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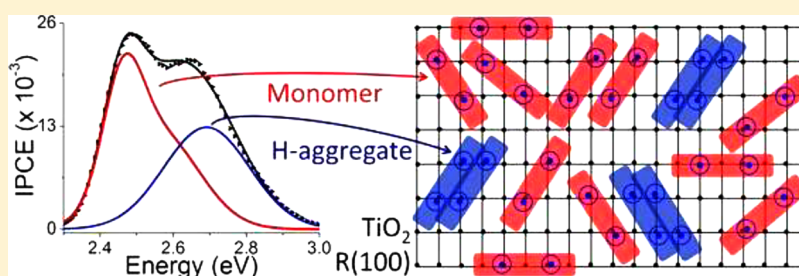
Dye Sensitization of Four Low Index TiO₂ Single Crystal Photoelectrodes with a Series of Dicarboxylated Cyanine Dyes

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S Supporting Information



ABSTRACT: Four dicarboxylated cyanine dyes were used to sensitize single-crystal anatase (001), anatase (101), rutile (001), and rutile (100) surfaces. Incident photon to current efficiencies (IPCE) spectra and isotherms were gathered for the different combination of dyes and surfaces. The maximum coverage of the surface-bound dyes on the TiO₂ crystal surfaces was determined by photochronocoulometric measurements. The IPCE spectra of the surface-bound dyes revealed that both the dye monomers and H-aggregates were both present and generated photocurrent. The relative abundance of dye monomers and H-aggregates was found to be strongly dependent on the crystallographic face used as the substrate for sensitization. The ratio of dye monomer to H-aggregate was quantified by fitting the IPCE spectra with a sum of the dye monomer and H-aggregate solution spectra.

The trends in surface coverage were explained using a simple “lattice matching” model where the distance between the coordinatively unsaturated Ti binding sites on the various TiO₂ crystallographic surfaces was compared with the distance between the carboxylate groups on the dyes. The rutile (100) surface had the highest coverage for all the dyes in agreement with the predictions of the lattice-matching model. Absorbed photon-to-current-efficiencies (APCEs) were calculated from the incident photon current efficiencies, the extinction coefficients and the measured surface coverages. The factors that affect the APCE values such as the relative injection yield for monomers and aggregate, the relative surface coverage values for monomers and aggregates, and semiconductor doping levels are discussed.

■ INTRODUCTION

Dye sensitized solar cells (DSSC) are a promising solar cell technology due to their relative high efficiency (>11% with laboratory scale cells), potentially low cost, and ease of manufacture. The highest efficiency DSSCs to this date have been fabricated using nanostructured wide-bandgap semiconductors as a substrate, Ru based dyes as sensitizers, and iodide containing electrolytes as the redox mediator.^{1,2} However some recent advances have produced high efficiencies with different sensitizers and different redox mediators.^{3–5}

One of many avenues of research, directed at improving the efficiency of DSSCs, has involved replacing ruthenium coordination compound sensitizers with organic dyes.^{6–12} Organic dye sensitizers could be superior to ruthenium based dyes due to their lower cost and higher extinction coefficients. Most organic dye sensitizers can be synthesized with multiple carboxylate groups, like the Ru based dyes, which bind covalently to coordinatively unsaturated titanium sites on the

TiO₂ surface in a bidentate configuration.^{13,14,16} This bidentate binding is very stable with respect to dissociation, due to the chelate effect, resulting in stable photocurrents. However, the bidentate configuration could restrict the ability of some dyes to bind to some surfaces since the distance between titanium binding sites may not match the distance between the carboxylate binding groups. Furthermore, the use of organic dye sensitizers as a replacement to Ru based dyes is complicated by the propensity of organic dyes to aggregate on the semiconductor surface with effects upon solar cell performance that are difficult to predict and control. Dye aggregation in sensitized solar cells has been shown to decrease overall power output,¹⁷ increase spectral response,¹⁸ or increase quantum yields.¹⁹

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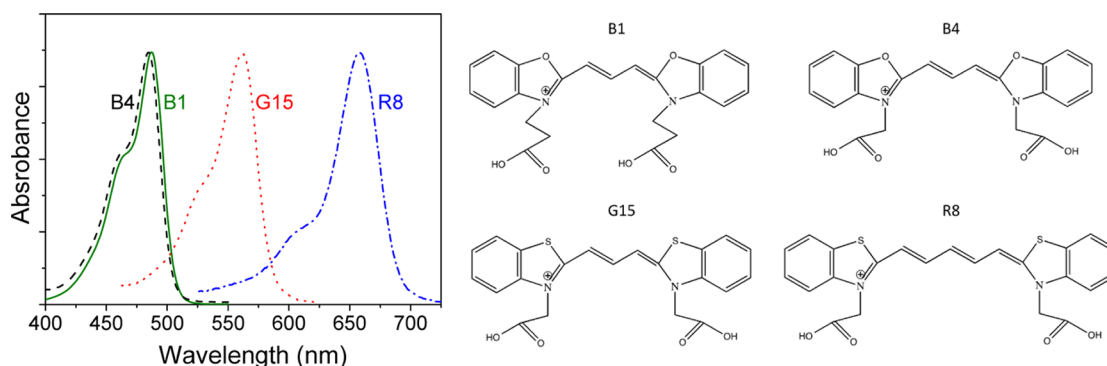


Figure 1. (left) UV-vis absorption spectra of the dicarboxylated cyanine dyes G15 (red dot), B1 (green solid), B4 (black dash), and R8 (blue dash dot). The dye concentrations are $<2.0 \times 10^{-5}$ M and the absorption spectra are predominantly the monomer form of the dye. (right) Structures of the dicarboxylated cyanine dyes employed in this study. The counterion (not shown) for all dyes was iodide.

Dye sensitized single crystal semiconductor electrodes provide an ideal experimental system for the elucidation of the models and parameters that control light absorption, charge separation, and transport at semiconductor/electrolyte interfaces. Such fundamental investigations can prove very valuable in the understanding of the more applied dye sensitized high-surface area nanocrystalline solar cells. The single crystal experimental system is much less complex than its nanocrystalline counterpart and the study of well-defined crystallographic surfaces allows for more definitive conclusions to be made concerning the relation between dye attachment and surface structure and the dye's performance as a sensitizer.

