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Impact of the molecular structure and adsorption mode of D- π -A dye sensitizers with a pyridyl group in dye-sensitized solar cells on the adsorption equilibrium constant for dye-adsorption on TiO₂ surface

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D- π -A dyes **NI-4** bearing a pyridyl group, **YNI-1** bearing two pyridyl groups and **YNI-2** bearing two thienylpyridyl groups as the anchoring group on the TiO₂ surface have been developed as dye sensitizers for dye-sensitized solar cells (DSSCs), where **NI-4** and **YNI-2** can adsorb onto the TiO₂ electrode through the formation of the coordinate bond between the pyridyl group of the dye and the Lewis acid site (exposed Tiⁿ⁺ cations) on the TiO₂ surface, but **YNI-1** is predominantly adsorbed on the TiO₂ electrode through the formation of the hydrogen bond between the pyridyl group of the dye and the Brønsted acid sites (surface-bound hydroxyl groups, Ti-OH) on the TiO₂ surface. The difference in the dye-adsorption mode among the three dyes on the TiO₂ surface has been investigated from the adsorption equilibrium constant (K_{ad}) based on the Langmuir adsorption isotherms. It was found that the K_{ad} values of **YNI-1** and **YNI-2** are higher than that of **NI-4**, and more interestingly, the K_{ad} value of **YNI-2** is higher than that of **YNI-1**. This work demonstrates that for the D- π -A dye sensitizers with the pyridyl group as the anchoring group to the TiO₂ surface the number of pyridyl groups and the dye-adsorption mode on the TiO₂ electrode as well as the molecular structure of the dye sensitizer affect the K_{ad} value for the adsorption of the dye to the TiO₂ electrode, that is, resulting in a difference in the K_{ad} value among the D- π -A dye sensitizers **NI-4**, **YNI-1** and **YNI-2**.

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Introduction

Twenty-five years have passed since Grätzel and co-workers developed high-performance dye-sensitized solar cells (DSSCs) employing a Ru-complex dye-adsorbed TiO₂ electrode in 1991,¹ but DSSCs are still receiving considerable attention as one of the most promising new renewable photovoltaic cells from chemists, physicists, and engineers.²⁻⁹ To further improve the photovoltaic performances of DSSCs, much effort has been made toward the development of various types of organic dye sensitizers bearing a carboxyl group,¹⁰⁻¹⁶ aldehyde,^{17,18} nitro group,¹⁹ 2-(1,1-dicyanomethylene)rhodanine,²⁰ pyridine,²¹⁻²⁴ or 8-hydroxyquinoline²⁵ as the electron-withdrawing anchoring group that possesses high dye loading and high surface coverage of the TiO₂ electrode, leading to good light-harvesting features over the wide spectral region of sunlight and high electron-injection efficiencies from the photoexcited dyes to the conduction

band (CB) of the TiO₂ electrode. In particular, many kinds of donor-acceptor π -conjugated (D- π -A) dyes bearing a carboxyl group have been designed and developed as one of the most promising classes of organic dye sensitizers because of their strong photoabsorption properties originating from the intramolecular charge transfer (ICT) excitation from the donor to the acceptor (carboxyl group) moiety in the D- π -A structures.^{3,4,6} The D- π -A dye sensitizers bearing a carboxyl group are adsorbed on the TiO₂ electrode through the bidentate bridging linkage between the carboxyl group of the dye and Brønsted acid sites (surface-bound hydroxyl groups, Ti-OH) on the TiO₂ surface (Fig. 1a and 2a; **NI-2**^{1b} as a typical D- π -A dye sensitizer bearing a carboxyl group). Thus, the photoabsorption properties associated with the ICT excitation of the D- π -A dye can lead to efficient electron transfer from the photoexcited dye through the carboxyl group to the CB of the TiO₂ electrode. As the result, the DSSCs based on the D- π -A porphyrin dye sensitizers bearing a carboxyl group have achieved a solar energy-to-electricity conversion yield (η) of up to 13%.^{11c,d}

On the other hand, we have designed and developed D- π -A dye sensitizers bearing a pyridyl group as the anchoring group

