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Enhanced Light-Harvesting Capability of a Panchromatic Ru(II) Sensitizer Based on π -Extended Terpyridine with a 4-Methylstyryl Group for Dye-Sensitized Solar Cells

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A novel Ru π -expanded terpyridyl sensitizer, referred to as HIS-2, is prepared based on the molecular design strategy of substitution with a moderately electron-donating 4-methylstyryl group onto the terpyridyl ligand. The HIS-2 dye exhibits a slightly increased metal-to-ligand charge transfer (MLCT) absorption at around 600 nm and an intense π - π * absorption in the UV region compared with a black dye. Density functional theory calculations reveal that the lowest unoccupied molecular orbital (LUMO) is distributed over the terpyridine and 4-methylstyryl moieties, which enhances the light-harvesting capability and is appropriate for smooth electron injection from the dye to the TiO₂ conduction band. The incident photon-to-electricity conversion efficiency spectrum of HIS-2 exhibits better photoresponse compared with black dye over the whole spectral region as a result of the extended π -conjugation. A DSC device based on black dye gives a short-circuit current (Jsc) of 21.28 mA cm⁻², open-circuit voltage (V_{OC}) of 0.69 V, and fill factor (FF) of 0.72, in an overall conversion efficiency (η) of 10.5%. In contrast, an HIS-2 based cell gives a higher J_{SC} value of 23.07 mA cm⁻² with V_{OC} of 0.68 V, and FF of 0.71, and owing to the higher J_{SC} value of HIS-2, an improved η value of 11.1% is achieved.

1. Introduction

In the last two decades, dye-sensitized solar cells (DSCs) have attracted increasing attention as promising alternatives to conventional silicon-based solar cells, because of their relatively

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high conversion efficiencies and low production costs. In DSC devices, the sensitizer is one of the key components for achieving higher power conversion efficiency, and therefore, extensive effort has been focused on developing new and superior sensitizers. Among various organic/ inorganic dyes, the most successful charge transfer (CT) sensitizers are those based on Ru polypyridyl complexes such as black dye, (TBA)₃[Ru(NCS)₃(Htctpy)]^[1] (Figure 1) and N719, (TBA)₂[Ru(NCS)₂(Hdcbpy)₂]^[2] (TBA = tetra-*n*-butylammonium, NCS = thiocyanato, tctpy = 4,4',4''-tricarboxyl-2,2':6',2"-terpyridyl, and dcbpy 4,4'-dicarboxyl-2,2'-bipyridyl). DSCs based on Ru polypyridyl complexes have broad light-absorption properties extending into the near-infrared (NIR) region and produce solar-to-electrical energy conversion efficiencies of up to 10% under standard air-mass (AM) 1.5G conditions.^[3] Recently, the best certified conversion efficiency of 11.4% was achieved using with black

dye combined with an organic co-adsorbent;^[4] however, the conversion efficiencies of the DSCs are still insufficient for the practical use. Therefore, the development of superior photosensitizers is being actively and extensively pursued.

The sensitizer molecules for the DSC applications require two inherent photophysical features to achieve high conversion efficiencies. First, a broad and intense absorption is necessary to ensure a good fit to the solar light spectrum in order to produce a large photocurrent response. Second, suitable energy levels of the ground- and excited-state oxidation potentials



Figure 1. Molecular structures of HIS-2 and black dye.

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of the sensitizers, which correspond to the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels, are required to match the iodine/ triiodide redox potential and the conduction band edge level of the TiO₂ semiconductor to ensure efficient charge injection and regeneration of the oxidized dye, respectively.^[5] The HOMO and LUMO energy levels and the band gap of Ru complexes can be finely tuned by exchange and/or substitution of ligands, and furthermore, introduction of π -conjugations into the dye molecules can increase their molar absorption coefficients. For example, many heteroleptic Ru(II) bis(bipyridyl) (NCS)2 complexes bearing various π -conjugations have been prepared.^[6] They are analogue complexes of N719, in which one dcbpy ligand has been exchanged with an ancillary bpy ligand substituted with electron-donating (ED) π -conjugations, such as thiophene, ethylenedioxythiophene, triarylamine, and their combined substituents, in order to improve light-harvesting capabilities in respect to both the molar extinction coefficient and the bathochromic shift of the absorption.

