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Introduction

Dye-sensitized solar cells (DSSCs) based on dye sensitizers adsorbed on nanocrystalline TiO2 electrodes have received considerable attention as a promising alternative to conventional solar cells based on silicon because they have interesting construction and operational principles, and colorful and decorative nature,1-18 since Grätzel and co-workers have reported high photovoltaic performances for DSSCs based on a Rucomplex dye in 1991.19 TiO2-based DSSCs can be classified into two types, I and II, depending on the electron-injection pathway from the dye to the conduction band (CB) of the TiO₂ (Fig. 1).^{6,7} The pathway for type-I DSSCs is photoexcitation of the local band of the adsorbed dye on TiO₂ followed by electron injection from the excited dye to the CB of TiO₂ (Fig. 1a: *i.e.*, an electron is excited from the HOMO to the LUMO level of the dye, followed by injection into the CB of TiO₂). This pathway can also be called the "two-step" or "indirect" electron-injection pathway. The dyes for type-I DSSCs are usually bound to the surface of

Development of D- π -Cat fluorescent dyes with a catechol group for dye-sensitized solar cells based on dye-to-TiO₂ charge transfer

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 $D-\pi$ -Cat fluorescent dyes YM-1 and YM-2 with a diphenylamine moiety as the electron-donating group, a catechol (Cat) unit as the anchoring group and fluorene or carbazole as the π -conjugated system were designed and developed as a photosensitizer for type-II dye-sensitized solar cells (DSSCs), which have a direct electron-injection pathway from the dye to the conduction band (CB) of the TiO₂ electrode by photoexcitation of the dye-to-TiO₂ charge transfer (DTCT) bands. Furthermore, not only to gain insight into the influence of the molecular structure of D- π -Cat dyes on the appearance of a DTCT band and the electron-injection mechanism, but also to investigate the impacts of the DTCT characteristics of D- π -Cat dyes on the photovoltaic performances of DSSCs, a D- π -Cat fluorescent dye YM-3 with carbazole-terthiophene as the π -conjugated system was also synthesized. It was found that the D- π -Cat dyes possess a good light-harvesting efficiency (LHE) in the visible region due to a broad absorption band corresponding to DTCT upon binding to a TiO₂ film. The incident photon-to-current conversion efficiency (IPCE) corresponding to the DTCT band for DSSCs based on YM-1 and YM-2 is higher than that for YM-3. This work indicates that the stabilization of the LUMO level and the expansion of the π -conjugated system by the introduction of a long π -bridge such as terthiophene on the Cat moiety can lead to an increase in the intramolecular charge transfer (ICT) excitation based on $\pi \to \pi^*$ transition with a decrease in the DTCT characteristics, resulting in enhancement of an indirect electron-injection pathway from the excited dye to the CB of TiO₂ by photoexcitation of the local band of the adsorbed dye on TiO₂.

> TiO_2 through carboxylic acid groups; a carboxylic acid group can form a chelating linkage or a bidentate bridging linkage at Brønsted acid sites (surface-bound hydroxy groups, Ti–OH) of the TiO₂ surface. Ru complexes, porphyrin dyes, phthalocyanine dyes, and organic dyes containing carboxylic acid groups have



Fig. 1 Schematic representation of (a) type-I DSSC (*i.e.*, an electron is excited from the HOMO to the LUMO level of the dye, followed by injection into the CB of the TiO_2) and (b) type-II DSSC (*i.e.*, an electron is injected directly from the HOMO of the dye into the CB of the TiO_2 upon photoexcitation).

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been known to inject electrons into TiO2, according to the type-I pathway.¹⁻¹⁹ Thus, the dyes for type-I DSSCs must have at least one carboxylic acid group as an anchoring group for adsorption onto the TiO₂ surface. Among dye sensitizers used so far in type-I DSSCs, donor-acceptor- π -conjugated (D- π -A) dyes possessing a diphenyl- or dialkylamino group as the electron donor (D) and a carboxylic acid group as the electron acceptor (A) and anchor linked by π -conjugated bridges, displaying broad and intense absorption spectral features, would be especially expected to be one of the most promising classes of organic dye sensitizers for type-I DSSCs.4-10 The photoabsorption properties of a D- π -A dye are associated with intramolecular charge transfer (ICT) excitation from the D to the A moiety of the dye, resulting in efficient electron transfer from the excited dye through the acceptor moiety (carboxylic acid group) into the CB of TiO₂. D- π -A dyes can facilitate the ICT and subsequent charge separation of the D and A moieties in the excited dye, and rapidly inject electrons into the CB of TiO₂ and effectively retard charge recombination because the cationic charge on the D moiety of the excited dye is spatially separated by the π -conjugated bridge from the TiO₂ surface with injected electrons. Therefore, much effort has been made on the development of various types of D- π -A organic dye sensitizers for type-I DSSCs and there has been a gradual accumulation of information about the relationship between the chemical structures and photovoltaic performances of type-I DSSCs. Consequently, type-I DSSCs have achieved solar energy-to-electricity conversion yields (η) of up to 12%.²

The pathway for type-II DSSCs, on the other hand, is a direct, "one-step" electron injection from the ground state of the dye to the CB of TiO₂ by photoexcitation of the dye-to-TiO₂ charge transfer (DTCT) bands (Fig. 1b: i.e., an electron is injected directly from the HOMO of the dye into the CB of TiO₂ upon photoexcitation).6,7,20 Catechol (Cat) dyes, such as dopamine and fluorine, numerous natural pigments, such as bromopyrogallol red, and anthocyanins containing Cat moieties show strong new absorption bands corresponding to DTCT in the visible region upon binding to TiO2.20-31 Cat dyes have been known to bind to the TiO₂ surface through bidentate mononuclear chelating and/or bidentate binuclear bridging linkages.²¹⁻⁴⁸ Thus, the advantages of type-II DSSCs over type-I DSSCs are as follows: (1) type-II DSSCs have efficient light-harvesting capabilities over the wide spectral range of sunlight because direct electron injection in type-II DSSCs can lead to the creation of a new DTCT band and ease of restrictions on the LUMO levels of the type-II dyes relative to type-I DSSCs with an indirect electron-injection pathway (for type-I DSSCs, to achieve electron injection from the excited dye to the CB of TiO₂, the LUMO levels of the type-I dyes must be higher than those of the CB of the TiO_2 electrode). (2) Type-II dyes can inject electrons into the CB of TiO₂ through only the type-II pathway or through type-I and type-II pathways and the electron-injection efficiency of the type-II pathway, in principle, should be unity. However, the photovoltaic performance of type-II DSSCs based on Cat dyes is significantly lower than that of type-I DSSCs based on organic dyes with a carboxylic acid group. To investigate the appearance of DTCT characteristics and the electron-injection

