

Preferred Molecular Orientation of Coumarin 343 on TiO₂ Surfaces: Application to Dye-Sensitized Solar Cells

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Abstract

The dye...TiO₂ interfacial structure in working electrodes of dye-sensitized solar cells (DSCs) is known to influence its photovoltaic device performance. Despite this, direct and quantitative reports of such structure remain sparse. This case study presents the application of X-ray reflectometry to determine the preferred structural orientation and molecular packing of the organic dye, coumarin 343, adsorbed onto amorphous TiO₂. Results show that the dye molecules are, on average, tilted by 61.1° relative to the TiO₂ surface, and are separated from each other by 8.2 Å. These findings emulate the molecular packing arrangement of a monolayer of coumarin 343 within its crystal structure. This suggests that the dye adsorbs onto TiO₂ in one of its lowest energy configurations, i.e. dye...TiO₂ self assembly is driven more by thermodynamic rather than kinetic means. Complementary DSC device tests illustrate that this interfacial structure compromises photovoltaic performance, unless a suitably sized co-adsorbant is interdispersed between the coumarin 343 chromophores on the TiO₂ surface.

Introduction

Since the breakthrough of dye-sensitized solar cells (DSCs) in 1991¹, the sensitization of titanium dioxide surfaces with photoactive dye molecules has become a topic of intense research interest. A DSC device employs the dye in a dual capacity: as its principal light absorber, rendering the dye in a photo-excited state via sunlight absorption; and as its source of electron current initiation, where the dye injects photo-excited electrons into the conduction band of the semiconducting TiO₂, to which dye molecules are adsorbed. This dye...TiO₂ composite represents the working electrode of the DSC. The structure, orientation and packing density of dyes at the TiO₂ interface can have a major impact on electron injection processes² and bulk TiO₂ surface passivation, thus heavily influencing the overall DSC performance. A variety of materials-characterization techniques that employ spectroscopy³⁻⁶, diffraction⁷ or imaging tools⁸⁻⁹, as well as computational methods¹⁰⁻¹¹ have all been used to infer these dye properties. However, the majority of these effects yield only indirect evidence of interfacial dye...TiO₂ structure. Results from direct physical measurement of dye surfaces remain scarce.

Recently, X-ray Reflectometry (XRR) was applied to the successful determination of molecular orientation and packing density for a range of metal-based dye complexes.¹² However, to the best of our knowledge, application of this technique to metal-free organic dyes so far remains unprecedented. Yet, such work is important since organic-dye functionalized DSC devices are now reaching comparable efficiencies to those that embed metal-based dye complexes¹³, and they offer added environmental and synthetic benefits¹⁴. A better understanding of the interfacial structure of organic dyes, as adsorbed onto the surface of TiO₂, is essential for determining how to enhance their associated photovoltaic property attributes. With this in hand, one stands to be able to establish rational molecular design protocols that will yield superior organic dyes for DSC applications.

This paper presents results obtained from XRR studies on the Coumarin 343 dye (C343, C₁₆H₁₅NO₄, Figure 1a) when bound to the surface of amorphous TiO₂. The photoelectronic and photophysical properties of C343 have already been investigated extensively: C343 possesses a large molar adsorption coefficient, ease of structural modification, high quantum-injection yields and near-instantaneous electron injection.¹⁵ In principle, these optoelectronic properties make this compound and its chemical derivatives well suited as

DSC sensitizers.¹⁶⁻¹⁸ However, it transpires that the overall photovoltaic device efficiency of C343 is low, especially relative to other coumarin-based chromophores.¹⁹ To explore this irregularity, the orientation and packing density of C343 about the TiO₂ surface is herein determined and is correlated with in-house device performance characteristics of DSCs functionalized by the C343 dye. To this end, the DSC device performance of this dye is enhanced by grafting deoxycholic acid as a co-adsorbate. These findings are rationalized within the context of the crystal packing of a monolayer of C343 dye molecules, suggesting that the self assembly of C343 onto amorphous TiO₂ is dictated by thermodynamic rather than kinetic factors.

