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2,1,3-Benzothiadiazole-containing donor-acceptor-acceptor dyes for dye-sensitized solar cells

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ABSTRACT

A series of organic dves with a donor-acceptor-acceptor (D-A-A) configuration, in which various diarylthienylamine donors and a cyanoacrylic acid acceptor are bridged by a low-band-gap 2,1,3benzothiadiazole acceptor, have been synthesized, characterized, and employed as photosensitizers for dye-sensitized solar cells (DSSCs). The adoption of 2,1,3-benzothiadiazole as the bridging acceptor endowed these tailor-made dyes with superior light-harvesting capabilities in comparison to their previously reported pyrimidine-based analogs. After fine-tuning the fabrication conditions, DSSCs based on these dyes showed solar spectral responses extending to the near-IR region and achieved power conversion efficiencies (PCEs) of up to 3.16% (OHexDPTB) under simulated AM 1.5G irradiation (100 mW cm⁻²).

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1. Introduction

Dye-sensitized solar cells (DSSCs) have been regarded as one of the most promising candidates for next-generation solar cells since their invention by Grätzel and co-workers in 1991¹ because of their ease of production, potential to allow low-cost manufacturing, and ability to be fabricated onto light-weight flexible substrates. During the last two decades, combined developments of new photosensitizers²⁻⁶ and electrolytes⁷⁻¹² have contributed to significant improvements both in power conversion efficiencies (PCEs) and long-term stability. At present, DSSCs based on ruthenium sensitizers have exhibited PCEs in the range of 11-12%.¹³⁻¹⁷ However, the rarity and high cost of the ruthenium metal may impede their further development for large-scale applications. Accordingly, metal-free organic sensitizers that are generally modeled on the donor-(π -spacer)-acceptor (D- π -A) system have also being intensely explored in DSSCs due to several predominant advantages over their ruthenium counterparts, such as larger molar extinction coefficients, flexibility in structural modification for manipulation of optoelectronic properties, facile synthesis, and relatively lower cost.¹⁸⁻³⁰ Although the performance of organic sensitizers has lagged behind those of ruthenium sensitizers over a long period of time, a record-high PCE of 12.3% has recently been realized for

DSSCs employing a D $-\pi$ -A porphyrin dye in conjunction with a Co^(II/III)tris(bipyridyl)-based redox electrolyte when co-sensitized with another organic D $-\pi$ -A dye, demonstrating a bright future for organic dye-based DSSCs.³¹

Previously, we reported a series of efficient organic dyes, where various diarylthienylamine donors are connected to a cyanoacrylic acid acceptor (also TiO2-anchoring group) through an electrondeficient pyrimidine π -spacer (Scheme 1).³² We later referred to such structural arrangement as the donor-acceptor-acceptor (D-A-A) molecular architecture. In comparison to a $D-\pi-A$ counterpart that adopts phenylene as a π -spacer, these dyes showed redshifted absorption and hence gave larger photocurrent as employed in DSSCs. From the point of view of energy levels, both frontier molecular orbital levels of the D-A-A dyes were lower than those of the D $-\pi$ -A counterpart, yet the degree of the shift on the lowest unoccupied molecular orbital (LUMO) level was larger than that on the highest occupied molecular orbital (HOMO) level, thus leading to narrower energy gaps for the D–A–A dyes. On the basis of the experimental observations mentioned above, we argued that such D-A-A architecture shows a potential ability to simultaneously enhance the short-circuit current density (J_{sc}) and open-circuit voltage $(V_{\rm oc})$ as utilized in the design of molecular donors for small-molecule organic solar cells (SMOSCs). Recently, two D–A–A donor molecules were practically synthesized and employed in SMOSCs, which indeed successfully demonstrated remarkable achievements with PCEs near or exceeding 6%.^{33,34} Remarkably, the donor molecule, DTDCTB, featuring a low-band-gap 2,1,3-benzothiadiazole (BT) exhibited





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a distinguished light-harvesting ability with absorption extending to the near-IR region.³³ The BT represents one of the most widely used electron-accepting units in optoelectronic materials,^{35–37} and several BT-containing organic DSSC dyes with different configurations have been reported.^{38–45} In this work, we report on a new series of organic D–A–A dyes, where the BT acceptor is used to replace the pyrimidine block (Scheme 2). Such structural modification is anticipated to enable these tailor-made dyes to show significant bathochromic shifts in absorption as compared to their pyrimidine-based analogs. This study also provides us with an opportunity to further assess the applicability of our D–A–A molecular design strategy on developing photosensitizers for DSSCs.



Scheme 1. Molecular structures of the reported pyrimidine-containing DSSC dyes.