Our earlier work on dye-sensitized TiO_2 single crystal electrodes has shown that ultraviolet (UV) phototreatments to clean the surface of the electrode prior to dye adsorption results in high and reproducible dye coverages. The high coverages produce a surface where the sensitized incident photon to current efficiencies (IPCE) of up to 1% can be measured for many sensitizing dyes.¹⁴ This advancement in the surface treatment of the TiO_2 electrodes, in concert with photochronocoulometric measurements of the amount of adsorbed dye, can translate into absorbed photon current efficiencies (APCE) of near 100% on TiO_2 .¹⁴

In this study we measured IPCE spectra on four different TiO_2 single crystal surfaces (anatase (001), anatase (101), rutile (001), and rutile (100)) with a structurally similar series of four dicarboxylated cyanine dyes. Spectral IPCE measurements revealed the degree of aggregation of the dyes on the four surfaces. Measurement of dye coverages with photochronocoulometry allowed us to further investigate the relationships between maximum dye coverage, surface aggregation, and compatibility of the binding geometry on the sensitized photocurrent. The control of dye aggregation on the surface could be important for maximizing dye coverage and extending the spectral response of the surface bound dyes.

EXPERIMENTAL SECTION

Dicarboxylated Cyanine Dye Characterization. The dicarboxylated cyanine dyes were synthesized as described previously.¹³ The structure and abbreviations used for the dyes are shown in Figure 1. The extinction coefficients in ethanol were measured to be: $2.2 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$, $6.2 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ and $2.5 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$ for B1, G15, and R8 respectively. Due to limited solubility in ethanol, the extinction coefficient for B4 was measured to be $8.6 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ in methanol. Cyanine dyes are known to form aggregates in solution but at low dye concentrations the monomer form of the dye dominates the spectra, Figure 1.

Single Crystal Electrode Preparation and Sensitization. The rutile(001) crystals were grown at DuPont Central Research and the rutile(100) crystals were obtained from Commercial Crystal Laboratories, Ltd. The anatase crystals with (001) and (101) surface orientations were mined in Hargvidda, Tyssedal, in Norway.

Electrodes were made by mounting the crystals on a copper disk using Ga/In eutectic for an ohmic contact and using epoxy (Epoxy Patch Hysol 1C) to isolate all except the front surface. After the epoxy set, the epoxy part of the electrode was sealed with silicone rubber (RTV) and permitted to dry for a few hours. Before photoelectrochemical measurements, the crystal was polished for 5 min with a soft polishing cloth using 20 nm colloidal silica (Buehler, Inc.) and cleaned with 0.2 M NaOH, followed by a Milli-Q (18 M Ω) water rinse. Atomically flat and reproducible surfaces are obtained by polishing, annealing and UV treatments.¹⁵ AFM images revealed that the terraces on the anatase crystal surfaces were less uniform across the surface compared with those of rutile crystal surfaces. Before and between the photocurrent measurements, UV treatment was carried out to remove any residual impurities and dyes on the surface. Repeated cycles of UV treatment and dye adsorption did not result in significant changes in the surface structure or surface area of the crystal.¹⁴ However after extended studies the crystals needed to be recovered, repolished, reannealed, and remounted.

The electrodes were then illuminated at 0.6 V vs Ag/AgCl in 1 M HCl (for anatase) or 10 mM NaClO_4 (for rutile) for 5 min using an Oriol 150 W Xe lamp followed by an ethanol (Pharmaco, ACS grade) rinse. A quartz cell was used to allow maximum UV illumination to reach the crystal surface. After UV treatment, the electrodes were rinsed with ethanol (for B1, G15, and R8) or methanol (for B4 dye) and promptly immersed in a dye solution in ethanol or methanol and left for 60 min to ensure equilibrium adsorption. Subsequent to dye adsorption, the electrodes were rinsed with ethanol or methanol and then photocurrent was measured in dye free electrolyte where dye desorption was not significant during the 10 min measurement time except for some fast desorption that appeared at very short times at high surface coverages that was earlier attributed to dyes that could only bind with one carboxylate.¹⁶

Photoelectrochemical and Transient Photocurrent Measurements. Photoelectrochemical measurements were carried out in a three-electrode configuration with a platinum gauze counter electrode and Ag/AgCl reference electrode. The incident photon to current efficiency (IPCE) spectra were measured for the dicarboxylated cyanine dye sensitized TiO_2 electrodes at seven different dye coverages. A bias of 0.6 V vs Ag/AgCl, on the light limited plateau of the photocurrent response, was applied during the collection of IPCE spectra. The IPCE spectra were measured in 10 mM tetrabutylammonium perchlorate (Fluka, electrochemical grade) and 4.5 mM hydroquinone in acetonitrile as a supporting electrolyte and as regenerator, respectively. The electrolyte was deoxygenated with nitrogen gas. Photocurrent spectroscopy was performed with PC control using a lock-in amplifier (Stanford Research, SR830), a