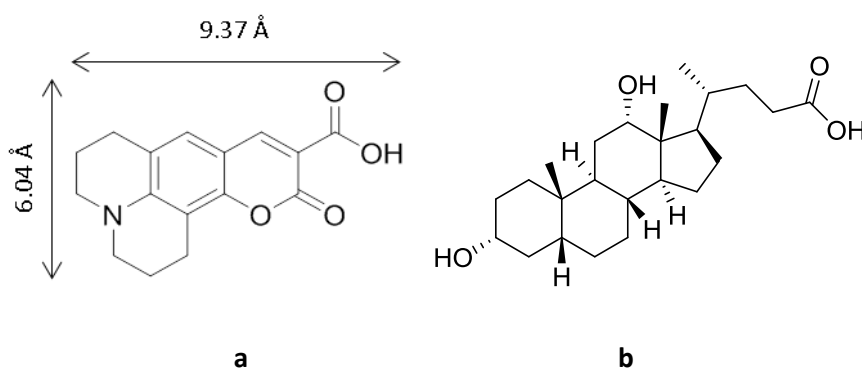


Figure 1 Structure of (a) Coumarin 343 and its corresponding molecular length and width; (b) deoxycholic acid (DCA).

Methods and Materials

Preparation and Sensitization of Amorphous TiO₂ Thin-films

Amorphous TiO₂ thin films were deposited on silicon (100) wafers, to provide the atomically flat surface required for XRR measurements. This was achieved using an ASM Microchemistry flow-type, hot-walled, F-120 atomic layer deposition (ALD) reactor, which was maintained at 1 mBar pressure and using a deposition temperature of 120 °C. Vaporous TiCl₄ and H₂O precursors were delivered from Peltier-cooled reservoirs maintained at 21°C, following a sequential dosing scheme of 0.4 s TiCl₄ exposure, a 1.0 s N₂ purge, a 1.0 s H₂O pulse and a final 1.5 s N₂ purge.²⁰ This process was repeated for 200 cycles. A TiO₂ growth rate of ~0.04 nm/cycle yielded a ~8 nm thick TiO₂ thin film. The surface appearance of this film was imaged via atomic force microscopy and its amorphous nature was confirmed by Bragg-Brentano X-ray diffraction measurements.

Prior to dye sensitization, these films were heated to 80 °C for a minimum of 30 minutes in order to remove any residual water on their surface. Sensitization was achieved by submersing the TiO₂ films in a 0.3 mM dye solution of C343 (97%, Sigma-Aldrich) in 1:1 acetonitrile:*t*-butanol for 20 hours. The resulting films were rinsed with neat acetonitrile and dried under a flow of nitrogen gas prior to being subject to X-ray reflectometry measurements.

X-ray Reflectometry (XRR)

XRR measurements were conducted using a Panalytical X'pert Pro reflectometer that employed a Cu K α X-ray source ($\lambda = 1.541 \text{ \AA}$). The X-ray beam was collimated using a Göbel mirror with a 0.1 mm slit and a post-sample parallel collimator. Reflectivity data were collected over a detector range of $0.1^\circ < 2\theta < 10.0^\circ$, incrementing in 0.02° steps, with a count time of 10 s per step. Data were acquired for the TiO₂ substrate before and after its dye sensitization, using the same substrate. The results were refined using the MOTOFIT package²¹ for Igor Pro (Wavemetrics) to reveal associated structural parameters, with X-ray reflectivity plotted as a function of the momentum transfer vector (Q) perpendicular to the TiO₂ surface (Equation 1).