The UV-vis absorption spectra of the dyes in dichloromethane (CH₂Cl₂) solutions are depicted in Fig. 1, and their pertinent photophysical parameters are summarized in Table 1. The photoluminescence data of these dyes are not provided here since the dves are almost non-luminescent. All three dves exhibit an intense absorption band in the long-wavelength region with a maximum around 613–654 nm and a molar extinction coefficient higher than $3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, which is assigned to the intramolecular charge transfer (ICT) transition. Apparently, the absorption of this series of dyes effectively extends the useful light-harvesting range to the near-IR region through incorporating BT as the bridging acceptor. The absorption bands of OMeDPTB and OHexDPTB are red-shifted as compared to that of **DPTB** by ca. 40 nm because of the stronger electron-donating nature of the dialkoxy substituents. This red shift is profitable for photon harvesting and thus photocurrent generation in DSSCs (vide infra). It is worth mentioning that in comparison to the reported D–A– π –A dye incorporating thiophene as an extra π -spacer to connect the BT and cyanoacrylic acid acceptors (λ_{max} at 541 nm in a tetrahydrofuran (THF) solution),³⁸ **DPTB** shows an evident bathochromic shift in absorption, corroborating again that enhanced solar spectral responses can be realized through our D-A-A molecular design concept (Fig. S1). Fig. 2 depicts the absorption spectra of the dyes anchoring on 7 µm porous TiO₂ nanoparticle films. The absorption maxima of these three dyes are blue-shifted compared to those observed in CH₂Cl₂ solutions. This phenomenon can be attributed to the deprotonation of carboxylic acid upon adsorption onto the TiO₂ surface, and the resulting carboxylate-TiO₂ unit is a weaker electron acceptor than the corresponding carboxylic acid.



Scheme 2. Synthesis of the dyes DPTB, OMeDPTB, and OHexDPTB.

2. Results and discussion

The synthetic pathways of the new dyes are illustrated in Scheme 2. Stille coupling reactions of triarylamine-functionalized tributylstannyl derivatives **1** and **4**,7-dibromo-2,1,3-benzothiadiazole afforded the mono-functionalized intermediates **2a**–**c**, which were directly reacted with copper cyanide to yield their corresponding cyano derivatives **3a**–**c** via the Rosenmund–von Braun reaction. Finally, the reduction of **3a**–**c** using diisopropylaluminum hydride followed by Knöevenagel condensation of the resulting aldehydes **4a**–**c** with cyanoacetic acid in the presence of ammonium acetate gave the target compounds **DPTB**, **OMEDPTB**, and **OHEXDPTB** in moderate overall yields. To gain more insight into the electronic structures of the dyes, density function theory (DFT) calculations were carried out on a B3LYP/6-31G(d) level for geometry optimization. As shown in Fig. 3, the HOMOs of the dyes are populated over the whole molecular conjugated backbone with substantial contributions from diarylamine and thiophene fragments, whereas LUMOs are delocalized through thiophene, BT, and cyanoacrylic acid blocks with considerable contributions from the latter two. The significant spatial overlap between the HOMO and LUMO as well as the coplanar conformation between the thiophene and BT rings is beneficial to enhance the efficiency of ICT transition, as evidenced in absorption spectra. Moreover, the HOMO–LUMO excitation shifts the electron density distribution from the diarylamine unit to the



Fig. 1. Absorption spectra of DPTB, OMeDPTB, and OHexDPTB measured in CH_2Cl_2 solutions (10 $^{-5}$ M).

Table 1

Photophysical and electrochemical parameters of the dyes

Dye	λ _{max} (nm) ^a	$^{\epsilon}(M^{-1} cm^{-1})^{a}$	λ_{max} on TiO ₂ $(nm)^b$	<i>E</i> ₀₋₀ (eV) ^с	E_{ox}^1 $(v)^d$	$E_{\rm red}$ $(v)^{\rm e}$	$E_{\text{ox}}^{*}(\nu)^{\text{f}}$
DPTB	613	32,800	513	1.74	1.02	-0.66	-0.72
OMeDPTB	650	34,442	548	1.65	0.87	-0.70	-0.78
OHexDPTB	654	32,292	547	1.64	0.87	-0.69	-0.77

^a Absorption spectra were measured in CH_2Cl_2 solutions (10⁻⁵ M). ^b Absorption spectra on TiO₂ were obtained through measuring the dyes adsor-

bed on 7 μ m TiO₂ nanoparticle films in chlorobenzene solutions. ^c E_{0-0} was estimated from the onset point of the absorption spectra in CH₂Cl₂

 E_{0-0} was estimated from the onset point of the absorption spectra in CH₂Cl₂ solutions.

 $^{\rm d}$ Measured in CH₂Cl₂ solutions with 0.1 M tetrabutylammonium hexa-fluorophosphate (TBAPF₆) as a supporting electrolyte. Scan rate: 100 mV/s; calibrated with ferrocene/ferrocenium (Fc/Fc⁺) as an external reference and converted to NHE by addition of 630 mV.⁴⁶

 $^{\rm e}$ Measured in THF solutions with 0.1 M tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte. Scan rate: 100 mV/s; calibrated with ferrocene/ferrocenium (Fc/Fc⁺) as an external reference and converted to NHE by addition of 630 mV. 46

^f $E_{\text{ox}}^* = E_{\text{ox}}^1 - E_{0-0}$.



Fig. 2. Absorption spectra of DPTB, OMeDPTB, and OHexDPTB anchoring on 7 μm porous TiO_2 nanoparticle films.

cyanoacrylic acid block, thus facilitating efficient electron injection from photoexcited dyes into the TiO₂ electrode.

