters include the dye structure,57–59 the chemical interactions between the anchoring groups on the dye molecules and the oxide surface,60,61 and the electronic character of the oxide substrates.62 One important factor that is known to govern the function of the dye at the molecular level53 is dye aggregation.52 Dye aggregates in DSCs that form upon adsorption onto the semiconductor have predominantly been examined indirectly by analyzing the solvatochromism in the UV/vis absorption spectra of these dyes (H- and J-type aggregates); however, it remains difficult to predict how solvatochromism affects DSC performance. Other optical techniques that have been used to indirectly examine dye aggregates in DSCs include emission spectroscopy, time-resolved spectroscopy, TAS, and photoelectron spectroscopy (at the molecular level)63 as well as IR, Raman, and electrochemical studies (bulk effects).53 Moreover, photoelectrochemical techniques (I−V curves, IPCE measurements, and impedance spectroscopy) have been used to quantify the collective effects of dye aggregation.54,60

However, AFM can be used to directly provide evidence for dye aggregation and quantify its size and shape characteristics on the dye–TiO2 interface. Thus, AFM can help to map the spatial distribution of such aggregates on the nanoscale. The nanostructural characterization of dye aggregates by AFM is usually carried out *ex situ*, having formed thin films of dye–TiO2 interfaces using various dye-sensitization conditions such as dye-solution concentrations and/ or sensitization times. Ultimately, AFM can afford a nanoscopic understanding of the sensitization process, i.e., in terms of its molecular origins (e.g., the size, functional groups, charges, and number and type of anchor groups in the dye) as well as mechanisms of dye aggregation. Such information can be expected to help devise molecular design guidelines on how to improve DSC device function.

**Application of AFM to Examine Dye–TiO2 Interfacial Structures.** Using AFM to Examine the Dye– TiO2 Interface of TiO2 Surfaces Sensitized with MK-2, N3, N749, or SQ-2. Our group has used AFM to image the nanoscopic formation of dye–TiO2 interfacial structures of N3, N749, MK-2, and the twitterionic squarine-based organic dye SQ-2 (Figure 8).52 All of these dyes form aggregates upon sensitization of TiO2, whereby the spatial distribution of the nanoaggregates is reproducible and dye-specific.

Beyond the formation of monomeric dye layers, all four dyes were found to exhibit higher-order aggregation in the lateral direction, whereby the formation of dimers was observed to be most common. When dye-sensitization solutions of low concentrations (0.005 mM) were employed, SQ-2 was found to preferentially form trimers; this suggests a predilection of the COO` group in SQ-2 to aggregate with another SQ-2 molecule over binding to the TiO2 surface. Conversely, the lateral height of N3 on TiO2 surfaces decreased with increasing concentration of the dye-sensitization solution. This was rationalized in terms of the severe steric congestion that is manifested on N3-adsorbed TiO2 surfaces. For N749, the formation of higher-order dye aggregates in the lateral direction was observed.

In the longitudinal direction, i.e., parallel to the TiO2 surface, dye molecules of N749, N3, and MK-2 assemble in lines of nanoaggregates, whereas clusters of dye molecules of SQ-2 are randomly distributed on the amorphous TiO2 substrates. The results observed for N749 and N3 are consistent with those of previously reported STM and AFM studies.54,59 The extent of dye aggregation within the plane of the TiO2 surface seems to be correlated to the number of
carboxylic acid groups present within the dye. It is worth noting here that relatively high concentrations of N3, N749, and MK-2 were required in the previously discussed XRR studies in order to observe the aggregates. (See the Characterizing Nanoaggregates of DSC Dyes on TiO2 Surfaces Using XRR section.) However, in this AFM study, the structural assembly of dye nanoparticles was observed even when the concentrations of the dye-sensitization solutions were two orders of magnitude lower (Figure 8).

In the same study, the formation of N749 nanoaggregates was additionally studied as a function of the dye-sensitization time to monitor the formation of N749 aggregates. This revealed that dye aggregation in N749 starts during the first hour of dye sensitization and that it is complete within 5 h. The large expanse of the dye nanoaggregates observed in this study suggests that dye--dye interactions are much more important than previously envisaged and that the nature of their spatial distribution can be related to different aggregation modes of the dye molecules, although AFM-based surmises about these dye--dye interactions remain more qualitative than quantitative in nature.

Combined AFM and XRR Study to Experimentally Validate New DSC Dyes. Recently, our group reported the first study in which a combination of AFM and XRR measurements of singly and cosensitized working electrodes was used to provide a quantitative analysis of how cosensitization affects dye aggregation and adsorption onto TiO2. This study formed the experimental-validation stage of a data-driven materials-discovery process that systematically mined a database of dyes to identify those that exhibit specific, desirable properties that might become useful for applications in DSC devices.60

Thereby, our text-mining tool ChemDataExtractor61 was used to autogenerate a database of 9431 potentially suitable dyes (including their chemical names, maximum absorption wavelengths, and molar extinction coefficients) from the scientific literature. This database was subsequently mined using high-throughput screening methods, which engaged algorithmic encodings of DSC dyes and dye--TiO2 structure--property relationships to predict organic dyes C1, 8c,62 XS6,63 15,64 and H365 as being promising prospective cosensitizers as well as six combinations of these dyes for cosensitization (Figure 9).