$$Q = 4\pi \left(\frac{\sin(\theta)}{\lambda} \right) \quad (1)$$

Nominal values for the scattering-length density (SLD) for each layer were used to prepare initial structural models, using a three-layer approach, whereby values of $20.1 \times 10^{-6} \text{ \AA}^{-2}$, $18.9 \times 10^{-6} \text{ \AA}^{-2}$ and $31.2 \times 10^{-6} \text{ \AA}^{-2}$ represented the silicon wafer, the native oxide layer and TiO_2 , respectively. An SLD of $13.6 \times 10^{-6} \text{ \AA}^{-2}$ was calculated for C343 using Equation 2, where r_e refers to the classical electron radius ($2.81 \times 10^{-15} \text{ m}$), Z is the sum of atomic numbers (*ie.* the total number of electrons) in the C343 molecule (150), and V is the molecular volume of the dye (309.02 \AA^3), determined from diffraction data.²²

$$SLD = \frac{r_e Z}{V} \quad (2)$$

Dye-sensitized Solar Cell Device Fabrication and Performance Testing

Working electrodes were fabricated by first depositing two layers of nanoparticulate TiO_2 paste (Dyesol, DSL 18NR-T) onto clean fluorine-doped tin oxide (FTO) glass (TEC7, Dyesol) using the doctor blade method. Sintering of this paste at 500°C for 30 minutes yielded $\sim 10 \text{ }\mu\text{m}$ -thick mesoporous TiO_2 films. These films were then submersed in a 0.3 mM 1:1 acetonitrile:t-butanol solution of C343 (97% Sigma Aldrich) for ~ 20 hours, before being rinsed with neat acetonitrile (Sigma-Aldrich, 99.5% ACS Reagent grade) and dried under a flow of nitrogen. An active dye... TiO_2 working-electrode surface area of $\sim 1 \text{ cm}^2$ was created via removal of excess TiO_2 from the parent-film periphery.

Counter electrodes were fabricated by first drilling two 0.6 mm diameter holes in clean FTO glass (TEC7, Dyesol). A 5 mM solution of chloroplatinic acid hydrate (Sigma Aldrich, 99.995%) in isopropanol (Fischer, Analytical reagent grade) was then prepared and drop cast onto the electrodes. These were subsequently heated to 390°C for 15 minutes in a box furnace.

Completed cells were assembled by sealing the electrodes together using a thermoplastic gasket (Solaronix, Meltonix 1170-25) and filling the inter-electrode volume with an I^-/I_3^-

electrolyte solution (Dyesol, EL-HPE) via the pre-drilled holes. These holes were subsequently blocked using two-part clear epoxy resin (Araldite).

J-V curves were measured for each DSC device under illumination using an Abet Technologies Sun 2000 solar simulator (AM1.5G spectrum), calibrated to 1 Sun intensity using an Oriel standard silicon reference cell (91150V). The open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}) and fill-factor (FF) of each cell was determined, from which the power-conversion efficiency (PCE, η) of the device was calculated according to Equation 3, where P_{in} refers to the power density of incident-light radiation (100 mW cm^{-2})

$$\eta = \frac{V_{oc} \cdot J_{sc} \cdot FF}{P_{in}} \quad (3)$$

Reported DSC device parameters were realized from averaging device performance characteristics from 5 individual cells (see Supplementary Information) in order to ensure good reproducibility and accuracy. PCEs are reported both as an absolute quantity as well as a % performance ratio relative to that of DSCs made in-house with N719 dye (*Di-tetrabutylammonium-cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II)*). This procedure was adopted since our previous findings show this ratio to be highly consistent across measurements duplicated across a range of laboratory fabrication conditions.²³ This obviates the renowned inconsistencies between absolute PCE values that result from inconsistent J_{sc} data obtained from preparing DSC devices in different laboratories, using different batches of raw materials and varying fabrication personnel.

Results and Discussion

X-Ray Reflectometry (XRR)

Figure 2 shows the experimentally observed and fitted XRR data for the C343-sensitized TiO_2 (red trace) and the corresponding untreated TiO_2 substrate (black trace). Structural parameters for the dye-sensitized TiO_2 (SLD; layer thickness; surface roughness) were obtained from model refinements using a three-layer approach, consisting of the dye layer, TiO_2 film, and native oxide layer on the silicon substrate whose SLD and thickness were fixed

(Table 1). In contrast, the untreated substrate required only a two-layer model, confirming the absence of any surface contamination such as residual trace amounts of water.¹² Relative to the untreated films, the additional layer in the dye-treated TiO₂ was easily detected due to a large contrast difference between the dye and TiO₂. Under these conditions, the XRR measurements were able to resolve the film thickness with an error of less than 0.2 Å.¹²