The electrochemical properties of these dyes were studied by cyclic voltammetry (CV). Representative cyclic voltammograms are shown in Fig. 4 and the relevant CV data are collected in Table 1. The three dyes all exhibit one reversible oxidation wave at lower potential and one irreversible (or quasi-reversible) oxidation wave at higher potential. The first waves can be ascribed to the oxidation of the diarylthienylamine donor moieties, whereas the second waves can be assigned to the oxidation of the conjugated backbones.⁴⁴ The oxidation potentials of **OMeDPTB** and **OHexDPTB** are less positive than those of **DPTB** due to the presence of the stronger electron-donating dialkoxy substituents. Moreover, the introduction of the dialkoxy substituents on the donor moieties increases the electron density of the conjugated backbones, thus making the second oxidation behaviors of OMeDPTB and OHexDPTB more reversible. On the other hand, one quasireversible reduction wave attributed to the reduction of the cyanoacrylic acid block was observed in the cathodic potential regime for the dyes, which is relatively insensitive to the structural alterations of the donor moieties even though the reduction potentials of **OMeDPTB** and **OHexDPTB** are slightly more negative than that of **DPTB**. The zero-zero excitation energy (E_{0-0}) estimated from the onset point of the absorption spectrum and the first oxidation potential (E_{ox}^1) was used to calculate the excited-state oxidation potential (E_{ox}^{*}) . The deduced E_{ox}^{*} values corresponding to the LUMO levels of these three dyes are more negative than the conduction band edge of the TiO₂ electrode (-0.5 V vs NHE),⁴⁷ indicating that the electron injection from photoexcited dyes into TiO₂ would be energetically favorable. The first oxidation potentials (E_{0x}^1) corresponding to the HOMO levels of the dyes are more positive than the redox potential of the iodide/triiodide (I^{-}/I_{3}^{-}) couple (0.4 V vs NHE). It suggests that the oxidized dyes formed after electron injection into TiO₂ should be able to thermodynamically accept electrons

In common with the photovoltaic characterization on the pyrimidine-based dyes,³² the photovoltaic performance of **DPTB**, OMeDPTB, and OHexDPTB as the photosensitizers for DSSCs was first evaluated with a sandwich DSSC cell using 0.6 M 1-butyl-3methylimidazolium iodide (BMII), 0.05 M LiI, 0.03 M I₂, 0.5 M 4tert-butylpyridine (TBP), and 0.1 M guanidinium thiocyanate in a mixture of acetonitrile–valeronitrile (85: 15, v/v) as the redox electrolyte (EL1) (details of the device preparation and characterization are described in the experimental section). The performance parameters of the DSSCs based on these organic dyes, including the Jsc, Voc, fill factor (FF), and PCEs, are summarized in Table 2. The preliminary results showed that the DSSCs exhibit extremely low PCEs (<0.06%). We attribute the poor photovoltaic performance to the addition of TBP into the electrolyte that can negatively shift the conduction band edge of TiO₂ about 0.3 V, 48,49 thus impeding efficient electron injection from the photoexcited dyes into the TiO₂ electrode.⁴⁶ Very recently, a few BT-containing sensitizers with similar structural features to our dyes (i.e., the BT acceptor directly adjacent to the cyanoacrylic acid) were also reported to show inferior performance to their analogs even though the origins of the low PCEs were different.^{44,45} For a fair comparison, the N719-sensitized DSSC was also fabricated under the same conditions and reached a PCE of 8.57%.

from I[–] ions in the electrolyte for effective dye regeneration.

To improve the poor device performance, the DSSCs were then fabricated in a TBP-free condition by merely using 0.6 M 1,2dimethyl-3-propylimidazolium iodide (DMPII), 0.05 M LiI, 0.03 M I₂ in acetonitrile as the redox electrolyte (EL2). The DSSCs based on these organic dyes exhibited remarkably improved performance, whereas the **N719**-based cell showed a lower PCE than the parent cell based on using the EL1 electrolyte, mainly due to the lower J_{sc} and V_{oc} values (Table 2). The decrease in V_{oc} for the **N719**-based cell can be partly attributed to the shift of the conduction band edge of TiO₂ toward positive potential.⁴⁹ Such phenomenon also qualitatively verifies our aforementioned speculation on the poor photovoltaic performance for the DSSCs based on our organic dyes in conjunction with the EL1 electrolyte. Fig. 5 shows the incident monochromatic photon-to-current conversion efficiency (IPCE)



Fig. 3. Frontier molecular orbitals (HOMOs and LUMOs) of the dyes calculated with DFT on a B3LYP/6-31G(d) level.



Fig. 4. Cyclic voltammograms of DPTB, OMeDPTB, and OHexDPTB recorded in solutions.

Table 2

Performance parameters of the DSSCs based on the organic dyes^a

Dye	$J_{\rm sc}$ (mA cm ⁻²)	$V_{\rm oc}\left({\sf V}\right)$	FF	PCE (%)
DPTB ^b	0.31	0.28	0.45	0.039
OMeDPTB ^b	0.42	0.25	0.45	0.045
OHexDPTB^b	0.44	0.30	0.45	0.059
N719 ^b	16.12	0.76	0.70	8.57
DPTB ^c	9.12	0.41	0.62	2.30
OMeDPTB ^c	13.06	0.39	0.62	3.13
OHexDPTB ^c	11.10	0.45	0.63	3.16
N719 ^c	14.05	0.57	0.67	5.39

^a The concentration of the organic dyes was maintained at 0.5 mM in a chlorobenzene solution, with 0.5 mM deoxycholic acid (DCA) as a co-adsorbent [**N719** was fabricated in a *tert*-butanol–acetonitrile (1:1, v/v) solution under the same conditions]. Performance of DSSCs was measured with a 0.125 cm² working area. Irradiating light: AM 1.5G (100 mW cm⁻²).

