

A solution-processable diketopyrrolopyrrole dye molecule with (fluoronaphthyl)thienyl endgroups for organic solar cells[☆]

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ABSTRACT

A solution-processable dye molecule DPP(TFNa)₂ that consists of diketopyrrolopyrrole (DPP) as the core and 5-(6-fluoro-2-naphthyl)thienyl as the endgroups is presented for bulk heterojunction organic solar cells. DPP(TFNa)₂ is a crystalline solid with a *T*_m of approximately 216 °C. X-ray diffraction experiments reveal that thermal annealing increases crystallinity of the as-cast film, thus beneficial to the absorption and charge-transport properties. DPP(TFNa)₂ exhibits two reversible one-electron oxidation waves at 0.87 and 1.16 V vs. Ag/AgCl reference electrode, respectively. Fitting the space-charge-limited current characteristics in a hole-only device results in a hole mobility of $\sim 2.7 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at low voltages for DPP(TFNa)₂. A preliminary characterization of the solar cell (ITO/PEDOT:PSS/DPP(TFNa)₂:PC₆₁BM/Al) yields a power conversion efficiency of approximately 3.0% under simulated AM 1.5G illumination (66.4 and 100 mW cm⁻², respectively). The fluorine effects on material properties such as morphology, absorption, electrochemistry, charge transport and the resulting device performance are discussed.

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1. Introduction

Solution-processable small molecule organic semiconductors have received increasing interest as electron donors in bulk heterojunction (BHJ) solar cells [1,2]. Tremendous efforts that have been invested in developing new materials and device technologies have contributed to reported power conversion efficiencies (PCEs) exceeding 7–8% very recently [3,4].

Among the various building blocks investigated, diketopyrrolopyrrole (DPP) remains an attractive strong electron-accepting

unit to construct potentially high-performance electron donors for BHJ organic solar cells (OSCs) due to its high planarity, photostability and facile availability [5–7].

In this context, a considerable number of solution-processable DPP-cored molecular donors with diverse endgroups have been reported (Fig. 1), producing a PCE of up to 4–5% [7–12]. These simple organic semiconductors provide valuable molecular structure-properties relationships, especially with the aid of X-ray single-crystal structural analysis [8a,12].

In this contribution, we further report a DPP-based molecular donor DPP(TFNa)₂ with (fluoronaphthyl)thienyl endgroups as well as an analogue compound without fluorine substituents DPP(TNa)₂ (Fig. 2) [9]. The early work [13,14] including ours [15] show that fluorination on a π -unit of an organic semiconductor may lead to an increase in intermolecular C–F $\cdots$ H and/or π – π interactions and hence in charge transport besides a decrease in HOMO and LUMO levels. Our results indicate that introducing the simple fluorine functionality contributes to improving the photovoltaic response of DPP(TFNa)₂.

[☆] Note that the compound DPP(TNa)₂ was published as Ref. 9 during our preparation of this work. Our results together with this earlier report show that DPP-based organic semiconductors that contain naphthyl components may provide an interesting class of solution-processable active materials for organic optoelectronics.

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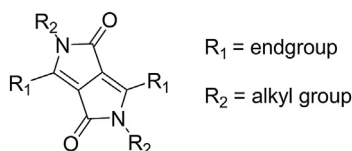


Fig. 1. Illustrative chemical structure of molecular donors based on DPP as the core.

2. Experimental

2.1. Materials and instructions

All manipulations involving air-sensitive reagents were performed under dry nitrogen. Tetrahydrofuran (THF) was dried with molecular sieves (3 Å). 2-Bromo-6-fluoronaphthalene was synthesized according to literature [16]. All the other starting materials were purchased commercially and used as received, unless otherwise specified.

^1H and ^{13}C NMR measurements were carried out on a Bruker 300 MHz DRX spectrometer with tetramethylsilane (TMS) as the internal reference. Mass Spectrometry (MS) data were obtained on a Bruker Daltonics BIFLEX III MALDI-TOF Analyzer using MALDI mode. Elemental analyses were carried out using a Vario EL CHNS elemental analyzer. UV–Vis absorption spectra were recorded on an HP 8453 UV–Vis spectrophotometer. Thermogravimetric analysis (TGA) measurements were carried out on Netzsch TG 209 under a nitrogen flow at a heating rate of $20\text{ }^\circ\text{C min}^{-1}$. Differential scanning calorimetry (DSC) measurements were performed on a Netzsch DSC 204 under nitrogen at a heating and cooling rate of $10\text{ }^\circ\text{C min}^{-1}$, respectively. Tapping-mode atomic force microscopy (AFM) was carried out on a Veeco Nanoscope V scanning probe microscope. Cyclic voltammetry was carried out on a CHI660A electrochemical workstation

using platinum working electrode and Ag/AgCl reference electrode at a scan rate of 100 mV s^{-1} in nitrogen-saturated mixed solvents $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (5:1 v/v) containing 0.1 M $n\text{-Bu}_4\text{NPF}_6$. The Fc^+/Fc couple was used as the internal standard. X-ray diffraction (XRD) was performed on a Panalytical Xpert PRO X-ray diffractometer at 40 kV/40 mA for the films spin-coated from CHCl_3 solutions onto glass substrates with or without thermal annealing. The radiation line was Cu K α ($k = 1.5418\text{ \AA}$).

