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Synthesis of triphenylamine-based thiophene-(*N*-aryl)pyrrole-thiophene dyes for dye-sensitized solar cell applications

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ABSTRACT

Two new triphenylamine-based metal-free organic dyes (**TPTDYE-1** and **TPTDYE-2**) containing 1-(2,6-diisopropylphenyl)-2,5-di(2-thienyl)pyrrole as a new π-conjugated chromophore were synthesized for dye-sensitized solar cell (DSSC) applications. **TPTDYE-1** containing three donor groups around the acceptor group was found to show relatively narrow absorption band from 300 nm to 470 nm while **TPTDYE-2** having extended π–π delocalization between the donor and acceptor group showed broad absorption band from 300 nm to 550 nm. The electrochemical studies indicate that the HOMO–LUMO energy gap of **TPTDYE-1** is considerably wider than that of **TPTDYE-2**. The dye-sensitized solar cell performance of each dye was investigated, and the **TPTDYE-2**-sensitized cell was found to show a maximum monochromatic incident photon-to-current conversion efficiency (IPCE) of 75%, a short-circuit photocurrent density (J_{sc}) of 13.50 mA/cm^2, an open-circuit voltage (V_{oc}) of 0.72 V, and a fill factor (FF) of 0.69, corresponding to an overall conversion efficiency of 6.71% under simulated AM 1.5 irradiation (100 mW/cm^2). Under the same condition the **TPTDYE-1**-sensitized cell showed the same IPCE value of 75% with a promising conversion efficiency of 6.00%, a J_{sc} of 11.11 mA/cm^2, a V_{oc} of 0.76 V, and a FF of 0.71.

1. Introduction

Dye-sensitized solar cells (DSSCs) are considered as the most attractive research area, because of their high performance in converting solar energy to electric energy at low cost and easy production.[1] In DSSCs so far two classes of dyes such as organometallic complexes and metal-free organic dyes were employed in the electrical energy production from sunlight. At present, DSSCs based on organometallic complexes (Ru(II)–polypyridyl complexes) showed maximum energy conversion efficiency (η) of 11% under simulated AM 1.5 irradiation (100 mW/cm^2).[2–5] On the other hand, DSSCs based on metal-free organic dyes have many advantages in lower cost, easier structural modification, and higher molar extinction coefficient of the dyes, and consequently, they have been considered as an excellent alternative for organometallic complex-based DSSCs. The DSSCs made from metal-free organic dyes showed maximum solar energy-to-electrical energy conversion efficiency in the range of 7–10%.[6–26] Among them, triphenylamine (TPA)-based metal-free organic dyes displayed promising performances up to 9–10%. [6–9] TPA has nonplanar structure and suppresses the dye aggregation when they are used in DSSC applications.[27] Previously, various thiophene or benzene derivatives were used as a bridging π-conjugation unit between the triphenylamine donor and cyanoacrylic acid acceptor group. Whereas pyrrole-based π-conjugated systems were rarely studied in DSSC applications. The DSSC performances of dyes incorporating *N*-alkylpyrrole as a bridging π-conjugation unit showed maximum conversion efficiency around 4–6%,[28] but at the same time the *N*-arylpyrrole-based dyes showed promising performances up to 7.2%, which is 91% of the standard cell from N719.[29] This inspires us to develop new *N*-arylpyrrole containing dyes for DSSC applications. There are two major factors influencing the performances of the DSSCs, the light harvesting ability of the dye and photo excited electron injection from the lowest unoccupied molecular orbital (LUMO) of the dye to the conduction band of the semiconductor in the anode. In order to enhance the DSSC performance finding new *N*-arylpyrrole-based π-conjugated chromophore having higher molar extinction coefficient is essential.

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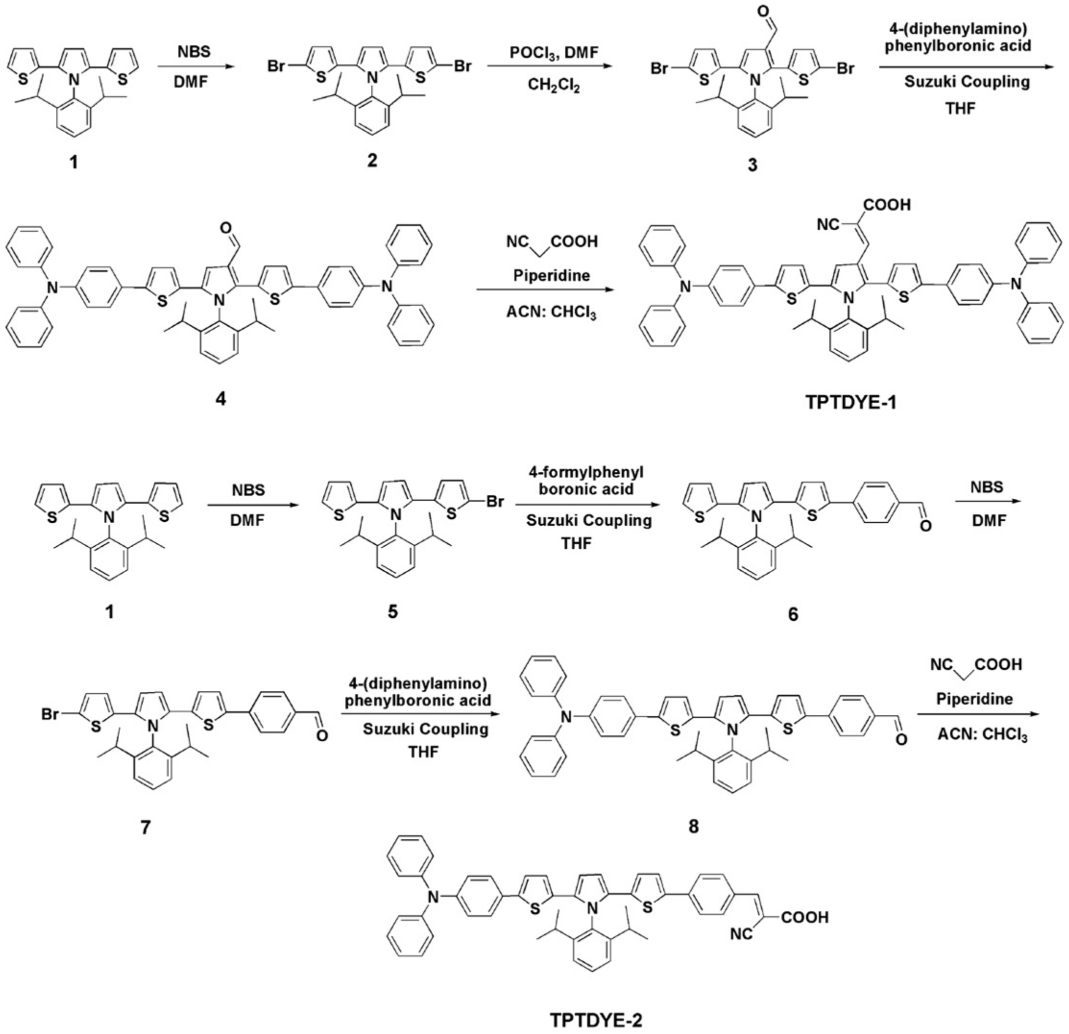
The molar extinction coefficient of 2,5-bis(2-thienyl)-*N*-2,6-diisopropylphenyl pyrrole (*N*-arylpyrrole TPT) was found to be relatively higher than 2,5-bis(2-thienyl)-*N*-4-octylphenyl pyrrole and 2,5-bis(2-thienyl)-*N*-dodecyl pyrrole.[30] Recently, we reported the use of *N*-arylpyrrole TPT-based polymers for bulk heterojunction (BHJ) solar cell applications.[30–33] The photovoltaic studies of the polymers clearly indicated that *N*-arylpyrrole TPT unit harvests the sunlight effectively.[30–33] From this result we expect that dyes utilizing the *N*-arylpyrrole TPT unit will show promising performance in DSSCs. In this study, we synthesized two new dyes incorporating *N*-arylpyrrole TPT unit namely **TPTDYE-1** and **TPTDYE-2** (Scheme 1). In **TPTDYE-1**, donor triphenylamine groups were attached on both side of the *N*-arylpyrrole TPT unit and cyanoacrylic acid acceptor bridged by a methine fragment was introduced on pyrrole back bone in *N*-arylpyrrole TPT unit. On the other hand, **TPTDYE-2** was constructed by serially connecting the acceptor group with donor groups such as benzene, *N*-arylpyrrole TPT unit, and triphenylamine. In terms of conjugation **TPTDYE-2** is expected to show better π–π conjugation than **TPTDYE-1**. In terms of electron donating ability from the donor to the acceptor group, **TPTDYE-1** is expected to be more effective than **TPTDYE-2** because two triphenylamine groups and one phenyl group are placed around the acceptor group. In this paper, we reported the detailed synthesis, characterization, and photovoltaic studies of two new metal-free organic donor–acceptor dyes (**TPTDYE-1** and **TPTDYE-2**). In addition, we also briefly discussed the influence of π-conjugation and electron donating strength on the energy conversion efficiency of the DSSCs.