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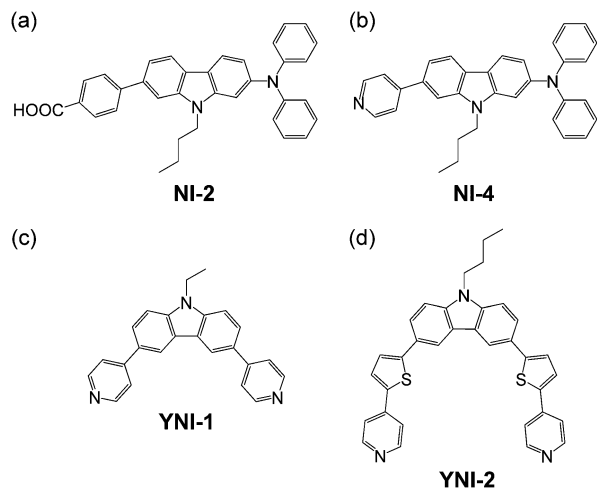


Fig. 1 Chemical structures of D- π -A dye sensitizers: (a) **NI-2** bearing a carboxyl group, (b) **NI-4** bearing a pyridyl group, (c) **YNI-1** bearing two pyridyl groups and (d) **YNI-2** bearing two thienylpyridyl groups.

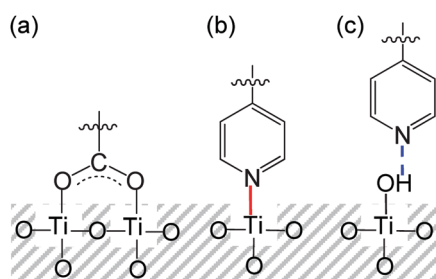


Fig. 2 Possible binding modes of the carboxyl group and pyridyl group on the TiO₂ surface. (a) A bidentate bridging linkage for the carboxyl group, (b) a coordination bond for the pyridyl group and (c) a hydrogen bond for the pyridyl group.

to the TiO₂ surface so far.²¹ It was found that the D- π -A dye sensitizer **NI-4** bearing a pyridyl group is predominantly adsorbed on the TiO₂ electrode through the coordination bond between the pyridyl group of the dye and the Lewis acid site (exposed Ti^{IV} cations) on the TiO₂ surface (Fig. 1b and 2b).^{21b,c} The difference in the dye-adsorption mode between **NI-2** and **NI-4** on the TiO₂ surface has been investigated from the Langmuir adsorption isotherms, and analysis of the Langmuir plots showed that the saturated dye-adsorption amounts (C_0) of **NI-2** and **NI-4** on the TiO₂ electrode are similar to each other. On the other hand, the adsorption equilibrium constant (K_{ad}) of **NI-4** is smaller than that of **NI-2**, that is, the fact indicates that the pyridyl group is a relatively weak anchoring ability to the TiO₂ surface compared with the carboxyl group.^{22a} Interestingly, the photovoltaic performance of DSSCs based on **NI-4** is higher than that based on **NI-2**. Thus, it was revealed that the D- π -A dye sensitizers bearing a pyridyl group can inject electrons efficiently from the pyridyl group to the CB of the TiO₂ electrode through the coordination bond, compared to the bidentate bridging linkages of the D- π -A dye sensitizers bearing a carboxyl group. Consequently, we demonstrated that the pyridyl group is a promising candidate as not only an electron-withdrawing

anchoring group but also an electron-injecting group for D- π -A dye sensitizers. More interestingly, we found that the D- π -A dye sensitizer **YNI-2** with two thienylpyridyl groups can adsorb onto the TiO₂ electrode through the formation of the coordinate bond between the pyridyl group of the dye and the Lewis acid site on the TiO₂ surface (Fig. 1d and 2b), but the D- π -A dye sensitizer **YNI-1** with two pyridyl groups is predominantly adsorbed on the TiO₂ electrode through the formation of the hydrogen bond between the pyridyl group of the dye and the Brønsted acid sites on the TiO₂ surface (Fig. 1c and 2c).^{21d} The photovoltaic performance of DSSCs based on **YNI-2** is higher than that based on **YNI-1**. Consequently, our previous work demonstrated that the higher photovoltaic performance of **YNI-2** is attributed to not only the red-shift and broadening of the photoabsorption band originating from the ICT and the stable oxidized state of the dye, but also to efficient electron injection by the formation of the coordinate bond at Lewis acid sites on the TiO₂ surface. Recently, some researchers have reported high-performance DSSCs based on porphyrin dyes or D- π -A dyes bearing pyridyl groups;^{22–24} as a result, the η value reached up to 8.2%.^{24e} However, a comprehensive understanding of the difference in the dye-adsorption modes among the dye sensitizers bearing the pyridyl group is still lacking.