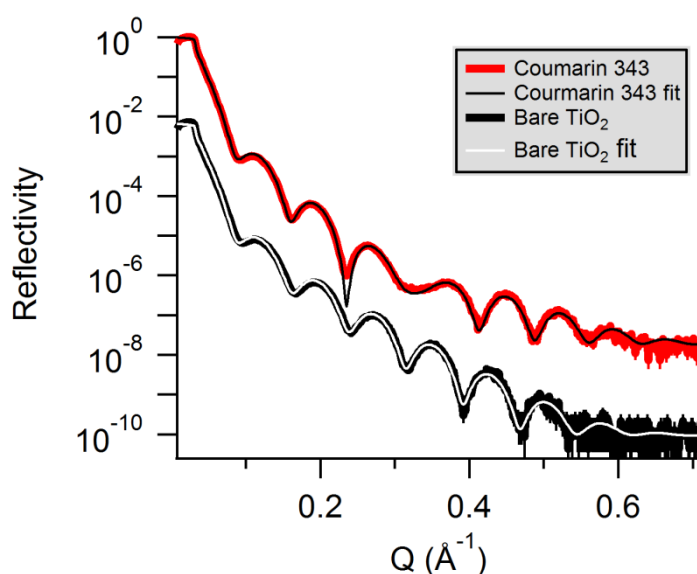


Figure 2 Representative reflectivity profile for Coumarin 343 on an amorphous TiO₂ thin-film (red) and the un-sensitized TiO₂ thin-film substrate (black). The dye-sensitized substrate results were derived from averaging four sets of raw data (see Supplementary Information).

Table 1 Structural data for Coumarin 343 on a TiO₂ thin-film substrate, as determined by reflectometry model refinement. The SLD and thickness of the third layer (SiO₂) was fixed at 5 Å and $18.9 \times 10^{-6} \text{ Å}^{-2}$ respectively, and has been omitted for clarity.

1	2	Coumarin 343
Dye layer	Formula	C ₁₆ H ₁₅ NO ₄
	Thickness / Å	10.0 ± 0.2
	SLD ($\times 10^{-6}$) / Å ⁻²	8.6 ± 0.3

	Surface roughness / Å	3.0 ± 0.4
	Mass density /g cm ⁻³	0.96
TiO₂ layer	Thickness / Å	80.0 ± 0.3
	SLD (×10 ⁻⁶) / Å ⁻²	30.1 ± 1.0
	Interfacial roughness / Å	4.6 ± 0.2

An SLD value of $8.6 \times 10^{-6} \text{ Å}^{-2}$ was observed for C343 on TiO₂. This is 35% lower than the calculated value for pure C343 ($13.6 \times 10^{-6} \text{ Å}^{-2}$) which suggests a dye layer with low density (0.96 g cm^{-3} ; Equation 4), relative to that of previously reported dyes, *e.g.* N719 (1.20 g cm^{-3}).¹²

$$SLD = \frac{r_e N_A \rho Z}{M} \quad (4)$$

where N_A is avogadro's number, ρ the mass density and M the molecular mass of Coumarin 343 (285.29 u) .

The measured average projected area-per-molecule (APM) on the TiO₂ surface is 49.3 Å^2 (Equation 5, where d is the dye layer thickness), resulting in a surface concentration, $[\text{dye}]_{\text{surf}}$, of $3.4 \times 10^{-10} \text{ mol cm}^{-2}$ (Equation 6). This is in good agreement with concentrations measured in previous dye absorption studies on amorphous TiO₂ films.²⁴

$$APM = \frac{r_e Z}{d(SLD)} \quad (5)$$

$$[\text{dye}]_{\text{surf}} = \frac{1}{N_A \times APM} \quad (6)$$

Similar coumarin derivatives have been shown to bind to the TiO₂ surface via a bidentate chelating carboxylate mode¹⁶. For modelling purposes, this carboxylate...TiO₂ separation is assumed to be 2.05 Å ;²⁵ this model is consistent with previous spectroscopic results²⁶, even