mechanism, the interfacial electron transfer dynamics of Cat dyes adsorbed on TiO₂ nanoparticles have been carefully studied by transient absorption spectroscopy and density functional theory (DFT) by some research groups. These fundamental studies have revealed that the back-electrontransfer (charge recombination) of electrons injected into TiO₂ for the type-II pathway takes place in a subpicosecond timescale,^{38,45} which was significantly faster than those (µs-ms) for the type-I pathway. Thus, type-II Cat dyes have rarely been employed as sensitizers for DSSCs and there have been few efforts to develop type-II dye sensitizers, compared with that of type-I DSSCs. In an attempt to overcome this problem, Yoon and co-workers found that attaching electron-donating moieties, such as (pyridin-4-yl)vinyl (v-P) and (quinolin-4-yl)vinyl (v-Q), to Cat led to 2- and 2.7-fold increases, respectively, in the η value, driven by large increases in the short-circuit photocurrent density $(I_{sc})^{23}$ As a result, the η values obtained with Cat-v-P and Cat-v-Q were 1.2 and 1.6%, respectively. They proposed that both the consecutive charge shift from the secondary donor (pyridine or quinoline unit) to a primary donor (4-vinylcatechol unit), leading to retardation of the back-electron-transfer rate and a dramatic increase in electron-injection efficiency, and a red-shift of the DTCT band caused by the increase in the donor strength of the dye through the attachment of a secondary donor to the primary donor were responsible for the increase in the η value. Thus, the application of the molecular design of D- π -Cat dye sensitizers with strong electron donors, such as triphenylamine, indoline, and carbazole is one of the most promising strategies not only to inhibit back electron transfer, but also to enhance direct electron-injection efficiency in type-II DSSCs based on Cat dyes.^{36,45h} They also reported that DSSCs based on Cat and dopamine as the sensitizers were typical type-II DSSCs. On the other hand, for DSSCs based on bromopyrogallol red, the photocurrent is generated not only by the type-I pathway, but also by the type-II pathway in the visible region. Therefore, the bromopyrogallol red-sensitized DSSC is a typical example in which both pathways operate over the whole spectral region. Two representative organic dye sensitizers for type-I and type-II DSSCs are alizarin and Cat, respectively. The appearance of DTCT characteristics and the electron-injection mechanism for both dyes have been extensively studied from experimental and theoretical methods by Prezhdo and co-workers.⁴⁶ Moreover, to study the electronic injection mechanism more in depth and to generalize the main differences between the type-I and type-II pathways, Sanz and co-workers studied five organic dyes of growing size, Cat, 2,3-naphthalenediol, alizarin, coumarin C343 having a carboxylic acid group, and coumarin derivative NKX-2311 having a cyanoacrylic acid group, and the electronic structures and optical response of the five dyes attached to TiO₂ were analyzed and compared by using time-dependent density functional theory (TDDFT).⁴⁷ From their analysis, NKX-2311 and Cat show purely indirect (type-I pathway) and direct (type-II pathway) electron-injection behavior, respectively. Nevertheless, intermediate ones are also possible. In the sequence from Cat to 2,3-naphthalenediol, C343, alizarin, and NKX-2311, the electron injection changes from a purely direct mechanism to a purely indirect mechanism. Alizarin and C343 represent



Scheme 1 Chemical structures of D $-\pi$ -Cat dye sensitizers YM-1, YM-2 and YM-3.

intermediate behavior in which both injection regimes are present. This is related to the relative position of the LUMO energy of the dye to the edge of the CB of TiO₂.

In this work, to provide a direction in molecular design toward creating efficient Cat dye sensitizers for type-II DSSCs, we have designed and synthesized D- π -Cat fluorescent dyes YM-1 and YM-2 with a diphenylamine moiety as the electrondonating group, a catechol (Cat) unit as the anchoring group, and fluorene or carbazole as the π -conjugated system (Scheme 1). Furthermore, not only to gain insight into the influence of the molecular structure of D- π -Cat dyes on the appearance of DTCT bands and the electron-injection mechanism, but also to investigate the impacts of the DTCT characteristics of D- π -Cat dyes on the photovoltaic performances of DSSCs, D- π -Cat fluorescent dye YM-3 with a carbazole-terthiophene as π -conjugated system was also synthesized. Here we reveal the impacts of the molecular structure of D- π -Cat dyes on the photovoltaic performances of type-II DSSCs, and demonstrate that the stabilization of the LUMO level and the expansion of the π -conjugated system by the introduction of terthiophene on the Cat moiety can lead to an increase in the ICT excitation based on $\pi \rightarrow \pi^*$ transition with a decrease in the DTCT characteristics, resulting in enhancement of an indirect electron-injection pathway from the excited dye to the CB of TiO₂ by photoexcitation of the local band of the adsorbed dye on TiO₂.

Results and discussion

Synthesis of D- π -Cat dyes YM-1, YM-2 and YM-3

D- π -Cat dyes **YM-1**, **YM-2** and **YM-3** were synthesized according to the stepwise synthetic protocol illustrated in Scheme 2. For **YM-1**, Suzuki coupling of 2,7-dibromo-9,9-dimethyl-9*H*-fluorene with 2 (ref. 49 and 50) gave compound 3. D- π -Cat dye **YM-1** was prepared by Buchwald–Hartwig C–N coupling of 3 with diphenylamine followed by treatment with acid. For **YM-2** and **YM-3**, the starting material 5 was prepared from 2,7-dibromo-9-butyl-9*H*-carbazole and diphenylamine through Buchwald–Hartwig C–N coupling according to the literature.⁵¹ Compound **6** was prepared by Suzuki coupling of 5 with 2. Compound **6** is hydrolyzed by treatment with acid to produce D– π -Cat dye **YM**-2. Compound 7 was prepared from 5 with bis(pinacolato) diboron by Miyaura boronation reaction. Compound **9** was prepared by Suzuki coupling of **1** with 2-([2,2':5',2''-terthiophen]-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane followed by bromination with*N*-bromosuccinimide (NBS). Compound**10**was prepared by Suzuki coupling of**9**with**7**. Compound**10** $was hydrolyzed by treatment with acid to produce <math>D-\pi$ -Cat dye **YM-3**.

Optical properties of YM-1, YM-2 and YM-3 in solution

The absorption and fluorescence spectra of YM-1, YM-2 and YM-3 in THF are shown in Fig. 2 and their spectral data are summarized in Table 1. The absorption and fluorescence spectra of YM-1 and YM-2 resemble each other very closely, but are significantly different from those of YM-3. The dye YM-3 shows a strong absorption band at around 430 nm, which is assigned to the ICT excitation based on $\pi \rightarrow \pi^*$ transition from the electron donor moiety (carbazole-diphenylamine) to the Cat unit through the terthiophene unit. Although the dyes YM-1 and YM-2 also show the ICT band at around 360 nm, the absorption maximum (λ_{max}^{abs}) for the ICT band of YM-3 occurs at a longer wavelength by ca. 70 nm than those of YM-1 and YM-2. Moreover, the molar extinction coefficient (ε) for the ICT band of YM-3 is 81 300 M^{-1} cm⁻¹, which is higher than those (*ca.* 33 000-43 000 M^{-1} cm⁻¹) of **YM-1** and **YM-2**. These results reveal that the introduction of a terthiophene unit on the carbazole skeleton expands the π -conjugation in the dye, and thus results in red-shift and broadening of the ICT band, and enhancement of the ε value. The dye **YM-3** shows a fluorescence maximum (λ_{max}^{fl}) at 478 nm, which occurs at a longer wavelength by ca. 80 nm than those of **YM-1** and **YM-2**. The dyes **YM-1** ($\Phi_{\rm f} = 0.56$) and **YM-2** ($\Phi_{\rm f} = 0.44$) exhibit a higher fluorescence quantum yield $(\Phi_{\rm f})$ than **YM-3** ($\Phi_{\rm f} = 0.27$).

Electrochemical properties of YM-1, YM-2 and YM-3

The electrochemical properties of YM-1, YM-2 and YM-3 were determined by cyclic voltammetry (CV) in acetonitrile containing 0.1 M tetrabutylammonium perchlorate (Bu₄NClO₄). The potentials were referenced to ferrocene/ferrocenium (Fc/Fc⁺) as the internal reference. The CV curves of the three dyes are shown in Fig. 3. For YM-3 the first oxidation peak was clearly observed at 0.41 V vs. Fc/Fc⁺, whereas for YM-1 and YM-2 the illdefined oxidation peak was observed at around 0.40 V. The corresponding reduction peak appeared at 0.30 V for both YM-1 and YM-2, and 0.26 V for YM-3, respectively. On the other hand, the second oxidation peak appeared at 0.47 V for YM-1, 0.48 V for YM-2, and 0.72 V for YM-3, respectively. The corresponding reduction peak for YM-1 was observed at 0.42 V, whereas no reduction peak was observed for YM-2 and YM-3. The HOMO energy levels of the dyes were estimated from the half-wave potential of oxidation ($E_{1/2}^{ox} = 0.35$ V for both YM-1 and YM-2 and 0.34 V for YM-3). The HOMO energy levels of YM-1, YM-2 and YM-3 were 0.98 V for both YM-1 and YM-2 and 0.97 V for YM-3 vs. the normal hydrogen electrode (NHE), respectively, thus indicating that the three dyes have comparable HOMO energy levels (Table 1). This result shows that the HOMO energy levels are more positive than the I_3^{-}/I^{-} redox potential (0.4 V), and



Scheme 2 Synthetic route to $D-\pi$ -Cat dye sensitizers YM-1, YM-2 and YM-3.