The cosensitization of XS6 and 15 by the cocktail method yielded DSC devices that exhibited the best photovoltaic performance, which was similar to that of N719 (ηN719 = 0.92). The high open-circuit voltage (VOC = 700 mV) in these cosensitized DSC devices suggested that minimal electron recombination is present. The AFM and XRR studies were employed to better understand the molecular origins of the photovoltaic results of the five short-listed DSC dye candidates. Their dye--TiO2, interfacial structures were characterized using AFM and XRR to quantify dye-aggregation effects, dye coverage, interdye spacing, and dye-layer thicknesses of the corresponding singly sensitized and cosensitized working electrodes (Table S4). This study was the first to use a combination of XRR and AFM on cosensitized working electrodes to provide a quantitative analysis of how cosensitization affects the aggregation and adsorption of dye molecules onto TiO2.

The AFM images of the singly sensitized and cosensitized working electrodes showed that the former lean toward higher levels of dye aggregation than the latter. For example, the working electrode sensitized with only 15 exhibits relatively large aggregates with a high mean height (8 nm) and a maximum height (15 nm) but a small number of aggregates (1.1 μm−2); this suggests that dye aggregation exists in both the longitudinal and lateral directions. In contrast, cosensitized XS6 and 15 revealed low levels of dye aggregation with low aggregate coverage (0.3–0.7%) as well as a small total number of aggregates (0.2–0.8 μm−2); these values are one order of magnitude lower than those for the working electrode sensitized only with 15. This low level of aggregation observed when TiO2 is cosensitized with XS6 and 15 suggested the formation of dye monolayers on TiO2; this would at least partially explain the good photovoltaic performance of DSCs that employ these cosensitized working electrodes.

Complementary XRR measurements afforded structural information on the adsorbed dye layers (dye-layer thickness, SLDoxy surface roughness, and surface coverage; cf. Table S4). Dye--TiO2 interfaces obtained from cosensitization employing XS6 and 15 were found to exhibit relatively low dye-layer thicknesses (dLB = 19 Å) at high surface coverage (>70%); these results are in good agreement with the minimal aggregation based on the AFM images. Overall, these results corroborated the formation of dense dye monolayers on the TiO2 surface.

Using Grazing Incidence Small-Angle X-ray Scattering (GIXSAXS) to Examine the DSC Dye--TiO2 Interfacial Structure. DSC-Specific GIXSAXS Methodologies. GIXSAXS is a scattering method designed to measure the structure and dynamics of matter at the nanoscale.
that is complementary to XRR and AFM given that it is sensitive to both the short- (SRO) and long-range order (LRO) of dye molecules on the TiO₂ surface. It is useful in the context of DSC research for studying structural characteristics such as the dye nanoaggregate separation, size, and distribution density within each dye self-assembly in the longitudinal and lateral directions relative to the semiconductor surface.

Certain experimental parameters have to be determined from the GISAXS geometry and the associated data-model fitting in order to extract meaningful information about the dye–TiO₂ interfacial structure. Such parameters include the critical angle of the layered substrate, α_c, the Yoneda peak position, and the Q_y profiles (Figure 10).

The effects of dye aggregation on the semiconductor and the magnitude and characteristics of the LRO and the SRO within the self-assembled dye–TiO₂ interface can be examined by GISAXS. The size of the dye nanoaggregates can also be quantified via GISAXS data. Such experiments can be carried out on dye-sensitized thin films of TiO₂ on silicon substrates, which are fabricated using varying dye-sensitization concentrations and dye-sensitization times. A typical GISAXS experimental setup, where the detector is aligned perpendicular to the incident X-ray beam. This geometry is applicable only to small scattering angles by which the incident X-ray beam is deflected relative to the y axis of a Cartesian coordinate system with its center on the incident spot. Reproduced with permission from ref 21. Copyright 2018 American Chemical Society.

Figure 10. (a) Typical GISAXS experimental geometry. (b) and (c) Side and top views of an approximated scattering geometry of a GISAXS experiment where the detector is aligned perpendicular to the incident X-ray beam. (d) Example of the extraction of Q_y at a horizontal cut at the Yoneda peak position. α_i: grazing angle of the incoming X-ray beam relative to the atomically flat surface of the thin dye film. α_f: out-of-plane scattering angle. α_c: critical angle. 2θ: angle by which the incident X-ray beam is deflected relative to the y axis of a Cartesian coordinate system with its center on the incident spot. Reproduced with permission from ref 21. Copyright 2018 American Chemical Society.

Quantifying the Size and Separation of Dye Nanoaggregate Particles in Dye–TiO₂ Interfaces and Their Extent of Short-Range Order (SRO) Using GISAXS. Our group has used GISAXS methods to examine the structural features of the dye–TiO₂ interface of working electrodes (amorphous TiO₂ films with atomically flat surfaces; thickness < 20 nm) sensitized with MK-2, N3, and N749. In particular, the size and separation of dye nanoaggregate particles that

$$Q_{y Yoneda} = \frac{2\pi}{\lambda} \sin(\alpha_c)$$  

where λ refers to the wavelength of the incident X-ray beam. The critical angle of the dominant TiO₂ layer, α_c, and the reflection angle, α_f, can be calculated on the basis of the fitted XRR data. Accordingly, the Q_y positions of the Yoneda peaks for different incident angles of the X-ray beam can be calculated.