^b The composition for the EL1 electrolyte is: 0.6 M 1-butyl-3-methylimidazolium iodide (BMII), 0.05 M LiI, 0.03 M I₂, 0.5 M 4-*tert*-butylpyridine (TBP), and 0.1 M guanidinium thiocyanate in a mixture of acetonitrile and valeronitrile (85/15, *v*/*v*). ^c The composition for the EL2 electrolyte is: 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.05 M LiI, 0.03 M I₂ in acetonitrile

spectra of the DSSCs based on the adoption of EL2 electrolyte. In agreement with the trend in absorption spectra, the IPCE spectra of the three cells all extend to the near-IR region, and the **OMeDPTB**-and **OHexDPTB**-based devices show red-shifted spectral responses as compared to the **DPTB**-based device. Fig. 6 shows the current density-voltage (J-V) curves of the DSSCs using the EL2 electrolyte under standard global AM 1.5G solar irradiation (100 mW cm⁻²). The J_{sc} values are well consistent with the IPCE spectra with



Fig. 5. IPCE spectra of DSSCs based on the EL2 electrolyte.



Fig. 6. Photocurrent density vs voltage for DSSCs based on the EL2 electrolyte under AM 1.5G simulated solar illumination (100 mW cm^{-2}).

a maximum value of 13.06 mA cm⁻² generated in the DSSC based on **OMeDPTB**, which showed both a broader spectral response and higher IPCE values. On the other hand, the **OHexDPTB**-based cell gave a higher V_{oc} than the other two cells, benefiting from the presence of two long aliphatic hexyloxy chains on the diarylthienylamine donor. It is now well known that the aliphatic alkyl chains can act as effective blocking units between the TiO₂ surface and electrolyte to prevent the approach of hydrophilic I_3^- ions to the TiO₂ surface, leading to suppressed charge recombination/dark current and lengthened electron lifetimes and thus an enhanced V_{oc} (see details in our previous works^{32,50} and Fig. S2).⁵¹ As a whole, the **OHexDPTB**-based cell showed the best PCE of 3.16% among these three DSSCs, with a J_{sc} of 11.10 mA cm⁻², V_{oc} of 0.45 V, and FF of 0.63.

3. Conclusion

In summary, three new organic dyes (DPTB, OMeDPTB, and **OHexDPTB**) with a D–A–A configuration have been synthesized, characterized, and applied in DSSCs. By making use of BT as the bridging acceptor, these tailor-made dyes showed superior lightharvesting capabilities to their previously reported pyrimidinebased analogs. The incorporation of dialkoxy substituents on the donor moieties endowed OMeDPTB and OHexDPTB with narrower bandgaps and higher HOMO levels than DPTB. In photovoltaic characterization, the use of the TBP-containing electrolyte (EL1) that can negatively shift the conduction band edge of TiO₂ about 0.3 V impeded efficient electron injection from the photoexcited dyes into the TiO₂ electrode because of their deep-lying LUMO levels, thus leading to poor photovoltaic performance. In contrast, the DSSCs based on these dyes in conjunction with the TBP-free electrolyte (EL2) showed markedly improved performance with solar spectral responses extending to the near-IR region, and the best cell based on OHexDPTB reached a PCE of 3.16% under simulated AM 1.5G irradiation (100 mW cm⁻²). The current results reveal that although the D-A-A dyes generally show better lightharvesting abilities than their analogs. DSSCs sensitized with D-A-A dyes may suffer from a trade-off between photocurrent and photovoltage owing to the possibly limited uses of TBP-containing electrolytes.

4. Experimental section

4.1. Synthetic procedures and characterization

4.1.1. *General methods*. All chemicals and reagents were used as received from commercial sources without purification. Solvents for chemical synthesis were purified by distillation. All chemical reactions were carried out under an argon or nitrogen atmosphere.

5-(*N*,*N*-diphenylamino)-2-(tri-*n*-butylstannyl)thiophene (**1a**),⁵² 5-[*N*,*N*-bis(4-methoxyphenyl)amino]-2-(tri-*n*-butylstannyl)thiophene (**1b**),^{53,54} and 5-[*N*,*N*-bis(4-hexyloxypheny)amino]-2-(tri-*n*butylstannyl)thiophene (**1c**)^{53,54} were synthesized by a procedure similar to that described in the next paragraph.