Fig. 2 (a) Absorption and (b) fluorescence spectra ($\lambda_{ex} = 362, 364$ and 429 nm for YM-1, YM-2 and YM-3, respectively) of YM-1, YM-2 and YM-3 in THF.

thus this ensures an efficient regeneration of the oxidized dyes by electron transfer from the I_3^-/I^- redox couple in the electrolyte. The LUMO energy levels of the three dyes were estimated from the $E_{1/2}^{\text{ox}}$ and an intersection of absorption and fluorescence spectra (381 nm; 3.25 eV for **YM-1**, 382 nm; 3.25 eV for **YM-2**, and 478 nm; 2.59 eV for **YM-3**). The LUMO energy levels were -2.27 for both **YM-1** and **YM-2** and -1.62 V for **YM-3**, respectively. Therefore, it was revealed that the red-shift of the ICT absorption band for **YM-3** relative to **YM-1** and **YM-2** is attributed to stabilization of the LUMO level by the introduction of a terthiophene unit on the carbazole skeleton of the dye, resulting in a decrease in the HOMO–LUMO band gap.

FTIR spectra of dye powders and dyes adsorbed on TiO₂ nanoparticles

To elucidate the adsorption states of **YM-1**, **YM-2** and **YM-3** on TiO_2 nanoparticles, we measured the FTIR spectra of the dye powders and the dyes adsorbed on TiO_2 nanoparticles (Fig. 4). For the powders of the dyes, the stretching vibrations of the phenolic group (C-OH) for the Cat unit was observed at 1272 and 1256 cm⁻¹ for **YM-1**, 1271 and 1256 cm⁻¹ for **YM-2** and 1264 and 1248 cm⁻¹ for **YM-3**, respectively. In the FTIR spectra of dyes adsorbed on TiO₂ nanoparticles, the stretching vibrations merge to one prominent or loose their hyperfine structure.

Table 1 Optical and electrochemical data, HOMO and LUMO energy levels, and DSSC performance parameters of YM-1, YM-2 and YM-3

Dye	$\lambda_{\max}^{abs \ a}/nm \left(\epsilon \ M^{-1} \ cm^{-1} \right)$	$\lambda_{\max}^{\mathrm{fl}}a/\mathrm{nm}\left(\Phi_{\mathrm{f}}\right)$	$E_{1/2}^{\operatorname{ox} b}/V$	HOMO ^c /V	LUMO ^c /V	$Molecules^d cm^{-2}$	$J_{\rm sc}{}^e/{ m mA~cm^{-2}}$	$V_{\rm oc}^{\ \ e}/{\rm mV}$	\mathbf{ff}^e	η^{e} (%)
YM-1	362 (43 100)	398 (0.56)	0.35	0.98	-2.27	$8.20 imes 10^{16\!f}$	1.36	416	0.51	0.29
						$6.36 imes10^{16g}$	1.56	456	0.50	0.36
YM-2	364 (33 800)	397 (0.44)	0.35	0.98	-2.27	$4.94 imes 10^{16f}$	1.51	416	0.50	0.31
						$2.86 imes10^{16g}$	1.46	448	0.49	0.32
YM-3	429 (81 300)	478 (0.27)	0.34	0.97	-1.62	$9.71 imes10^{16f}$	0.75	316	0.47	0.11
						$5.50 imes10^{16g}$	0.82	328	0.50	0.13

^{*a*} In THF, fluorescence quantum yields (Φ_f) were determined by using a calibrated integrating sphere system ($\lambda_{ex} = 362, 364$ and 429 nm for YM-1, YM-2 and YM-3, respectively). ^{*b*} Half-wave potential for the oxidation ($E_{1/2}^{ox}$) vs. Fc/Fc⁺ was recorded in acetonitrile/Bu₄NClO₄ (0.1 M) solution. ^{*c*} Vs. normal hydrogen electrode (NHE). ^{*d*} Adsorption amount per unit area of the TiO₂ electrode. ^{*e*} Under simulated solar light (AM 1.5, 100 mW cm⁻²). ^{*f*} 0.1 mM dye solution in THF. ^{*g*} 0.1 mM dye and 5 mM CDCA solution in THF.



Fig. 3 Cyclic voltammograms of YM-1, YM-2 and YM-3 in acetonitrile containing 0.1 M Bu₄NClO₄ at a scan rate of 50 mV s⁻¹. The arrow denotes the direction of the potential scan.



Fig. 4 FTIR spectra of the dye powders and the dyes adsorbed on TiO_2 nanoparticles for (a) YM-1, (b)YM-2 and (c) YM-3. (d) Possible binding modes for catechol on a TiO_2 surface: a bidentate mononuclear chelating linkage (left) and a bidentate dinuclear bridging linkage (right).

Thus, these observations indicate that the three dyes are adsorbed on the TiO_2 surface through the formation of a bidentate mononuclear chelating linkage and/or a bidentate

binuclear bridging linkage between the Cat unit of dye and $\rm TiO_2$ (Fig. 4d).40

Theoretical calculations

To examine the electronic structures of YM-1, YM-2 and YM-3 and their Ti-Cat chelate complexes (Ti-YM-1, Ti-YM-2 and Ti-YM-3), the molecular orbitals of the three dyes were calculated using density functional theory (DFT) at the B3LYP/6-31G(d,p) level. The DFT calculations indicate that the HOMO is mostly localized on the fluorene-diphenylamine moiety for YM-1, the carbazole-diphenylamine moiety for YM-2 and the carbazolediphenylamine moiety containing the terthiophene unit for YM-3, and the LUMO is mostly localized on the fluorene-Cat moiety for YM-1, the carbazole-Cat moiety for YM-2 and the terthiophene-Cat moiety for YM-3 (Fig. 5). On the other hand, for the Ti-Cat chelate complexes the LUMOs of Ti-YM-1, Ti-YM-2 and Ti-YM-3 are mostly localized on the titanium of chelating linkage, although the HOMOs are mostly localized on almost the same moiety as those of YM-1, YM-2 and YM-3. Accordingly, the DFT calculations reveal that when YM-1, YM-2 and YM-3 were adsorbed on the TiO₂ surface, dye excitations upon light irradiation induce an efficient direct electron injection from the HOMO of the dye to the CB of TiO₂, resulting in the appearance of a DTCT band.

Photoabsorption properties of YM-1, YM-2 and YM-3 adsorbed on the TiO_2 film

The absorption spectra of the dyes adsorbed on the TiO₂ film are shown in Fig. 6a. In addition to the ICT band based on $\pi \rightarrow \pi^*$ transition observed in THF, YM-1, YM-2 and YM-3 adsorbed on the TiO₂ film show the broad absorption band corresponding to DTCT upon binding to the TiO₂ film, that is, the DTCT band appears in the region of 450 to 650 nm for both YM-1 and YM-2 and 550 to 800 nm for YM-3. Thus, the DTCT band of YM-3 appears in a longer wavelength region than those of YM-1 and YM-2. The red-shift of absorption peak wavelengths for Cat dyes upon binding to the TiO₂ film can attributed to the stabilization of the LUMO level of Ti–Cat dye complexes. In fact, as shown in Fig. 5, the DFT calculations reveal that the LUMO energy level of YM-3 is lower than those of YM-1 and YM-2, and the three dyes have comparable HOMO energy levels, which are in good agreement with the



Fig. 5 Energy level diagram and HOMO and LUMO of YM-1, YM-2 and YM-3 and their Ti–Cat chelate complexes Ti–YM-1, Ti–YM-2 and Ti–YM-3.