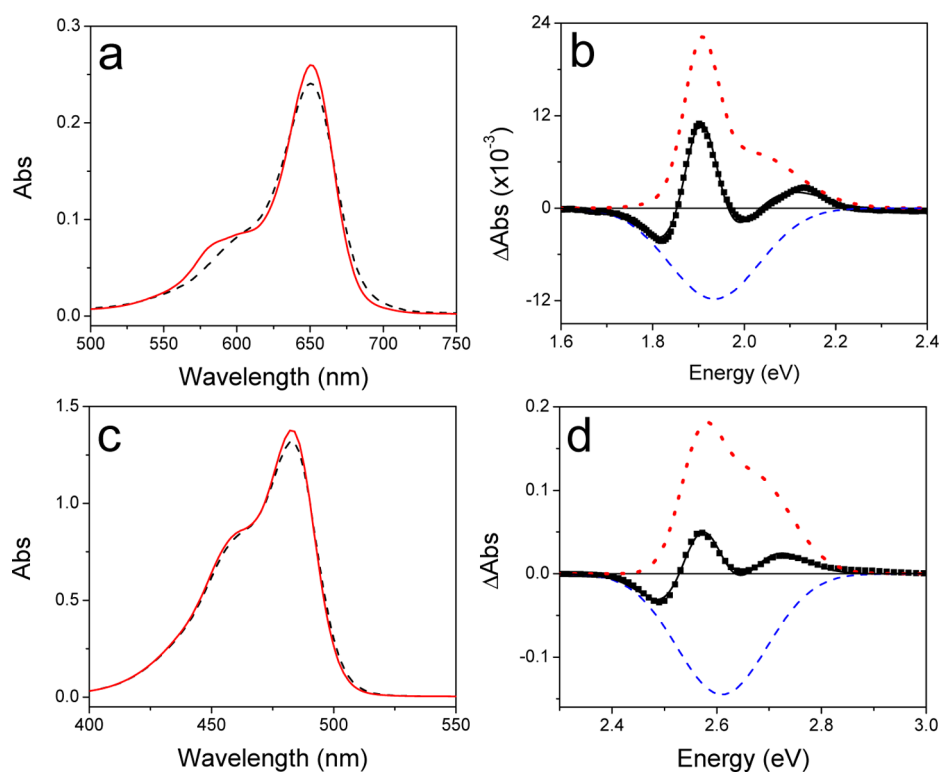


Figure 2. (a) The absorption spectra of R8 in aqueous solution. The spectra were obtained at a series of temperatures from 70 °C (black dash) to 25 °C (red solid), other temperatures are not shown. (b) The 70 °C absorption spectrum was subtracted from the 25 °C absorption spectrum resulting in the absorption change spectrum (black dots). The absorption change spectrum was fit (black solid) with a sum of the monomer spectrum (red dots) and the H-aggregate spectrum (blue dash). (c) The absorption spectra of B1 in aqueous solution. The spectra were obtained at a series of temperatures from 70 °C (black dash) to 25 °C (red solid), other temperatures are not shown. (d) The 70 °C absorption spectrum was subtracted from the 25 °C absorption spectrum resulting in the absorption change spectrum (black dots). The absorption change spectrum was fit (black solid) with a sum of the monomer spectrum (red dots) and the H-aggregate spectrum (blue dash).

potentiostat (EG&G, 174A) and monochromator (Jarrel Ash Fisher) with a Stanford Research optical chopper at 13 Hz.

Mott–Schottky measurements were carried out with a EG&G PAR173 polarographic analyzer, a Stanford Research SR830 lock-in amplifier and a Stanford Research DS345 function generator under PC control in acetonitrile solution saturated with tetramethylammonium chloride (Sigma-Aldrich). The doping densities were determined to be $1.5 \times 10^{18} \text{ cm}^{-3}$ for anatase (001), $5.8 \times 10^{19} \text{ cm}^{-3}$ for anatase (101), $2.0 \times 10^{18} \text{ cm}^{-3}$ for rutile (001), and $5.4 \times 10^{18} \text{ cm}^{-3}$ for rutile (100). The flatband potentials (vs Ag/AgCl) are 0.0 V for anatase (001), −0.40 V for anatase (101), −0.18 V for rutile (001), and −0.15 V for rutile (100).

Photochronocoulometry measurements of the TiO_2 electrodes sensitized with dicarboxylated cyanine dyes were made in acetonitrile solution with 10 mM tetrabutyl-ammonium perchlorate. Chart v4 software (AD Instruments) running on a Macintosh computer was used to record the transient photocurrent signal from a RDE4 potentiostat (Pine Instrument Company) using a 532 nm (5 mW) diode laser for G15 dye, a 473 nm (6 mW) diode laser for B1, and B4 dye, and a 630 nm (13 mW) diode laser for R8 dye as the light source with the beam expanded to illuminate the entire crystal surface. The electrolyte was deoxygenated with nitrogen gas. The transient photocurrent, resulting from illumination of the crystal surface, was integrated over time to obtain the total photocharge passed. In the absence of a regenerator all surface bound sensitizers injected electrons and then were converted to their oxidized state. The integrated photocurrent is then representative of the total number of dye molecules bound to the surface assuming that the entire crystal surface is electrochemically active and a one-electron reaction with no following electrochemical steps. More details for the photochronocoulometric measurement were described in a previous paper.¹⁶

Data Analysis and Simulations. Spectral simulation to determine the relative monomer and H-aggregate contribution of the dicarboxylated cyanine dyes were performed in Origin 7.0 using error minimization routines. With energy (in eV) as the independent variable the spectra were simulated using the sum of multiple Gaussian functions. The highest quality fits were achieved when the dye monomer spectrum was represented by the sum of two Gaussian functions with a fixed peak separation. The H-aggregate spectrum required only one Gaussian function for high quality fits.

Simulations for the lattice-matching model were performed in Excel 2010 using the “solver” suite to perform error minimization routines. Intramolecular carboxyl-carboxyl distances were estimated using molecular modeling software (Gaussian ver. 0.9).

RESULTS AND DISCUSSION

The dicarboxylated cyanine dyes employed in this study are known to bind to the TiO_2 single crystal electrodes as both monomers and H-aggregates.¹⁴ The complex equilibrium between dye monomers and aggregates makes it challenging to determine the distinct absorption spectra of the various dye species. The pure monomer and H-aggregate spectra of the dye were determined by changing the temperature of a dye solution causing a shift in the equilibrium ratio of dye monomers and H-aggregates resulting in changes in the UV-vis absorption spectrum of the dye solutions.²⁰ The UV-vis absorption spectra for the four dyes were measured at temperatures between 25° and 70 °C in aqueous solutions at concentrations of: B1 ($5.0 \times 10^{-5} \text{ M}$), B4 ($2.0 \times 10^{-5} \text{ M}$), G15 ($5.0 \times 10^{-6} \text{ M}$), and R8 ($1.0 \times 10^{-5} \text{ M}$). The 70 °C absorption spectrum was subtracted from the 25 °C absorption spectrum resulting in the absorption