2. Results and discussions

2.1. Synthesis and characterization of the dyes

The synthetic procedure for **TPTDYE-1** and **TPTDYE-2** is shown in Scheme 1. Compounds **1** and **2** were synthesized according to the known procedure reported from our group.[30] Vilsmeier formylation of compound **2** gave compound **3**. Suzuki coupling reaction of compound **3** with 4-(diphenylamino)phenylboronic acid yielded compound **4**. By treating compound **1** with 1 equiv of *N*-bromosuccinimide (NBS) yielded a mixture of mono and dibrominated products. The mono-brominated product (**5**) was separated and treated with 4-formylphenylboronic acid via Suzuki coupling reaction to afford compound **6**. The bromination of compound **6** with 1 equiv of NBS gave compound **7**. Suzuki coupling reaction of compound **7** with 4-(*N*,*N*-diphenylamino)phenylboronic acid yielded compound **8**. The Knoevenagel condensation reaction of compounds **4** and **8** with cyanoacetic acid in the presence of piperidine yielded **TPTDYE-1** and **TPTDYE-2**, respectively. All



Scheme 1. Synthetic route for the synthesis of dyes **TPTDYE-1** and **TPTDYE-2**.

compounds prepared newly in this study were well characterized, and the spectral data are summarized in the Experimental Section. The two dyes were found to be well soluble in chloroform, dichloromethane, tetrahydrofuran, and ethanol.

2.2. Optical properties

The UV–visible absorption spectra of dyes in tetrahydrofuran (THF, 1.0×10^{-5} M) solution are shown in Fig. 1. The absorption spectrum of the **TPTDYE-1** was quite sharp covering the region from 300 nm to 470 nm, whereas that of **TPTDYE-2** was relatively broad from 300 nm to 550 nm. Though there are several electron donor groups around the acceptor group, the relatively short π-conjugation length of **TPTDYE-1** between the triphenylamine and cyanoacrylic acid groups leads the blue shifted absorption maximum (418 nm, $\varepsilon=5.9\times10^4$) compared to that (455 nm, $\varepsilon=5.8\times10^4$) of **TPTDYE-2**. The extended π–π delocalization between the donor (triphenylamine) and acceptor (cyanoacrylic acid) group in **TPTDYE-2** results 37 nm red-shifted absorption maximum compared to that of **TPTDYE-1**. We expect that the absorption band of **TPTDYE-1** is derived from the localized π–π* transition. On the other hand the broad absorption band of **TPTDYE-2** is expected to be originated from the overlap of the π–π* transition in donor units and the donor–acceptor intramolecular charge transfer (ICT) between the donor and the cyanoacrylic acid anchoring moiety.[24,28,29] The solvent dependent absorption spectra of dyes **TPTDYE-1** and **TPTDYE-2** presented in Fig. 2 might support the possibility of the overlap of the π–π* transition in donor units and the donor–acceptor ICT between the donor and the cyanoacrylic acid anchoring moiety. The UV–visible absorption spectra of dyes **TPTDYE-1** and **TPTDYE-2** adsorbed on TiO_2 are also presented in Fig. 1. The absorption maximum of **TPTDYE-1** or **TPTDYE-2** adsorbed on TiO_2 was found to be 463 nm or 507 nm, respectively. Compared to the spectra in THF solution, the red-shifted absorption maxima and broad absorption band of the dyes adsorbed on TiO_2 might to be attributed to the formation of J-type aggregate.[28,34–36] Fig. 3 shows the normalized absorption and photoluminescence (PL) spectra of dyes **TPTDYE-1** and **TPTDYE-2** in THF solution. The photoluminescence maximum was observed at 521 nm and 622 nm, respectively, and the optical band gaps (E_{0-0}) of dyes **TPTDYE-1** and **TPTDYE-2** were estimated to be 2.65 eV and 2.27 eV, respectively, from the intersection of absorption and emission spectra in solution. The photo-physical properties of the dyes **TPTDYE-1** and **TPTDYE-2** are summarized in Table 1.