On the other hand, to the best of our knowledge, only few examples of π -expansion of the acceptor tpy ligand on the Ru-tpy complex with comparably high conversion efficiencies to that of black dye have been reported. Recently, new π -expanded black dye analogue sensitizers bearing ED π -conjugations, as well as heteroleptic Ru-bpy dyes, have been reported to have more intense molecular absorption coefficients and bathochromically shifted absorption. They have achieved relatively high conversion efficiencies of approximately 10%,[7] but no such Ru-tpy based dye has exceeded the best conversion efficiency of over 11%. For the Ru-bpy dyes, even when the carboxyl groups of one bpy are substituted with ED groups, another dcbpy can behave as an electron acceptor and anchoring group, and electron injection from the dcbpy can occur efficiently via a coordination bond between the carboxylate and TiO₂. In contrast, for the Ru-tpy dyes, if the tpy ligand is substituted with ED groups such as thiophenes or triarylamines, it is expected that the strongly ED substituent increases the electron density on the pyridyl ring, and as a result, the electron-accepting character of the pyridyl ring may be lost. Actually, theoretical calculations

indicate that the LUMOs of the Ru–tpy sensitizers with a highly electron-rich π -spacer were mainly localized on the carboxylbipyridine part and not on the pyridyl ring substituted with the ED π -conjugate.^[7a,b] Meanwhile, it has been reported that the LUMO level of black dye, –3.93 eV, was located at almost the lowest acceptable level for efficient electron injection from the dye into the TiO₂ conduction band,^[5,7a,7c,8] and thus, electron-withdrawing groups, which decrease the LUMO level of the sensitizer, are inappropriate as the substituent. Therefore, alternative π -conjugation substituents on the tpy ligand would be moderately ED groups.

Based on our expectations, we designed a new π -expanded dicarboxylterpyridyl ligand with a moderately ED 4-methylstyryl moiety, which analogues employed in Ru–polypyridyl sensitizers as π -conjugate antennas on the co-ligands,^[9] and synthesized its Ru complex, HIS-2 (Figure 1) to achieve a higher molar absorption coefficient, appropriate energy levels, and a higher conversion efficiency. HIS-2 exhibited a higher molar absorption coefficient in the EtOH solution than that of black dye over the whole spectral region, and as we expected, the DSC device based on HIS-2 successfully achieved an excellent conversion efficiency of 11.1%. Herein, we report the synthesis, photochemical properties, computational chemistry, and photovoltaic properties of HIS-2.

2. Results and Discussion

2.1. Synthesis of the Ru Complex HIS-2

HIS-2 was prepared according to the conventional synthesis method of black dye using a 4,4'-bis(methoxycarbonyl)-4"-(4-methylstyryl)-2,2':6',2"-terpyridine (L^{Me}) instead of Me₃tctpy ligand (Scheme 1). RuCl₃·3H₂O and L^{Me} were refluxed in an EtOH solution for 3 h and [RuCl₃(L^{Me})] was precipitated as a dark red powder. [RuCl₃(L^{Me})] was reacted with NH₄NCS in a DMF solution at 145 °C for 4 h, and then, the solution was cooled to 60 °C and methyl esters were hydrolyzed with Et₃N.



Scheme 1. Synthetic protocol of HIS-2.

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Figure 2. UV (solid line) and emission (dashed line) spectra of HIS-2 (\bullet) and black dye (\circ). UV spectra were measured in MeOH (inset: magnified spectrum in the range of 600–750 nm) and emission spectra were measured in MeOH/EtOH (1:4 v/v) at 77 K.

The product was purified on a Sephadex LH-20 column using water as the eluent. To the purple fraction, TBANCS was added, and the pH of the solution was acidified to 5.0 using 0.1 M HNO₃ to yield dark green precipitates. The suspension was kept in the refrigerator overnight. The precipitates were filtered, washed with water and diethylether, and dried under vacuum to obtain HIS-2 at a 12% yield as a dark green powder. HIS-2 was fully characterized by ¹H NMR and HRMS spectroscopy. By ¹H NMR spectroscopy, the molecular ratio of Ru dye and TBA⁺ was determined to be 1:2, and therefore, one carboxylic acid in HIS-2 is deprotonated.