though alternative geometries have been speculated via computation.²⁷ With diffraction data published by Honda *et al.*²² the maximum possible dye-layer thickness corresponds to the sum of this dye...TiO₂ separation and the fully extended length of the dye molecule (Figure 1), i.e. the longest dimension of the dye along its molecular mean plane ($d_{\text{max}} = 11.42$ Å). Conceptually, this corresponds to the case where all dye molecules would be aligned perpendicular to the TiO₂ surface. The XRR measurements reveal a dye-layer thickness (d_{obs}) value of 10.0 Å (Table 1), indicating that C343 actually adopts a tilt angle, α , of $61.1 \pm 2.3^\circ$ with respect to the lateral TiO₂ surface, according to basic trigonometric considerations, c.f. Figure 3(a).

C343 features a molecular width of 6.04 Å (defined as the distance between atoms O1 and C5 perpendicular to the molecular length (Figure 1), from diffraction data.²² This indicates a theoretical APM of 33.12 Å², (Figure 4(a)), which is 16.18 Å² smaller than the area per molecule derived from the measurements using Equation (2). Consequently, it is feasible to assume that C343 molecules adopt a special configuration containing an average intermolecular spacing between parallel planes that are separated by 8.2 Å (Figure 3(b)). This is much larger than anticipated, due to the high propensity of C343 to form π - π stacking interactions which should involve an intermolecular distance of approximately 3-4 Å.²⁸ It should be noted here that this spacing is significantly larger than the longest molecular dimension in I₃⁻ (~5.27 Å) and acetonitrile (2.59 Å)²⁹, which means that facile access to the TiO₂ surface should still be possible. It is therefore reasonable to assume that C343 does not fully passivate the TiO₂ surface, which could lead to a significant reduction in overall cell performance due to unwanted electron decay pathways via electrolyte recombination reactions.³⁰ It should then offer a reasonable explanation for the low voltage (~0.41 V) obtained by this dye³¹ relative to other high-performance dyes such as N3 (*cis-Bis(isothiocyanato) bis(2,2'-bipyridyl)-4,4'-dicarboxylato ruthenium(II)*)¹¹, which show higher surface density.¹²

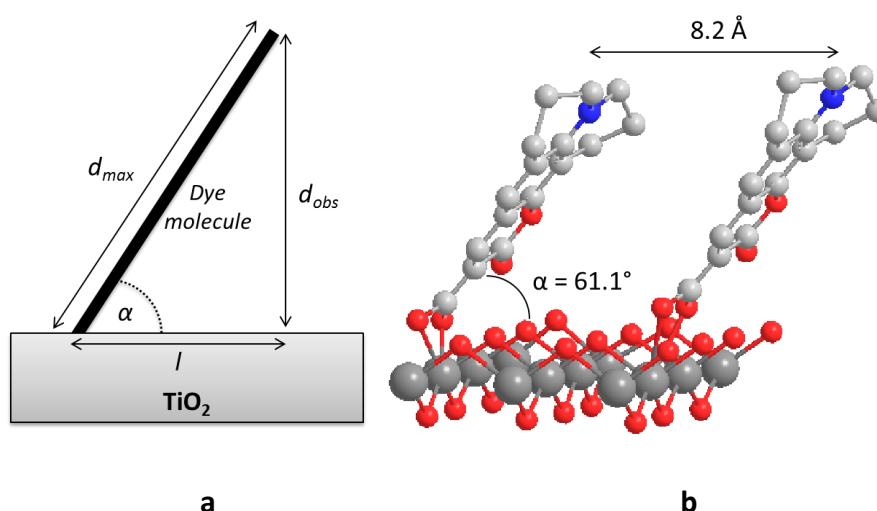


Figure 3 (a) Tilt angle, α , of the dye subtending the TiO_2 surface, calculated from reference to d_{max} and d_{obs} via basic trigonometric considerations; the theoretical area-per-molecule of the dye on the TiO_2 surface calculated by multiplying the molecular width of C343 by $l = d_{\text{max}}\cos(\alpha)$. (b) Visualization of C343 molecules bound to the surface. Perpendicular height and intermolecular distance are set in accordance with XRR data