Fig. 6 (a) Absorption spectra of YM-1, YM-2 and YM-3 in THF (–) and adsorbed on the TiO_2 film (…). (b) Photographs of YM-1, YM-2 and YM-3 in THF and (c) YM-1, YM-2 and YM-3 adsorbed on the TiO_2 film.

experimental results from the CV and the spectral analyses (Fig. 2 and 3). On the other hand, the LUMO energy levels for the surface-bound Ti-YM-1, Ti-YM-2 and Ti-YM-3 complexes are lower than those of YM-1, YM-2 and YM-3, although the HOMO energy levels for the Ti-Cat dye complexes are almost the same energy levels as those of YM-1, YM-2 and YM-3. It is worth mentioning here that the LUMO energy level of Ti-YM-3 is lower than those of Ti-YM-2 and Ti-YM-3. Thus, this result clearly shows that the expansion of the π -conjugated system by the introduction of the terthiophene unit on the Cat can lead to the stabilization of the LUMO energy levels of the Ti-Cat dye complexes, resulting in the red-shift of the DTCT band. As shown in Fig. 6b and c, the colors of the Cat dyes in THF are colorless for YM-1 and YM-2 and yellow for YM-3, respectively, but the colors of the Cat dyes adsorbed on the TiO₂ film are dark-orange for YM-1 and YM-2 and dark brown for YM-3, respectively, which indicates a decrease in the transition energy by the appearance of the DTCT band associated with the formation of the surface-bound Ti-Cat complex.

Photovoltaic performances of DSSCs based on YM-1, YM-2 and YM-3

The DSSCs were prepared by using the dye-adsorbed TiO₂ electrode, Pt-coated glass as a counter electrode, and an acetonitrile solution with iodine (0.05 M), lithium iodide (0.1 M), and 1,2-dimethyl-3-propylimidazolium iodide (0.6 M) as an electrolyte. The photocurrent-voltage (I-V) characteristics were measured under simulated solar light (AM 1.5, 100 mW cm^{-2}). The incident photon-to-current conversion efficiency (IPCE) spectra and the I-V curves are shown in Fig. 7. The photovoltaic performance parameters are summarized in Table 1. It is worth mentioning here that the adsorption amounts of YM-1, YM-2 and YM-3 adsorbed on the TiO₂ electrode are 8.20×10^{16} , 4.94×10^{16} and 9.71×10^{16} molecules per cm², respectively, which is comparable to that of conventional D- π -A dye sensitizers with carboxyl groups. The IPCE spectra of YM-1 and YM-2 resemble each other very closely, and are in good agreement with the observed absorption spectra on the TiO₂ film, that is, the IPCE spectra coincide with the DTCT band (Fig. 7a). The IPCE values of both YM-1 and YM-2 exceed 10% through the



Fig. 7 (a) IPCE spectra and (b) I-V curves of DSSCs based on YM-1, YM-2 and YM-3 with (...) and without (–) CDCA as a coadsorbent.

wavelength region of 580 nm. The onset of IPCE for both YM-1 and YM-2 reached 700 nm. Therefore, it is clear that the photocurrents for DSSCs based on YM-1 and YM-2 are mainly generated by a direct electron-injection pathway from the Ti-Cat chelate complexes (Ti-YM-1 and Ti-YM-2) to the CB of the TiO₂. On the other hand, the IPCE corresponding to the DTCT band for DSSCs based on YM-3 is below 10% in the wavelength region over 500 nm, and is much lower than those of YM-1 and YM-2. However, it is worth mentioning here that the maximum IPCE value of YM-3 reaches 20% at around 430 nm, which corresponds to the $\pi \to \pi^*$ transition based on the local band of the adsorbed dye on TiO₂. Consequently, the photocurrent for DSSCs based on YM-3 is mainly generated by an indirect electron-injection pathway from the excited dye to the CB of TiO₂. Sanz and co-workers reported that whether the dve sensitizers exhibit a purely indirect electron-injection behavior or a purely direct electron-injection behavior is related to the relative position of the LUMO energy of the dye to the edge of the CB of TiO₂.⁴⁷ Thus, this result indicates that the stabilization of the LUMO level and the expansion of the π -conjugated system by the introduction of terthiophene on the Cat moiety can lead to an increase in the ICT excitation based on $\pi \to \pi^*$ transition with a decrease in the DTCT characteristics,48 resulting in enhancement of an indirect electron-injection pathway from the excited dye to the CB of TiO₂ by photoexcitation of the local band of the adsorbed dye on TiO₂, that is, type-I DSSCs. In addition, the maximum IPCE value (20%) of **YM-3** is much lower than those of conventional D- π -A dyes having the carboxylic acid group. It is suggested that the electron-injection efficiency of D- π -Cat dyes through the type-I pathway is lower than those of D- π -A dyes having the carboxylic acid group through the type-I pathway. This may be attributed to the difference in the binding mode onto the TiO₂ surface between D- π -Cat dyes and D- π -A dyes having the carboxylic acid group. The *I*–*V* curves show that the J_{sc} and η values for **YM**-1 (1.36 mA cm⁻² and 0.29%) and YM-2 (1.51 mA cm⁻² and 0.31%) are much higher than those for **YM-3** (0.75 mA cm⁻² and 0.11%) (Fig. 7b). Thus, this shows that the expansion of the π -conjugated system by the introduction of terthiophene on the Cat moiety results in the facilitation of the back-electrontransfer rate from electrons injected into TiO₂ to the oxidized dye, leading to a decrease in photovoltaic performances. On the other hand, the open-circuit photovoltage (V_{oc}) of Cat dye sensitizers is lower than that of the conventional organic dye sensitizers.^{32,36} It is assumed that the low V_{oc} values (ca. 300-400 mV) for YM-1, YM-2 and YM-3 are attributed to faster charge recombination between the injected electrons in the CB of TiO₂ and I_3^- ions in the electrolyte, arising from the approach of $I_3^$ ions to the TiO2 surface due to the electrostatic interactions between the D- π -Cat and I₃⁻ ions due to the formation of Ti-Cat chelate complexes, as with the case of catechol-thiophene sensitizers by Burn and Meredith.³² Moreover, the Voc value (316 mV) for YM-3 with terthiophene is smaller than those (416 mV) for YM-1 and YM-2. This is attributed to the fact that expansion of the π -conjugated systems of dyes by introducing thiophene units often facilitates the approach of I_3^- ions to the TiO₂ surface because of complexation between the dye and I_3^- ions,

and also produces the result that it can no longer form a compact blocking layer (larger surface coverage) to the approach of I_3^- ions to the TiO₂ surface, resulting in faster charge recombination and a lower $V_{\rm oc}$ value.^{4,10,52,53} When chenodeoxycholic acid (CDCA) was employed as a coadsorbent to prevent dye aggregation on the TiO₂ surface, the $J_{\rm sc}$, $V_{\rm oc}$ and η values slightly increased (Fig. 7b). Under the adsorption conditions of 0.1 mM dye and 5 mM CDCA, the $J_{\rm sc}$, $V_{\rm oc}$ and η values for DSSCs with CDCA are 1.56 mA cm⁻², 456 mV and 0.36% for **YM-1**, 1.46 mA cm⁻², 448 mV and 0.32% for **YM-2** and 0.82 mA cm⁻², 328 mV and 0.13% for **YM-3**, respectively (Table 1).