2.2. Photophysical Properties

The absorption spectra in EtOH, and the luminescent spectra in EtOH/MeOH (4:1, v/v) measured at 77 K for HIS-2 and black dye are shown in Figure 2, and selected parameters are summarized in Table 1. The HIS-2 dye showed a broad absorption spectrum covering a wide spectral range in the visible and near-IR regions with higher molecular absorption coefficients compared to black dye over the whole spectral region, which is a result of the wider π -conjugation owing to the presence of the 4-methylstyrene moiety on the terpyridyl ligand. Lowlying absorption bands, which can reasonably be assigned to a metal-to-ligand charge transfer (MLCT) transition to the terpyridyl ligand (discussed in Section 2.3), are exhibited for HIS-2 at 597 nm with a molar extinction coefficient (ϵ) of 8.2 \times 10³ M⁻¹ cm⁻¹, which is slightly blue-shifted compared with the corresponding absorption of black dye, at 613 nm with ε of 7.0 \times $10^3~{
m M}^{-1}~{
m cm}^{-1}$. Additionally, at 685 nm, a small shoulder with arepsilonof 4.2×10^3 M⁻¹ cm⁻¹ was appeared for HIS-2 (Figure 2 inset). In the UV region, the HIS-2 dye showed an intense absorption band at around 350 nm, which is assigned to the ligand-centered π - π * transition of the 4,4'-bis(carboxyl)-4"-(4-methylstyryl)-2,2':6',2"-terpyridine ligand. All of these features render HIS-2

Table 1. Photophysical and electrochemical properties of HIS-2 and

HIS-2	329 (sh)	32700	850	-5.47	1.77	-3.70
	348	38900				
	414	14800				
	597	8200				
	685 (sh)	4200				
BD	328	20900	890	-5.46	1.53	-3.93
	340	19900				
	411	9700				
	613	7000				

^{a)}Measured in EtOH; ^{b)}Measured in EtOH/MeOH (4:1, v/v) at 77 K; ^{c)}Measured by AC-3E, dyes were adsorbed onto the transparent TiO₂ films; ^{d)}0-0 transition energies, $E_{0.0}$ were estimated from the intersection of the absorption and emission spectra; ^{e)}LUMO levels were calculated from the HOMO level and $E_{0.0}$ energy.

an attractive sensitizer for the nanocrystalline TiO_2 -based solar cells. When adsorbed onto a transparent thin TiO_2 film, HIS-2 shows a broad absorption spectrum similar to that in solutions, but with the absorption peak slightly blue-shifted (supporting information). When excited into the charge-transfer absorption band of HIS-2 in EtOH/MeOH (4:1, v/v) at 77 K, a broad emission band with a maximum at 850 nm was observed as shown in Figure 2, and is attributed to the luminescence from the lowest energy ³MLCT state. The excited-state lifetimes of HIS-2 were determined to be 17 and 443 ns at 298 and 77 K, respectively.

In order to obtain information on the frontier energy levels, the ionization potential of HIS-2 bound to a nanocrystalline TiO_2 film was determined using a photoemission yield spectrometer (Riken Keiki, AC-3E). An oxidation potential of -5.47 eV, which corresponds to the HOMO level, was obtained for the sensitizer HIS-2 adsorbed on a TiO₂ electrode and was low enough for efficient regeneration of the oxidized dye through reaction with iodide. The excited-state oxidation potential estimated from the HOMO level and the 0-0 transition energy of the HIS-2 sensitizer was -3.70 eV, which lies sufficiently above the conduction band edge (-4.2 eV)^[10] of the nanocrystalline TiO₂. Therefore, an efficient electron injection into the conduction band of TiO₂ is expected to occur with sensitizer HIS-2.

2.3. Computational Chemistry

In order to gain insight into the electronic structure of HIS-2, calculations of the molecular orbital distribution and electronic transitions were carried out with density functional theory (DFT) using the Gaussian 03 software^[11] at the PBE1PBE/D95 (for C, H, and N) and LANL2DZ (for Ru) levels. The ground-state structure of HIS-2 was first optimized in vacuo, followed by excitation calculations using time-dependent (TD)-DFT. To mimic the perturbation due to the environment, a polarizable continuum model (PCM) was employed using EtOH as the solvent.