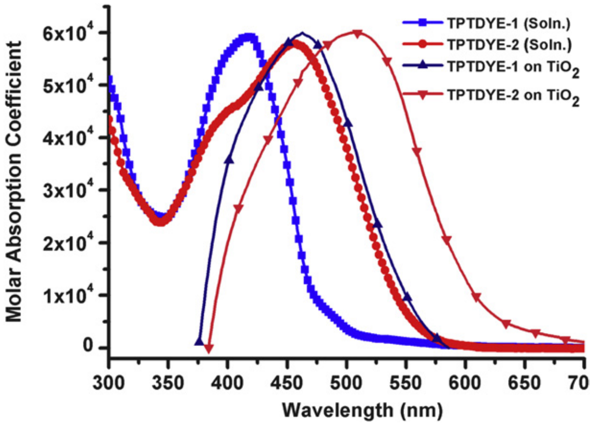


Fig. 1. UV–visible absorption spectra of dyes **TPTDYE-1** and **TPTDYE-2** in THF solution (1.0×10^{-5} M) and on TiO_2 film (the spectra on TiO_2 film are normalized to 6×10^4).

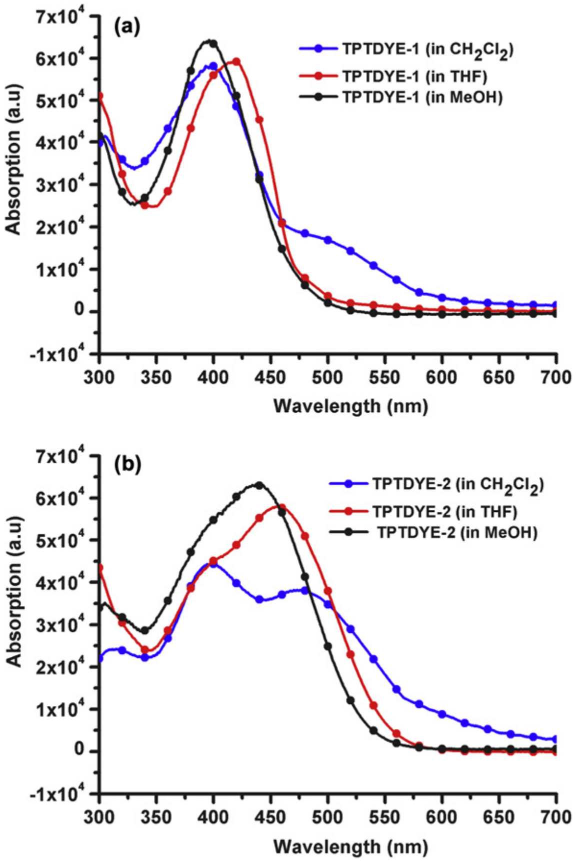


Fig. 2. Comparison of UV–visible absorption spectra of dyes **TPTDYE-1** and **TPTDYE-2** in methylene chloride (CH_2Cl_2), THF, and methanol (MeOH) (1.0×10^{-5} M).

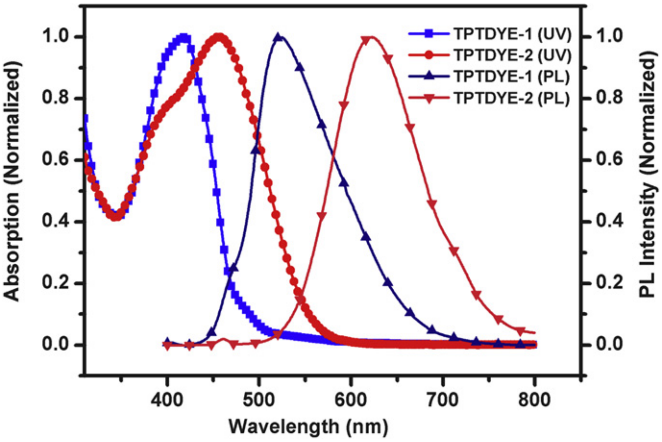


Fig. 3. Normalized absorption and photoluminescence spectra of dyes **TPTDYE-1** and **TPTDYE-2** in THF.

Table 1
Optical and electrochemical properties of **TPTDYE-1** and **TPTDYE-2**

Sensitizer	Abs max in solution[a] (nm)	ε[b]	Abs max on TiO_2[c] (nm)	PL max[d] (nm)	E_{0-0}[e] (eV)	E_{ox}[f] (V)	E_{LUMO}[g] (V)
TPTDYE-1	418	5.9×10^4	463	521	2.65	1.00	−1.65
TPTDYE-2	455	5.8×10^4	507	622	2.27	0.83	−1.44

[a] Measurements from dye dissolved in THF (1×10^{-5} M).
[b] Molar absorptivity ($M^{-1}\,cm^{-1}$) of the dyes measured in THF (1×10^{-5} M).
[c] Measurements from the dye adsorbed on TiO_2.
[d] Measurements from dye dissolved in THF (1×10^{-5} M).
[e] The optical band gap (E_{0-0}) estimated at the intersection of absorption and emission spectra in solution.
[f] The onset oxidation potentials were estimated from cyclic voltammetry analysis.
[g] The E_{LUMO} level was calculated using the following equation, $E_{LUMO}=E_{ox}-E_{0-0}$.

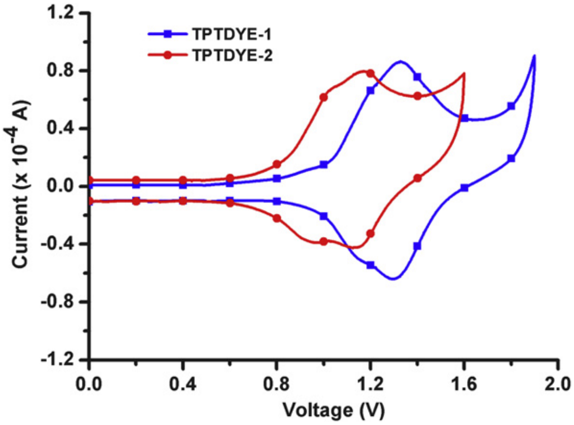


Fig. 4. Cyclic voltammograms of dyes **TPTDYE-1** and **TPTDYE-2**, platinum working electrode in 0.1 M Bu_4NBF_4/acetonitrile at 100 mV/s, potential versus Ag/AgCl.

2.3. Electrochemical properties

Fig. 4 shows the cyclic voltammetry (CV) diagrams of dyes **TPTDYE-1** and **TPTDYE-2**. The onset oxidation potential (E_{ox}), which reflects the highest occupied molecular orbital (HOMO) of the dye, was calculated to be 1.00 V and 0.83 V, respectively, and the lowest unoccupied molecular orbital (LUMO) levels estimated from the values of E_{ox} and E_{0-0} were −1.65 V and −1.44 V, respectively. The electrochemical properties of dyes **TPTDYE-1** and **TPTDYE-2** are included in Table 1. In order to utilize the synthesized dyes as sensitizers in DSSCs, it is necessary to ensure their energy levels are suitable. For the efficient electron injection from dye to TiO_2, the conduction band energy level of the dye should be positioned above the conduction band of TiO_2.[35] According to the literature the conduction band of TiO_2 is positioned at −0.5 V, which is located 1.15 V and 0.94 V, respectively, lower than the LUMO level of **TPTDYE** dyes. Consequently, the possibility of excited electron injection from the LUMO of the dye to the LUMO of TiO_2 can be ensured. In addition, the HOMO levels of the dyes were sufficiently lower than that of electrolyte (I_3^-/I^-) redox couple (0.4 V), ensuring a smooth electron flow from the electrolyte to the dyes. Consequently, newly synthesized dyes were expected to show promising photovoltaic properties as sensitizers in DSSC applications.