The most structured Q_y profiles along the Yoneda line usually belong to the dye–TiO₂ interfaces that have been created using dye-sensitization concentrations that generate the least-dense dye layers; these often feature dye self-assembly with the most significant levels of SRO. Diffraction peaks that are observed along the Q_y profiles, corresponding to an X-ray beam incident angle α_i,X-ray < α_c,TiO₂, should be attributed to the dye layer. Then, interparticle separations, d, can be calculated from the peak position, q, in the scattering profile according to

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

The size of nanoaggregate particles can be determined from the GISAXS data via the Guinier approximation. For that purpose, the low-q data of the Yoneda cut are analyzed within its Guinier region, which is the part of the Q_y profile before the onset of the first diffraction peak. According to Guinier’s law, the radius of gyration (R_g) for each dye nanoaggregate is

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

where q is the scattering vector, I_q is the scattering intensity at low q, and I_0 is the zero-angle scattering intensity, which provides information about the molecular mass and structure. Thus, R_g values can be obtained from plotting ln(I_q) as a function of q².
can form within the dye self-assemblies on the TiO2 surface were quantified by GISAXS perpendicular and parallel to the TiO2 surface, i.e., in the lateral and longitudinal directions. The extent of SRO in these self-assembled dye–TiO2 interfacial structures was also determined by GISAXS. Moreover, the interfacial structures were also studied as a function of fabrication conditions using different sensitization concentrations.

The XRR results showed that at high dye-sensitization concentrations (e.g., 1.00 mM) relatively thick dye layers of low density are generated, while at low concentrations relatively thin and dense dye layers were obtained. This result agrees well with those obtained in our previous XRR study, which was discussed earlier (vide supra).40

In other words, when dyes with a wider vertical span on TiO2 self-assemble, packing is less efficient and more disordered, which results in extensive lateral dye aggregation commensurate with that of dye layers of low density and high XRR-fitted thickness. In contrast, N749 exhibits a higher dye-layer density at high sensitization concentration (1.00 mM); this was tentatively attributed to the markedly large intermolecular spacing of N749 (APM_{TiO2} 176.23 Å^2 for 0.5 mM N749 to 104.25 Å^2 for 1 mM N749), which can be expected to permit a higher degree of dye adsorption at higher sensitization concentration. However, a clear trend in the variation of the dye-layer thickness upon varying the sensitization concentration (0.05–1.00 mM) was not observed for N749, which suggests that the lateral self-assembly of N749 on TiO2 is significantly different from that of MK-2 and N3; this was tentatively ascribed to a potential buffering effect from the counterion in N749, given that the other two dyes lack such a counterion.

When sensitized at 1.00 mM (MK-2, N3) or 0.5 mM (N749), i.e., at concentrations where XRR data suggested the formation of the least-dense dye layers, dye nanoaggregates form along the dye self-assemblies with maximum interparticle separations of 203 nm (MK-2), 158 nm (N3), and 199 nm (N749). Under these sensitization conditions, the nanoaggregate separations along the dye self-assembly are regular for N3. In contrast, additional smaller interparticle separations of ca. 67 and 61 nm (MK-2) as well as 104 and 46 nm (N749) were observed for MK-2 and N749. The average particle size of N3 nanoaggregates in the longitudinal direction was comparable to its interparticle separation. In other words, the dye self-assembly is saturated given that there is no space to fit additional dye particles into the gaps between N3 particles. Moreover, N3 exhibited a monodisperse particulate structure and MK-2 and N749 exhibited polydisperse structures, which was reflected in an apparent lack of monodispersity in the Guinier region. The particle diameters of the three dyes were estimated to be 156–198 nm. In the longitudinal direction, N3 shows the highest degree of SRO. The SRO is thus correlated with higher dye-sensitization concentrations for MK-2 and N3 in both the longitudinal and lateral directions.

These experimental results were supported by theoretical GISAXS simulations based on the distorted-wave Born approximation, which suggested strong correlations between the density of the dye layers and the particle distribution density or the particle size, when particles are assumed to lie at the bottom of the dye layer. These results thus suggest that the dye layer is “bottom-heavy”, particularly when there are expanses of dye molecules in the lateral direction on TiO2 owing to the occurrence of dye aggregation along this trajectory.

The obtained results thus show that, when the sensitization time remained constant (20 h), the thickness and density of the MK-2 and N3 dye layers strongly depend on the sensitization concentration.

Limits of GISAXS and Associated Methods in Determining the Nature of SRO. So far, we have shown how XRR, AFM, and GISAXS experiments can be used to qualitatively and quantitatively examine the dye–TiO2 interface in various regards, including the thickness, density, and roughness of the dye layers on TiO2, as well as the formation, size, and separation of dye nanoaggregates in the longitudinal and lateral directions relative to the TiO2 surface and
the extent of SRO in these nanoaggregates. However, all of these techniques fail to offer a consistent, quantitative, and reliable method to probe the local atomically resolved structure of dyes on TiO₂. The local atomic structure would provide a geometric measure of the SRO, whose structural quantification within the dye−TiO₂ interfaces would be particularly valuable with respect to the binding configuration of dye molecules that adsorb onto TiO₂ surfaces. This is especially pertinent considering recent STM/STS studies where it has been suggested that dye molecules can exist in multiple dye conformations on the dye−TiO₂ interfacial structure. It should be noted here that STM imaging is not generally suitable for atomic resolution.