To a stirring solution of 2-(*N*,*N*-diphenylamino)thiophene (5.02 g, 20 mmol) in anhydrous THF (60 mL) was dropwise added *n*-BuLi (1.6 M, 16.25 mL, 26 mmol) at -78 °C under an argon atmosphere. The reaction mixture was stirred for 15 min at -78 °C, quickly warmed to room temperature by removing the cooling bath, and stirred for another 15 min. Tri-*n*-butyltin chloride (7.05 mL, 26 mmol) was then added to the mixture in one portion. After stirring at ambient temperature overnight, the reaction mixture was poured into water and extracted with diethyl ether. The combined extracts were washed with brine, dried over anhydrous magnesium sulfate, and filtered. The solvent of the extracts was removed by rotary evaporation to afford **1a** as a sticky green oil, which was used for the next step without further purification.

4.1.2. [5-(7-Cyano-2,1,3-benzothiadiazol-4-yl)-thiophen-2-yl]-N,Ndiphenylamine (**3a**). A mixture of **1a** (20 mmol), 4,7-dibromo-2,1,3benzothiadiazole (5.88 g, 20 mmol), and PdCl₂(PPh₃)₂ (281 mg, 0.4 mmol) in anhydrous *N*,*N*-dimethylformamide (30 mL) was stirred and heated at 80 °C under an argon atmosphere overnight. After cooling to room temperature, the reaction mixture was

poured into methanol. The resulting precipitate was filtered, washed with methanol, and dried. The crude product mixture consisting of **2a** and the disubstituted byproduct was used for the next step without further separation. A mixture of the crude product mixture and copper cyanide (4.48 g, 50 mmol) in N,Ndimethylformamide (108 mL) was stirred and heated to reflux overnight. The cooled reaction mixture was added into an icv solution of concentrated hydrochloric acid (12 mL, 12 N), iron (III) chloride (21.87 g), and water (122 mL). The mixture was then heated at 70 °C for 0.5 h, after which the mixture was extracted with toluene and water. The combined extracts were washed with brine, dried over anhydrous magnesium sulfate, and filtered. The solvent of the filtrate was removed by rotary evaporation, and the crude product was purified by column chromatography on silica gel with dichloromethane/hexane (v/v, 1:1) as eluent to afford **3a** as a black solid (2.82 g, 34%). Mp 220–222 °C; IR (KBr) v 3037, 2224, 1584, 1531, 1492, 1461, 1370, 1206, 1054, 898 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 8.15 (d, J=4.0 Hz, 1H), 7.91 (d, J=7.6 Hz, 1H), 7.59 (d, J=7.6 Hz, 1H), 7.37-7.33 (m, 4H), 7.27 (d, J=7.2 Hz, 4H), 7.16 (t, J=7.2 Hz, 2H), 6.64 (d, J=4.0 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 157.5, 153.7, 151.0, 146.8, 135.9, 132.6, 131.0, 129.4, 127.7, 124.6, 124.2, 121.2, 117.2, 116.0, 100.7; HRMS (*m*/*z*, FAB⁺) Calcd for C₂₃H₁₄N₄S₂ 410.0660, found 410.0657.

4.1.3. [5-(7-Cyano-2,1,3-benzothiadiazol-4-yl)-thiophen-2-yl]-N,Nbis(4-methoxyphenyl)amine (**3b**). The synthetic procedure was similar to that of **3a**, except that the eluent for column purification was dichloromethane/hexane (ν/ν , 2:1). **3b** was isolated as a black solid (29%). Mp 156–158 °C; IR (KBr) ν 3040, 2929, 2831, 2225, 1605, 1567, 1541, 1421, 1354, 1241, 1170, 1036, 829 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 8.11 (d, J=4.4 Hz, 1H), 7.84 (d, J=7.6 Hz, 1H), 7.46 (d, J=7.6 Hz, 1H), 7.24 (d, J=8.8 Hz, 4H), 6.90 (d, J=8.8 Hz, 4H), 6.37 (d, J=4.4 Hz, 1H), 3.83 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ 159.9, 157.0, 153.8, 150.9, 139.7, 135.9, 132.8, 131.8, 126.3, 124.6, 120.2, 116.2, 114.8, 112.4, 99.4, 55.6, 55.5; HRMS (m/z, FAB⁺) Calcd for C₂₅H₁₈N₄O₂S₂ 470.0871, found 470.0868.

4.1.4. [5-(7-Cyano-2,1,3-benzothiadiazol-4-yl)-thiophen-2-yl]-N,N-bis(4-hexyloxypheny)amine (**3c**). The synthetic procedure was similar to that of **3a**. The crude product was purified by column chromatography on silica gel twice using dichloromethane/hexane (ν/ν , 1:1) and then with ethyl acetate/hexane (ν/ν , 1:12) as eluent to afford **3c** as a black solid (34%). Mp 107–109 °C; IR (KBr) ν 3043, 2957, 2854, 2222, 1605, 1543, 1470, 1352, 1233, 1178, 1025, 835 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 8.11 (d, *J*=4.4 Hz, 1H), 7.83 (d, *J*=8.0 Hz, 1H), 7.44 (d, *J*=8.0 Hz, 1H), 7.23 (dd, *J*=2.4, 7.2 Hz, 4H), 6.88 (dd, *J*=2.4, 7.2 Hz, 4H), 6.36 (d, *J*=4.4 Hz, 1H), 3.96 (t, *J*=6.8 Hz, 4H), 1.82–1.78 (m, 4H), 1.50–1.46 (m, 4H), 1.39–1.34 (m, 8H), 0.95–0.91 (m, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ 160.1, 156.6, 153.7, 150.8, 139.4, 135.8, 132.8, 131.9, 126.3, 124.2, 119.9, 116.2, 115.2, 112.1, 99.1, 68.2, 31.6, 29.3, 25.8, 22.7, 14.1; HRMS (*m*/*z*, FAB⁺) Calcd for C₃₅H₃₈N₄O₂S₂ 610.2436, found 610.2435.