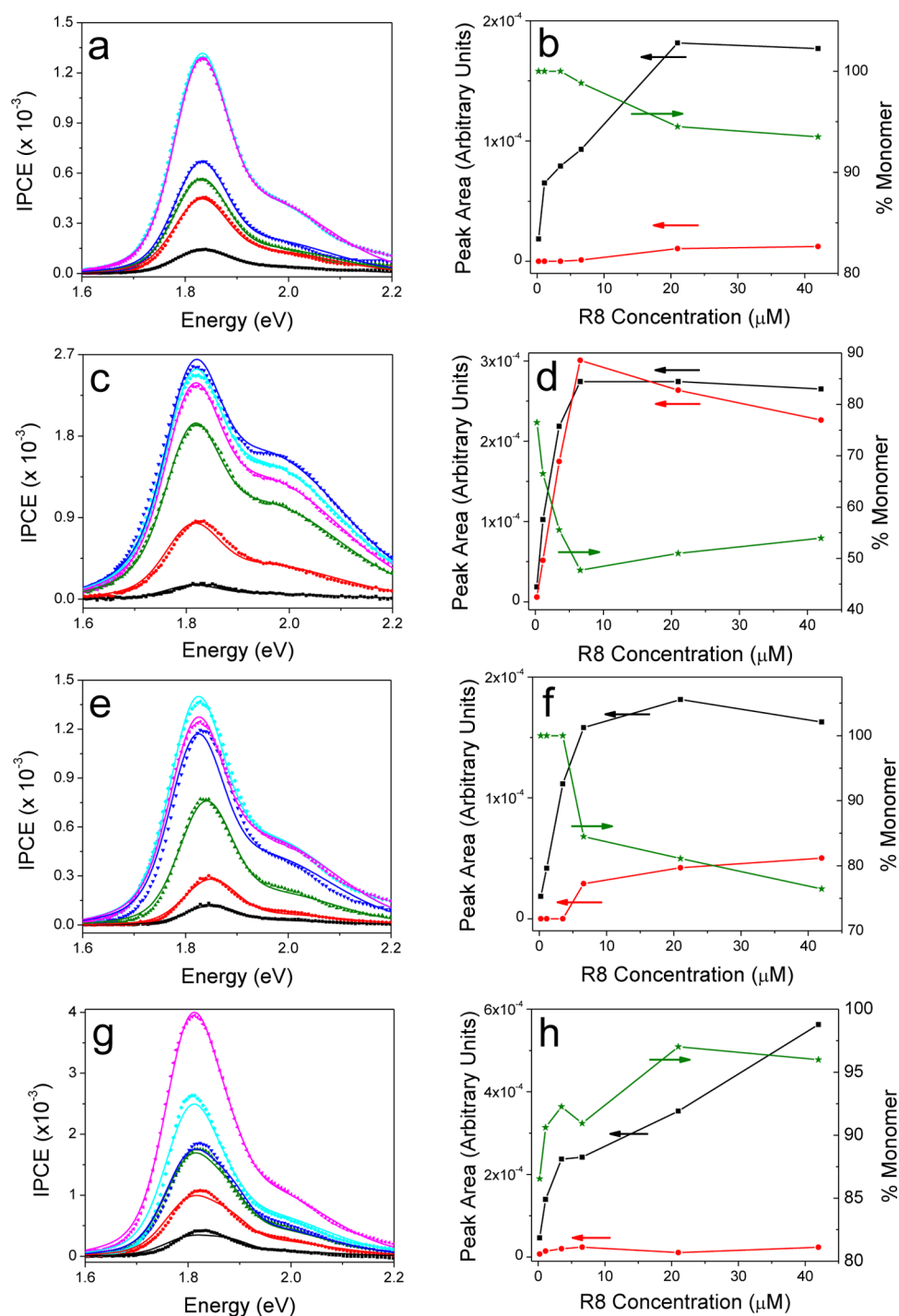


Figure 3. The IPCE spectra (symbols) and corresponding spectral fitting (solid lines) for R8 on the four different crystallographic TiO_2 single crystal surfaces. (a) on anatase (100), (c) on anatase (101), (e) on rutile (001), and (g) on rutile (100). The IPCE spectra were gathered at R8 concentrations of: 42 μM (magenta), 21 μM (cyan), 6.6 μM (blue), 3.5 μM (olive), 1.1 μM (red), and 0.21 μM (black). The corresponding figure on the right shows the total contributions of the photocurrent from monomer (black squares) and H-aggregation (red circles) as a function of dye the concentration in the sensitization solution. Also shown is the percent monomer (green stars) contribution to the IPCE as a function of the dye concentration in the sensitization solution. The monomer and H-aggregate contributions were calculated from the spectral simulations.

change spectrum. Distinct isobestic points were observed in the absorption change spectrum indicating the equilibrium between two chemical species. The absorption change spectrum was simulated by summing the pure monomer and H-aggregate spectra. As the aqueous dye solution warms the equilibrium favors the formation of monomers over H-aggregates, therefore the H-aggregate spectra contribution to

the absorption change spectrum simulation has a negative intensity reflecting the loss of the H-aggregate species (Figure 2).

We assume that in solution at low concentration the dye exists in only two forms, monomer and dimers in an H-aggregated geometry. The monomer spectrum could be simulated with two Gaussian curves (one for main monomer