We have already discussed in a preceding section (vide supra) how we have used XRR data to determine the thickness of dye layers of MK-2 and MK-44 on TiO₂.40 In that study, the significant deviation of the thickness of the dye layers of MK-44 from the theoretically expected thickness of a monolayer of perpendicularly aligned molecules of MK-44 was rationalized in terms of an APM that suggested that the dye molecules adopt a substantial tilt angle (61.2 ± 2.2°) relative to the TiO₂ surface. This tilt angle was, in turn, attributed to an anchoring mode that is different from the conventionally anticipated bidentate bridging mode via one COO− group, i.e., to a binding mode that also includes the CN group of the cyanocrylate anchor. Although this argument is feasible, it remains an indirect rationalization of experimental observations.

Structural data from a method that probes the SRO of dye molecules on TiO₂ with atomic resolution would thus be highly complementary to the nanoscopically resolved local structure of dye nanoaggregates determined by GISAXS and AFM that we have discussed in the previous sections (vide supra).21,25 Indeed, the self-assembly of dyes on TiO₂ surfaces seems to exhibit short-, medium-, and long-range order.

Our group overcame this experimental limitation by developing a method to examine the local atomic structure of DSC working electrodes based on atomic pair distribution function (PDF) analysis. PDF analysis is a powerful technique for the characterization of nanostructures in liquid42,74−77 and glasses,47,48,78,79 i.e., materials that exhibit little to no medium-range order (MRO) to LRO. We therefore explored the feasibility of using PDF analysis to obtain direct information on the (preferred) anchoring mode of dyes in the dye−TiO₂ interface.

Using the Glancing-Angle Pair Distribution Function (gaPDF) to Examine Dye-Anchoring Modes in Dye−TiO₂ Interfaces. DSC-Relevant gaPDF Methodology. A glancing-angle pair distribution function (gaPDF) analysis of synchrotron-based X-ray diffraction patterns has been employed to characterize intact DSC working electrodes using the experimental setup shown in Figure 11a. A detailed comparison between experimentally obtained gaPDF signatures and calculated PDF models of suspected interfacial structures allows the identification of preferred dye-anchoring modes.

The methodology involves an initial conversion of the raw diffraction intensity (I(q)) to the interference function, i(Q), via eq 9, where f refers to the atomic X-ray scattering (form) factor:

\[ i(Q) = \frac{I(q) - f^2}{\langle f^2 \rangle} \]  

Then, a PDF is generated by converting i(Q) into D(r) using a Fourier transform according to eq 10; for details, see Keen et al.80 This PDF describes the average number density of atoms at a given interatomic distance, r.

\[ D(r) = \frac{2}{\pi} \int_0^{\infty} Q(Q) \sin(Qr) \, dQ \]  

The background-adjusted subtraction of data of the unsensitized TiO₂ films from the dye-sensitized TiO₂ films then affords ∆PDF according to eq 11.

\[ \Delta D(r) = D(r)_{\text{sensitized}} - D(r)_{\text{unsensitized}} \]  

Such ∆D(r) profiles (∆PDFs) represent the structural features of the dye−TiO₂ interface. These experiments are designed to determine the (preferred) anchoring modes of dyes on the TiO₂ surface. Thus, conventional PDF analysis of the X-ray diffraction patterns of the dyes in their bulk phase are used as control experiments to subtract all contributions to the gaPDF scattering pattern that may arise from the dyes alone but not from the dye−TiO₂ anchoring. The experimentally obtained ∆PDF results can be compared to density functional theory (DFT)-derived simulated X-ray diffraction patterns to determine possible dye-anchoring modes that exist on a given dye−TiO₂ interface.

Application of gaPDF Analysis to Ru-Bipyridyl-Based Dyes (N3 and N749). N3 and N749 contain four and three carboxylic acid groups, respectively. In general, carboxylic acid groups and their deprotonated carboxylate groups are considered to be very good anchoring groups for adsorbing dyes onto TiO₂ surfaces.81 Several binding-mode configurations of carboxylate ions on TiO₂ have been proposed for such Ru-based dyes. Some optical82 and vibrational82,83 spectroscopy studies have suggested that adsorption occurs predominantly via the bidentate-chelating (BC) or bidentate-bridging (BB) mode, while other optical and vibrational studies82,83 have proposed the coexistence of monodentate ester (ME), BB, and BC modes (Figure 11c). Moreover, DFT studies42,84 have revealed a strongly unfavorable adsorption energy associated with the BC mode. Experimental gaPDF structural signatures were obtained for N3- and N749-sensitized TiO₂ substrates and compared to DFT calculated PDF models of various viable interfacial structures. The comparison revealed a preference for N3 and N749 dyes to adopt BB anchoring modes, which are sometimes supported by an auxiliary monodentate carboxylic acid anchor.85

The experimental setup for the gaPDF measurements is shown in Figure 11a. Samples of dye−TiO₂ interfaces (20-μm-thick mesoporous films) were generated by immersing TiO₂ surfaces in 0.5 mM solutions (-BuOH/McCN, 1:1 v/v) of N3 or N749 dyes for 24 h. The samples were then rinsed using pure McCN and briefly dried under a flow of nitrogen.