Thus, in this work, to gain insight into the molecular structure and the adsorption mode of D- π -A dye sensitizers with a pyridyl group on the TiO₂ surface, the difference in the dye-adsorption mode among **NI-4**, **YNI-1** and **YNI-2** on the TiO₂ surface has been investigated from the K_{ad} value based on the Langmuir adsorption isotherms. The Langmuir plots showed that the C_0 value of **NI-4** on the TiO₂ electrode is slightly larger than those of **YNI-1** and **YNI-2**, but the C_0 values of **YNI-1** and **YNI-2** are similar to each other. Moreover, it was found that the K_{ad} values of **YNI-1** and **YNI-2** are higher than that of **NI-4**, and more interestingly, the K_{ad} value of **YNI-2** is higher than that of **YNI-1**. Here, we report that the impacts of the molecular structure and adsorption mode of D- π -A dye sensitizers with a pyridyl group for DSSCs on the adsorption equilibrium constant for dye-adsorption to the TiO₂ surface.

Results and discussion

A 9 μm (1.5 cm^2) thick TiO₂ electrode was immersed into THF solutions containing various concentrations (0.02, 0.04, 0.06, 0.08, 0.1, 0.2, 0.5, 1.0 or 1.0 mM) of **NI-4**, **YNI-1** or **YNI-2** for dye-adsorption on the TiO₂ surface. In all cases, dye-adsorption was performed for 24 h in an incubator kept at 25 °C. The dye-adsorbed TiO₂ electrode was immersed in a 1 M THF-DMSO-NaOH aq. mixed solvent (5:4:1) to desorb the dye molecules, that is, the adsorption amount of **NI-4**, **YNI-1** and **YNI-2** was determined by recording the photoabsorption spectra of the solutions on a spectrophotometer. Consequently, the amount (C_{ad}) of dyes adsorbed on the TiO₂ electrode is expressed by the number of dye molecules per unit area of the TiO₂ surface calculated using a specific surface area of 830 $\text{cm}^2 \text{mg}^{-1}$. The C_{ad}^{-1} versus $[\text{Dye}]^{-1}$ (the concentration of the dye solution) plots



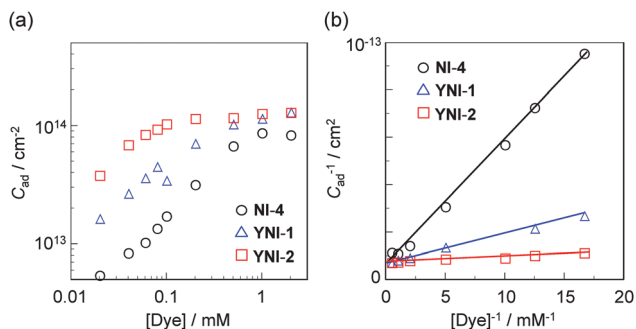


Fig. 3 (a) Adsorption isotherms of **NI-4**, **YNI-1** and **YNI-2** on the TiO_2 electrode. (b) Double-reciprocal Langmuir plots of the data shown in (a). Best fitting lines were obtained from the linear-least-squares method.

in the double-logarithmic representation depicts the adsorption isotherms for **NI-4**, **YNI-1** and **YNI-2** adsorbed on the TiO_2 surface (Fig. 3a). The adsorption isotherms showed that for the three dyes the adsorption amount of dye molecules adsorbed on the TiO_2 electrode increased with the increasing concentration of the dye solution. However, it is seen clearly from the adsorption isotherms that the adsorption trends of the three dyes differ greatly from each other, reflecting the differences in the molecular structure and the adsorption mode among **NI-4**, **YNI-1** and **YNI-2**. Thus, to investigate the difference in the adsorption trends among the three dyes from the Langmuir plots, the three adsorption isotherms were analyzed by using the following equation:

$$C_{\text{ad}}^{-1} = (K_{\text{ad}}C_0)^{-1}[\text{Dye}]^{-1} + C_0^{-1} \quad (1)$$

derived from a Langmuir isotherm:²⁶

$$C_{\text{ad}}/C_0 = K_{\text{ad}}[\text{Dye}]/(1 + K_{\text{ad}}[\text{Dye}]) \quad (2)$$