2.1.1. 2,5-bis(2-ethylhexyl)-3,6-bis(5-(2-naphthyl)thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H, 5H)-dione (DPP(TNa) $_2$) [9]

$\text{Pd}(\text{PPh}_3)_4$ (35 mg, 0.03 mmol) was added to a mixture of 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (0.35 g, 0.51 mmol) and 2-naphthyl boronic acid (0.22 g, 1.29 mmol) in toluene (25 mL), ethanol (10 mL) and aqueous Na_2CO_3 solution (2 M, 5 mL) under N_2 . After the reaction was heated overnight at $90\text{ }^\circ\text{C}$, the volatile was evaporated. The residue was treated with water and extracted with CH_2Cl_2 . The organic layer was separated, dried over anhydrous MgSO_4 , filtered and then concentrated. The crude product was purified by column chromatography using petroleum ether/dichloromethane (v/v = 3/1) as eluent to afford a deep mulberry solid in 89% yield (0.36 g). ^1H NMR (300 MHz, CDCl_3): δ 9.00 (d, $J = 4.14\text{ Hz}$, 2H), 8.13 (s, 2H), 7.76–7.90 (m, 8H), 7.60 (d, $J = 4.14\text{ Hz}$, 2H), 7.48–7.56 (m, 4H), 4.12 (m, 4H), 1.99 (m, 2H), 1.31–1.45 (m, 16H), 0.87–0.96 (m, 12H). ^{13}C NMR (75 MHz, CDCl_3): δ 10.63, 14.09, 23.14, 23.78, 28.66, 30.46, 39.32, 46.06, 108.35, 123.99, 124.80, 124.95, 126.68, 126.91, 127.80, 128.25, 128.92, 129.06, 130.58, 133.34, 133.52, 136.80, 139.83, 149.72, 161.77. Anal. Calcd. for $\text{C}_{50}\text{H}_{52}\text{N}_2\text{O}_2\text{S}_2$: C, 77.28; H, 6.74; N, 3.6; S, 8.25. Found: C, 77.07; H, 6.744; N, 3.57; S, 8.378. MALDI-TOF: m/z 777.631 (100%) M^+ (calcd. 777.347).

2.1.2. 6-Fluoro-2-naphthyl boronic acid pinacol ester

A solution of $n\text{-BuLi}$ in $n\text{-hexane}$ (2.5 M, 1.86 mL, 4.67 mmol) was added dropwise to a solution of 2-bromo-6-fluoronaphthalene (1.00 g, 4.44 mmol) in anhydrous THF (20 mL) under nitrogen at $-78\text{ }^\circ\text{C}$. After the reaction was kept at $-78\text{ }^\circ\text{C}$ for 1 h, isopropoxyboronic acid pinacol ester (1.12 mL, 5.56 mmol) was added. The mixture was left to warm up to room temperature overnight. Then it was evaporated under vacuum. The residue was treated with water and extracted with CH_2Cl_2 . The organic phase was further washed with water and brine, and dried over MgSO_4 . Upon concentration under vacuum, the crude product was purified by column chromatography on silica gel using CH_2Cl_2 as the eluent to obtain a white solid (0.785 g, 65%). ^1H NMR (300 MHz, DMSO): δ 8.25 (s, 1H), 8.09–8.14 (m, 1H), 7.88 (d, $J = 8.28\text{ Hz}$, 1H), 7.68–7.75 (m, 2H), 7.40–7.46 (m, 1H), 1.31 (s, 12H).

2.1.3. 2,5-bis(2-ethylhexyl)-3,6-bis(5-(6-fluoronaphthalen-2-yl)thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H, 5H)-dione (DPP(TFNa) $_2$)

Prepared according to the procedure of compound **1** using 6-fluoro-2-naphthyl boronic acid pinacol ester instead. Yield: 83%. ^1H NMR (300 MHz, CDCl_3): δ 8.97 (d, $J = 4.08\text{ Hz}$, 2H), 8.10 (s, 2H), 7.89–7.77 (m, 6H), 7.56 (d, $J = 4.08\text{ Hz}$, 2H), 7.45 (d, $J = 7.74\text{ Hz}$, 2H), 7.30 (t, $J = 8.73\text{ Hz}$, 2H), 4.11 (m, 4H), 1.97 (m, 2H), 1.31–1.41 (m, 16H), 0.87–0.96 (m, 12H). ^{13}C NMR (75 MHz, CDCl_3): δ 10.62, 14.08, 23.12, 23.78, 28.65, 30.44, 39.30, 46.05, 108.38, 110.95, 111.23, 117.19, 117.53, 124.76, 124.86, 125.04, 128.21, 128.27, 129.08, 130.01, 130.51, 130.59, 130.71, 134.02, 134.14, 136.72, 139.80, 149.34, 161.75 (The F–C coupling was observed). Anal. Calcd. for $\text{C}_{50}\text{H}_{50}\text{F}_2\text{N}_2\text{O}_2\text{S}_2$: C, 73.86; H, 6.20; N, 3.45; S, 7.89. Found: C, 73.70; H, 6.21; N, 3.40; S, 7.987. MALDI-TOF: m/z 812.601 (100%) M^+ (calcd. 812.328).

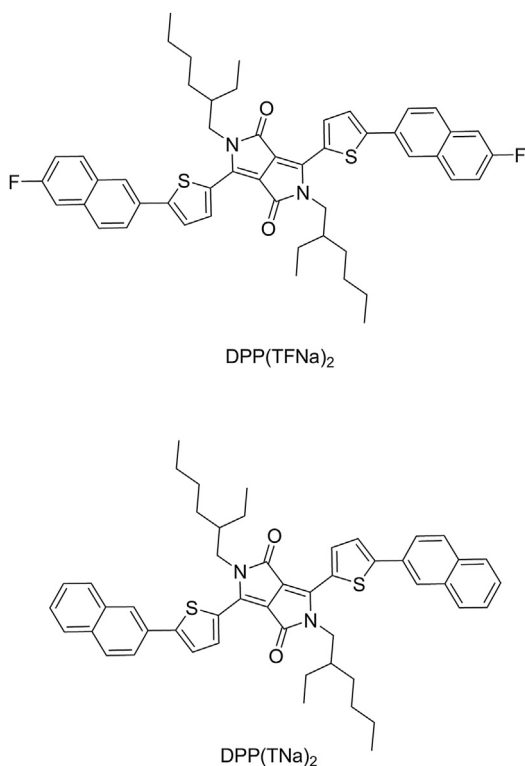


Fig. 2. Chemical structure of DPP(TFNa) $_2$ and DPP(TNa) $_2$.