Thus, electrochemical impedance spectroscopy (EIS) analysis was performed to study the electron recombination process in DSSCs based on these three dyes under -0.6 V bias applied voltage in the dark. The Nyquist plots and Bode phase plots are shown in Fig. 8. The small semicircle at around Z' = 20 ohm in the Nyquist plot, which corresponds to the high-frequency peaks in the Bode phase plots, represents the electron transfer from the Pt counter-electrode to I_3^- ions in the electrolyte, that is, the charge-transfer resistances at the Pt/electrolyte interface. The large semicircle in the Nyquist plot, which corresponds to the midfrequency peaks in the Bode phase plots, represents the charge recombination between the injected electrons in TiO₂ and I_3^- ions in the electrolyte, that is, the charge-transfer resistances at the TiO₂/dye/electrolyte interface.⁵⁴⁻⁵⁷ The Nyquist plots (Fig. 8a) show the resistance value for the large semicircle to increase in the order of YM-3 (14.6 Ω) < YM-1 (37.0 Ω) \approx YM-2



Fig. 8 (a) Nyquist plots and (b) Bode phase plots of DSSCs based on YM-1, YM-2 and YM-3 with and without CDCA as a coadsorbent.



Fig. 9 Photovoltaic parameters (J_{sc} , V_{oc} , ff, and η) for DSSCs based on YM-2 during light soaking (AM 1.5, 100 mW cm⁻²).

 (37.3Ω) , indicating that the electron recombination resistance increases in the order of YM-3 < YM-1 \approx YM-2. The electron recombination lifetimes (τ_e) expressing the electron recombination between the injected electrons in TiO₂ and I₃⁻ ions in the electrolyte, extracted from the angular frequency ($\omega_{rec} = 2\pi f$) at the midfrequency peak in the Bode phase plot using $\tau_{\rm e} = 1/\omega_{\rm rec}$, are 20.0 ms for YM-1, 15.9 ms for YM-2 and 6.3 ms for YM-3, respectively (Fig. 8b), which is consistent with the sequence of Voc values in the DSSCs. When CDCA was employed as a coadsorbent, the τ_e values in the presence of CDCA slightly increased $(\tau_{\rm e} = 25.2 \text{ ms for YM-1}, 20.0 \text{ ms for YM-2}, \text{ and } 8.0 \text{ ms for YM-3}),$ compared with those in the absence of CDCA, that is, coadsorption of CDCA with D- π -Cat dyes can effectively retard charge recombination between the injected electrons in the CB of TiO_2 and I_3^- ions. Moreover, we examined the durability of the DSSCs based on D- π -Cat dyes to light soaking. As the result, it was demonstrated that the DSSC based on the dye YM-2 shows a good light-soaking stability under simulated solar light: there is little change in the J_{sc} , V_{oc} , ff, and η values during 24 h of

Conclusions

light soaking (Fig. 9).

In this work, to provide a direction in molecular design toward creating efficient catechol (Cat) dye sensitizers for type-II DSSCs, we have designed and synthesized D- π -Cat fluorescent dyes YM-1 with fluorene, YM-2 with carbazole, and YM-3 with carbazole-terthiophene as a π -conjugated system. D- π -Cat dyes YM-1, YM-2 and YM-3 adsorbed on the TiO_2 film show the broad absorption band corresponding to dye-to-TiO₂ charge transfer (DTCT) upon forming Ti-Cat chelate complexes (Ti-YM-1, Ti-YM-2 and Ti-YM-3). It was found that the photocurrents for DSSCs based on YM-1 and YM-2 are mainly generated by a direct electron-injection pathway from the Ti-Cat chelate complexes (Ti-YM-1 and Ti-YM-2) to the CB of the TiO₂, that is, type-II DSSCs. On the other hand, the photocurrent for DSSC based on YM-3 is mainly generated by an indirect electroninjection pathway from the excited dye to the CB of TiO₂, that is, type-I DSSCs. We demonstrate that the stabilization of the LUMO level and the expansion of the π -conjugated system by the introduction of a long π -bridge such as terthiophene on the Cat moiety can lead to an increase in the intramolecular charge transfer (ICT) excitation based on $\pi \rightarrow \pi^*$ transition with a decrease in the DTCT characteristics, resulting in enhancement of an indirect electron-injection pathway from the excited dye to the CB of TiO₂ by photoexcitation of the local band of the adsorbed dye on TiO₂.

Experimental

Melting points were measured with an MP model Yanaco micro melting point apparatus. IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer by using the ATR method. High-resolution mass spectral data were acquired on a Thermo Fisher Scientific LTQ Orbitrap XL. ¹H NMR spectra were recorded on a Varian-400 (400 MHz) or Varian-500 (500 MHz) FT-NMR spectrometer. Absorption spectra were recorded with a Hitachi U-2910 spectrophotometer and fluorescence spectra were recorded with a HORIBA FluoroMax-4 spectrofluorometer. The fluorescence quantum yields in solution were determined by using a HORIBA FluoroMax-4 spectrofluorometer with a calibrated integrating sphere system ($\lambda_{ex} = 362$, 364 and 429 nm for **YM-1**, **YM-2** and **YM-3**, respectively). Cyclic voltammetry (CV) curves were recorded in an acetonitrile/Bu₄NClO₄ (0.1 M) solution with a three-electrode system consisting of Ag/Ag⁺ as the reference electrode, Pt plate as the working electrode, and Pt wire as the counter electrode by using a AMETEK Versa STAT 4 potentiostat. Electrochemical impedance spectroscopy (EIS) for DSSCs in the dark under a forward bias of -0.60 V with a frequency range of 10 MHz to 100 kHz was measured with an AMETEK Versa STAT 3.

Synthesis

4-Bromo-1,2-bis(methoxymethoxy)benzene (1).49 A solution of iPr₂NH (18.5 mL, 0.1 mol) in dry THF (30 mL) was added slowly to a solution of 4-bromobenzene-1,2-diol (5.0 g, 26.5 mmol) in dry THF (88 mL) under an argon atmosphere. The reaction mixture was stirred for 30 min at room temperature and then chlorodimethyl ether (8.1 g, 0.1 mol) was added. The resulting mixture was stirred for 14 h at room temperature. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane and washed with water. The dichloromethane extract was evaporated under reduced pressure. The residue was chromatographed on silica gel (dichloromethane as eluent) to give 1 (5.99 g, yield 82%) as a colorless viscous solid; ¹H NMR (500 MHz, acetone-d₆) $\delta = 3.51$ (s, 3H), 3.52 (s, 3H), 5.20 (s, 2H), 5.22 (s, 2H), 7.09 (d, *J* = 8.7 Hz, 1H), 7.13 (dd, J = 2.2 and 8.7 Hz, 1H), 7.30 (d, J = 2.2 Hz, 1H) ppm; HRMS (ESI): m/z: (M + Na⁺) calcd for C₁₀H₁₃O₄BrNa, 298.98894; found 298.98907.

2-(3,4-Bis(methoxymethoxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2).⁵⁰ A solution of 1 (12.3 g, 44.0 mmol), bis(pinacolato)diboron (13.2 g, 52.0 mmol), PdCl₂(dppf) (1.1 g, 1.3 mmol), and KOAc (10.2 g, 0.1 mol) in DMF (150 mL) was stirred for 15 h at 80 °C. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane and washed with water. The dichloromethane extract was evaporated under reduced pressure. The residue was chromatographed on silica gel (hexane to remove bis(pinacolato)diboron and then ethyl acetate-hexane = 3 : 8 as eluent) to give 2 (9.58 g, yield 67%) as a colorless solid; ¹H NMR (400 MHz, acetone-d₆) δ = 1.32 (s, 12H), 3.46 (s, 3H), 3.58 (s, 3H), 5.20 (s, 2H), 5.24 (s, 2H), 7.14 (d, *J* = 8.0 Hz, 1H), 7.38 (dd, *J* = 1.6 and 8.0 Hz, 1H), 7.47 (d, *J* = 1.6 Hz, 1H) ppm; HRMS (ESI): *m/z*: (M + Na⁺) calcd for C₁₆H₂₅BO₆Na, 347.16364; found 347.16409.