4.1.5. 7-(5-N,N-Diphenylaminothiophen-2-yl)-2,1,3-benzothiadiazole-4-carbaldehyde (**4a**). To a stirring solution of **3a** (616 mg, 1.5 mmol) in anhydrous THF (30 mL) was dropwise added diisopropylaluminum hydride (1 M in THF, 3.75 mL, 3.75 mmol) at 0 °C under an argon atmosphere. After stirring at this temperature for 2 h, the reaction was quenched with saturated aqueous ammonium chloride solution (15 mL), and the cooling bath was removed. After stirring at ambient temperature for another 1 h, the reaction mixture was poured into water and extracted with ethyl acetate. The combined extracts were washed with brine, dried over anhydrous magnesium sulfate, and filtered. The solvent of the filtrate was removed by rotary evaporation, and the crude product was purified by column chromatography on silica gel with dichloromethane/ hexane (ν/ν , 2:1) as eluent to afford **4a** as a black solid (200 mg, 32%). Mp 175–177 °C; IR (KBr) ν 3035, 2839, 2729, 1690, 1587, 1537, 1490, 1369, 1265, 1154, 1058, 837 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 10.59 (s, 1H), 8.16 (d, *J*=4.0 Hz, 1H), 8.09 (d, *J*=7.6 Hz, 1H), 7.68 (d, *J*=7.6 Hz, 1H), 7.34–7.30 (m, 4H), 7.26–7.23 (m, 4H), 7.15–7.11 (m, 2H), 6.63 (d, *J*=4.0 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 188.1, 157.4, 153.6, 151.9, 146.8, 133.3, 133.0, 130.9, 129.4, 128.4, 124.6, 124.2, 123.9, 121.6, 117.3; HRMS (*m/z*, FAB⁺) Calcd for C₂₃H₁₅N₃OS₂ 413.0657, found 413.0658.

4.1.6. 7-[5-N,N-bis(4-methoxyphenyl)aminothiophen-2-yl]-2,1,3benzothiadiazole-4-carbaldehyde (**4b**). The synthetic procedure was similar to that of **4a**. The crude product was purified by column chromatography on silica gel twice using ethyl acetate/toluene (ν/ν , 1:40) and then with ethyl acetate/hexane (ν/ν , 1:3) as eluent to afford **4b** as a black solid (37%). Mp 150–152 °C; IR (KBr) ν 3070, 2960, 2837, 1665, 1604, 1546, 1418, 1349, 1235, 1182, 1008, 840 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 10.55 (s, 1H), 8.15 (d, *J*=4.4 Hz, 1H), 8.04 (d, *J*=8.0 Hz, 1H), 7.56 (d, *J*=8.0 Hz, 1H), 7.24 (dd, *J*=2.4, 6.8 Hz, 4H), 6.90 (dd, *J*=2.4, 6.8 Hz, 4H), 6.38 (d, *J*=4.4 Hz, 1H), 3.83 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ 187.9, 160.0, 157.0, 153.7, 151.8, 139.7, 133.7, 133.3, 131.9, 126.3, 125.3, 123.1, 120.5, 114.7, 112.6, 55.5; HRMS (m/z, FAB⁺) Calcd for C₂₅H₁₉N₃O₃S₂ 473.0868, found 473.0875.

4.1.7. 7-[5-N,N-bis(4-hexyloxypheny)aminothiophen-2-yl]-2,1,3benzothiadiazole-4-carbaldehyde (**4c**). The synthetic procedure was similar to that of **4a**, except that the eluent for column purification was toluene. **4c** was isolated as a black solid (24%). Mp 106–108 °C; IR (KBr) ν 3066, 2956, 2854, 1673, 1605, 1538, 1435, 1346, 1239, 1179, 1051, 832 cm⁻¹; ¹H NMR (CD₂Cl₂, 400 MHz) δ 10.57 (s, 1H), 8.13 (d, *J*=4.4 Hz, 1H), 8.05 (d, *J*=7.6 Hz, 1H), 7.62 (d, *J*=7.6 Hz, 1H), 7.23 (d, *J*=8.8 Hz, 4H), 6.90 (d, *J*=8.8 Hz, 4H), 6.36 (d, *J*=4.4 Hz, 1H), 3.97 (t, *J*=6.4 Hz, 4H), 1.83–1.76 (m, 4H), 1.50–1.45 (m, 4H), 1.38–1.36 (m, 8H), 0.93 (t, *J*=6.8 Hz, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ 187.9, 160.2, 156.6, 153.7, 151.8, 139.5, 133.7, 133.3, 132.0, 126.3, 125.1, 123.2, 120.4, 115.2, 112.4, 68.3, 31.7, 29.3, 25.8, 22.7, 14.2; HRMS (*m*/*z*, FAB⁺) Calcd for C₃₅H₃₉N₃O₃S₂ 613.2433, found 613.2432.