2.2. Device fabrication and characterization

Photovoltaic cells: ITO-coated glass substrates were cleaned by sonification in acetone, detergent, deionized water, and isopropyl alcohol and dried in a nitrogen stream, followed by an oxygen plasma treatment. To fabricate photovoltaic devices, a hole-transport thin layer (ca. 40 nm) of PEDOT:PSS (Baytron PVPAl 4083, filtered at 0.45 μm) was spin-cast on the pre-cleaned ITO-coated glass substrates at 4000 rpm and baked at 140 $^{\circ}\text{C}$ for 10 min under ambient conditions. The active layer DPP(TNa)₂ or DPP(TFNa)₂:PC₆₁BM was prepared by spin-casting chloroform solution (total concentration, 20 mg mL^{-1}) at 2500 rpm for 30 s in dry box and thermally annealed at 110 $^{\circ}\text{C}$ for 10 min. Subsequently, the aluminum cathode (90 nm) was thermally evaporated onto the active layer under high vacuum ($<3 \times 10^{-4}$ Pa). The cell was encapsulated by a thin glass slice. The effective device area was defined as 0.16 cm^2 by a shadow mask. The current density–voltage (*J*–*V*) characteristics were measured using a Keithley 2400 source meter. The photovoltaic devices were characterized using a calibrated AM 1.5G solar simulator (Oriel model 91192), under light intensity of 66.4 mW cm^{-2} .

The PCE of the device ITO/PEDOT:PSS/DPP(TFNa)₂:PC₆₁BM(3:2 w/w, thermally annealed) was further measured under illumination intensity of 100 mW cm^{-2} .

Single carrier hole-only device (ITO/PEDOT:PSS(40 nm)/DPP(TNa)₂ or DPP(TFNa)₂ (80 nm)/MoO₃(10 nm)/Al) was fabricated to measure hole mobility of the molecular donors. PEDOT:PSS was used as a hole-injection layer at the anode, and a vacuum-deposited molybdenum trioxide (MoO₃) layer was used as an electron-blocking layer at the cathode. DPP(TNa)₂ and DPP(TFNa)₂ were spin-cast from CHCl₃ solution at 1000 rpm (10 mg mL^{-1}), thermally annealed at 110 $^{\circ}\text{C}$ for 10 min.

3. Results and discussions

3.1. Synthesis, optical and electrochemical properties

DPP(TFNa)₂ is facilely obtained by a two-fold Suzuki coupling of 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)dione with 6-fluoro-2-naphthyl boronic pinacol ester (Fig. 3). The identity and purity are evidenced by ¹H and ¹³C NMR, MS and microanalysis (See also Fig. S1 and S2 in Supporting Information).

DPP(TNa)₂ and DPP(TFNa)₂ show very similar absorption in dilute solution, with two absorption maxima in the visible at ca. 570 and 610 nm (Fig. 4), while the former compound has a higher molar absorptivity of $6.63 \times 10^{-4} \text{ L mol}^{-1} \text{ cm}^{-1}$ at 610 nm vs. $5.44 \times 10^{-4} \text{ L mol}^{-1} \text{ cm}^{-1}$ of the latter fluorinated compound. The absorption spectra of their as-cast films are considerably redshifted and hence reveal a considerable difference. Thus, two new peaks

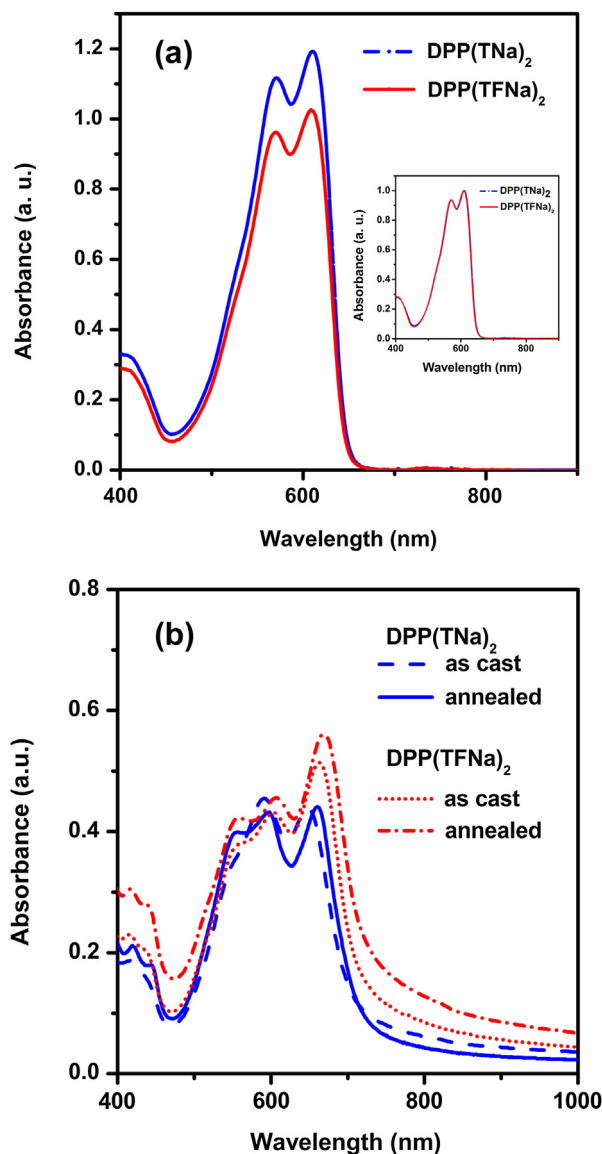


Fig. 4. (a) The UV–Vis–NIR absorption spectra of DPP(TNa)₂ and DPP(TFNa)₂ in dilute CH₂Cl₂ solution ($2 \times 10^{-5} \text{ mol L}^{-1}$) with the normalized spectra shown in the inset and (b) as-cast films from CHCl₃ solution (10 mg mL^{-1} , spin speed of 1000 rpm) and subsequently thermally annealed films at 110 $^{\circ}\text{C}$ for 10 min.

appear at 591 and 647 nm for DPP(TNa)₂ and 604 and 663 nm for DPP(TFNa)₂. In addition to an emerging absorption peak at 558 nm, thermal annealing the as-cast films produces a further redshift of the absorption spectra, in particular for DPP(TNa)₂, (Table 1). These