2-(3,4-Bis(methoxymethoxy)phenyl)-7-bromo-9,9-dimethyl-9*H*-fluorene (3). To a mixture of 2,7-dibromo-9,9-dimethyl-9*H*fluorene (4.85 g, 13.78 mmol), 2 (2.23 g, 6.89 mmol), and $PdCl_2(PPh_3)_2$ (0.24 g, 0.34 mmol) under an argon atmosphere were added aqueous 1 M Na₂CO₃ (3 mL) and DMF (100 mL) and stirred for 6 h at 100 °C. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane and washed with water. The dichloromethane extract was evaporated under reduced pressure. The residue was chromatographed on silica gel (ethyl acetate–hexane = 1 : 5 as eluent) to give 3 (0.96 g, yield 30%) as a white solid; mp 128–129 °C; IR (ATR): $\tilde{\nu} = 1514$, 1455, 1246 cm⁻¹; ¹H NMR (500 MHz, acetone-d₆) $\delta = 1.56$ (s, 6H), 3.50 (s, 3H), 3.51 (s, 3H), 5.25 (s, 2H), 5.30 (s, 2H), 7.23 (d, J = 8.5 Hz, 1H), 7.34 (dd, J = 2.0 and 8.5 Hz, 1H), 7.62 (dd, J = 1.5 and 8.0 Hz, 1H), 7.73 (dd, J = 1.5 Hz, 1H), 7.62 (dd, J = 1.5 and 8.0 Hz, 1H), 7.74 (d, J = 1.5 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 1.5 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H) ppm; ¹³C NMR (125 MHz, acetone-d₆) $\delta = 27.91$, 48.0, 57.07, 57.16, 97.11, 97.3, 118.27, 119.57, 122.23, 122.25, 122.74, 122.77, 123.40, 127.69, 127.83, 131.82, 137.46, 138.57, 139.79, 142.13, 149.13, 149.64, 155.81, 158.0 ppm; HRMS (ESI): m/z: (M + Na⁺) calcd for C₂₅H₂₅O₄BrNa, 491.08284; found 491.08301.

7-(3,4-Bis(methoxymethoxy)phenyl)-9,9-dimethyl-N,N-diphenyl-9H-fluoren-2-amine (4). To a mixture of 3 (0.96 g, 2.05 mmol), diphenylamine (0.69 g, 4.10 mmol), Pd(OAc)22 (0.018 g, 0.08 mmol), and tBuONa (0.59 g, 0.08 mmol) under an argon atmosphere were added (tBu)₃P (10 wt% in hexane, 0.166 g, 0.082 mmol) and toluene (45 mL), and stirred for 19 h at 100 °C. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane and washed with water. The dichloromethane extract was evaporated under reduced pressure. The residue was chromatographed on silica gel (ethyl acetate-hexane = 3:10 as eluent) to give 4 (1.09 g, yield 92%) as a white solid; mp 127–128 °C; IR (ATR): $\tilde{\nu} = 1583$, 1485, 1463 cm⁻¹; ¹H NMR (500 MHz, acetone-d₆) $\delta = 1.47$ (s, 6H), 3.50 (s, 3H), 3.52 (s, 3H), 5.25 (s, 2H), 5.30 (s, 2H), 7.02 (dd, J = 2.0 and 8.2 Hz, 1H), 7.05-7.07 (m, 2H), 7.09-7.12 (m, 4H), 7.23 (d, J = 8.5 Hz, 1H), 7.26 (d, J = 2.0 Hz, 1H), 7.29-7.34 (m, 5H),7.49 (d, *J* = 2.2 Hz, 1H), 7.58 (dd, *J* = 1.6 and 8.0 Hz, 1H), 7.73 (d, J = 8.2 Hz, 1H), 7.75 (d, J = 1.6 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H) ppm; ¹³C NMR (100 MHz, acetone-d₆) $\delta = 27.35, 47.62, 56.3,$ 56.39, 96.3, 96.45, 117.29, 118.77, 119.43, 120.69, 121.75, 121.82, 121.84, 123.7, 124.21, 124.85, 126.71, 130.24, 134.76, 136.9, 138.77, 140.04, 148.13, 148.33, 148.82, 148.93, 155.17, 156.33 ppm; HRMS (APCI): m/z: (M + H⁺) calcd for C₃₇H₃₆NO₄, 558.26389; found 558.26361.

4-(7-(Diphenylamino)-9,9-dimethyl-9H-fluoren-2-yl)benzene-1,2-diol (YM-1). To compound 4 (0.136 g, 0.29 mmol) were added THF (2 mL) and 1N HCl (2 mL), and refluxed for 3 h. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane and washed with water. The dichloromethane extract was evaporated under reduced pressure. The resulting residue was subjected to reprecipitation from ethyl acetate-hexane to give YM-1 (0.106 g, yield 92%) as a white powder; mp 107–108 °C; IR (ATR): $\tilde{\nu} = 3385$ (br), 1586, 1489, 1465 cm⁻¹; ¹H NMR (400 MHz, acetone-d₆) $\delta = 1.46$ (s, 6H), 6.92 (d, J = 8.4 Hz, 1H), 7.01 (dd, J = 2.0 and 8.4 Hz, 1H), 7.06–7.11 (m, 7H), 7.21 (d, J = 2.4 Hz, 1H), 7.27 (d, J = 2.0 Hz, 1H), 7.28–7.33 (m, 4H), 7.53 (dd, *J* = 1.6 and 8.0 Hz, 1H), 7.69 (d, J = 1.6 Hz, 1H), 7.71 (d, J = 8.4 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H) ppm; ¹³C NMR (100 MHz, acetone-d₆) δ = 27.38, 47.57, 114.81, 116.53, 119.33, 119.56, 120.6, 121.48, 121.62, 123.64, 124.3, 124.78, 126.33, 130.22, 134.38, 134.99, 138.22, 140.63, 145.64, 146.3, 148.14, 148.96, 155.08, 156.27 ppm; HRMS (APCI): m/z: $(M + H^{+})$ calcd for $C_{33}H_{28}NO_2$, 470.21146; found 470.21109.

7-Bromo-9-butyl-N,N-diphenyl-9H-carbazol-2-amine (5).51 To a mixture of 2,7-dibromo-9-butyl-9H-carbazole (1.13 g, 2.96 mmol), diphenylamine (1.0 g, 5.92 mmol), Pd(dba)₂ (0.081 g, 0.09 mmol), dppf (0.148 g, 0.27 mmol) and tBuONa (0.796 g, 8.28 mmol) under an argon atmosphere was added toluene (5 mL), and stirred for 6 h at 80 °C. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane and washed with water. The dichloromethane extract was evaporated under reduced pressure. The residue was chromatographed on silica gel (dichloromethane-hexane = 1 : 6 as eluent) to give 5 (1.02 g, yield 74%) as a white solid; 1 H NMR (400 MHz, acetone-d₆, TMS) $\delta = 0.86$ (t, J = 7.4 Hz, 3H), 1.26–1.32 (m, 2H), 1.72–1.76 (m, 2H), 4.29 (t, J = 7.0 Hz, 2H), 6.94 (dd, J = 1.5 and 8.2 Hz, 1H), 7.03-7.07 (m, 2H), 7.10-7.13 (m, 4H), 7.23 (d, J = 1.1 Hz, 1H), 7.28–7.33 (m, 5H), 7.23 (d, J = 1.3 Hz, 1H), 8.00 (d, J = 8.2 Hz, 1H), 8.05 (d, J = 8.5 Hz, 1H) ppm; HRMS (APCI): m/z: (M + H⁺) calcd for C₂₈H₂₆N₂Br, 469.12739; found 469.12830.