4.1.8. 2-Cyano-3-[7-(5-N,N-diphenylaminothiophen-2-yl)-2,1,3benzothiadiazol-4-yl] acrylic acid (DPTB). A mixture of 4a (207 mg, 0.5 mmol), cyanoacetic acid (128 mg, 1.5 mmol), ammonium acetate (27 mg) in glacial acetic acid (9 mL) was stirred and heated at 80 °C for 2 h. After cooling to room temperature, the resulting precipitate was collected by filtration and thoroughly washed with water, methanol, and hexane to afford DPTB as a black solid (225 mg, 94%). Mp 255–257 °C; IR (KBr) v 3023, 2225, 1694, 1588, 1533, 1490, 1377, 1235, 1153, 1053, 904, 812 cm⁻¹; ¹H NMR (Acetone- d_6 , 400 MHz) δ 9.13 (s, 1H), 8.77 (d, J=8.0 Hz, 1H), 8.23 (d, *J*=4.4 Hz, 1H), 8.04 (d, *J*=8.0 Hz, 1H), 7.41 (t, *J*=8.0 Hz, 4H), 7.31–7.29 (m, 4H), 7.21 (t, J=7.2 Hz, 2H), 6.66 (d, J=4.4 Hz, 1H); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ 163.3, 158.0, 154.3, 150.2, 146.5, 146.1, 131.1, 130.5, 130.0, 129.8, 127.5, 125.0, 124.2, 122.5, 120.1, 116.5, 102.5; HRMS $(m/z, FAB^+)$ Calcd for C₂₆H₁₆N₄O₂S₂ 480.0715, found 480.0712.

4.1.9. 2-Cyano-3-{7-[5-N,N-bis(4-methoxyphenyl)aminothiophen-2yl]-2,1,3-benzothiadiazol-4-yl} acrylic acid (**OMeDPTB**). The synthetic procedure was similar to that of **DPTB** and afforded **OMeDPTB** as a black solid (80%). Mp 235–237 °C; IR (KBr) ν 3047, 2951, 2219, 1693, 1582, 1536, 1454, 1324, 1213, 1149, 1070, 817 cm⁻¹; ¹H NMR (DMSO-*d*₆, 400 MHz) δ 8.92 (s, 1H), 8.61 (d, *J*=8.0 Hz, 1H), 8.14 (d, *J*=4.4 Hz, 1H), 8.00 (d, *J*=8.0 Hz, 1H), 7.29 (d, *J*=8.8 Hz, 4H), 7.00 (d, *J*=8.8 Hz, 4H), 6.30 (d, *J*=4.4 Hz, 1H), 3.78 (s, 6H); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ 163.6, 161.4, 157.2, 154.5, 150.0, 146.0, 139.2, 131.7, 130.0, 126.9, 124.1, 121.1, 118.8, 116.7, 115.1, 111.0, 101.0, 55.3; HRMS $(m/z, FAB^+)$ Calcd for C₂₈H₂₀N₄O₄S₂ 540.0926, found 540.0933.

4.1.10. 2-Cyano-3-{7-[5-N,N-bis(4-hexyloxypheny)aminothiophen-2-yl]-2,1,3-benzothiadiazol-4-yl} acrylic acid (**OHexDPTB**). The synthetic procedure was similar to that of **DPTB** and afforded **OHexDPTB** as a black solid (90%). Mp 152–154 °C; IR (KBr) ν 3058, 2928, 2860, 2219, 1692, 1579, 1534, 1439, 1349, 1228, 1061, 828 cm⁻¹; ¹H NMR (CD₂Cl₂, 400 MHz) δ 9.05 (s, 1H), 8.66 (d, *J*=8.4 Hz, 1H), 8.08 (d, *J*=4.0 Hz, 1H), 7.55 (d, *J*=8.4 Hz, 1H), 7.22 (d, *J*=8.8 Hz, 4H), 6.90 (d, *J*=8.8 Hz, 4H), 6.32 (d, *J*=4.0 Hz, 1H), 3.97 (t, *J*=6.4 Hz, 4H), 1.83–1.76 (m, 4H), 1.48 (m, 4H), 1.38–1.36 (m, 8H), 0.93 (t, *J*=6.8 Hz, 6H); ¹³C NMR (CD₂Cl₂, 100 MHz) δ 162.5, 157.9, 156.0, 151.5, 148.7, 140.0, 133.8, 133.1, 131.8, 127.4, 125.6, 121.4, 119.6, 117.0, 116.0, 112.5, 69.0, 32.2, 29.8, 26.3, 23.2, 14.4; HRMS (*m*/*z*, FAB⁺) Calcd for C₃₈H₄₀N₄O₄S₂ 680.2491, found 680.2491.

4.2. Measurements of UV-vis absorption spectra of dyes in CH₂Cl₂ solutions

UV-vis absorption spectra of dyes in CH₂Cl₂ solutions were recorded with a spectrophotometer (JASCO V-670).