DSC Device Performance

Details on the photovoltaic performance of C343 in a DSC³¹, as well as the effects of incorporating the anti-aggregating agent deoxycholic acid (DCA) into DSC devices as a co-adsorber to various dyes have been reported previously.^{17, 32-33} However, a systematic study of the co-operative effects of pairing C343 and DCA in DSC devices is unprecedented, to the best of our knowledge. Systematic investigation of the effects of such co-sensitization on photovoltaic behaviour stands to provide some further insight into the nature of the dye... TiO_2 interfacial structure observed via XRR; in particular, a rationale behind the larger-than-expected C343 intermolecular distance. C343-based DSC devices were fabricated with the photo-inactive DCA co-adsorbate according to one of four dyeing methods, as outlined in Table 2; 1:1 acetonitrile:*t*-butanol was used as a solvent throughout. DCA (Figure 1b) was chosen on the basis of its similarity in size and shape to C343, and the lack of discernible planar π -moieties, ensuring passivation to electronic intermolecular interactions.

Table 2 Details of the four dyeing methods employed and photovoltaic device performance characteristics of C343:DCA co-sensitized DSCs at 1 Sun intensity (AM1.5G spectrum). The N719 performance ratio is calculated using an internal-reference N719 device efficiency obtained by the authors (3.7%) to normalize the subject results; see Supporting Information.

Method	Dyeing Process	V _{oc} /V	J _{sc} /mA cm ⁻²	FF /%	PCE /%	N719 performance ratio /%
A	0.3 mM C343 for 20 hours	0.27 ± 0.03	0.09 ± 0.01	41.1 ± 0.9	0.010 ± 0.002	0.3
B	As for 'A', but repeated for further 20 hours	0.28 ± 0.03	0.10 ± 0.01	40.2 ± 0.7	0.011 ± 0.001	0.3
C	Mixture of 0.3 mM C343 and 0.2 mM DCA for 20 hours	0.333 ± 0.004	0.12 ± 0.01	44.3 ± 0.4	0.018 ± 0.001	0.5
D	0.3 mM C343 for 20 hours, then subsequently 0.2 mM DCA for 20 hours	0.39 ± 0.03	0.15 ± 0.02	48.0 ± 1.5	0.027 ± 0.008	0.7

DSCs obtained from method A exhibited a power conversion efficiency (PCE, η) of 0.010 % (Table 2; Figure 4) which is low when compared to literature values, and should be

attributed to the simplified fabrication process used for this work.³¹ Exposing devices to a more lengthy dyeing process (e.g. method B) did not affect their performance significantly, indicating saturated surface coverage, with respect to C343 after the first cycle.

Devices obtained from method C showed a significantly higher PCE, resulting predominantly from an improvement in V_{OC} and J_{SC} (see Table 2; Figure 4). The highest performance was achieved when using method D, with an almost 3-fold increase in PCE over devices following methods A or B. A $V_{OC} = 0.386$ V was attained, attributed to a reduction in recombination reactions owing to improved surface passivation.³⁴ J_{SC} also increased to 0.15 mA cm^{-2} and FF went up to 48.0 %. This is attributable to a positive shift of the TiO_2 conduction-band edge in the presence of DCA, and suppression of quenching processes, resulting in increased electron-injection yields.³⁴ Both of these effects indicate successful co-adsorption of DCA to the TiO_2 surface (Figure 5). This DSSC fabrication method also ensured that DCA co-adsorption was not accompanied by concurrent C343 desorption, as evidenced by the colorless DCA solutions that persisted upon the co-adsorbant sensitization step in the sequential dyeing process, *c.f.* contamination from C343 would afford a green solution. As DCA adsorption occurs after C343 sensitization, and no C343 desorption was observed, these results support the XRR results which indicate that sufficient space should exist between the dye molecules to allow DCA to adsorb. As repeated sensitization with C343 yielded insignificant improvement in the device efficiency compared to devices containing DCA, it is reasonable to assume that the limiting factor for the dye adsorption is the electronic interaction between the π -electrons in the C343 molecules, rather than steric congestion with respect to the surface, which may be expected intuitively.