2.4. Computational studies

The structure of the dyes was optimized by using B3LYP hybrid functional and 6-31G∗ basis sets for the better understanding of the correlation between the structure and the photophysical property as well as the device performance.[6–36] The optimized structures of dyes **TPTDYE-1** and **TPTDYE-2** are shown in Fig. 5. The geometrically optimized structure of the dyes clearly indicates that the coplanarity between the donor and acceptor group is greater in **TPTDYE-2** than in **TPTDYE-1**. In **TPTDYE-1**, two big nonplanar triphenylamine groups, sterically hindered isopropyl groups in the phenyl ring on the pyrrole nitrogen and the presence of acceptor group increase the twist angles between the aryl groups. The twist angles between the triphenylamine and thiophene were found to be 17.8° and 19.0°, respectively, and that between the less hindered thiophene and pyrrole plane was found −17.1°. However, the presence of acceptor group on the pyrrole ring decreases the coplanarity quite much, the twist angle being −38.1° between the thiophene and pyrrole in the other side of **TPTDYE-1**. In contrast, the sterically hindered isopropyl groups play a vital role in the formation of planar structure of **TPTDYE-2**. The isopropyl groups prevent the bond rotation between the thiophene and pyrrole units and, consequently, enhance the coplanarity between the donor and acceptor group in **TPTDYE-2**. The twist angle between the triphenylamine and thiophene was calculated to be 16.2°, and those between the other aromatic groups were found to be less than 1.6°. Consequently, in **TPTDYE-2**, all aromatic groups and the acceptor group are laid almost in same plane except for the triphenylamino group. The electronic distributions in the HOMO and LUMO of the dyes are displayed in Fig. 6. At the ground state (HOMO) of the dyes, electron density is homogeneously distributed on the electron donor groups

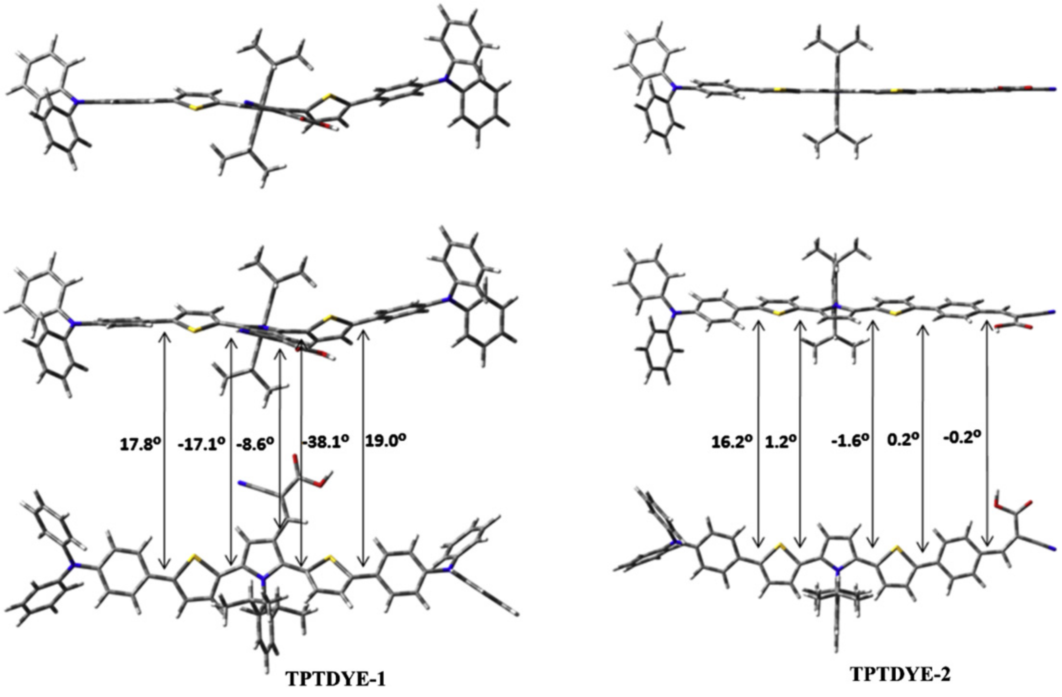


Fig. 5. Optimized structures of dyes **TPTDYE-1** and **TPTDYE-2**.

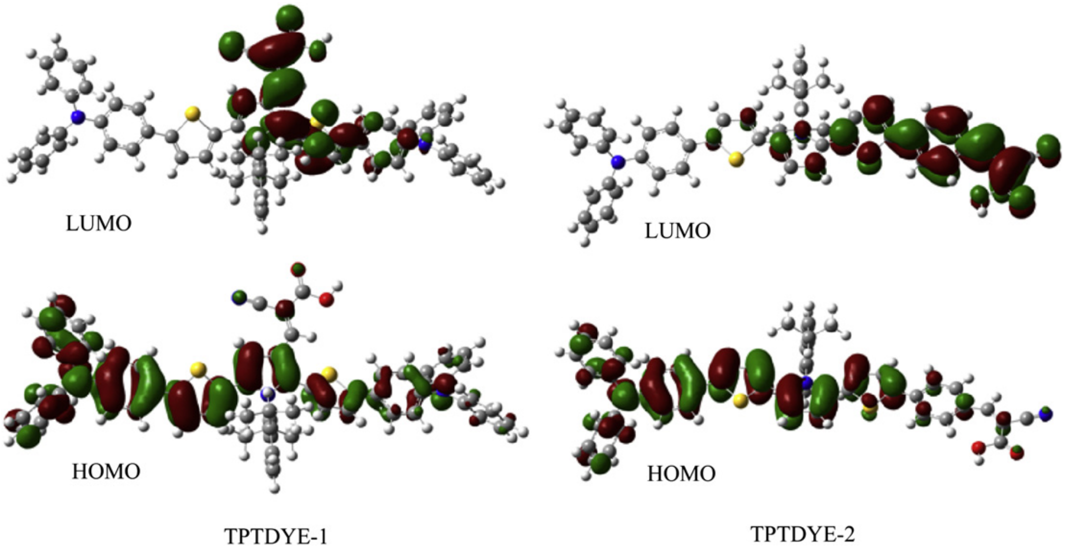


Fig. 6. The frontier orbital plots of the HOMO and LUMO of dyes **TPTDYE-1** and **TPTDYE-2**.

such as triphenylamine and *N*-aryl TPT. At the excited state (LUMO) of the dyes, the electron density is distributed on the electron acceptor group (cyanoacrylic acid). The electronic distribution over the *N*-aryl TPT unit in both HOMO and LUMO suggests that an effective intramolecular charge transfer occurs from the donor to acceptor through *N*-aryl TPT unit. The frontier molecular orbital of the dyes reveals that HOMO–LUMO excitation moves the electron density distribution from donor moiety to cyanoacrylic acid.