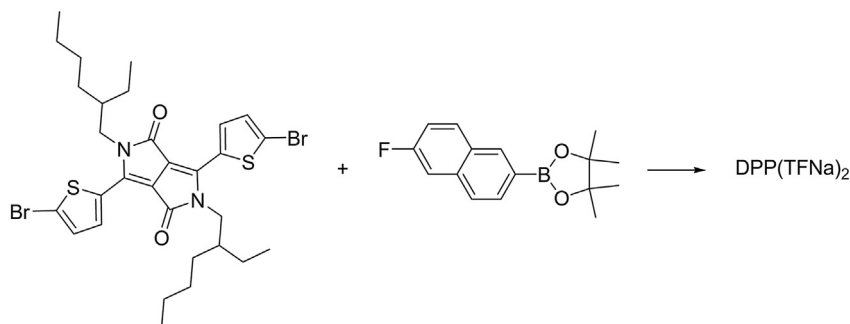


Fig. 3. Synthetic route to DPP(TFNa)₂.

Table 1
UV–Vis and cyclic voltammetric data for DPP(TNa)₂ and DPP(TFNa)₂.

	$\lambda_{\text{max}}^{\text{abs}}$ (nm) ^a			$E_{\text{ox}}^{\text{ex}}$ (V) ^b		HOMO ^c (eV)	LUMO ^d (eV)
	Solution	As-cast films	Thermally annealed films	1 st	2 nd		
DPP(TNa) ₂	570, 610	591, 647	558, 596, 660	0.85	1.14	−5.18	−3.47
DPP(TFNa) ₂	570, 609	604, 663	558, 607, 669	0.87	1.16	−5.20	−3.56

^a In CH₂Cl₂.

^b Vs. Ag/AgCl reference electrode.

^c Derived from E_{ox} values with reference to the energy level of ferrocene (Fc) of −4.8 eV vs. vacuum level.

^d Derived from E_{HOMO} and the absorption onset of the solid films.

observations suggest that monofluorination of the naphthyl group provides more efficient intermolecular stacking in solid state, which further benefits from thermal treatment.

Cyclic voltammetry performed in CH₂Cl₂/CH₃CN in the presence of Bu₄NPF₆ as supporting electrolyte shows that DPP(TNa)₂ and DPP(TFNa)₂ undergo two consecutive reversible one-electron oxidations at ~0.85 V and 1.14 V vs. Ag/AgCl (Fig. 5). This reversibility indicates that the positively charged species are stable, which can be important as far as charge transport is concerned. The electrochemical data lead to estimated HOMO levels of −5.18 eV for DPP(TNa)₂ and −5.20 eV for DPP(TFNa)₂, with reference to the energy level of ferrocene. The LUMO levels were derived as −3.47 and −3.56 eV from the HOMO levels and the UV–Vis absorption onset of each compound.

Furthermore the HOMO and LUMO energy levels of DPP(TNa)₂ and DPP(TFNa)₂ were estimated with the basis set of 6-31G(d,p) using the Gaussian 09 program. For saving computation time, model compounds with methyl groups replacing the 2-ethylhexyl moieties were used instead. The simulated HOMO and LUMO orbitals as well as the corresponding energy levels are presented in Fig. S3 and Table S1, respectively. The obtained data from the DFT calculations agree quite well with those derived from the cyclic voltammograms. Thus, introducing fluorine atoms in DPP(TFNa)₂ lowers the HOMO and LUMO levels.

3.2. Thermal and morphological properties

Thermogravimetric analysis shows that DPP(TNa)₂ and DPP(TFNa)₂ are thermally stable well over 400 °C (see Fig. S4 in

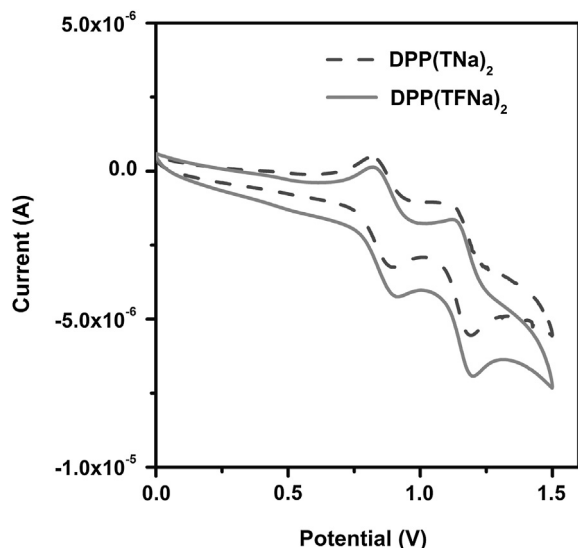


Fig. 5. Cyclic voltammograms of DPP(TNa)₂ and DPP(TFNa)₂ in CH₂Cl₂/CH₃CN (5:1 v/v). Supporting electrolyte: 0.1 M Bu₄NPF₆; Scan rate: 0.1 V s^{−1}.