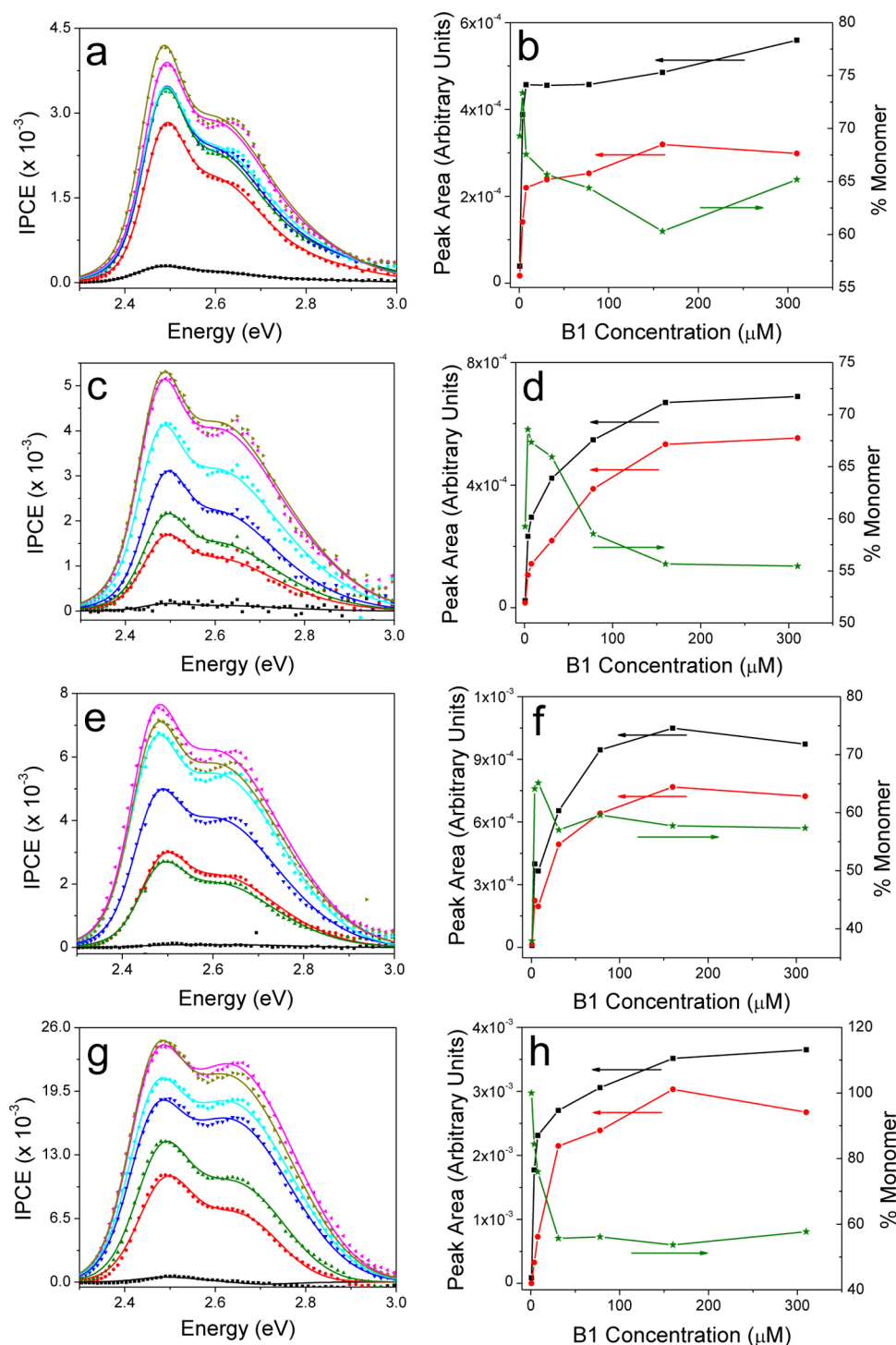


Figure 4. The IPCE spectra (symbols) and corresponding spectral fitting (solid lines) for B1 on the four different crystallographic TiO_2 single crystal surfaces. (a) on anatase (100), (c) on anatase (101), (e) on rutile (001), and (g) on rutile (100). The IPCE spectra were gathered at B1 concentrations of: 310 μM (dark yellow), 160 μM (magenta), 78 μM (cyan), 31 μM (blue), 7.8 μM (olive), 3.9 μM (red), and 0.78 μM (black). The corresponding figure on the right shows the total contributions of the photocurrent from monomer (black squares) and H-aggregation (red circles) as a function of dye concentration in the sensitization solution. Also shown is the percent monomer (green stars) contribution to the photocurrent as a function of the dye concentration in the sensitization solution. The monomer and H-aggregate contributions were calculated from the spectral simulations.

peak and the other for the shoulder) whereas the H-aggregate spectrum is fit using only one Gaussian curve for all dyes employed in this study (Figure 2b and d). We also assume that the UV-vis spectrum of the H-aggregate in solution is similar to that of the H-aggregate on the TiO_2 surface despite the fact that

on the surface higher order aggregation is likely. Therefore for the rest of the discussion the term H-aggregate will be used to refer to dimers and all higher order aggregates both in solution and on the TiO_2 surface. We find that the fit of the subsequent

Table 1. Saturation Coverage in mol/cm² of the Four Dyes on the Four Crystal Surfaces Calculated from Photochronocoulometric Measurements Organized from Highest Coverage (Left) to Lowest Coverage (Right)

dye	highest coverage						lowest coverage				
B1	rutile (100)	6.0×10^{-10}	>	anatase (001)	2.2×10^{-10}	>	anatase (101)	1.2×10^{-10}	>	rutile (001)	1.1×10^{-10}
B4	rutile (100)	3.3×10^{-10}	>	anatase (001)	1.7×10^{-10}	>	anatase (101)	1.2×10^{-10}	>	rutile (001)	5.9×10^{-11}
G15	rutile (100)	1.7×10^{-10}	>	anatase (101)	7.0×10^{-11}	>	anatase (001)	4.9×10^{-11}	>	rutile (001)	3.9×10^{-11}
R8	rutile (100)	7.0×10^{-11}	>	anatase (001)	1.5×10^{-11}	>	anatase (101)	1.2×10^{-11}	>	rutile (001)	9.6×10^{-12}

IPCE spectra is good enough to give us confidence in these assumptions.

IPCE spectra for the R8 and B1 dyes indicate that both the monomer and H-aggregates of the dye are present on the surface and are capable of generating photocurrent on the four different low index TiO₂ surfaces (Figures 3 and 4). The IPCE spectra were gathered over a range of dye concentrations and in all cases the photocurrent increased with increasing dye surface coverage reaching saturation at higher coverages.

The IPCE spectra of the R8 dye shows a strong face dependence on the various TiO₂ crystals. The IPCE spectra closely resemble the solution monomer spectra on the anatase (001), rutile (001), and rutile (101) surfaces (Figure 3a, e, g), whereas on the anatase (101) surface the spectra is broad and contains substantial contributions from H-aggregated dye (Figure 3c). In contrast the IPCE spectra of the B1 dye does not show a strong dependence on the TiO₂ crystal face (Figure 4).

The isotherm-like behavior for B1 and R8 reached saturation at 0.2 mM and 0.02 mM respectively. Saturation was in similar concentration regimes reached for the other two dyes studied (<0.03 mM for B4 and <0.2 mM for G15) (Supporting Information (SI) Figures S1 and S2).

The IPCE absorbance spectra in Figures 3 and 4 were simulated using a linear sum of the dicarboxylated cyanine dye monomer and H-aggregate absorbance spectra calculated in Figure 2b and d. Interestingly, in no case were J-aggregates observed in the IPCE spectra despite the well-known tendency for cyanine dyes to form J-aggregates.^{14,22–25} The spectral fitting was in good agreement with the IPCE spectra for B4 (SI Figure S1), and G15 (SI Figure S2) dyes, however the spectral agreement was of lower quality for the B1 dye (Figure 3). The B1 dye is unique among the four dicarboxylated cyanine dyes studied; the additional methylene spacer on the carboxylated appendage may afford the B1 dye more flexibility to bind to the TiO₂ surface.

The contributions of dye monomers and H-aggregate were obtained from the spectral simulations (Figures 3 and 4). Small spectral shifts were observed between the solution spectra and surface bound IPCE spectra of the dicarboxylated cyanine dyes. SI Table S1 lists the peak wavelengths and peak widths used in the spectral fitting. Interestingly in almost all cases the percent monomer contribution to the IPCE spectra decreased as the dye concentration increased. This suggests that dyes initially bind as spatially isolated monomers, then as the number of possible isolated binding sites decrease dyes are forced to bind at surface sites near other dyes in H-aggregate forming geometries.

The contribution of H-aggregates to the IPCE spectra was higher on the anatase(101) surface than compared to the other TiO₂ crystallographic surfaces for all the studied dyes. The unusually high contribution from H-aggregates to the IPCE spectrum suggests that the anatase(101) surface promotes H-aggregate formation or that the band alignment of the anatase

(101) face favors charge transfer from an H-aggregate excited state.