where C_{ad} , C_0 , K_{ad} , and $[\text{Dye}]$ denote the adsorption amount of dye, adsorption amount of dye at saturation, adsorption equilibrium constant, and equilibrium concentration of dye, respectively. Fig. 3b (C_{ad}^{-1} versus $[\text{Dye}]^{-1}$ plots) represents the Langmuir plots obtained from the data of Fig. 3a for **NI-4**, **YNI-1** and **YNI-2**. The plots fit straight lines very well, demonstrating that adsorption of the three dyes on the TiO_2 surface follows a Langmuir isotherm. The Langmuir isotherm holds when the following conditions are valid: monolayer adsorption, equivalent adsorption site, and negligible interaction between the adsorbed molecules. Thus, the C_0 and K_{ad} values were obtained by the linear least squares method as $1.7 \times 10^{14} \text{ cm}^{-2}$ and $1.1 \times 10^3 \text{ M}^{-1}$ for **NI-4**, $1.4 \times 10^{14} \text{ cm}^{-2}$ and $6.1 \times 10^3 \text{ M}^{-1}$ for **YNI-1**, and $1.3 \times 10^{14} \text{ cm}^{-2}$ and $33.1 \times 10^3 \text{ M}^{-1}$ for **YNI-2**, respectively. The adsorption parameters of the three dyes from the Langmuir isotherms are summarized in Table 1, together with correlation coefficients (R) in the linear regression analysis. It was found that the C_0 value of **NI-4** on the TiO_2 electrode is slightly larger than those of **YNI-1** and **YNI-2**, but the K_{ad} values of **YNI-1** and **YNI-2** are higher than that of **NI-4**. This result indicates that a rod-shaped D- π -A dye sensitizer with a pyridyl group such as **NI-4** can effectively cover the TiO_2 surface compared with relatively bulky bifurcation-shaped D- π -A dye sensitizers with

Table 1 Adsorption parameters of **NI-4**, **YNI-1** and **YNI-2** obtained from Langmuir isotherms

Dye	C_0/cm^{-2}	$K_{\text{ad}}/\text{M}^{-1}$	R^a
NI-4	1.7×10^{14}	1.1×10^3	0.9969
YNI-1	1.4×10^{14}	6.1×10^3	0.9980
YNI-2	1.3×10^{14}	33.1×10^3	0.9653

^a R denotes a correlation coefficient.

two pyridyl groups such as **YNI-1** and **YNI-2**, on the other hand, the bifurcation-shaped structure with the two pyridyl groups can strongly adsorb on the TiO_2 surface compared with the rod-shaped D- π -A structure with a pyridyl group. Moreover, it is worth noting here that the C_0 values of **YNI-1** and **YNI-2** are similar to each other, but the K_{ad} value of **YNI-2** is higher than that of **YNI-1**. Thus, these results indicate that the adsorption ability of **YNI-2** onto the TiO_2 surface is superior to that of **YNI-1**. The fact may be attributed to the difference in binding modes between the two dyes on the TiO_2 electrode.

Therefore, to gain insight into the impact of the molecular structure and the adsorption mode of D- π -A dye sensitizers with a pyridyl group on the adsorption equilibrium constant for dye-adsorption to the TiO_2 surface, we evaluated the photovoltaic performance of DSSCs based on the co-adsorbed TiO_2 electrode with the dye **YNI-1** or **YNI-2** and chenodeoxycholic acid (CDCA) capable of adsorbing at the Brønsted acid sites on the TiO_2 electrode. For co-adsorption the concentration of CDCA was changed, with that of **YNI-1** or **YNI-2** kept constant at 0.1 mM, where 0.1 mM dye and 1.0 mM CDCA solution, and 0.1 mM dye and 5.0 mM CDCA solution were used. The photocurrent-voltage (I - V) characteristics of DSSCs based on the co-adsorbed TiO_2 electrode with the dye **YNI-1** or **YNI-2** and CDCA were measured under simulated solar light (AM 1.5, 100 mW cm^{-2}) and the I - V curves are shown in Fig. 4. The photovoltaic performances of the DSSCs are summarized in Table 2. We expected that for the co-adsorption of **YNI-1** and CDCA the adsorption of **YNI-1** onto the TiO_2 electrode may compete with that of CDCA because **YNI-1** and CDCA adsorb on the same acid sites (Brønsted acid sites), leading to a decrease in the short-circuit photocurrent density (J_{sc}) and the solar energy-to-electricity conversion yield (η) with the increase in the concentration of CDCA. On the other hand, **YNI-2** and

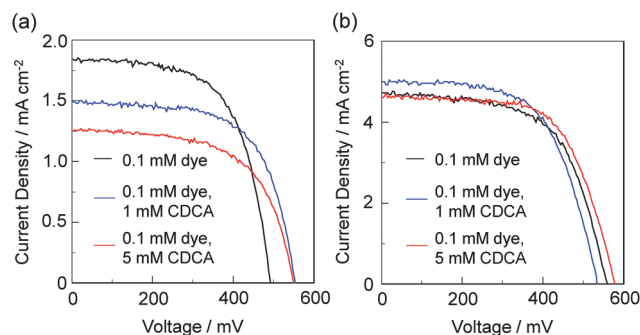


Fig. 4 I - V curves of DSSCs based on (a) **YNI-1** and (b) **YNI-2** with and without CDCA as a co-adsorbent.