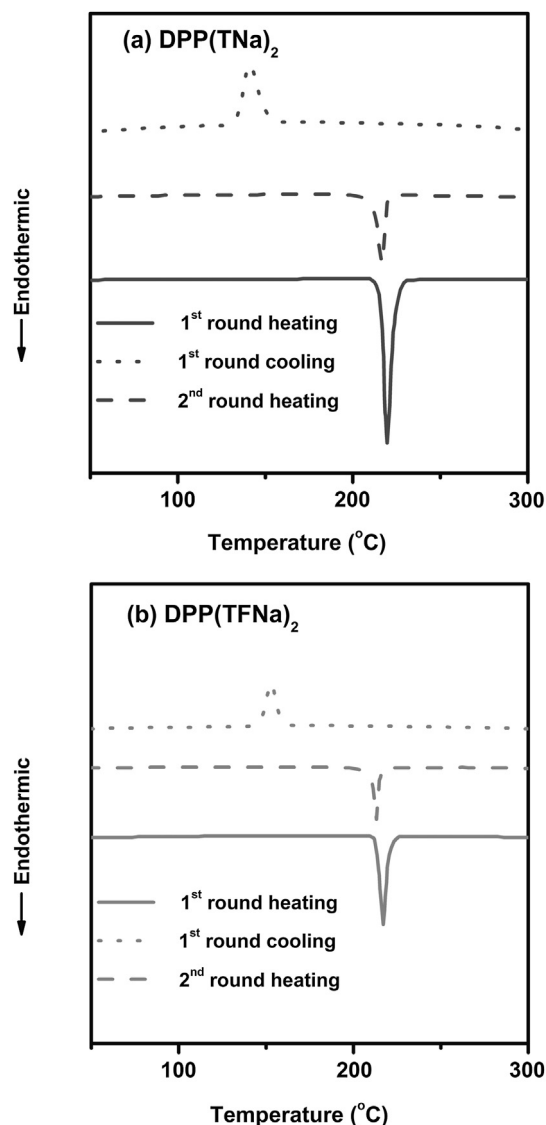


Fig. 6. DSC diagrams of DPP(TNa)₂ (a) and DPP(TFNa)₂ (b).

Supporting information). Differential scanning calorimetry (DSC) measurements reveal that both compounds are crystalline solids (Fig. 6). They melt approximately at 220 °C, and re-melt after crystallization upon cooling.

The morphologies of the as-cast and thermally-annealed films of DPP(TNa)₂ and DPP(TFNa)₂ studied by atomic force microscopy (AFM) are shown in Fig. 7. Relative to DPP(TFNa)₂, thermal annealing for a short period, e.g. 10 min, imposes a dramatically greater effect on the as-cast film of DPP(TNa)₂. Notably, the grain domain size is grown typically from ~30 nm × 150 nm ~ 150 nm × 350 nm, with a large increase of the surface roughness R_{rms} from 1.82 nm to 70.52 nm. These morphological changes are indicative of the increasingly growing crystallinity of the resulting thermally treated films, as confirmed by the XRD measurement (See Fig. S5 in Supporting Information), hence accounting for the observed evolution of the absorption spectra of the corresponding films upon heating (Fig. 4).

3.3. Hole-mobility measurement

Single carrier hole-only devices ITO/PEDOT:PSS/DPP(TNa)₂ or DPP(TFNa)₂/MoO₃/Al were fabricated to measure hole mobility of the molecular semiconductors. A vacuum-deposited molybdenum

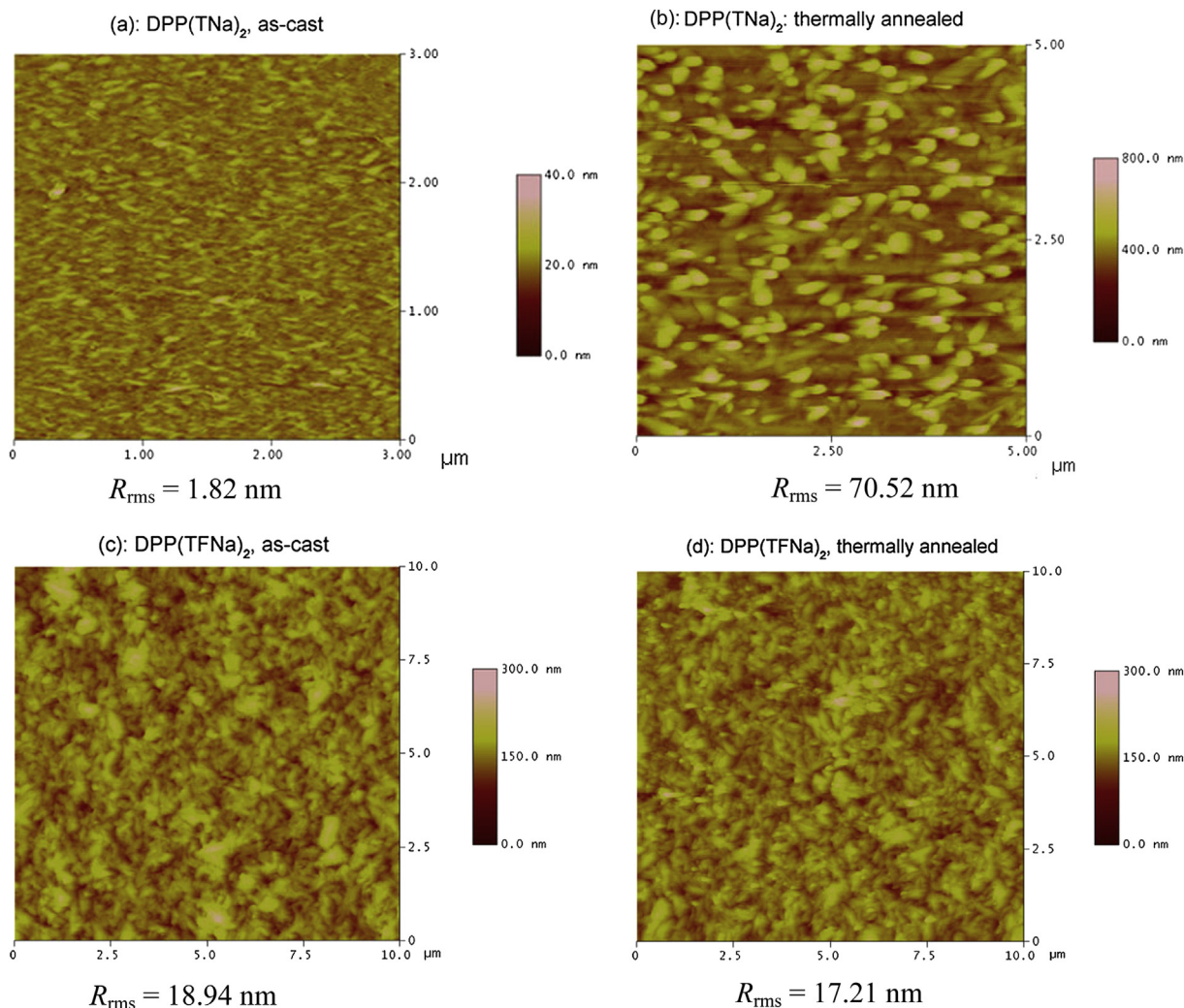


Fig. 7. (a) Topographic atomic force microscopy (AFM) images of the as-cast and thermally annealed thin films of DPP(TNa)₂ and DPP(TFNa)₂ from CHCl₃ solution (10 mg mL⁻¹, at a spin speed of 1000 rpm) on ITO. Thermal annealing was performed at 110 °C for 10 min.

trioxide (MoO₃) layer was used as an electron-blocking layer at the cathode.