gaPDF data were collected for both sensitized and unsensitized DSCs in order to isolate the specific contributions from the dye−TiO₂ interfacial structure using ∆PDF analysis, i.e., by subtracting out PDF contributions from the bare TiO₂ substrate. These ∆D(r) profiles were compared to simulated ∆D(r) profiles, which were generated from models of the interfacial structure using DFT calculations. Pearson correlation coefficients between ∆D(r)exp and ∆D(r)sim were only moderate, which meant that various models had to be tested against ∆D(r)exp. A detailed analysis of the discrepancy between ∆D(r)exp and ∆D(r)sim implied shorter-than-expected average bond lengths and characteristic structural features at r values that are associated with dye−TiO₂ anchoring. In particular, the location of the second peak in each ∆D(r) exhibited marked differences between ∆D(r)exp and ∆D(r)sim, i.e., a shift to shorter distances from the most energetically favorable simulation (BB + MC=O) to the experiment for N3 (2.06 Å → 2.00 Å) and N749 (2.04 Å → 1.96 Å). This was rationalized in terms of a shorter-than-expected average length of the direct dye−TiO₂ interaction in ∆D(r)exp, which may indicate predominantly single-anchor binding configurations, such as BB and ME. Meanwhile, DFT calculations showed that a neighboring carboxylic acid group may sometimes support this BB-binding mode in its capacity as an auxiliary anchor via monodentate binding through its C=O substituent (Figure 11d). This study demonstrates the successful application of the gaPDF method to characterize dye−TiO₂ interfacial structures in DSCs and underscores the need for further investigations into dye anchoring groups.

Using In-Situ Neutron Reflectometry (NR) to Examine Buried Dye−TiO₂ Interfaces. DSC-Specific In-Situ NR Methodology. The materials-characterization methods that we have discussed so far depend on either the scattering of X-rays (XRR, GIXS, and X-PDF) or the imaging of the dye-sensitized surface (AFM). Although all of these techniques undoubtedly deliver interesting results, they all suffer from the intrinsic shortcoming that they are (pseudo) ex-situ techniques. In other words, they describe the dye−TiO₂ interface under conditions that are significantly different from those in fully
assembled DSC devices. Given the delicate interplay between the dye-TiO₂ interfacial structure on the atomic scale and the effects of solvent, electrolyte, and/or light, materials-characterization techniques that emulate the device environment more accurately must be developed.

One strategy to accomplish this goal is to employ ex-situ XRR and in-situ neutron reflectometry (NR) as complementary structural-characterization techniques. In-situ NR can be used to probe the buried interfacial structure of a DSC working electrode within a solid-liquid environment, and the thus-obtained results can be interpreted by considering complementary techniques such as ex-situ XRR measurements or indirect methods such as UV/vis absorption spectroscopy and DFT calculations.

In-situ NR can access buried interfaces of a device for several key reasons. First, neutrons carry no charge, so they can penetrate samples easily. Second, neutrons interact with the nuclei of atoms, in contrast to X-rays which interact with electrons. Accordingly, the scattering-length density of neutrons (SLD) depends upon the isotopic nature of each element within a material structure. In turn, this depends on the coherent scattering length of the nuclei of each isotope, which varies in a complex fashion for each element. Thereby,

\[
\text{SLD}_n = \frac{\sum b_i}{V} = \frac{N_A \rho \sum b_i}{M}
\]

where \(\sum b_i\) refers to the sum of isotopic coherent scattering lengths in a material, \(N_A\) is the Avogadro constant, \(\rho\) is the mass density, \(V\) is the molecular volume of the material, and \(M\) the molecular mass of the molecules involved.

In the context of a dye-TiO₂ interfacial structure, \(V\) is the molecular volume of the dye which is determined from its crystal structure, \(M\) is the molecular mass of the dye, and \(\Sigma b_i\) is quantified according to the sum of the coherent scattering lengths of the elements that comprise a given layer of material, e.g., the dye layer. Therefore, different isotopes of the same element may exhibit significantly different SLD values; this variation can be used to carry out isotope-labeling experiments.

Applying In-Situ NR to Examine the Dye-TiO₂ Interfacial Structure of the Organic Dyes MK-2 and MK-44 Buried Under Solvent and/or Electrolyte. In 2017, our group reported the first application of in-situ NR to DSC research whereby the electrolyte (\(\Gamma^-/I^-\) in this case) was incorporated into the structural model of the buried dye-TiO₂ interface of the organic dyes MK-2 and MK-44.³⁰ Complementary ex-situ XRR measurements were first used in this study on air-exposed dye-TiO₂ interfaces to determine the average ex-situ orientation of the dye molecules relative to the TiO₂ surface, the dye coverage of the surface, and the intermolecular spacing between dye molecules on the TiO₂ surface. The thus-obtained data revealed that MK-2 and MK-44 dyes self-assemble into monolayers on the TiO₂ surface, with a dye coverage of 75–90%, whereby the dye molecules adopt tilt angles of 56.6–65.1°. The hexyl chains of MK-2 seem to be interdigitated, which results in an effective passivation of the TiO₂ surface against electron recombination, as evidenced during photovoltaic testing. Conversely, the MK-44 dye molecules do not possess hexyl chains; as such, their intermolecular spacing on TiO₂ is too large for \(\pi-\pi\) interactions to form. The correspondingly lower photovoltaic performance of DSCs that contain MK-44 dyes, as opposed to MK-2, was attributed to ineffective passivation (Figure 12).

These ex-situ XRR results provided preparational information for the subsequent in-situ NR measurements, which were used to examine how the addition of LiI and Li₃IO₃ to the dye-TiO₂ interface affects the binding configuration of MK-2 and MK-44 dyes. These iodine-based compounds were added as they react with one another to form the \(\Gamma^-/I^-\) redox couple, which acts as the most common electrolyte in DSC research. Three electrolyte solutions were prepared and individually tested with MK-2 or MK-44 sensitized TiO₂ substrates in solid-liquid cells that contained either neat deuterated acetonitrile (d₃-MeCN), 0.7 M LiI in d₃-MeCN, or 0.7 M LiI and 0.05 M Li₃IO₃ in d₃-MeCN. The in-situ-NR-derived structural results are summarized in Table S5.