In addition to the monomer and H-aggregate contributions to the IPCE spectra, the total coverage of the dyes on the TiO₂ single crystal surface was also measured. Grätzel et al. have measured the amount of adsorbed dye on nanocrystalline anatase films using the electrochemical oxidation of the dye²⁵ and Fillinger et al used dye desorption followed by UV-vis spectroscopy to determine dye coverages.²⁶ However both of these studies were done on high surface area nanocrystalline electrodes resulting in substantial currents or absorption signals. These methods are problematic on single crystal electrodes due to the low total absorption and adsorption of dye monolayers. Therefore we used a photochronocoulometric technique that was used to measure adsorbed triiodide on WSe₂ electrodes²⁷ and to measure dye coverages on TiO₂ single crystals.¹⁶ Herein the surface coverage of dye on a sensitized single-crystal electrode under depletion was determined by exposing it to a light pulse that, in the absence of a regenerating redox couple, irreversibly photooxidized the adsorbed dye due to electron injection into the conduction band of the TiO₂. The total injected charge, determined by integrating the photocurrent transient, should be equal to the number of adsorbed dye molecules assuming that it is a one-electron oxidation (Table 1).

A simple model to account for dye adsorption trends was formulated with two underlying assumptions. The first assumption is that stabilized photocurrents were the result of both carboxylate groups binding to the TiO₂ surface. Previous work in our lab showed that there was an initial decrease in the photocurrent immediately upon immersing the dye saturated electrode into the electrolyte attributed to desorption of the dye molecules attached by only one carboxylate group.¹⁶ Therefore stable photocurrents are attributed to bidentate coordination of dyes. The second assumption is a “lattice matching model” where the highest dye coverages are obtained when the distance between the carboxylate groups closely matches a distance between unsaturated four or five coordinate Ti atoms on an unreconstructed TiO₂ surface.^{14,16,28} Hints about the organization of the dyes on the surface, such as surface aggregate formation, might then be obtained from the packing structures resulting in H-aggregate like interactions between neighboring dye molecules and the percentage of aggregate measured in the photocurrent spectra. This model is very simplified since it does not take into account complications such as the terraced nature of the surfaces where kink sites and step edges may influence the binding and nucleation of aggregates.

Molecular mechanics software (Gaussian ver. 0.9) was used to estimate the average intramolecular distance between carboxylic acid groups in the bidentate cyanine dyes. Due to the different possible binding modes of the carboxylate to the oxide surface the average distance between the carbon atoms in the carboxylate groups was used. The distances for the dyes

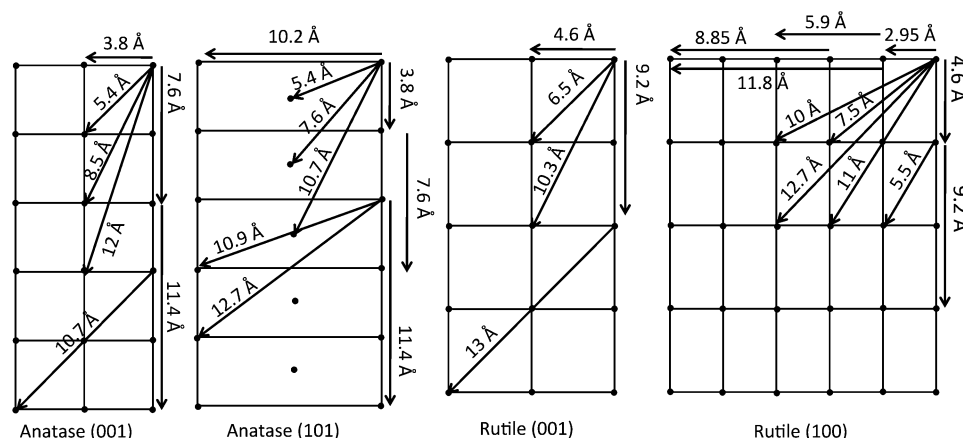


Figure 5. The possible distances for bidentate binding for the dicarboxylated cyanine dyes between the five-coordinate Ti sites on the four TiO₂ crystal surfaces. The dots represent the location of the five-coordinate Ti sites.

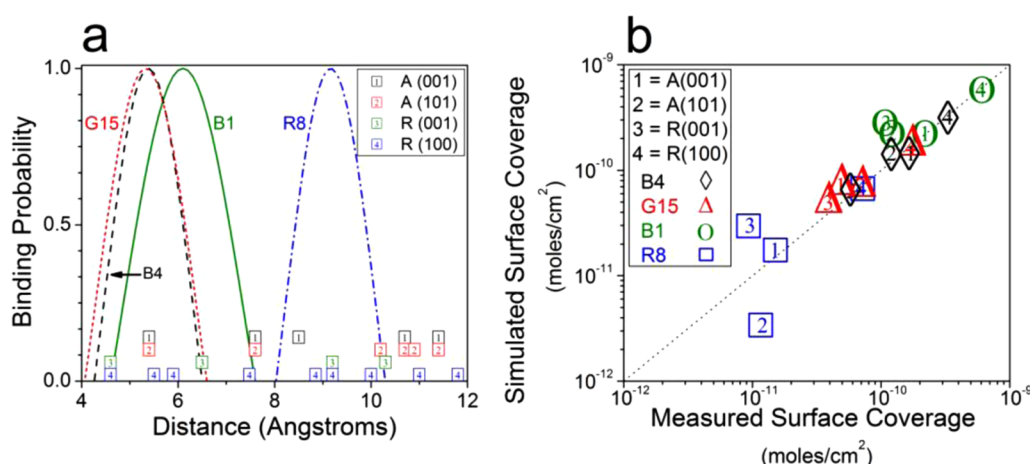


Figure 6. (a) Simulation of binding probability of all four dyes on four crystallographic faces of TiO₂. The approximately parabolic intramolecular carboxyl-carboxyl distance curves for G15 (red dot), B1 (green solid), B4 (black dash) and R8 (blue dash dot) are shown. The distances between the five-coordinate Ti sites on the TiO₂ single-crystal surfaces used to simulate surface compatibility are shown for anatase (001) (1 in black square), anatase (101) (2 in red square), rutile (001) (3 in green square), and rutile (100) (4 in blue square). (b) Plot of the simulated surface coverage (mol/cm²) for the various cyanine dyes vs the measured surface coverage (mol/cm²).

were 8.5 ± 2 Å for B1, 8.5 ± 1 Å for B4 and G15, and 10.5 ± 1 Å for R8. Figure 5 shows the possible bidentate binding distances on the four crystal surfaces that are close to the distance between the two carboxylate groups on the dyes used in this study.