4.3. Measurement of UV–vis absorption spectra of dyeloaded nanoporous TiO₂ films

A 7- μ m-thick transparent porous TiO₂ nanoparticle layer (adopting 20-nm anatase TiO₂ nanoparticles) was coated on a glass plate by the doctor-blade method. After sintering at 500 °C for 30 min, the TiO₂ film was immersed into a dye solution (0.5 mM dye in chlorobenzene) at room temperature for 24 h. Then the UV–vis absorption spectrum of the dye-loaded TiO₂ film was recorded on a spectrophotometer.

4.4. Theoretical calculation

Density functional theory (DFT) calculations were conducted by using the hybrid B3LYP function for geometry optimization. The molecular orbital levels of HOMO and LUMO were achieved with the 6-31G(d) basis set implemented in the Gaussian 03 package.

4.5. Cyclic voltammetry measurement

The electrochemical properties of dyes were investigated by cyclic voltammetry (CV). The measurement of oxidation potentials was carried out in anhydrous CH_2Cl_2 solutions (1.0 mM) containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as a supporting electrolyte, and the measurement of the reduction potentials was conducted in anhydrous THF solutions (1.0 mM) containing 0.1 M tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte, purged with argon prior to conduct the experiments. A glassy carbon electrode and a platinum wire were used as the working and counter electrodes, respectively. All potentials were recorded versus Ag/AgCl (saturated) as a reference electrode and calibrated with the ferrocene/ferrocenium redox couple. All measurement was performed at a scan rate of 100 mV s⁻¹.

4.6. Fabrication of dye-sensitized solar cells

To prepare the DSSC working electrodes, the FTO glass plates were first cleaned in a detergent solution under ultrasonication for 15 min, and then rinsed with water and ethanol. A layer of 20-nm-sized anatase TiO_2 nanoparticles as the transparent nanocrystalline layer was first coated on the FTO glass plate by the doctor-blade method. After drying the film at 120 °C, another layer of 400-nm-

sized anatase TiO₂ nanoparticles was then deposited as the light scattering layer. The resulting working electrode was composed of a 12-µm-thick transparent TiO₂ nanoparticle layer (particle size: 20 nm) and a 4-µm-thick TiO₂ scattering layer (particle size: 400 nm). The nanoporous TiO₂ electrodes were then sequentially heated at 150 °C for 10 min, at 300 °C for 10 min, at 400 °C for 10 min, and finally at 500 °C for 30 min. After cooling, the nanoporous TiO₂ electrodes were immersed into a chlorobenzene solution containing organic dyes (0.5 mM) or acetonitrile/tert-butanol mixture (1:1) containing N719 (0.5 mM) with deoxycholic acid (0.5 mM, DCA) as a co-adsorbent at room temperature for 24 h. Counter electrodes of the DSSCs were prepared by depositing 40nm-thick Pt films on the FTO glass plates by e-beam evaporation. The dye-adsorbed TiO₂ working electrode and a counter electrode were then assembled into a sealed DSSC cell with a sealant spacer between the two electrode plates. A drop of electrolyte solution (EL1: 0.6 M 1-butyl-3-methylimidazolium iodide (BMII), 0.05 M LiI, 0.03 M I₂, 0.5 M 4-tert-butylpyridine, 0.1 M guanidinium thiocyanate in a mixture of acetonitrile and valeronitrile (85/15, v/v) or EL2: 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.05 M LiI, 0.03 M I₂ in acetonitrile) was injected into the cell through a drilled hole. Finally, the hole was sealed using the sealant and a cover glass. An anti-reflection coating film was adhered to the DSSC. A mask with an aperture area of 0.125 cm² was covered on a testing cell during photocurrent-voltage and incident photon-tocurrent conversion efficiency measurements.

4.7. Photocurrent-voltage measurement

The photocurrent—voltage characteristics of the DSSCs were measured under illumination of AM 1.5G solar light from a 300-W Xenon lamp solar simulator. The incident light intensity was calibrated as 100 mW/cm². Photocurrent—voltage curves were obtained by applying an external bias voltage to the cell and measuring the generated photocurrent.

4.8. Incident monochromatic photon-to-current conversion efficiency measurement

The incident monochromatic photon-to-current conversion efficiency (IPCE) spectra were measured by using a 75-W Xenon arc lamp as the light source coupled to a monochromator. The IPCE data were taken by illuminating monochromatic light on the solar cells (with a wavelength sampling interval of 10 nm from 300 nm to 800 nm) and measuring the short-circuit current of the solar cells. The IPCE measurement was performed with a lock-in amplifier, a low speed chopper, and a bias light source under the full computer control.

4.9. Electrochemical impedance spectroscopy measurement

The electrochemical impedance spectroscopy (EIS) of the cells was measured by using an impedance analyzer with a frequency range of 20 Hz–1 MHz. In this study, during the impedance measurement, the cell was under the constant AM 1.5G 100 mW/cm² illumination. The impedance of the cell (throughout the frequency range of 20 Hz to 1 MHz) was then measured by applying a bias at the open-circuit voltage V_{oc} of the cell (namely, under the condition of no dc electric current) and by using an AC amplitude of 10 mV.

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Supplementary data

These data include an absorption spectrum of **DPTB** in a THF solution, electrochemical impedance spectra, and copies of ¹H and ¹³C NMR spectra. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2012.05.052.

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