The in-situ NR results suggest that the interdigitated hexyl chains of the MK-2 dye molecules stabilize them from complexation with the Li⁺ cations; as such, the MK-2 dye adopts the BB anchoring mode, which is consistent with its ex-situ dye-TiO₂ binding configuration. In contrast, the –CN group of its chemical congener MK-44 engages in complexation with Li⁺ cations; this results in a change in the MK-44-TiO₂ anchoring mode from a CN/COO configuration with TiO₂ to the BB configuration upon addition of LiI (Figure 12). This structural rearrangement, commensurate with a more upright alignment of the molecules of MK-44, exposes the TiO₂ surface to solvent and electrolyte attack. This will limit the photovoltaic performance of the corresponding DSC on account of electron-recombination effects.

It should be noted here that the most salient results of this case study, i.e., the change in binding mode of MK-44 upon addition of Li⁺...
ions to the dye solution, involve the cyanocrylate anchor; this anchoring group is arguably the most prevalent anchoring group in DSC research. These results can thus be expected to have broader relevance to DSC research. However, this study also showed that (i) the spatial resolution of the dye layer and the precision of the SLD parameters need to be improved and (ii) the experimental errors need to be reduced. Regardless, the differences between the in-situ NR and ex-situ XRR results were, as far as MK-44 is concerned, significant. This result highlights the need to characterize dye···TiO2 interfaces in a fully assembled DSC device.

**Applying In-Situ NR to Examine the Dye···TiO2 Interfacial Structure of MK-2, N3, and N749 Buried Under Solvent and/or Electrolyte.** To improve the spatial resolution and experimental accuracy of in-situ NR measurements that characterize dye···TiO2 interfacial structures within fully assembled DSC devices, our group has recently developed an in-situ NR method based on contrast matching. Contrast matching more fully exploits the isotope-specific neutron-scattering cross sections of an element to discriminate scattering from atomic structures within a particular part of a device. For example, neutron scattering from an individual layer of a multilayer structure can be blended into that of a neighboring layer by partially deuterating it in such a fashion that the overall SLD of that layer matches that of this neighboring layer. Effectively, the resulting zero differential-scattering contribution between the two device layers highlights the structural features of layers in between the contrast-matched layers and reduces the number of apparent fringe features at higher Q values.

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**Figure 13.** (a) Variation in SLD for each dye···TiO2 interface as a function of the position in the device relative to the distance from the silicon surface; it should be noted here that the fitting of the first trough in the reflectivity of the Si-contrast-matched data is compromised on account of a trade-off between the cost of background subtraction and the benefits of more apparent fringe features at higher Q values. (b) Dye···TiO2 device interfaces sandwiched between a silicon layer (for good neutron transmission) and a solvent layer whose H/D ratio provides high contrast variation (left), contrast matching to the silicon layer (middle), or contrast matching to the TiO2 layer (right). (c) Ensemble model of the MeCN···dye···TiO2 and I⁻/I₃⁻···dye···TiO2 interfacial structure based on the results of this in-situ NR study. It should be noted here that the position of the Li⁺ cations (top layer) was attributed tentatively to charge neutrality, given the lack of evidence that they ingress into the dye layer. Reproduced with permission from ref 86. Copyright 2021 American Chemical Society.
of data-refinement parameters that are required to model a multilayered structure; it also provides multiple refinement options between differently contrast-(mis)matched data sets of that structure. This is the essence of the methodology used in this in-situ NR experiment, whereby partial deuteration of the acetonitrile solvent is used to tailor a contrast match between layers within a DSC device. Dye···TiO₂ interfacial structures that contain N₃, N749, or MK-2 dyes were chosen as subject materials.⁶⁶

Initially, we investigated the solvent···dye···TiO₂ interfacial structures to establish accurate dye-layer thickness and SLD values for the baseline solvent···dye···TiO₂ interface before adding the electrolyte. Thereby, dye···TiO₂ interfaces on silicon substrates were immersed in three solutions: (i) pure d₃-MeCN, (ii) d₄-MeCN/MeCN = 20.8:79.2, and (iii) d₄-MeCN/McCN = 29.7:70.3. The H/D isotopic ratios of the partially deuterated acetonitrile solutions were designed to contrast match the solvent to the silicon or TiO₂ layer (Figure 13a,b). The resulting three independent in-situ NR data sets per dye were applied to a triple core refinement to generate fits to structural models of the solvent···dye···TiO₂ interface for each dye (Figure 13a); these results are summarized in Tables S6 and S7.

The refined data acquired from this part of the in-situ NR experiment revealed dye-layer-thickness values that are essentially consistent with the following anchoring modes: N₃ (BB), N749 (BB via its central carboxylate group), and MK-2 (BB). The refined SLD values furthermore suggested that N₃ and MK-2 self-assemblies cover >90% of the TiO₂ surface, while the refined N749/McCN ratio (55.7:44.3) indicated that N749 self-assemblies suffer from substantial levels of solvent ingestion, which results in dye layers of significantly lower density; this was tentatively attributed to the presence of bulky and weakly coordinating [nBu₃N]⁺ cations that persist in the sensitization process.