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Figure 3. Calculated isodensity surface plots of the frontier orbitals (LUMO + 2, LUMO + 1, LUMO, HOMO, HOMO-1, and HOMO-2) of HIS-2 (isodensity value = 0.03)

The calculated frontier orbital distributions of HIS-2 are shown in Figure 3. The HOMO, HOMO-1, and HOMO-2 are delocalized over the Ru metal and the NCS ligands, and the dominant amplitudes are located primarily on the sulfur atoms of the NCS ligands. The NCS groups pointing in the direction of the bulk solution may facilitate reduction of the oxidized dve (Ru³⁺) through the reaction with I⁻ in the electrolyte. In contrast, the LUMO and LUMO+1 are distributed over a terpyridyl and the 4-methylstyryl moiety, suggesting that an expansion of the conjugation length of the terpyridyl ligand has effectively occurred as a result of the moderately ED property of the 4-methylstyryl moiety. The LUMO distribution on the terpyridyl ligand facilitates electron injection from the photo-excited sensitizer to the TiO₂ semiconductor via the anchoring carboxyl groups.

The TD-DFT calculations (calculation results are summarized in Table 2; see also the Supporting Information) reveal that HIS-2 shows lower-lying electronic transitions in which electrons are promoted mainly from antibonding orbitals between the Ru^{II} d π orbital and π orbitals of the thiocyanato group to the π^* orbitals of the dicarboxyterpyridyl and 4-methylstyryl groups. For HIS-2, the lowest electronic transition responsible for the intense absorption in the NIR region involves a combination of the HOMO-1 \rightarrow LUMO and HOMO \rightarrow LUMO transitions. An analysis of the transition dipole moments indicates that the intensity of the former transition corresponds to an inter-ligand CT from the 4-methylstyrene moiety to the carboxylpyridine, and the latter to that of an MLCT from Ru to the 4-methylstyrene moiety.

2.4. Photovoltaic Properties

The incident monochromatic photon-to-current conversion efficiency (IPCE) spectra of the cells based on HIS-2 and black dye are shown in Figure 4a. The IPCE at each incident wavelength was calculated from Equation 1, where I_{sc} is the photocurrent density at the short-circuit condition in mA cm⁻² under monochromatic irradiation, *q* is the elementary charge, λ is the wavelength of the incident radiation in nm, and P_0 is the incident radiative flux in W cm⁻².

 Table 2. Selected results for the TD-DFT singlet to singlet excited-state
 transitions for the MLCT band of HIS-2 in EtOH.

State	Wavelength [nm]	f	Assignment	
1	715.14	0.0619	HOMO–1 to LUMO	(17%)
			HOMO to LUMO	(74%)
2	632.51	0.1106	HOMO-1 to LUMO	(63%)
			HOMO-1 to LUMO+1	(7%)
			HOMO to LUMO	(16%)
			HOMO to LUMO+1	(5%)
4	538.26	0.0969	HOMO-1 to LUMO+1	(42%)
			HOMO to LUMO+1	(52%)
5	501.18	0.0366	HOMO-2 to LUMO+1	(2%)
			HOMO-1 to LUMO	(5%)
			HOMO-1 to LUMO+1	(38%)
			HOMO-1 to LUMO+3	(3%)
			HOMO to LUMO	(2%)
			HOMO to LUMO+1	(32%)

IPCE $(\lambda) = 1240 (I_{SC}/q\lambda P_0)$

(1)

The IPCE of the HIS-2-sensitized cell reaches a maximum of about 80% at 610 nm, and the onset of the IPCE spectra is above 900 nm. These are anticipated to be optimal parameters for the best DSCs.^[12] It is well known that the valley at around 390 nm in the IPCE spectrum of the black dye exists owing to the strong absorption of iodide in the electrolyte as seen in Figure 4a.^[4,13] In contrast, because of the more intense absorptions of HIS-2 in the spectral range of 300-400 nm compared to those of the black dye and attributed to the 4-methylstyryl group, the IPCE spectrum of HIS-2 exhibited superior photoresponses in that spectral region. As a result, HIS-2 surprisingly achieved higher IPCE values than those of black dye over almost the whole spectral region, which is consistent with the absorption spectra of HIS-2 and black dye.

The characteristic photocurrent density-photovoltage (I-V)curves measured under the illumination of the standard AM 1.5

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Figure 4. a) IPCE spectra and b) J–V curves of DSCs based on HIS-2 (\bullet) and black dye (\circ).