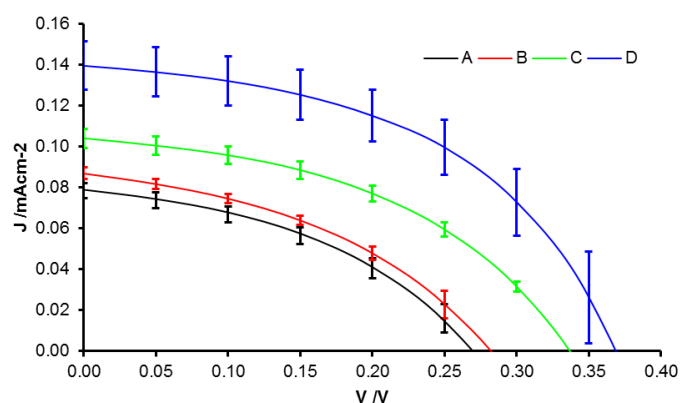


Figure 4 J-V curves for DSCs resulting from method A (black); method B (red); method C (green) and method D (blue).

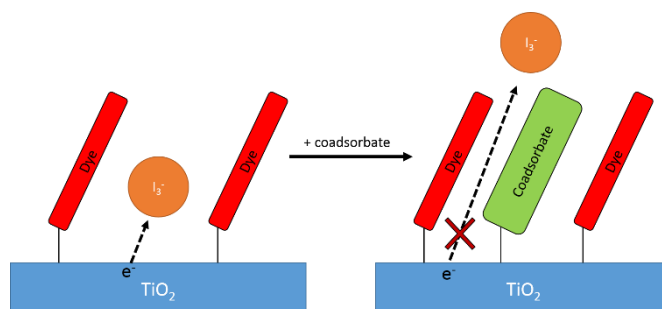


Figure 5 Schematic diagram showing the approach of the I₃⁻ to the TiO₂ surface and inducing recombination with electrons in the TiO₂ conduction band (left); and (right) how the inclusion of a co-adsorbate can prevent this recombination.

A Proposed Justification for the Dye...TiO₂ Interfacial Structure Observed by XRR.

Considering these XRR and DSC device results, along with *a priori* knowledge of the behaviour of C343 in the solid state and in solution, an indication to a possible justification for the larger-than-expected intermolecular spacing of C343 molecules can be proposed. Previous studies have focused on the behaviour of C343 in solution and have shown J-aggregates in the presence of non-polar solvents.³⁵ However, details surrounding the possible formation of H-aggregates of this dye, and of DSC dyes generally, are less well-known. One example by Nuesch and Grätzel has shown that the H-aggregation of merocyanine dyes, formed upon adsorption onto TiO₂ nanoparticle surfaces, presents a similar configuration to the crystal packing of the dye.³⁶ When one considers the crystal structure of C343 (Figure 6),²² a distinct layering is observable along the *c*-axis of the unit cell, with carboxylic-acid groups on adjacent molecules facing alternating directions.

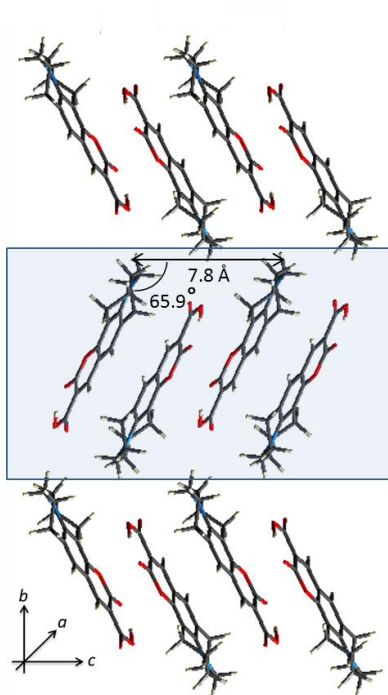


Figure 6 Crystal Structure of C343²² looking down the *a*-axis of the unit cell. Image generated using CrystalExplorer, Version 3.1³⁷