Table 2 DSSC performance parameters of **YNI-1** and **YNI-2**

Dye	CDCA/mM	J_{sc}^d /mA cm ⁻²	V_{oc}^d /mV	ff ^d	η^d (%)
YNI-1	0 ^a	1.84	492	0.63	0.57
	1 ^b	1.49	552	0.51	0.42
	5 ^c	1.25	548	0.61	0.42
YNI-2	0 ^a	4.72	556	0.61	1.60
	1 ^b	5.00	532	0.60	1.60
	5 ^c	4.60	576	0.65	1.72

^a A 9 μ m thick TiO₂ electrode was used. 0.1 mM dye solution in acetonitrile. ^b A 9 μ m thick TiO₂ electrode was used. 0.1 mM dye and 1 mM CDCA solution. ^c A 9 μ m thick TiO₂ electrode was used. 0.1 mM dye and 5 mM CDCA solution. ^d Under simulated solar light (AM 1.5, 100 mW cm⁻²).

CDCA adsorb independently on the TiO₂ surface because **YNI-2** and CDCA adsorb at different acid sites, the Lewis acid sites and Brønsted acid sites on the TiO₂ surface, respectively, and thus regardless of the concentration of CDCA the co-adsorption of **YNI-2** and CDCA has little influence on the J_{sc} value and the η value. As is shown in Table 2, for the co-adsorption of **YNI-1** and CDCA, with the increase in the concentration of CDCA, the η value as well as the J_{sc} value of DSSCs based on the co-adsorbed TiO₂ electrode with **YNI-1** and CDCA decreases. Therefore, the adsorption of **YNI-1** onto the TiO₂ surface may compete with that of CDCA, that is, by increasing the concentration of CDCA the adsorption amount of **YNI-1** may decrease, being accompanied by an increase in that of CDCA. This may be explained by the fact that **YNI-1** and CDCA adsorb on the same acid sites (Brønsted acid sites), and thus the increase in the concentration of CDCA leads to a decrease in the adsorption amount of **YNI-1** by the competitive adsorption of CDCA. On the other hand, for the co-adsorption of **YNI-2** and CDCA there are no appreciable changes in the J_{sc} value and the η value with the increase in the concentration of CDCA, suggesting that **YNI-2** and CDCA adsorb independently on the TiO₂ surface because **YNI-2** and CDCA adsorb on different acid sites (Lewis acid sites for **YNI-2** and Brønsted acid sites for CDCA, respectively). Therefore, the increase in the concentration of CDCA does not cause a decrease in the adsorption amount of **YNI-2** without the competitive adsorption of CDCA, consistent with our previous result for **NI-4**.^{22a} Consequently, these results indicate that the co-adsorption of **YNI-1** and CDCA causes the competitive adsorption between the dye and CDCA, leading to a decrease in the amount of the dye adsorbed on the TiO₂ electrode, thus resulting in a reduction of the photovoltaic performance of the DSSCs, but for the co-adsorption of **YNI-2** and CDCA the competitive adsorption was not observed and thus the co-adsorption has little influence on the photovoltaic performance of the DSSCs.

On the basis of the Langmuir isotherms and the co-adsorption of the dye **YNI-1** or **YNI-2** and CDCA onto the TiO₂ electrode, it is concluded that the high K_{ad} value of **YNI-2** relative to that of **YNI-1** is attributed to the reasonable angle between two thienylpyridine moieties (based on MO calculations (MOPAC and AM1 method),^{21c,d} it is defined as the angle between the two pyridines as the corner N2 for the nitrogen atom (N2) of carbazole and the nitrogen atoms (N1 and N3) of the two pyridyl groups, that is *ca.* 90° for **YNI-1** and *ca.* 67° for **YNI-2**) as well as the accumulated