G sunlight (100 mW cm⁻²) condition (as illustrated in Figure 4b and summarized in **Table 3**), yield a short-circuit current density (J_{SC}) of 23.07 mA cm⁻², an open-circuit voltage (V_{OC}) of 0.68 V, and a fill factor (FF) of 0.71, resulting in an overall conversion efficiency of 11.1% for the HIS-2-sensitized device. Under the same device fabrication conditions and efficiency evaluation procedure, the photovoltaic parameters (J_{SC} , V_{OC} , FF) of the cell based on black dye are 21.28 mA cm⁻², 0.69 V and 0.72, respectively, giving an efficiency of 10.5%. Reflecting the increase in the IPCE values, for HIS-2, the improved J_{SC} value for HIS-2 is mainly responsible for the higher conversion efficiency than

Table 3. Photovoltaic properties of DSCs based on HIS-2 and black dye.

Dye	J _{sc} [mA cm ⁻²]	V _{oc} [V]	FF	η [%]
HIS-2	23.07	0.68	0.71	11.1
BD	21.28	0.69	0.72	10.5

Photovoltaic measurements were performed under AM 1.5 G (100 mW cm⁻²) irradiation on the DSC devices with 0.25 cm² active area defined by a metal mask.

that of black dye. The results demonstrate that the moderately electron-donating 4-methylstyrene unit can enhance the light harvesting capability of a Ru–tpy based sensitizer, and the HIS-2 dye is a promising candidate as a panchromatic sensitizer used in DSCs.

3. Conclusion

We have successfully developed a new Ru-tpy sensitizer HIS-2 based on the molecular design strategy of substitution with a moderately electron-donating π -conjugated 4-methylstyryl group onto the terpyridyl ligand. HIS-2 exhibited more intense absorption over the whole spectral region compared to black dye owing to the extended π -conjugation resulting from the 4-methylstyryl moiety. The TD-DFT calculation reveals that the LUMO and LUMO + 1 of HIS-2 are distributed over the terpyridine and 4-methylstylene moieties, and the lowest energy ¹MLCT was composed of a combined transition of the HOMO to LUMO and the HOMO-1 to LUMO transitions. The DSC based on the HIS-2 dye achieved a conversion efficiency of 11.1%, which is higher than the efficiency of 10.5% of the reference cell based on black dye under the same standard AM 1.5 G conditions. In the IPCE spectra, HIS-2 displayed a better photoresponse, particularly, in the UV and NIR regions compared to the black dye, and this was attributed to the intense absorption in the corresponding spectral regions. Our results show that this is a promising molecular design strategy for the development of panchromatic sensitizers for the DSC applications with high conversion efficiencies exceeding 11%. In addition to the development of new dicarboxylterpyridine sensitizers with various styryl units based on different ED groups, the device optimization for HIS-2 is in progress to fully explore its potential in dye-sensitized solar cell applications.

4. Experimental Section

General Procedures: 4,4'-Bis (methoxycarbonyl)-4"-(4-methylstyryl)-2,2':6',2"-terpyridine (L^{Me}) was purchased from Tokyo Chemical Industry (TCI) Co., Ltd. using custom synthesis service. All chemicals were used as received from chemical companies without further purification. Anhydrous solvents were degassed by Ar bubbling for 20 min before use. All syntheses were carried out under argon atmosphere unless stated. Work functions of the dyes adsorbed onto TiO₂ film was measured using with AC-3E Photoemission yield spectrometer (RIKEN KEIKI). The ¹H and ¹³C NMR measurements were performed by a DRX-600 spectrometer (Bruker BioSpin). UV spectra was measured using with UV-3600 UV-vis-NIR spectrometer (SHIMAZDU).

Synthesis of $[RuCl_3(L^{Me})]$: Ruthenium trichloride (130 mg, 0.84 mmol) was dissolved in EtOH (30 mL), and the solution was stirred for 2 min at 50 °C. To the solution, a solution of L^{Me} (236 mg, 0.51 mmol) in dichloromethane (20 mL) was added, and the mixture was refluxed for 3 h. The solution was concentrated to ca. 10 mL, and then cooled to room temperature. The precipitated complex was collected by filtration, washed with cold EtOH to remove unreacted ruthenium trichloride, and air-dried. [RuCl_3(L^{Me})] was yielded as a dark brown powder (268 mg, 80%).