Table 2
Photovoltaic properties of **TPTDYE-1** and **TPTDYE-2**

Sensitizer	V_{oc}[a] (V)	J_{sc}[b] (mA/cm^2)	FF[c] (%)	η[d] (%)	IPCE[e] (%)
TPTDYE-1	0.76	11.11	0.71	6.00	75
TPTDYE-2	0.72	13.50	0.69	6.71	75

[a] Open-circuit voltage.
[b] Short-circuit current density.
[c] Fill factor.
[d] Power conversion efficiency.
[e] Incident photon-to-collected electron efficiency.

2.5. Photovoltaic performance of DSSCs

Fig. 7 represents the current–density/voltage (*J*–*V*) characteristics of the DSSCs obtained with the two dyes, and the detailed photovoltaic performance parameters (J_{sc}, V_{oc}, FF, and η) are listed in Table 2. The photovoltaic performances of the DSSCs were measured at 100 mW/cm^2 under simulated AM 1.5 G solar light conditions. The **TPTDYE-1**-sensitized cell gave a short-circuit photocurrent density (J_{sc}) of 11.11 mA/cm^2, an open-circuit voltage (V_{oc}) of 0.76 V, and a fill factor (FF) of 0.71, corresponding to an overall conversion efficiency (η) of 6.00%. Under the same conditions, the **TPTDYE-2**-sensitized cell gave a J_{sc} value of 13.50 mA/cm^2, a V_{oc} of 0.72 V, and an FF of 0.69, corresponding to a η value of 6.71%. The V_{oc} and FF of the **TPTDYE**-sensitized cells were found to be almost identical. On the other hand, **TPTDYE-2**-sensitized cell showed enhanced photocurrent and energy conversion efficiency than **TPTDYE-1**-sensitized cell. The photocurrent is mainly correlated with sunlight absorption ability of sensitizer. The optical studies indicate that both dyes **TPTDYE-1** and **TPTDYE-2** have similar absorption coefficient, but the broader absorption ability of **TPTDYE-2** enhances the light harvesting, and consequently offered higher J_{sc} in their DSSCs studies. The relatively higher J_{sc} value of the **TPTDYE-2**-based DSSC is expected to induce higher performance up to 6.71%.

Fig. 8 shows the action spectra of monochromatic IPCEs (Incident Photon-to-electron Conversion Efficiencies) for the sandwiched DSSCs. The IPCE value of **TPTDYE-1**-sensitized cell exceeds

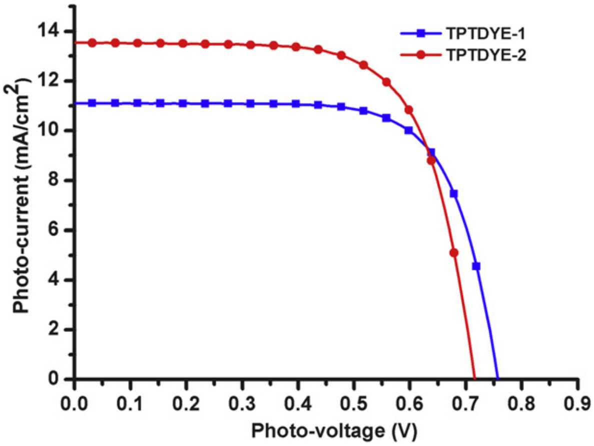


Fig. 7. *J*–*V* Characteristics of DSSCs made from **TPTDYE-1** and **TPTDYE-2** under AM 1.5 irradiation (100 mW/cm^2).

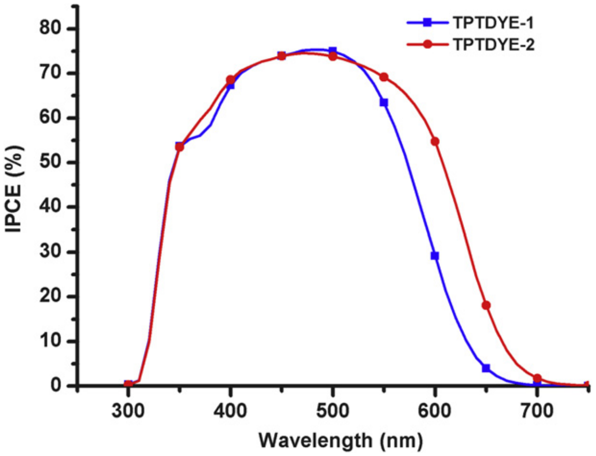


Fig. 8. IPCE characteristics for DSSCs made from **TPTDYE-1** and **TPTDYE-2**.

60% in a spectral range from 390 nm to 560 nm and reaches its maximum of 75% at 490 nm, and the DSSC made from **TPTDYE-2** gave the maximum IPCE value of 75% at 470 nm with over 60% in a range from 370 nm to 590 nm. The IPCE maximum values of the **TPTDYE**-sensitized cells were identical, though the 60% energy conversion region was found to be quite broad for **TPTDYE-2**-sensitized cell. The broader IPCE spectrum of **TPTDYE-2**-sensitized cell evidently supports its higher energy conversion efficiency compared to that of **TPTDYE-1**-sensitized cell.

3. Conclusions

Two new metal-free organic dyes incorporating 1-(2,6-diisopropylphenyl)-2,5-di(2-thienyl)pyrrole were synthesized and used as sensitizers in DSSCs. The dye (**TPTDYE-1**) containing three donor groups around the acceptor group showed narrow absorption band in the range from 300 nm to 470 nm. The maximum electrical energy conversion efficiency of the DSSC based on **TPTDYE-1** was 6.00% with a J_{sc} of 11.11 mA/cm^2, a V_{oc} of 0.76 V, and an FF of 0.71. The dye (**TPTDYE-2**) having the extended $\pi-\pi$ delocalization between the donor and acceptor group showed quite broader absorption band from 300 nm to 550 nm. The overall photovoltaic performance of the DSSC based on **TPTDYE-2** was 6.71% with a J_{sc} of 13.50 mA/cm^2, V_{oc} of 0.72 V, and an FF of 0.69. The lower photovoltaic performance of the DSSC based on **TPTDYE-1** compared to that of the DSSC based on **TPTDYE-2** might be attributed to the decreased light harvesting ability of the dye. From this study, we conclude that the effective π-conjugation between the donor and acceptor group of the dye is more important than the electron donating strength from the donor to the acceptor group to enhance the photovoltaic performances of DSSCs.