electron density on the nitrogen atom of the pyridyl groups due to a large planar π -conjugated system extending from the electron donor moiety to the electron acceptor moiety by the introduction of a thiophene unit, leading to the construction of molecular structures capable of forming strong coordinate bonds between the two pyridyl groups of dyes and the Lewis acid sites on the TiO₂ surface. On the other hand, **YNI-1** is constructed with the rigid D- π -A structure due to the pyridyl groups directly bound to the carbazole skeleton. Therefore, it is reasonable to presume that the rigid molecular structure of **YNI-1** makes it difficult to form the coordination bond between the pyridyl group of the dye and the Lewis acid site on the TiO₂ surface, but instead prefers to form the hydrogen bond between the pyridyl group of the dye and the flexible surface-bound hydroxyl groups (Brønsted acid sites) on the TiO₂ surface, resulting in a relatively low K_{ad} value. Consequently, this work demonstrates that for the D- π -A dye sensitizers with the pyridyl group as the anchoring group to the TiO₂ surface, the number of pyridyl groups and the dye-adsorption mode on the TiO₂ electrode as well as the molecular structure of the dye sensitizer affect the K_{ad} value for the adsorption of the dye to the TiO₂ electrode, that is, resulting in a difference in the K_{ad} value among the D- π -A dye sensitizers **NI-4**, **YNI-1** and **YNI-2**.

Conclusions

The difference in the dye-adsorption modes among D- π -A dye sensitizers **NI-4** with a pyridyl group, **YNI-1** with two pyridyl groups and **YNI-2** with two thienylpyridyl groups on the TiO₂ electrode has been investigated from the adsorption equilibrium constant (K_{ad}) based on the Langmuir adsorption isotherms. It was found that a rod-shaped D- π -A dye sensitizer with a pyridyl group such as **NI-4** can effectively cover the TiO₂ surface compared with relatively bulky bifurcation-shaped D- π -A dye sensitizer with two pyridyl groups such as **YNI-1** and **YNI-2**; on the other hand, the bifurcation-shaped structure with the two pyridyl groups can strongly adsorb on the TiO₂ surface compared with the rod-shaped D- π -A structure with a pyridyl group. More interestingly, the K_{ad} value of **YNI-2** is higher than that of **YNI-1**, which indicates that the adsorption ability of **YNI-2** onto the TiO₂ surface is superior to that of **YNI-1**. Thus, it was revealed that the number of pyridyl groups and the dye-adsorption mode on the TiO₂ electrode as well as the molecular structure of the dye sensitizer affect the K_{ad} value for the adsorption of the dye to the TiO₂ electrode, resulting in a difference in the K_{ad} value among the D- π -A dye sensitizers **NI-4**, **YNI-1** and **YNI-2**. Consequently, this work provides useful knowledge of the molecular design of D- π -A dye sensitizers bearing a pyridyl group capable of controlling the dye-adsorption mode on the TiO₂ electrode for DSSCs.

Experimental

Preparation of the dye-adsorbed TiO₂ electrode and DSSCs

The TiO₂ paste (JGC Catalysts and Chemicals Ltd, PST-18NR) was deposited on a fluorine-doped-tin-oxide (FTO) substrate by



doctor-blading, and sintered for 50 min at 450 °C. The 9 μm (1.5 cm²) thick TiO₂ electrode was immersed into 0.02, 0.04, 0.06, 0.08, 0.1, 0.2, 0.5, 1.0 or 1.0 mM dye solution in THF for 24 h in an incubator kept at 25 °C. For the co-adsorption of the dye and chenodeoxycholic acid (CDCA), 0.1 mM dye and 1.0 mM CDCA solution, and 0.1 mM dye and 5.0 mM CDCA solution were used. BET surface areas of the TiO₂ particles were 830 cm² mg⁻¹. Consequently, the total area for 1 cm² geometric area of the electrode was ca. 1577 cm² for 9 μm thick TiO₂ electrode. The dye-coated electrode was immersed in a mixed solvent of THF–DMSO–NaOH aq. 1 M (5 : 4 : 1), which was used to determine the amount of dye molecules adsorbed onto the electrode by measuring the absorbance. The quantification of dye was made based on the molar extinction coefficient for λ_{max}^{abs} of dye in the above solution. Photoabsorption spectra were observed with a Shimadzu UV-3150 spectrophotometer.

The DSSCs were fabricated by using the dye-adsorbed TiO₂ electrode (0.5 × 0.5 cm² in photoactive area), Pt-coated glass as a counter electrode, and a solution of 0.05 M iodine, 0.1 M lithium iodide, and 0.6 M 1,2-dimethyl-3-propylimidazolium iodide in acetonitrile as the electrolyte. The photocurrent–voltage characteristics were measured using a potentiostat under a simulated solar light (AM 1.5, 100 mW cm⁻²).

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