Synthesis of HIS-2: The complex HIS-2 was synthesized under an argon atmosphere by refluxing at 130 °C, an aqueous solution of ammonium thiocyanate (1 g, 13.16 mmol) in H₂O (5 mL) and [RuCl₃(L^{Me})] (260 mg, 0.39 mmol) in DMF (25 mL) for 4 h. Then, triethylamine (10 mL) and

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H₂O (5 mL) were added, and the solution was refluxed for a further 24 h to hydrolyze the ester groups on the terpyridine ligand. The reaction mixture was allowed to cool and the solvent volume was reduced on a rotary evaporator to about 5 mL. Water was added to the flux, and the insoluble solid was filtered and dried under vacuum. The isolated solid was further purified on a Sephadex LH-20 column with water as an eluent. Obtained complex HIS-2 was suspended into 10 mL of water and dissolved by the addition of a minimum amount of 0.1 M aqueous tetrabutylammonium hydroxide (TBAOH). To this solution, tetrabutylammonium thiocyanate (100 mg, 0.33 mmol) was added. The resulting solution was filtered, the pH was adjusted to 4.5 with dilute hydrochloric acid, and then dark green powder was precipitated. The resulting precipitate was filtered and dried under vacuum to vield HIS-2 (55 mg, 12%). ¹H NMR (600 MHz, CD₃OD, δ): 9.02 (d, J = 5.4 Hz, 1H), 8.87 (d, J = 5.4 Hz, 1H), 8.79 (s, 1H), 8.78 (s, 1H), 8.76 (bs, 1H), 8.46 (bs, 1H), 8.06 (dd, J = 5.4 and 1.8 Hz, 1H), 7.79 (bd, J = 5.4 Hz, 1H), 7.65 (d, J = 16.2 Hz, 1H), 7.58 (d, J = 7.8 Hz, 2H), 7.32 (d, J = 16.2 Hz, 1H), 7.24 (d, J = 7.8 Hz, 2H), 3.22 (m, 16H), 2.39 (s, 3H), 1.65 (m, 16H), 1.39 (m, 16H), 1.00 (t, / = 7.2 Hz, 24H); HRMS (ESI, m/z): [M-H]⁻ calcd for C₆₁H₈₉N₈O₄S₃Ru, 1195.5218; found, 1195.5243.

Computational Methods: Calculations of the geometry of complex HIS-2 and its excitation energies were carried out at density functional theory (DFT) and time-dependent (TD)-DFT levels using Gaussian 03 suite.^[11] The density functional employed in the computations was a hybrid density functional PBE1PBE. The basis functions used were the Dunning–Hay split valence double- ξ for the C, H, and N atoms (D95) and the Hay-Wadt double- ξ with the Los Alamos relativistic effective core potential for Ru atom (LANL2DZ). To mimic environmental perturbation, a polarizable continuum model (PCM) was employed using EtOH as solvent. TD-DFT excited-state calculation of the lowest 50 singlet-singlet electronic transitions for the HIS-2 was performed also at the PBE1PBE/LANL2DZ level for the geometry optimization.

Device Fabrication: A nanocrystalline TiO₂ photoelectrode (area: 0.25 cm²; thickness: 25 μ m) was prepared by screen-printing on conducting glass as previously described.^[14] The films were further treated 0.1 M HCl aqueous solutions before examination.^[15] Coating of the TiO₂ film was carried out by immersing for 24 h in a sensitizer solution of 3×10^{-4} M acetonitrile/*tert*-butyl alcohol (1:1, v/v). Deoxycholic acid (20 mM) was added to the dye solution as a co-adsorbent to prevent aggregation of the dye molecules. Fabrication of DSCs composed of 0.25 cm² dye-adsorbed TiO₂ film, an electrolyte (0.05 M l₂, 0.1 M LiI, dimethylpropylimidazolium iodide (DMPII), 0.2 M *tert*-butylpyridine (TBP) in acetonitrile and a platinum-coated counter electrode. The two electrodes were separated by a Surlyn spacer (40-µm-thick) and sealed by heating the polymer frame.

Photovoltaic Characterization: Incident photon-to-current conversion efficiency (IPCE) spectra were measured by a CEP-200BX spectrometer (Bunko Keiki). The photocurrent-photovoltage (*J*–*V*) curves were obtained by a WXS-90S-L2 Super solar simulator (WACOM). Photovoltaic parameters were obtained by the measurements on two different cells of each experimental condition. Measurements were performed under AM 1.5 G irradiation (100 mW cm⁻²) on the DSC devices with 0.25 cm² active surface area defined by a metal mask.^[16]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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