7-(3,4-Bis(methoxymethoxy)phenyl)-9-butyl-N,N-diphenyl-9H-carbazol-2-amine (6). To a mixture of 5 (0.69 g, 2.13 mmol), 2 (1.0 g, 2.13 mmol), and Pd(PPh₃)₄ (0.123 g, 0.107 mmol) under an argon atmosphere were added aqueous 1 M Na₂CO₃ (2 mL) and DMF (10 mL) and stirred for 10 h at 100 °C. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane and washed with water. The dichloromethane extract was evaporated under reduced pressure. The residue was chromatographed on silica gel (ethyl acetate-hexane = 2:1 as eluent) to give 6 (0.696 g, yield 56%) as a light yellow solid; mp 107–110 °C; IR (ATR): $\tilde{\nu} = 1583$, 1515, 1491, 1462 cm⁻¹; ¹H NMR (400 MHz, acetonitrile-d₃) $\delta = 0.87$ (t, J = 7.4 Hz, 3H), 1.28–1.34 (m, 2H), 1.77–1.81 (m, 2H), 3.51 (s, 3H), 3.53 (s, 3H), 4.36 (t, J = 7.0 Hz, 2H), 5.26 (s, 2H), 5.31 (s, 2H), 6.93 (dd, J = 1.8 and 8.4 Hz, 1H), 7.02–7.06 (m, 2H), 7.11– 7.14 (m, 4H), 7.24–7.33 (m, 6H), 7.39 (dd, J = 2.2 and 8.4 Hz, 1H), 7.46 (dd, J = 1.4 and 8.1 Hz, 1H), 7.55 (d, J = 2.2 Hz, 1H), 7.74 (d, J = 1.0 Hz, 1H), 8.06 (d, J = 8.4 Hz, 1H), 8.11 (d, J = 8.3 Hz, 1H) ppm; ¹³C NMR (125 MHz, acetonitrile-d₃) $\delta = 13.95$, 20.84, 31.52, 42.9, 56.42, 56.5, 96.17, 96.45, 106.06, 107.85, 117.62, 117.65, 118.52, 119.03, 119.14, 120.84, 121.74, 122.22, 122.55, 123.46, 124.58, 130.12, 137.32, 138.38, 142.26, 142.87, 147.09, 147.74, 148.42, 149.09 ppm; HRMS (APCI): m/z: (M + H⁺) calcd for C38H39N2O4, 587.29043; found 587.29041.

4-(9-Butyl-7-(diphenylamino)-9*H*-carbazol-2-yl)benzene-1,2diol (YM-2). To compound 6 (0.102 g, 0.18 mmol) were added THF (2 mL) and 1N HCl (2 mL), and refluxed for 3 h. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane and washed with water. The dichloromethane extract was evaporated under reduced pressure. The resulting residue was subjected to reprecipitation from ethyl acetate–hexane to give YM-2 (0.079 g, yield 89%) as a white powder; mp 80–82 °C; IR (ATR): $\tilde{\nu} = 3367$ (br), 1593, 1488, 1456 cm⁻¹; ¹H NMR (400 MHz, acetone-d₆) $\delta = 0.73$ (t, J = 7.4Hz, 3H), 1.15–1.21 (m, 2H), 1.63–1.68 (m, 2H), 4.22 (t, J = 7.0 Hz, 2H), 6.79 (dd, J = 1.8 and 8.3 Hz, 1H), 6.80 (d, J = 8.2 Hz, 1H), 6.88–6.92 (m, 2H), 6.97–7.00 (m, 4H), 7.02 (d, J = 2.2 Hz, 1H), 7.10 (d, J = 1.7 Hz, 1H), 7.14 (d, J = 2.2 Hz, 1H), 7.15–7.19 (m, 4H), 7.28 (dd, J = 1.5 and 8.1 Hz, 1H), 7.54 (d, J = 1.0 Hz, 1H), 7.90 (d, J = 8.3 Hz, 1H), 7.94 (d, J = 8.5 Hz, 1H) ppm; ¹³C NMR (100 MHz, acetone-d₆) $\delta = 14.93$, 21.77, 32.62, 43.7, 107.06, 108.21, 115.94, 117.25, 118.61, 119.73, 120.43, 120.46, 121.47, 122.42, 123.09, 124.07, 125.26, 130.85, 135.79, 140.14, 143.26, 143.67, 146.26, 147.0, 147.64, 150.01 ppm; HRMS (APCI): m/z: (M + H⁺) calcd for C₃₄H₃₁N₂O₂, 499.23800; found 499.23767.

9-Butyl-N,N-diphenyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazol-2-amine (7). A solution of 5 (0.93 g, 1.97 mmol), bis(pinacolato)diboron (0.5 g, 1.97 mmol), PdCl₂(dppf) (0.04 g, 0.05 mmol), and KOAc (0.39 g, 3.94 mmol) in DMF (4 mL) was stirred for 15 h at 80 °C. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane, and washed with water. The dichloromethane extract was evaporated under reduced pressure. The residue was chromatographed on silica gel (hexane to remove bis(pinacolato)diboron and then ethyl acetate-hexane = 1 : 1 as eluent) to give 7 (0.52 g, yield 51%) as a white solid; mp 60-63 °C; IR (ATR): $\tilde{\nu} = 1625, 1587, 1492, 1433 \text{ cm}^{-1}$; ¹H NMR (400 MHz, acetone-d₆) $\delta = 0.84$ (t, J = 7.3 Hz, 3H), 1.24–1.30 (m, 2H), 1.38 (s, 12H), 1.72–1.78 (m, 2H), 4.29 (t, J = 7.0 Hz, 2H), 6.92 (dd, J = 1.8 and 8.4 Hz, 1H), 7.02–7.06 (m, 2H), 7.10–7.13 (m, 4H), 7.22 (d, J = 1.8 Hz, 1H), 7.27–7.32 (m, 4H), 7.61 (d, J = 7.8 Hz, 1H), 7.85 (s, 1H), 8.04–8.06 (m, 2H), 8.07 (d, J = 8.3 Hz, 2H) ppm; ¹³C NMR (100 MHz, acetone-d₆) $\delta = 14.89, 21.75, 26.0, 32.67,$ 43.72, 85.15, 106.64, 116.53, 118.36, 120.01, 120.51, 122.99, 124.29, 125.51, 126.87, 127.0, 130.88, 141.93, 143.77, 148.5, 149.89 ppm (one aromatic carbon signal was not observed owing to overlapping resonances); HRMS (APCI): m/z: (M + H⁺) calcd for C34H38BN2O2, 517.30209; found 517.30328.

5-(3,4-Bis(methoxymethoxy)phenyl)-2,2':5',2''-terthiophene (8). To a mixture of 1 (0.37 g, 1.34 mmol), 2-([2,2':5',2"-terthiophen]-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.5 g, 1.34 mmol) and Pd(PPh₃)₄ (0.077 g, 0.067 mmol) under an argon atmosphere were added aqueous 1 M Na₂CO₃ (1.2 mL) and DMF (5 mL) and stirred for 8 h at 100 °C. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane and washed with water. The dichloromethane extract was evaporated under reduced pressure. The residue was chromatographed on silica gel (ethyl acetate-hexane = 1:1 as eluent) to give 6 (0.27 g, yield 46%) as a yellow solid; mp 110-111 °C; IR (ATR): $\tilde{\nu} = 1514, 1495 \text{ cm}^{-1}$; ¹H NMR (400 MHz, acetone d_6) $\delta = 3.49$ (s, 3H), 3.52 (s, 3H), 5.25 (s, 2H), 5.30 (s, 2H), 7.11 (dd, J = 3.6 and 5.2 Hz, 1H), 7.20 (d, J = 8.5 Hz, 1H), 7.24-7.27(m, 2H), 7.28–7.35 (m, 4H), 7.45–7.47 (m, 2H) ppm; ¹³C NMR (100 MHz, acetone-d₆) $\delta = 57.08, 57.16, 96.94, 97.13, 116.41,$ 119.49, 121.3, 125.45, 125.62, 126.06, 126.27, 126.56, 126.71, 129.83, 130.0, 136.95, 137.53, 137.58, 138.25, 144.55, 149.34, 149.66 ppm; HRMS (ESI): m/z: (M + Na⁺) calcd for C₂₂H₂₀O₄NaS₃, 467.04159; found 467.04163.