At low voltages, the device current shows a clear quadratic dependence on the voltage, indicating a space-charge-limited current (Fig. 8). Consequently, fitting the *J*–*V* curve in accord with Mott–Gurney’s square law (Eqn. (1)) [17] yields a mobility value of $1.24 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for DPP(TNa)₂ and $2.7 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for DPP(TFNa)₂, which is among the highest obtained for solution-processed small molecule donors [2,7–12].

$$J = \frac{9}{8} \varepsilon \mu \frac{V^2}{d^3} \quad (1)$$

where ε and d are permittivity and thickness of the active layer ($\varepsilon = \varepsilon_0 \varepsilon_r$, ε_0 the permittivity of the free space, ε_r the relative permittivity and assumed as approximately 3.0, μ the mobility and V the effective voltage corrected by subtracting from the applied voltage (V_{appl}) the built-in voltage (V_{bi}) and the voltage drop (V_s) resulting from the series resistance.

3.4. Photovoltaic performances

The photovoltaic responses of solution-processed thin films of DPP(TNa)₂ and DPP(TFNa)₂ were first tentatively investigated in

conventional bulk-heterojunction photovoltaic cells (ITO/PEDOT:PSS/active layer/Al). The active layer consists of a blend of DPP(TNa)₂ or DPP(TFNa)₂ as electron donor and PC₆₁BM as electron acceptor, thermally annealed at 110 °C for 10 min. The current density–voltage (*J*–*V*) characteristics of photovoltaic devices involving various electron donor:acceptor ratios, namely 2:1, 3:2, 1:1, 2:3 (w/w) are shown in Fig. 9, under simulated AM 1.5G with an illumination intensity of 66.4 mW cm^{-2} . The relevant data are summarized in Table 2.

PCE of DPP(TNa)₂ remains approximately at 2.5% in a range of donor:acceptor ratios from 2:1 to 1:1 (w/w). For instance, the open-circuit voltage (V_{oc}) = 0.84 V, short-circuit current density (J_{sc}) = 4.06 mA cm^{-2} , Filled factor (*FF*) = 52.1% for a blend of 3:2 (w/w), thus providing a PCE of 2.61%. This PCE is comparable to that of the photovoltaic device (ITO/PEDOT:PSS/DPP(TNa)₂:PC₇₁BM/Ca/Al) [9]. Further increasing the content of PC₆₁BM to 2:3 (w/w) leads to a sharp decrease of PCE to 1.49%, due mainly to the loss of *FF*.

By contrast, DPP(TFNa)₂ shows a generally higher PCE. For a blend of 3:2 (w/w), V_{oc} = 0.92 V, J_{sc} = 4.18 mA cm^{-2} , *FF* = 54.4%, yielding a PCE of 3.15% (Table 2).

Film morphology of the active layer plays a critical role in determining the photovoltaic response. Fig. S6 shows the surface morphology of the thermally annealed active layer that consisted of

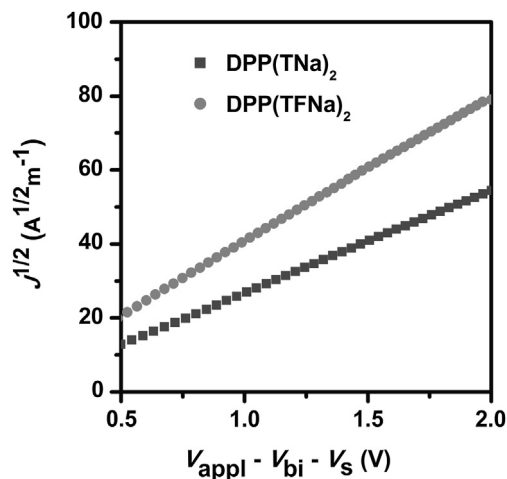


Fig. 8. $J^{1/2}$ – V characteristics of the hole-only device: ITO/PEDOT:PSS(40 nm)/DPP(TNa)₂ or DPP(TFNa)₂(80 nm)/MoO₃(10 nm)/Al. PEDOT:PSS was used as a hole-injection layer at the anode, and a vacuum-deposited molybdenum trioxide (MoO₃) layer as an electron-blocking layer at the cathode. The active layer was spin-cast from CHCl₃ solution, thermally annealed at 110 °C for 10 min.

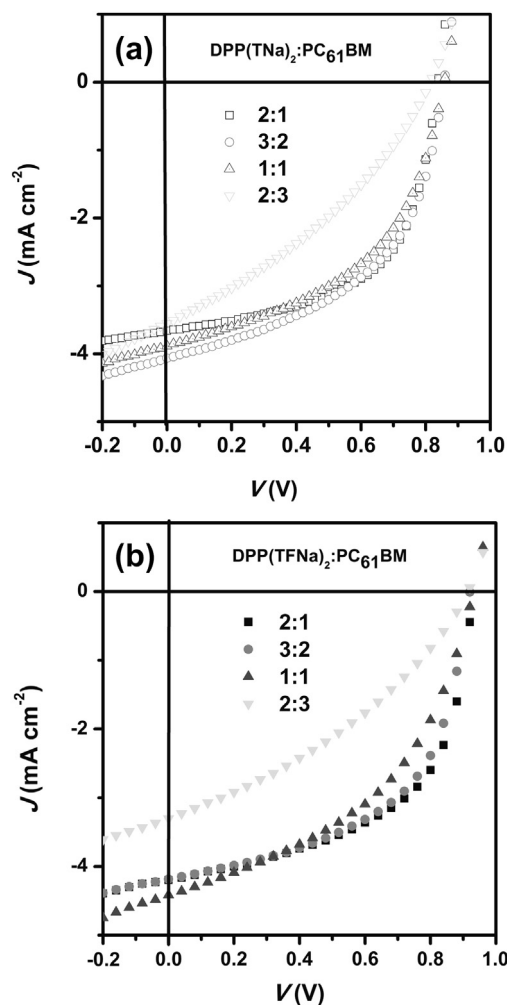


Fig. 9. Current density (J)–voltage (V) of photovoltaic devices that consisted of different solution-processed active layers, thermally annealed at 110 °C for 10 min (a) DPP(TNa)₂:PC₆₁BM and (b) DPP(TFNa)₂:PC₆₁BM.