4. Experimental section

4.1. Materials and instruments

All reagents were commercially available from Aldrich or TCI chemicals and used without further purification. Solvents purified by normal procedure were handled in a moisture-free atmosphere. Flash column chromatography was performed on silica gel (Merck Kieselgel 60, 70–230 mesh). ^{1}H and ^{13}C NMR spectra were recorded using a 300-MHz Varian Mercury Plus spectrometer in deuterated chloroform. The absorption spectra of dyes were recorded at 25 °C in THF solution using a JASCO V-570 spectrophotometer, and the absorption spectra of dyes adsorbed on a TiO_2 film were measured using Cary 5 spectrophotometer. The photoluminescence spectra were recorded using a Hitachi F-4500 fluorescence spectrophotometer at 25 °C in THF solution. The cyclic voltammograms of dyes **TPTDYE-1** and **TPTDYE-2** were recorded by using a CH Instruments Electrochemical Analyzer. Cyclic voltammetry (CV) experiments were conducted on a drop-cast dye film on a platinum working electrode in acetonitrile (ACN) containing 0.1 M tetrabutylammonium tetrafluoroborate (TBATFB) as the supporting electrolyte at room temperature and ambient atmosphere at a scan rate of 100 mV/s with the use of Ag/AgCl and platinum wire as the reference and counter electrode, respectively. The CV instrument calibration was performed by using the ferrocene/ferrocenium (FOC) redox couple as an internal standard before and after the analysis. Infrared spectra were obtained on a Nicolet 380 FTIR spectrophotometer with samples prepared as KBr pellets.

4.2. Fabrication of dye-sensitized solar cell

Fluorine-doped tin oxide (FTO) glass plates (Pilkington TEC Glass-TEC 8, Solar 2.3 mm thickness) were cleaned in a detergent solution using an ultrasonic bath for 30 min and then rinsed with water and ethanol. Then, the plates were immersed in 40 mM $TiCl_4$ (aqueous) at 70 °C for 30 min and washed with water and ethanol. A transparent nanocrystalline layer was prepared on the FTO glass plates by using a doctor blade printing TiO_2 paste (Solaronix, Ti-Nanoxide T/SP), which was then dried for 2 h at 25 °C. The TiO_2 electrodes were gradually heated under an air flow at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min, and at 500 °C for 15 min. The thickness of the transparent layer was measured by using an Alpha-step 250 surface profilometer (Tencor Instruments, San Jose, CA). A paste containing 400 nm sized anatase particles (CCIC. PST-400C) was deposited by means of doctor blade printing to obtain the scattering layer, and then dried for 2 h at 25 °C. The TiO_2 electrodes were gradually heated under an air flow at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min, and at 500 °C for 15 min. The resulting film was composed of a 6 μm thick transparent layer and a 4 μm thick scattering layer. The TiO_2 electrodes were treated again with $TiCl_4$ at 70 °C for 30 min and sintered at 500 °C for 30 min. Then, they were immersed into the dye (**TPTDYE-1** or **TPTDYE-2**) solution and kept at room temperature for 12 h. FTO plates for the counter electrodes were cleaned in an ultrasonic bath in H_2O, acetone, and 0.1 M aqueous HCl, subsequently. The counter electrodes were prepared by placing a drop of an H_2PtCl_6 solution (2 mg Pt in 1 mL ethanol) on an FTO plate and heating it (at 400 °C) for 15 min. The dye adsorbed TiO_2 electrodes and the Pt counter electrodes were assembled into a sealed sandwich-type cell by heating at 80 °C using a hot-melt ionomer film (Surlyn) as a spacer between the electrodes. A drop of the electrolyte solution was placed in the drilled hole of the counter electrode and was driven into the cell via vacuum backfilling. Finally, the hole was sealed using additional Surlyn and a cover glass (0.1 mm thickness). The electrolyte was then introduced into the cell, which is composed of 0.6 M 3-propyl-1,2-dimethyl imidazolium iodide, 0.05 M iodine, 0.1 M LiI and 0.5 M 4-*tert*-butylpyridine in acetonitrile.

4.3. Characterization of DSSCs

The cell performance was measured using 1000 W xenon light source, whose power of an AM 1.5 Oriel solar simulator was calibrated by using KG5 filtered Si reference solar cell. The incident photon-to-current conversion efficiency (IPCE) spectra for the cells were measured on an IPCE measuring system (PV Measurements).

4.4. Synthesis of dyes

The new organic dyes, **TPTDYE-1** and **TPTDYE-2**, were synthesized as outlined in Scheme 1. Compounds **1** and **2** were synthesized according to the known procedure reported from our group.[30] The detailed synthetic procedure and characterization of the intermediates and final dyes are given below.

*4.4.1. 2,5-Bis(5-bromothiophen-2-yl)-1-(2,6-diisopropylphenyl)-1H-pyrrole-3-carbaldehyde (**3**).* *N,N*-Dimethylformamide (DMF, 0.16 mL, 2.0 mmol) was added to a cooled solution (0 °C) of $POCl_3$ (0.20 mL, 2.0 mmol) in dry CH_2Cl_2 (10 mL). The solution was refluxed for 30 min, cooled in an ice bath. To the cooled solution was added 2,5-bis(5-bromothiophen-2-yl)-1-(2,6-diisopropylphenyl)-1*H*-pyrrole (**2**) (1.0 g, 1.82 mmol). The reaction mixture was refluxed with stirring for 2 h, cooled, and then, the solution of $MeCOONa\cdot 2H_2O$ (0.2 g, 3.0 mmol) in water (10 mL) was added. The emulsion obtained was refluxed for 1 h, and then cooled. The organic layer was separated, and the aqueous layer was extracted twice with CH_2Cl_2. The combined organic solution was washed with a small amount of water, dried over anhydrous $NaSO_4$, filtered, evaporated on a rotary evaporator to dryness, and the residue was then triturated in a small volume of hexane. The precipitated crystals of product **3** were filtered off and dried. Yield 0.8 g (75%). Mp 175–176 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 9.97 (s, 1H), 7.56 (t, 1H), 7.26 (d, 2H), 7.12 (s, 1H), 6.93 (d, 1H), 6.75 (d, 1H), 6.71 (d, 1H), 6.22 (d, 1H), 2.30–2.44 (m, 2H), 0.92 (d, 6H), 0.90 (d, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 186.1, 147.8, 135.9, 135.0, 132.0, 131.6, 131.3, 131.2, 131.0, 130.2, 130.0, 125.3, 125.2, 125.0, 115.6, 112.2, 107.8, 28.6, 24.1, 24.0; IR (KBr, cm^{-1}): 3107, 3079, 2962, 2926, 2867, 2837, 1658, 1444, 1414; HRMS (EI$^+$, *m*/*z*) [M$^+$] calcd for $C_{25}H_{23}Br_2NOS_2$ 574.9588, found 574.9583.