The intermolecular distance between these molecular layers is 3.5(4) Å, consistent with parallel displaced $\pi\cdots\pi$ stacking.²⁸ By taking just a single layer of molecules (Figure 6, shaded box), it is also observable that the intermolecular distance between molecules of the same orientation is 7.8(4) Å and have an angle relative to each other of 65.9(6)°. These observations are very close to the values of 8.2 Å and 61.1° for C343 on TiO₂ as derived from XRR results. It would therefore seem that, close to the TiO₂ surface, a similar molecular arrangement is occurring, with every other molecule being of an unfavourable orientation to formulate a bond between its carboxylic acid and TiO₂. This may also be influenced by adsorption of solvent molecules to the surface. In either case, the eventual removal of these non-adsorbed species, during the cell fabrication process, would result in molecular orientation and packing as measured by XRR. While the surface structure inferences of dye packing on TiO₂ from XRR were also compared with other molecular layer configurations in the C343 crystal structure (see Supporting Information), their good correspondence with molecular layers along the *c*-axis was unique.

This link between crystal structure and dye...TiO₂ surface structure has significant implications for the energetics associated with self assembly of dye molecules adsorbing

onto TiO₂. The crystal structure of a material is naturally one of, if not, the lowest-energy configurations of a molecule. The rationale for this is the need for a driving energy that overcomes a decrease in free energy to induce crystallization. Accordingly, crystal structures are most commonly represented by the most thermodynamically-stable state of the molecule. The fact that the XRR-derived parametrics of the dye...TiO₂ interfacial structure relate so closely to that of a monolayer of the C343 crystal structure along the c-axis indicates a thermodynamic mechanism behind dye..TiO₂ self assembly. At first sight, this might seem counter-intuitive given that dye molecules are drawn to the TiO₂ surface somewhat dynamically given that they reside in a solution environment. Yet, dye...TiO₂ interfaces and the associated dye loading onto TiO₂ are poorly understood. So it is entirely possible that local-field forces associated with the dye are substantially modulated as they approach the TiO₂ surface, to the extent that they emulate crystal-field forces. As such, dye...TiO₂ self assembly could readily be controlled by thermodynamic rather than kinetic origins, as indicated by the XRR results herein. This proposed self-assembly mechanism not only rationalizes the poor DSC performance of C343 relative to other coumarin derivatives, but is also entirely consistent with the observed improvement in DSC photovoltaic output once a DCA co-adsorbant was added to fill the interstices which would form as a result of thermodynamically-driven self assembly.

Conclusions

The interfacial structure of the coumarin 343 dye...TiO₂ composite, that forms the working electrode of a DSC, has been determined by X-ray reflectometry. The molecular orientation and packing of the dye on the TiO₂ surface have been quantified, revealing that C343 dyes self assemble on TiO₂ via thermodynamic rather than kinetic energy constraints. The large lateral dye...dye separation (8.2 Å) on C343-sensitized TiO₂ working electrode surfaces that is observed has significant implications for the photovoltaic device performance of the corresponding DSCs. In its native state, inefficient dye loading onto the TiO₂ surface is afforded, exposing the working electrode to electrolyte-to-TiO₂ based electron recombination, and compromising electron injection; this explains the poor device efficiency of C343-based DSCs. Fortunately, this situation can be rectified by co-sensitizing the C343-

based DSC with deoxycholic acid, which fills the interstices on the TiO₂ surface which arose from the thermodynamically-driven C343 self-assembly process.

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Supporting Information

Supporting Information Available: Tables of photovoltaic device performance characteristics from individual tests of multiplicate DSCs prior to their averaging; raw XRR data for the dye-sensitized substrate; modelled structural parameters for the bare TiO₂ film; and further discussion of surface structure versus crystal structure configurations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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