Table 2

Summary of photovoltaic data (ITO/PEDOT:PSS/active layer(thermally annealed)/Al), under light intensity of 66.4 mW cm^{−2}.

	SM:PC ₆₁ BM (w/w)	J_{sc} (mA cm ^{−2})	V_{oc} (V)	FF (%)	PCE (%)
DPP(TNa) ₂	2:1	3.65	0.82	56.0	2.52
	3:2	4.06	0.84	50.9	2.61
	1:1	3.88	0.86	48.1	2.41
	2:3	3.55	0.82	34.0	1.49
DPP(TFNa) ₂	2:1	4.20	0.92	52.1	3.03
	3:2	4.18	0.92	54.4	3.15
	1:1	4.41	0.92	44.4	2.71
	2:3	3.30	0.92	35.2	1.61
	3:2 ^a	6.22	0.90	54.3	3.04

^a under an illumination light intensity of 100 mW cm^{−2}.

a donor:PC₆₁BM ratio of 3:2 and 2:3 (w/w), respectively (See [Supporting Information](#)). In the case of a higher PC₆₁BM content, a large “bright” domain size is observed in particular for DPP(TNa)₂, concurrent with a rougher surface.

The active layer of DPP(TFNa)₂:PC₆₁BM (3:2 w/w) nevertheless shows a dominant fine fiber structure with a least surface roughness of approximately 1.70 nm, which may contribute to its highest photovoltaic performance.

On the other hand, the photovoltaic devices provide severely reduced PCEs without thermal annealing of the active layer. At the same donor:acceptor ratio of 3:2 (w/w), PCE = 0.23% with V_{oc} = 0.65 V, J_{sc} = 0.88 mA cm^{−2}, FF = 26.7% for DPP(TNa)₂, and PCE = 0.3% with V_{oc} = 0.75 V, J_{sc} = 0.99 mA cm^{−2}, FF = 26.8% for DPP(TFNa)₂ (See [Fig. S7](#) in Supporting Information).

Finally, PCE of the device ITO/PEDOT:PSS/DPP(TFNa)₂:PC₆₁BM(3:2 w/w, thermally annealed)/Al remained at ca. 3.0% with V_{oc} = 0.90 V, J_{sc} = 6.22 mA cm^{−2}, FF = 54.3%, under illumination intensity of 100 mW cm^{−2} (See [Table 2](#) and [Fig. S8](#) in Supporting Information). This result for a BHJ solar cell comprised of a solution-processed active layer appears of considerable significance on account of the facile synthesis/availability of the donor compound and the utilization of PC₆₁BM as an electron acceptor [[5a,7–12,18](#)].

4. Conclusions

In summary, we have described a linear solution-processable DPP-cored molecular semiconductor DPP(TFNa)₂ with 5-(6-fluoro-2-naphthyl)thienyl endgroups for BHJ solar cells. This new electron donor shows lower HOMO and LUMO levels, relative to the analogue compound DPP(TNa)₂ without fluorine substitution. Thermally-annealed thin film of DPP(TFNa)₂ possesses more smooth morphology and better hole mobility as well as red-shifted absorption. Consequently, DPP(TFNa)₂ can afford a substantially improved PCE to approximately 3.0% with high V_{oc} (≈0.90 V) and FF (≈54%) in a simple photovoltaic device (ITO/PEDOT:PSS/small molecule donor:PC₆₁BM/Al). Further attempt to improve the photovoltaic response of DPP(TFNa)₂ as well as molecular design is underway in our laboratory.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.dyepig.2013.09.022>.