*4.4.2. 2,5-Bis(5-(4-(diphenylamino)phenyl)thiophen-2-yl)-1-(2,6-diisopropylphenyl)-1H-pyrrole-3-carbaldehyde (**4**).* The solution of compound **3** (0.38 g, 0.66 mmol) and 4-(diphenylamino)phenylboronic acid (0.4 g, 1.4 mmol) in 30 mL THF was purged well with nitrogen for 45 min and then $Pd(PPh_3)_4$ (2 mol %) and aqueous 2 M K_2CO_3 solution (7 mL) was added to the solution. The whole mixture was refluxed with vigorous stirring for 48 h under nitrogen. The solvent was concentrated by using a rotary evaporator and the residue was dissolved in CH_2Cl_2. The organic solution was washed well with water and brine solution and then, dried over anhydrous Na_2SO_4. The solvent was concentrated and the residue was purified by column chromatography (silica gel, hexane/ethyl acetate=80:20, v/v) to afford compound **4** as a pure product. Yield is 0.45 g (75%). Mp 244–245 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 10.11 (s, 1H), 7.53 (t, 1H), 7.21–7.33 (m, 16H), 7.00–7.11 (m, 16H), 6.90 (d, 1H), 6.83 (d, 1H), 6.29 (d, 1H), 2.42–2.60 (m, 2H), 0.94 (dd, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 186.6, 148.1, 147.9, 147.6, 147.5, 147.2, 143.5, 137.1, 133.0, 132.1, 131.9, 131.5, 131.1, 129.6, 129.5, 128.0, 128.0, 127.4, 126.7, 126.5, 125.7, 125.0, 124.9, 124.8, 123.7, 123.6, 123.4, 123.4, 122.4, 122.2, 107.4, 28.7, 24.2, 24.0; IR (KBr, cm^{-1}): 3064, 3032, 2961, 2928, 2925, 2867, 2839, 1661, 1591, 1490; HRMS (EI$^+$, *m*/*z*) [M$^+$] calcd for $C_{61}H_{51}N_3OS_2$ 905.3474, found 905.3476.

*4.4.3. (E)-3-(2,5-Bis(5-(4-(diphenylamino)phenyl)thiophen-2-yl)-1-(2,6-diisopropylphenyl)-1H-pyrrol-3-yl)-2-cyanoacrylic acid (**TPTDYE-1**).* Compound **4** (0.36 g, 0.4 mmol) was dissolved in the mixed solvent of $CHCl_3$ and acetonitrile (30 mL, 1:1, v/v) and then piperidine (2 mmol) and cyanoacetic acid (2 mmol) were added at room temperature. The solution was slowly heated to reflux temperature. After 18 h, the solution was cooled to room temperature and concentrated by using a rotary evaporator. The residue was dissolved into 10 mL of CH_2Cl_2 and poured into 100 mL water. To this stirred mixture was added 2 N HCl solution until the reaction mixture became acidic. The aqueous layer was extracted with CH_2Cl_2 and the organic layer was washed with water and brine solution, dried over anhydrous $NaSO_4$, filtered, evaporated on a rotary evaporator to dryness, and the residue was purified by column chromatography (silica gel, CH_2Cl_2/CH_3OH=90:10, v/v) to afford **TPTDYE-1**. Yield is 0.33 g (85%). Mp 269–270 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 8.02 (s, 1H), 7.66 (t, 1H), 7.25–7.40 (m, 16H), 7.12 (d, 1H), 6.60–7.08 (m, 11H), 6.70 (d, 1H), 6.18 (d, 1H), 2.28–2.42 (m, 2H), 0.86 (t, 12H). IR (KBr, cm^{-1}): 3433, 3061, 3029, 2962, 2927, 2866, 2210, 1590, 1491; HRMS (EI$^+$, *m*/*z*) [M$^+$] calcd for $C_{64}H_{52}N_4O_2S_2$ 972.3532, found 972.3536.

*4.4.4. 2-(5-Bromothiophen-2-yl)-1-(2,6-diisopropylphenyl)-5-(thiophen-2-yl)-1H-pyrrole (**5**).* 1-(2,6-Diisopropylphenyl)-2,5-di(thiophen-2-yl)-1*H*-pyrrole (**1**) (2.69 g, 6.87 mmol) was dissolved in 10 mL of DMF. The solution was cooled with ice bath and then *N*-bromosuccinimide (NBS, 1.23 g, 6.87 mmol) in 10 mL of DMF was added drop by drop to the stirred solution at 0 °C. The solution was stirred for 6 h. The solvent was concentrated by using a rotary evaporator and the residue was dissolved in 50 mL of CH_2Cl_2. The organic solution was washed with water and brine solution, and then dried over anhydrous Na_2SO_4. The organic solvent was evaporated by using a rotary evaporator and the unreacted starting material, dibrominated product, and expected mono-brominated product were separated using column chromatography (silica gel, hexane) to afford compound **5** as a sticky mass. Yield is 1.3 g (40%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.57 (t, 1H), 7.30 (d, 2H), 6.99 (dd, 1H), 6.78 (dd, 1H), 6.72 (d, 1H), 6.64 (dd, 2H), 6.42 (dd, 1H), 6.15 (d, 1H), 2.42–2.58 (m, 2H), 0.95 (d, 6H), 0.91 (d, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 148.2, 137.1, 135.1, 134.1, 130.8, 130.7, 130.0, 129.4, 127.2, 125.0, 123.6, 123.2, 122.9, 109.9, 109.5, 109.4, 28.5, 24.0, 23.9; IR (KBr, cm^{-1}): 3102, 3069, 2962, 2927, 2866, 1468; HRMS (EI$^+$, *m*/*z*) [M$^+$] calcd for $C_{24}H_{24}BrNS_2$ 469.0534, found 469.0530.