5-(3,4-Bis(methoxymethoxy)phenyl)-5"-bromo-2,2':5',2"-terthiophene (9). A solution of 8 (0.52 g, 1.16 mmol) and *N*-bromosuccinimide (0.21 g, 1.16 mmol) in chloroform (100 mL) was stirred for 2 h at 0 °C. To a reaction mixture dichloromethane was added and washed with water. The dichloromethane extract was evaporated under reduced pressure. The residue was chromatographed on silica gel (chloroform as eluent) to give **9** (0.53 g, yield 87%) as a yellow solid; mp 139–142 °C; IR (ATR): $\tilde{\nu}$ = 1515, 1500 cm⁻¹; ¹H NMR (400 MHz, acetone-d₆) δ = 3.49 (s, 3H), 3.52 (s, 3H), 5.25 (s, 2H), 5.29 (s, 2H), 7.13–7.21 (m, 3H), 7.24–7.31 (m, 4H), 7.35 (d, *J* = 3.7 Hz, 1H), 7.45 (d, *J* = 1.7 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ = 56.41, 56.47, 95.51, 95.71, 111.14, 113.35, 117.01, 120.09, 123.57, 123.82, 124.16, 124.77, 124.83, 128.8, 130.84, 135.0, 135.69, 136.89, 138.74, 143.3, 147.18, 147.66; HRMS (APCI): *m*/*z*: (M + H⁺) calcd for C₂₂H₂₀O₄S₃Br, 522.97016; found 522.96979.

7-(5"-(3,4-Bis(methoxymethoxy)phenyl)-[2,2':5',2"-terthiophen]-5-yl)-9-butyl-N,N-diphenyl-9H-carbazol-2-amine (10). To a mixture of 9 (0.22 g, 0.41 mmol), 7 (0.21 g, 0.41 mmol) and $Pd(PPh_3)_4$ (0.024 g, 0.02 mmol) under an argon atmosphere were added aqueous 1 M Na2CO3 (0.4 mL) and DMF (10 mL) and stirred for 2 h at 90 °C. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane and washed with water. The dichloromethane extract was evaporated under reduced pressure. The residue was chromatographed on silica gel (ethyl acetate-hexane = 1:2 as eluent) to give 10 (0.23 g, yield 66%) as a yellow solid; mp 160-164 °C; IR (ATR): $\tilde{\nu} = 1594, 1491, 1461 \text{ cm}^{-1}$; ¹H NMR (400 MHz, acetone-d₆) $\delta = 0.88$ (t, J = 7.2 Hz, 3H), 1.28–1.35 (m, 2H), 1.77– 1.82 (m, 2H), 3.50 (s, 3H), 3.52 (s, 3H), 4.37 (t, J = 6.8 Hz, 2H), 5.25 (s, 2H), 5.30 (s, 2H), 6.94 (dd, J = 1.8 and 8.4 Hz, 1H), 7.04-7.07 (m, 2H), 7.11-7.14 (m, 4H), 7.19-7.23 (m, 2H), 7.29-7.36 (m, 10H), 7.47 (d, J = 1.8 Hz, 1H), 7.53–7.57 (m, 2H), 7.85 (s, 1H), 8.05 (d, J = 8.4 Hz, 1H), 8.11 (d, J = 8.1 Hz, 1H) ppm; ¹³C NMR (100 MHz, acetone-d₆) $\delta = 14.17, 21.00, 31.87, 56.34, 96.19,$ 96.38, 106.02, 106.48, 115.66, 117.95, 118.03, 118.74, 119.4, 120.56, 121.15, 121.9, 123.55, 123.6, 124.68, 124.75, 124.78, 125.04, 125.35, 125.36, 125.44, 125.84, 125.95, 129.25, 130.16, 131.61, 136.25, 136.3, 136.7, 136.88, 142.31, 143.26, 143.83, 145.55, 147.48, 148.6, 148.91, 149.16 ppm; HRMS (APCI): m/z: $(M + H^{+})$ calcd for $C_{50}H_{45}N_2O_4S_3$, 833.25360; found 833.25452.

4-(5"-(9-Butyl-7-(diphenylamino)-9H-carbazol-2-yl)-[2,2':5',2"terthiophen]-5-yl)benzene-1,2-diol (YM-3). To compound 10 (0.09 g, 0.1 mmol) were added THF (5 mL) and 1 N HCl (2 mL), and refluxed for 8 h. After concentrating under reduced pressure, the resulting residue was dissolved in ethyl acetate and washed with water. The dichloromethane extract was evaporated under reduced pressure. The organic extract was concentrated to afford YM-3 as a greenish yellow powder in quantitative yield; mp 260–263 °C; IR (ATR): $\tilde{\nu} = 3369, 1593,$ 1491, 1460 cm⁻¹; ¹H NMR (400 MHz, acetone-d₆) $\delta = 0.88$ (t, J =7.3 Hz, 3H), 1.29–1.33 (m, 2H), 1.77–1.83 (m, 2H), 4.36 (t, J = 7.0 Hz, 2H), 6.86 (d, I = 8.1 Hz, 1H), 6.93 (dd, I = 1.8 and 8.4 Hz, 1H), 7.03-7.07 (m, 3H), 7.11-7.15 (m, 5H), 7.23-7.35 (m, 10H), 7.53–7.55 (m, 2H), 7.85 (s, 1H), 8.04 (d, J = 8.4 Hz, 1H), 8.10 (d, J= 8.1 Hz, 1H); ¹³C NMR (100 MHz, acetone-d₆) $\delta = 14.15, 20.98,$ 31.85, 43.01, 106.03, 106.47, 113.53, 116.75, 117.95, 118.03, 118.38, 119.4, 121.14, 121.9, 123.55, 123.58, 123.67, 124.74, 125.03, 125.16, 125.33, 125.79, 125.86, 126.92, 130.16, 131.63, 135.31, 136.37, 136.61, 136.95, 142.32, 143.26, 144.83, 145.45, 146.43, 146.44, 147.47, 149.16 ppm; HRMS (ESI): m/z: (M + H⁺) calcd for C₄₆H₃₇N₂O₂S₃, 745.20117; found 745.20020.

Preparation of DSSCs based on dyes YM-1, YM-2 and YM-3. 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 thick TiO₂ electrode (0.5 \times 0.5 cm² in photoactive area) was immersed into a 0.1 mM dye solution in THF for a number of hours to adsorb the photosensitizer. The DSSCs were fabricated by using the TiO₂ electrode thus prepared, 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 photocurrentvoltage characteristics were measured using a potentiostat under simulated solar light (AM 1.5, 100 mW cm⁻²). IPCE spectra were recorded under monochromatic irradiation with a tungsten-halogen lamp and a monochromator. The amount of adsorbed dye on TiO2 nanoparticles was determined from the calibration curve by absorption spectral measurement of the concentration change of the dye solution before and after adsorption. Absorption spectra of the dyes adsorbed on TiO₂ nanoparticles were recorded on the dye-adsorbed TiO₂ film (thickness of 9 μ m) in the transmission mode with a Shimadzu UV-3150 spectrophotometer equipped with a calibrated integrating sphere system.

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