This simple “lattice matching” model provides a quantitative way to compare the intramolecular carboxyl-carboxyl distance of the cyanine dye with the distance between any pair of five-coordinate Ti atoms at the TiO₂ surface that act as possible bidentate binding sites. In the simulation one carboxyl group of the dicarboxylated cyanine dye was fixed on a five-coordinate Ti site at a distance defined as zero, while the location of the second carboxyl group was allowed to rotate and sample possible five-coordinate Ti binding sites across the TiO₂ surface. The dicarboxylated cyanine dyes are not expected to be completely rigid, therefore the model used to simulate the intramolecular carboxyl-carboxyl distance accounted for flexibility due to rotations about bonds mostly in the alkyl chains attached to the carboxylate binding groups. The model treats molecular bonds as simple springs and employs an approximately parabolic probability of the intramolecular carboxyl-carboxyl separation distance varying from the equilibrium length.

The binding probability is highest for the dicarboxylated cyanine dye when the approximately parabolic intermolecular carboxyl-carboxyl distance matches a Ti–Ti crystallographic distance, Figure 6a. The numerical value of the approximately parabolic probability curve evaluated at the Ti–Ti crystallographic distance is the probability of the dicarboxylated cyanine dye binding that specific location. The binding probability to any one Ti–Ti distance was a number between zero and one. On any TiO₂ surface there are many possible Ti–Ti crystallographic sites to which the flexible dicarboxylated cyanine dye could bind, therefore the numerical value of the approximately parabolic probability curve was evaluated at every possible Ti–Ti crystallographic distance and added to calculate the summed binding probability for each dye on each TiO₂ crystal face. In the simulation the summed binding probability was a number between 0 and 2.3 for the dyes studied (SI Figure S3). The summed binding probability was highest when many crystallographic Ti–Ti binding distances corresponded to the maximum dye binding probability distance. The summed dimensionless binding probability value was converted to the simulated surface coverage value by multiplying by a normalization constant. The normalization constant was chosen such that the simulated surface coverage

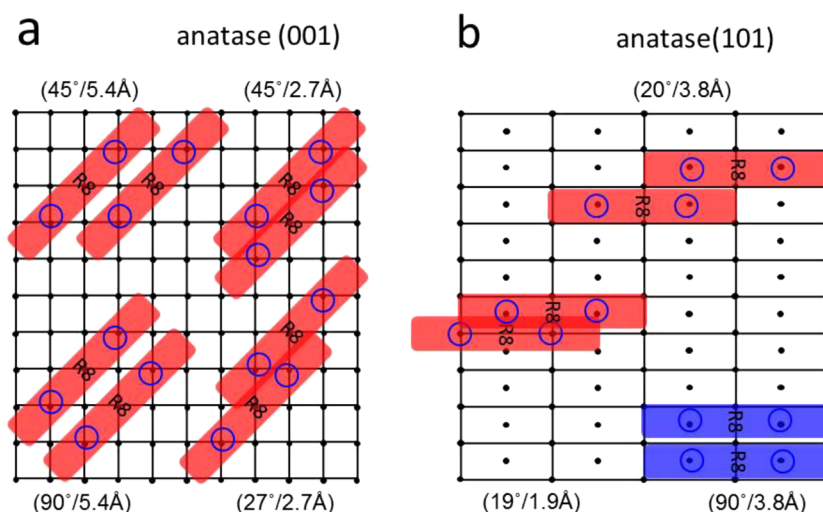


Figure 7. Possible surface bound confirmations for R8 on (a) anatase (001) and (b) anatase (101) that fall within the approximately parabolic binding probability curve shown in Figure 6a. The grids show surface unit cells for the crystallographic face with the dots corresponding to Ti binding sites. The long rectangles represent R8 dye molecules, the two circles within the rectangle represent the approximate location of the two carboxylate binding groups. R8 molecules bind to the TiO_2 surface as monomers (red rectangles) or H-aggregates (blue rectangles). The surface bound R8 dyes form H-aggregates with neighboring molecules only if they meet the geometric requirements: $>55^\circ$ slip angle and approximate spacing of 3.6 Å. Blue rectangles represent R8 molecules that meet or the geometric requirements for H-aggregate formation. The parentheses contain the slip angle and intermolecular distance between neighboring R8 molecules.

equaled the experimentally measured surface coverage for the TiO_2 crystallographic face with the highest summed binding probability. The crystal face with the highest summed binding probability was rutile (100) for all dyes studied. The simulated surface coverage for each dicarboxylated cyanine dye was calculated on each TiO_2 crystallographic face and compared with the measured surface coverage, Figure 6b.

In the simulation the average distance and width of the approximately parabolic intramolecular carboxyl-carboxyl distance curves were allowed to float until the simulated surface compatibility most closely matched the experimentally measured surface coverage; the best agreement between the measured surface coverage and the simulated surface coverage was achieved with the parameters shown in SI Table S2. The trend in the simulated values agrees well with the molecular modeling simulations of the intramolecular carboxyl-carboxyl distance.

The “lattice matching” model correctly simulates the measured surface coverage of any one dye on each of the TiO_2 crystallographic faces; however the model does not accurately predict the surface coverage of different dyes relative to each other on any one TiO_2 crystallographic face.

Rutile (100) showed the highest surface coverage both experimentally and in the “lattice matching” model for all dyes, presumably because the rutile (100) surface has the most five-coordinate Ti sites separated by a distance that is similar to the intramolecular carboxyl-carboxyl distance of the dicarboxylated cyanine dyes used in this study (Figure 6a). By the same logic the rutile (001) almost always showed the lowest coverage because it has the fewest matching Ti sites.

For the R8 dye the lowest surface coverage is expected for the anatase (101) surface where only one Ti-Ti crystallographic distance falls under the simulated approximately parabolic intermolecular carboxyl-carboxyl dye stretching distance. Additionally this Ti-Ti crystallographic distance is not located near the equilibrium carboxyl-carboxyl distance for the R8 dyes. The highest surface coverage for R8 is expected on

the rutile (100) surface where three lattice distances all fall within the simulated dye carboxyl-carboxyl stretching distance. For the other dyes on the four surfaces, the results were also in agreement with the expectation based on the analysis described above.

The simple “lattice matching” model did not accurately predict the surface coverage of different dyes relative to each other on any one TiO_2 crystallographic face. The simulation predicts that the longer dye (R8) should have a slightly larger total surface coverage in comparison to most of the shorter dyes due to the higher number of surface sites that the longer dyes can sample and potentially bind to. We attribute the lower overall experimentally measured surface coverage of the longer dye to the ability of the R8 dye to bridge across and block five-coordinate sites, thus rendering those sites unusable for other dyes, a factor not accounted for in our simple model. The shorter dyes, on the other hand, would not bridge across and block as many possible binding sites, and thus not impede the binding of additional dyes. It is also interesting that the B1 dye, expected to have the most flexibility due to its additional methylene spacer in the anchoring group, had the highest experimentally measured surface coverage on all four surfaces.