The results of these solvent···dye···TiO₂ interfacial structures were then compared to those from complementary ex-situ XRR as well as concerted ex-situ X-ray and ex-situ NR corefineds of data that were collected on the air···dye···TiO₂ interface. The dye-layer-thickness values from the in-situ experiments are, except for those from the ex-situ XRR measurements for N749, all larger (by at least 1.2 Å) than those obtained from complementary ex-situ measurements. Although the ex-situ XRR and ex-situ NR data display similar errors, the ex-situ XRR data were considered to be more reliable, given that their Q range is by a factor of four larger than that of the NR data and that the reflectivity of the former extends two more orders of magnitude. However, the errors associated with the triple corefineds of the contrast-matched in-situ NR data are less than half of those achieved in the previous in-situ NR study that did not seek contrast matching.

Moreover, the thickness values of the MK-2 layer that were determined from the in-situ NR experiments were closer to those of the ex-situ measurements than to those of the previous in-situ NR measurements. Hence, this contrast-matching strategy allows a triple corefined of data of the solvent···dye···TiO₂ interface to generate reliable baseline accuracy for in-situ NR experiments.

Subsequently, we sought to examine the electrolyte···dye···TiO₂ interfacial structure via a second contrast-matching strategy, which was based on a deuterated MeCN solution of the I⁻/I₃⁻ electrolyte that was formed in situ in a two-stage process: (i) the electrolyte precursor LiI was injected into the MeCN-based solvent that lies atop each dye···TiO₂ interface to generate I⁻ ions and (ii) I₂ was added to form the fully functional I⁺/I₃⁻ electrolyte. In-situ NR data were acquired (i) after the addition of LiI and (ii) after the formation of I⁺/I₃⁻. Data sets for each two-stage process, for each dye, were collected in two solvent environments: fully deuterated d₄-MeCN and the silicon-matched D/H ratio (20.8:79.2).

The contrast-matching strategy used in this in-situ NR study delivers sufficiently accurate data to resolve a four-layer structural model to describe the I⁺/I₃⁻···dye···TiO₂ interfacial structure. Moreover, this contrast-matched in-situ NR study allowed a study of these interactions on a molecular level within DSC devices.

It was found that the anchoring for N₃ on TiO₂ surfaces changes upon addition of I₂, as is evident from the changing dye-layer thickness. This change was rationalized in terms of the formation of [NCS]···I and [NCS]···I₂ interactions and corroborated by XPS S 2p and Ti 2p results. The magnitude of change in dye-layer thickness upon addition of I₂ was interpreted in terms of a tentative change of the anchoring mode from BB via two COO⁻ groups on different
N749 exhibited a similarly increased dye-layer thickness upon addition of I$_2$, albeit that the nature of its anchoring should be different from that of N3 prior to the addition of I$_2$. Furthermore, while N3 showed complete oxidation of the sulfur in its NCS ligands, those atoms were only partially oxidized in N749. Meanwhile, the molecular behavior of MK-2 was found to change only minimally in response to the addition of the electrolyte. Importantly, these electrolyte-induced structural changes can be expected to affect dye regeneration and electron-injection in *in operando* DSC devices.

The structural results showed that the electrolyte components ingress into the self-assembled monolayers of MK-2, MK-44, and N749 dyes that are adsorbed onto TiO$_2$ (Figure 13c). Interestingly, only some dye...TiO$_2$ anchoring configurations are modulated by the interactions between the dye molecules and the electrolyte.

The thus-obtained results were corroborated by *ex-situ* RRR and NR, FTIR, and XPS experiments and are consistent with those of molecular-dynamics simulations.89 Taken together, this afforded the overarching structural model of N3, N749, and MK-2 dye...TiO$_2$ interfaces under various environments that is shown in Figure 13c.

### CONCLUSIONS

This feature article has reviewed the application of *ex-situ* XRR, AFM, GISAXS, and gaPDF and *in-situ* NR metrological methods to determine the dye...TiO$_2$ interfacial structures of DSC working electrodes. Two of these methods (gaPDF and *in-situ* NR) needed to be developed specifically, hence these represent first-of-a-kind experiments. A summary of all of the dyes that were used in these dye...TiO$_2$ structural studies is provided in Figure 14.

The structural nature of these dye...TiO$_2$ interfaces has afforded information on key characteristic properties of DSCs, which include dye anchoring, dye aggregation, molecular dye orientation, intermolecular spacing between dyes, interactions of the dyes with the TiO$_2$ surface, interactions between the dye and electrolyte, and electrolyte precursors.

Looking ahead, it would naturally be good to study the dye...TiO$_2$ interfacial structures for DSC working electrodes that contain other dyes. Indeed, there are a multitude of other dyes that could be studied by these methods to afford a better understanding of structure–property relationships in DSC working electrodes. It would also be good to study more dye...TiO$_2$ interfacial structures that arise from cosensitization. On the one hand, our data-driven consensitization study by Cooper et al.60 has demonstrated the value of such a study. On the other hand, cosensitization has been the fabrication method of choice to tip the photovoltaic performance of DSC devices into world-record-breaking outputs.90–99 Yet, alas, the structural characteristics of cosensitization remain poorly understood at the molecular scale.

The use of these systematically designed methodologies in the experimental-validation process of data-driven materials discovery also presents an attractive avenue of research to pursue. This excitement is being fueled by the fast-advancing developments in “big data” and machine-learning capabilities that aim to furnish “design-to-device” pipelines for materials discovery.100 These aims are very much in the spirit of the Materials Genome Initiative.