*4.4.5. 4-(5-(1-(2,6-Diisopropylphenyl)-5-(thiophen-2-yl)-1H-pyrrol-2-yl)thiophen-2-yl)benzaldehyde (**6**).* The solution of compound **5** (1.2 g, 2.55 mmol) and 4-formylphenylboronic acid (0.40 g, 2.65 mmol) in 30 mL THF was purged well with nitrogen for 45 min and then $Pd(PPh_3)_4$ (2 mol %) and aqueous 2 M K_2CO_3 solution (7 mL) were added to the solution. The whole mixture was refluxed with vigorous stirring for 48 h under nitrogen. The solvent was concentrated by using a rotary evaporator and the residue was dissolved in CH_2Cl_2. The organic solution was washed well with water and brine solution, and then dried over anhydrous Na_2SO_4. The solvent was concentrated and the residue was purified by column chromatography (silica gel, hexane/ethyl acetate=95:5, v/v) to afford compound **6**. Yield is 1.0 g (79%). Mp 157–158 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 9.94 (s, 1H), 7.81 (d, 2H), 7.58 (d, 3H), 7.31 (d, 3H), 7.13 (d, 1H), 7.00 (dd, 1H), 6.78 (dd, 1H), 6.72 (dd, 2H), 6.45 (dd, 1H), 6.28 (d, 1H), 2.42–2.62 (m, 2H), 0.94 (d, 6H), 0.91 (d, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 191.5, 148.2, 140.2, 139.3, 137.3, 135.0, 134.9, 134.3, 131.2, 130.8, 130.6, 129.6, 127.2, 125.5, 125.5, 125.0, 123.7, 123.4, 110.2, 109.6, 28.6, 24.0, 23.8; IR (KBr, cm^{-1}): 3068, 2959, 2924, 2864, 2818, 2732, 1694, 1600, 1561, 1439; HRMS (EI$^+$, *m*/*z*) [M$^+$] calcd for $C_{31}H_{29}NOS_2$ 495.1691, found 495.1694.

*4.4.6. 4-(5-(5-(5-Bromothiophen-2-yl)-1-(2,6-diisopropylphenyl)-1H-pyrrol-2-yl)thiophen-2-yl)benzaldehyde (**7**).* Compound **6** (0.75 g, 1.51 mmol) was dissolved in 10 mL of DMF. The solution was cooled with ice bath and then NBS (0.27 g, 1.52 mmol) in 5 mL of DMF was added drop by drop to the stirred solution at 0 °C. The solution was stirred for 6 h. The solvent was concentrated by using a rotary evaporator and the solid was dissolved in 50 mL of CH_2Cl_2. The organic solution was washed with water and brine solution, and then dried over anhydrous Na_2SO_4. The solvent was concentrated on a rotary evaporator and dried under vacuum to afford compound **7**. Yield is 0.83 g (95%). Mp 149–150 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 9.95 (s, 1H), 7.81 (dd, 2H), 7.54–7.62 (m, 3H), 7.32 (d, 2H), 7.21 (t, 1H), 7.13 (d, 1H), 6.86 (dd, 1H), 6.63–6.74 (m, 3H), 6.19–6.29 (m, 1H), 2.42–2.62 (m, 2H), 0.95 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 191.5, 148.1, 140.1, 139.6, 136.9, 136.6, 134.9, 133.9, 131.1, 130.6, 130.2, 130.0, 125.8, 125.5, 125.2, 123.9, 123.2, 110.3, 110.2, 109.7, 28.6, 24.0, 23.9; IR (KBr, cm^{-1}): 3069, 2960, 2926, 2866, 2814, 2726, 1697, 1599, 1562, 1469, 1439; HRMS (EI$^+$, *m*/*z*) [M$^+$] calcd for $C_{31}H_{28}BrNOS_2$ 573.0796, found 573.0798.

*4.4.7. 4-(5-(5-(5-(4-(Diphenylamino)phenyl)thiophen-2-yl)-1-(2,6-diisopropylphenyl)-1H-pyrrol-2-yl)thiophen-2-yl)benzaldehyde (**8**).* The solution of compound **7** (0.7 g, 1.22 mmol) and 4-(diphenylamino)phenylboronic acid (0.38 g, 1.32 mmol) in 30 mL THF was purged well with nitrogen for 45 min, and then $Pd(PPh_3)_4$ (2 mol %) and aqueous 2 M K_2CO_3 solution (7 mL) were added to the solution. The whole mixture was refluxed with vigorous stirring for 48 h under nitrogen. The solvent was concentrated by using a rotary evaporator and the residue was dissolved in CH_2Cl_2. The organic solution was washed with water and brine solution, and then dried over anhydrous Na_2SO_4. The solvent was concentrated and the residue was purified by column chromatography (silica gel, hexane/ethyl acetate=80:20, v/v) to afford compound **8**. Yield is 0.7 g (78%).

Mp 193–194 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 9.95 (s, 1H), 7.81 (d, 2H), 7.54–7.62 (m, 3H), 7.23–7.34 (m, 10H), 7.00–7.14 (m, 7H), 6.89 (d, 1H), 6.73 (dd, 2H), 6.30 (d, 1H), 6.28 (d, 1H), 2.48–2.62 (m, 2H), 0.98 (d, 6H), 0.96 (d, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 191.5, 148.2, 147.7, 147.3, 141.9, 140.2, 139.3, 137.2, 134.9, 134.4, 133.5, 131.2, 130.9, 130.6, 129.7, 129.5, 128.5, 126.4, 125.5, 125.1, 124.7, 124.0, 123.9, 123.7, 123.3, 123.1, 122.5, 110.3, 109.6, 28.6, 24.0; IR (KBr, cm^{-1}): 3064, 3031, 2962, 2927, 2867, 2839, 2729, 1698, 1598, 1491, 1445; HRMS (EI^+, m/z) [M^+] calcd for $C_{49}H_{42}N_2OS_2$ 738.2739, found 738.2742.

*4.4.8. (E)-3-(4-(5-(5-(5-(4-(Diphenylamino)phenyl)thiophen-2-yl)-1-(2,6-diisopropylphenyl)-1H-pyrrol-2-yl)thiophen-2-yl)phenyl)-2-cyanoacrylic acid (**TPTDYE-2**).* Compound **8** (0.59 g, 0.8 mmol) was dissolved in a mixed solvent of $CHCl_3$ and acetonitrile (30 mL, 1:1, v/v), and then piperidine (4 mmol) and cyanoacetic acid (4 mmol) were added at room temperature. The solution was slowly heated to reflux temperature. After 18 h, the solution was cooled to room temperature and concentrated by using a rotary evaporator. The residue was dissolved into 10 mL of CH_2Cl_2 and the resulting solution was poured into 100 mL water. To this stirred mixture was added 2 N HCl solution until the reaction mixture became acidic. The aqueous layer was extracted with CH_2Cl_2 and the organic layer was washed with water and brine solution, and then dried over anhydrous $NaSO_4$, filtered, evaporated on a rotary evaporator to dryness. The residue was purified by column chromatography (silica gel, CH_2Cl_2/CH_3OH=90:10, v/v) to give **TPTDYE-2**. Yield: 0.57 g (88%). Mp 289–290 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 7.82 (d, 4H), 7.66 (t, 1H), 7.25–7.54 (m, 12H), 6.89–7.11 (m, 8H), 6.80 (d, 2H), 6.49 (d, 1H), 6.41 (d, 1H), 2.34–2.44 (m, 2H), 0.90 (d, 12H). IR (KBr, cm^{-1}): 3438, 3062, 3030, 2960, 2925, 2866, 2214, 1627, 1591, 1491; HRMS (EI^+, m/z) [M^+] calcd for $C_{52}H_{43}N_3O_2S_2$ 805.2797, found 805.2785.

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