References

- [1] Mishra A, Bäuerle P. Small molecule organic semiconductors on the move: promises for future solar energy technology. *Angew Chem Int Ed* 2012;51: 2020–67.
- [2] (a) Li Y-W, Guo Q, Li Z-F, Pe J-N i, Tian W-J. Solution processable D–A small molecules for bulk-heterojunction solar cells. *Energy Environ Sci* 2010;3: 1427–36; (b) Walker B, Kim C, Nguyen T-Q. Small molecule solution-processed bulk heterojunction solar cells. *Chem Mater* 2011;23:470–82; (c) Lin Y, Li Y, Zhan X-W. Small molecule semiconductors for high-efficiency organic photovoltaics. *Chem Soc Rev* 2012;41:4245–72; (d) Roncali J. Molecular bulk heterojunctions: an emerging approach to organic solar cells. *Acc Chem Res* 2009;42:1719–30.
- [3] Zhou JY, Zuo Y, Wan XJ, Long GK, Zhang Q, Ni W, et al. Solution-processed and high-performance organic solar cells using small molecules with a benzodithiophene unit. *J Am Chem Soc* 2013;135:8484–7.
- [4] Kyaw AKK, Wang DH, Gupta V, Zhang J, Chand S, Bazan GC, et al. Efficient solution-processed small-molecule solar cells with inverted structure. *Adv Mater* 2013;25:2397–402.
- [5] Recent reviews on DPP-based materials for organic photovoltaics: (a) Qu S-Y, Tian H. Diketopyrrolopyrrole (DPP)-based materials for organic photovoltaics. *Chem Commun* 2012;48:3039–51; (b) Li Y-N, Sonar P, Murphy L, Hong W. High mobility diketopyrrolopyrrole (DPP)-based organic semiconductor materials for organic thin film transistors and photovoltaics. *Energy Environ Sci* 2013;6:1684–710.
- [6] (a) Wienk MM, Turbiez M, Gilot J, Janssen RAJ. Narrow-bandgap diketopyrrolo-pyrrole polymer solar cells: the effect of processing on the performance. *Adv Mater* 2008;20:2556–60; (b) Bijleveld JC, Zoombelt AP, Mathijssen SGJ, Wienk MM, Turbiez M, de Leeuw DM, et al. Poly(diketopyrrolopyrrole-terthiophene) for ambipolar logic and photovoltaics. *J Am Chem Soc* 2009;131:16616–7.
- [7] (a) Tamayo AB, Walker B, Nguyen T-Q. A low band gap, solution processable oligothiophene with a diketopyrrolopyrrole core for use in organic solar cells. *J Phys Chem C* 2008;112:11545–51; (b) Tamayo AB, Dang X-D, Walker B, Seo J, Kent T, Nguyen T-Q. A low band gap, solution processable oligothiophene with a dialkylated diketopyrrolopyrrole chromophore for use in bulk heterojunction solar cells. *Appl Phys Lett* 2009;94:103301; (c) Walker B, Tamayo AB, Dang X-D, Zalar P, Seo JH, Garcia A, et al. Nanoscale phase separation and high photovoltaic efficiency in solution-processed small-molecule bulk heterojunction solar cells. *Adv Funct Mater* 2009;19: 3063–9.
- [8] (a) Lee OP, Yiu AT, Beaujuge PM, Woo CH, Holcombe TW, Millstone JE, et al. Efficient small molecule bulk heterojunction solar cells with high fill factors via pyrene-directed molecular self-assembly. *Adv Mater* 2011;23:5359–63; (b) Jeong B-S, Choi H, Cho N, Ko HM, Lim W, Song K, et al. Molecular engineering of diketopyrrolopyrrole-based photosensitizer for solution processed small molecule bulk heterojunction solar cells. *Sol Energy Mater Sol Cells* 2011;95:1731–40; (c) Wu Z-L, Li A, Fan B, Xue F, Adachi C, Ouyang J-Y. Phenanthrene-functionalized 3,6-dithiophen-2-yl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-diones as donor molecules for solution-processed organic photovoltaic cells. *Sol Energy Mater Sol Cells* 2011;95:2516–23; (d) Mei J, Graham KR, Stalder R, Tiwari SP, Cheun H, Shim J, et al. Self-assembled amphiphilic diketopyrrolopyrrole-based oligothiophenes for field-effect transistors and solar cells. *Chem Mater* 2011;23:2285–8; (e) Mazzio KA, Yuan MJ, Okamoto K, Luscombe CK. Oligoselenophene derivatives functionalized with a diketopyrrolopyrrole core for molecular bulk heterojunction solar cells. *ACS Appl Mater Interfaces* 2011;3:271–8.
- [9] Liu Y, Du X-Y, Xiao Z, Cao J-M, Tan S-T, Zuo Q-Q, et al. Solution processable low bandgap small molecule donors with naphthalene end-groups for organic solar cells. *Synth Met* 2012;162:1665–71.
- [10] (a) Chen M-R, Fu W-F, Shi M-M, Hu X-L, Pan J-Y, Ling J, et al. An ester-functionalized diketopyrrolopyrrole molecule with appropriate energy levels for application in solution-processed organic solar cells. *J Mater Chem A* 2013;1:105–11; (b) Liu S-Y, Shi M-M, Huang J-C, Jin Z-N, Hu X-L, Pan J-Y, et al. C–H activation: making diketopyrrolopyrrole derivatives easily accessible. *J Mater Chem A* 2013;1:2795–805.
- [11] (a) Shin W, Yasuda T, Watanabe G, Yang YS, Adachi C. Self-organizing mesomorphic diketopyrrolopyrrole derivatives for efficient solution-processed organic solar cells. *Chem Mater* 2013;25:2549–56; (b) Bura T, Leclerc N, Bechara R, Lévesque P, Heiser T, Ziesler R. Triazatruxene-diketopyrrolopyrrole dumbbell-shaped molecules as photoactive electron donor for high-efficiency solution processed organic solar cells. *Adv Energy Mater* DOI: 10.1002/aenm.201300240.
- [12] Walker B, Tamayo AB, Dang X-D, Zalar P, Seo JH, Garcia A, et al. Structure–property relationships: effects of heteroatom substitutions on the crystal structure, film formation, and optoelectronic properties of diketopyrrolopyrrole-based materials. *Adv Funct Mater* 2013;23:47–56.
- [13] Review on fluorinated organic materials for electronic and optoelectronic applications: Babudri F, Farinola GM, Naso F, Ragni R. Fluorinated organic materials for electronic and optoelectronic applications: the role of the fluorine atom. *Chem Commun* 2007;43:1003–22.
- [14] Delgado MCR, Pigg KR, da Silva Filho DA, Gruhn NE, Sakamoto Y, Suzuki T, et al. Impact of perfluorination on the charge-transport parameters of oligoacene crystals. *J Am Chem Soc* 2009;131:1502–12.
- [15] Zhao L, Zou J-H, Huang J, Li C, Zhang Y, Sun C, et al. Asymmetrically 9,10-disubstituted anthracenes as soluble and stable blue electroluminescent molecular glasses. *Org Electron* 2008;9:649–55.
- [16] Collina S, Azzolina O, Vercesi D, Sbacchi M, Scheideler MA, Barbieri A, et al. Synthesis and antinociceptive activity of pyrrolidinyl-naphthalenes. *Bioorg Med Chem* 2000;8:1925–30.
- [17] Lampert MA, Mark P. Current injection in solids. New York: Academic Press; 1970.
- [18] Lin Y, Ma L, Li Y, Liu Y, Zhu D, Zhan X. A solution-processable small molecule based on benzodithiophene and diketopyrrolopyrrole for high-performance organic solar cells. *Adv Energy Mater* 2013;3:1166–70.