The further development of experimental methodologies to determine structural characteristics of DSC devices is also desirable. To this end, the development of in *operando* materials-characterization methods would be particularly useful in understanding the function of dye...TiO$_2$ interfacial structures within operating DSC devices. This prospect is yet to be realized, although it would be a natural extension of our *in-situ* NR methodological developments.

With that said, all distinct metrological methods presented in this feature article have been applied in isolation from each other. This is despite the fact that their results are often used to complement data analysis of other methods. We collate the results from multiple metrologies to construct an overarching model of a DSC device environment (e.g., Figure 13c). Ultimately, though, it would be much better if we could develop new metrological instrumentation that would explicitly combine formally disparate materials-characterization methods in such a way that it would act as a “one-stop shop” for determining the surface, interfacial, and bulk structures of a device.

For example, one could envisage a new type of metrological instrument that scans the surface of a dye...TiO$_2$ interface with an AFM tip, while an X-ray beam is shone on the same surface at a glancing angle to conduct either GISAXS or gaPDF measurements. The dye...TiO$_2$ interface could then be covered with solvent, electrolyte, and its FTO-glass counter electrode to form a full device assembly. Thereupon, the unique scattering contrast that is available from neutrons could be employed via *in-situ* NR methods to extract complementary bulk structural information from the buried interface that will then have formed from the device-assembly construct. One could even combine optical spectroscopy methods with these direct structural tools to obtain concerted electronic information about DSC characteristics such as electron recombination. Currently, such an example is just a hypothetical construct, but it aims to illustrate and stimulate the essence of such an idea. Pending the development of such instrumentation, data acquired for each metrology could then be combined via an entirely interoperable procedure, and the data would arise from the same sample under the same environmental conditions. This would make the structural results far more accurate and thus informative for DSC operation. As such, one could far better tailor the molecular design of DSCs and indeed model other types of device technologies.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.langmuir.1c02165.

Schematic illustration of a representative reflectivity experiment (Figure S1); refined structural parameters for thin films of TiO$_2$ sensitized with N3 using EtOH, EtOH/t-BuOH (1:1 v/v), DMSO, or MeCN/t-BuOH (1:1 v/v) (Table S1); refined structural parameters for XRR data on thin films of TiO$_2$ sensitized with MK-2 or MK-44 (Table S2); thickness, density, SLD, and dye volume fraction values for thin films of TiO$_2$ sensitized with solutions of MK-2, N3, or N749 of different concentration (Table S3); AFM and XRR parameters for dye layers on thin films of TiO$_2$ singly sensitized with 1S and cosensitized with XS6 and 1S (Table S4); structural parameters determined by *in-situ* NR for TiO$_2$ substrates sensitized with MK-2 or MK-44 dyes, submerged in a solution of d$_{7}$-MeCN, 0.7 M LiI in d$_{7}$-MeCN, or 0.7 M LiI and 0.05 M I$_2$ in d$_{7}$-MeCN (Table S5); corefined structural parameters of the dye (MK-2, dcbpy ligands to BB via the same COO$^-$ group. This hypothesis was corroborated by the results of XPS Ti 2p measurements and electronic-structure calculations, which suggested that these changes require relatively low activation energies.88
N3, or N749) layers for two contrast-matching scenarios (d$_{L}$-MeCN and Si-contrast-matched d$_{L}$-MeCN/MeCN) in the presence of LiI or LiI/I$_{2}$ under consideration of the solvent ingress in the dye layer (Table S6); and dye-layer thickness for MK-2, N3, and N749 determined by various forms of NR and XRR carried out on the same dyes at the same sensitization concentration (0.3 mM) and time (20 h) using the same solvents (Table S7).}

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**Notes**

The authors declare no competing financial interest.

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Jacqueline M. Cole is Head of Molecular Engineering at the University of Cambridge, where she currently holds the BASF/Royal Academy of Engineering Research Chair in Data-Driven Molecular Engineering of Functional Materials. Her research focuses on data science and computational methods that predict materials for photovoltaic, magnetic, and catalytic applications, which she then experimentally validates by developing and applying advanced materials-characterization methods. Accordingly, she holds two Ph.D. degrees: one in physics from the University of Cambridge and one in chemistry from the University of Durham. Her interdisciplinary work has been recognized by numerous international and national awards and honors, which include the American Crystallographic Association Bertram Eugene Warren Diffraction Physics Award (2021), the Royal Society Clifford Paterson Medal and Lecture (2020), the BASF/Royal Academy of Engineering Research Chair in Data-Driven Molecular Engineering of Functional Materials (2019–2024), the 1851 Royal Commission 2014 Fellowship in Design (2015–2018), a UK–US Fulbright Award (2013 and 2014), the Royal Society of Chemistry SAC Silver Medal and Lecture (2009), and the 18th Franco-British Science Prize (2006) for international collaboration.

Ulrich F. J. Mayer conducted postgraduate studies with Prof. Ian Manners (FRS) at the University of Bristol (U.K.) on highly strained metallocenophanes containing late transition metals. After postdoctoral work with Prof. Duncan Wass at the University of Bristol (U.K.) on autonomously self-healing composite materials for aerospace-engineering applications, he was a JSPS research fellow at the Institute for Chemical Research of Kyoto University (Japan), where he worked in the group of Prof. Norihiro Tokitoh on main-group catalysts. In 2012, he founded an independent language-editing service (www.mayerscientificediting.com), where he works predominantly with Japanese academics in the fields of chemistry and materials sciences. In 2014, he accepted a position as a scientific writer in the molecular-engineering group at the University of Cambridge (U.K.).

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