We also investigated the relationship between the monomer to H-aggregate ratio observed in the IPCE spectrum and geometry of neighboring dyes on the TiO_2 surface. In Figure 7, we show several models for R8 dye aggregates on anatase (001), where 93% monomers are observed, and anatase (101), where only 53% monomer is observed in the IPCE spectra (see Table 2). The models take into account the 3.6 Å “face-to-face” packing distance of the cyanine dye molecules, obtained from the crystal structure of a similar cyanine dye,^{22,29,30} and the “slippage angle” of $>55^\circ$ required for H-aggregates.¹³

The “lattice matching model” indicates that on the anatase (101) H-aggregate formation is possible for the R8 dye, whereas on the anatase (001) surface the R8 dyes are too far apart or have too small of a slip angle for H-aggregate formation (the models for R8 on rutile (001) and (100) shown

Table 2. Monomer Percentage in Photocurrent Spectra at the Saturation Taken from the Fitting for Peak Area

dye	anatase(001)	anatase(101)	rutile(001)	rutile (100)
B1	65%	55%	57%	58%
B4	74%	59%	80%	73%
G15	68%	40%	59%	75%
R8	93%	53%	76%	96%

in SI Figure S4). This model does not account for the possibility that dyes may bind in a monodentate fashion and are stabilized on the surface via H-aggregation.

Having measured both dye coverages and the IPCE values, we can calculate absorbed photon to current efficiency (APCE) values for the dicarboxylated cyanine dyes on the four crystallographic faces of TiO₂. The APCE is important both for constructing dye sensitized solar cells and for understanding the fundamentals of charge transfer between the excited dye and the semiconductor substrate. The APCE is related to the light harvesting efficiency (LHE) and IPCE, and can be calculated as follows:

$$\text{abs}(\lambda) = \varepsilon(\lambda)\Gamma \quad (1)$$

$$\text{LHE} = 1 - 10^{-\text{abs}(\lambda)} \quad (2)$$

$$\text{APCE} = \text{IPCE}/\text{LHE} \quad (3)$$

where $\varepsilon(\lambda)$ is the extinction coefficient of the dye and Γ is the dye coverage on the surface of semiconductors. The extinction coefficient for the H-aggregate was obtained from the simulations of the temperature dependent absorption spectra in Figure 2. The IPCE values were obtained from the photocurrent measurements in Figures 3 and 4. The total dye coverage (Γ_{total}) was calculated from the photochromocoulometric measurements described above. The total dye coverage was taken to be the sum of the monomer and H-aggregate contributions:

$$\Gamma_{\text{M}} + \Gamma_{\text{H}} = \Gamma_{\text{total}} \quad (4)$$

where Γ_{M} and Γ_{H} represent the surface coverage of the dye monomers and dye H-aggregates respectively. The total dye surface coverage is known. However under these experimental conditions there is no direct measurement of the sensitized surface absorbance spectrum, and therefore no direct measurement of the dye monomer and dye H-aggregate contributions to the total surface coverage. If the APCE values for the dye monomer and H-aggregate are assumed to be equal, then the IPCE spectra reports directly on the abundance of monomers and H-aggregates at the sensitized TiO₂ surface. Equations 1–4 were combined to give an expression of the total surface coverage as a function of the measured IPCE values.

$$\begin{aligned} & -\frac{1}{\varepsilon_{\text{M}}(\lambda)} \log_{10} \left(1 - \frac{\text{IPCE}_{\text{M}}(\lambda)}{\text{APCE}(\lambda)} \right) \\ & - \frac{1}{\varepsilon_{\text{H}}(\lambda)} \log_{10} \left(1 - \frac{\text{IPCE}_{\text{H}}(\lambda)}{\text{APCE}(\lambda)} \right) \\ & = \Gamma_{\text{total}} \end{aligned} \quad (5)$$

The APCE values were obtained using Newton's method with the Matlab program. The trend of the APCE values (Table 3) differed from the trend in total surface coverage observed for dicarboxylated cyanine dyes sensitizing the four crystallographic faces of TiO₂.

Table 3. APCE Values for the Highest Dye Coverages on the Four Crystal Surfaces

	anatase (001)	anatase (101)	rutile (001)	rutile (100)
B1	4.6%	9.7%	16%	11%
B4	18%	23%	37%	31%
G15	37%	52%	58%	52%
R8	15%	43%	26%	11%

APCE values of near 100% are expected for dyes covalently bound to the surface with strong electronic coupling to the semiconductor. There are several possible factors that affect the difference between the two trends. First, the assumption of equal APCE values for the dye monomer and H-aggregates may not be true especially for the larger H-aggregates that may be present on the surface. Second it is known that the doping density of the crystal influences the electric field gradient at the surface and this can affect the APCE if the doping density is too low.³¹ Third, inaccurate measurement of the total dye surface coverage due to the assumption that only one electron is involved in the photooxidation of the dye. A subsequent current doubling effect from an additional electron injection from a dye radical would result in a reduction by one-half of the amount of dye calculated to be present, thus doubling the APCE values in Table 3. The result would be APCE values near 100% for four dye/crystal face combinations. The origin of the unexpectedly low APCE values is currently under study for our lab. Specifically attenuated total reflectance (ATR) studies will allow the simultaneous measurement of photocurrent and absorbance spectra for the dyes on the semiconductor surface providing a direct measurement of APCE values for dye monomers aggregates and dye oxidation products.

CONCLUSIONS

We have studied the sensitization of four different TiO₂ single-crystal surfaces with a series of four dicarboxylated cyanine dyes. Direct measurement of the incident photon to current efficiencies (IPCE) spectra, adsorption isotherms, and saturated surface coverages are reported. The IPCE spectra indicated that both the monomer and H-aggregated form of the dyes were capable of generating photocurrent. The relative abundance of dye monomers and H-aggregates was found to be strongly dependent on the crystallographic face used as the substrate for sensitization. Simulations of the IPCE spectra were used to quantify the dye monomer/H-aggregate ratios.

The sensitization of TiO₂ single crystal substrates with dicarboxylated cyanine dyes has provided insight into preferential binding of bidentate sensitizers to specific surfaces of TiO₂. A simple model was developed to predict the compatibility of bidentate binding sensitizers for any semiconductor crystallographic face and thus explain the observed trends in dye surface coverage. In addition to dye binding, the propensity of cyanine dyes to form H-aggregates with neighboring dyes was also rationalized using simple geometric arguments. Structural models for H-aggregate on the surface were proposed.

ASSOCIATED CONTENT

Supporting Information

Additional information as noted in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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