Supporting Information

2-Alkyl-2-thienyl–Substituted Benzo[1,2-*b*:4,5-*b*´]dithiophene-Based Donor Molecules for Solution-Processed Organic Solar Cells

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1. Materials

All chemicals and solvents were purchased in reagent grade from Aldrich, ACROS, Fluka, or Lancaster, except $Pd(PPh_3)_4$, which was obtained from Strem Chemical. Tetrahydrofuran (THF), toluene, and Et_2O were distilled over Na/benzophenone; all reagents were used as received. The syntheses of trimethyl(4-octylthien-2-yl)stannane and compounds **1**–**7** were slightly modified versions of procedures reported in the literature.[1–3]

2. Measurements and Characterization

^1H and ^{13}C NMR spectra were recorded from $CDCl_3$ solutions using a Varian Unity 300 MHz spectrometer; chemical shifts are reported as δ values (ppm) relative to an internal tetramethylsilane (TMS) standard. Elemental analyses, determined using a HERAEUS CHN-OS RAPID elemental analyzer, and mass spectra, determined using matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS; Applied Biosystems, DE-PRO, Texas, USA), were performed in the Academia Sinica mass spectrometry laboratory. UV–Vis absorption spectra were recorded using an HP G1103A apparatus from dilute solutions in $CHCl_3$ or from solid films that had been spin-coated onto glass substrate from $CHCl_3$ solutions (10 mg mL^{-1}). Cyclic voltammetry (CV) was performed in 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in MeCN at room temperature using a BAS 100 electrochemical analyzer with a standard three-electrode electrochemical cell operated at a scanning rate of 100 mV s^{-1}. During CV measurements, the solutions were purged with N_2 for 30 s. In each case, a C working electrode was coated with a thin layer of small molecule, a Pt wire was used as the counter electrode, and a Ag wire was used as the quasi-reference electrode; a Ag/AgCl (3 M KCl) electrode served as the reference electrode for all potentials quoted herein. The redox couple of ferrocene/ferrocenium ion (Fc/Fc^+) was used as an external standard. The

corresponding energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were calculated from the experimental values of $E_{ox/onset}$ and $E_{red/onset}$ for the solid films of TBDTCNR and TBDTCN, formed by drop-casting films at a similar thickness from THF solutions (ca. 5 mg mL^{-1}). The onset potentials were determined from the intersections of two tangents drawn at the rising currents and background currents of the CV measurements. For DFT calculations, we employed the B3LYP functional,[4,5] as implemented in the Gaussian03 package,[6] in conjunction with the 3-21G(d) split-valence basis set. All DFT calculations were carried out on the ALPS cluster at the National Center for High-Performance Computing of Taiwan. Atomic force microscopy (AFM) images of the thin films (on glass substrates) were obtained using a Digital Instruments NS 3a controller and a D3100 stage. The transmission electron microscope (TEM) investigation was performed on a JEOL EM-2100F TEM operated at 200 kV. The specimen for TEM measurement were prepared by spin casting the TBDTCNR /PC61BM (w:w, 1:0.4) blend solution at 3000 rpm on glass substrate, then floating the film on a water surface, and transferring to TEM grids.

3. Synthesis

4,8-Bis(2-octyl-2-thienyl)benzo[1,2-*b*:4,5-*b*′]dithiophene (2)

In a clean and dry two-neck flask equipped with a condenser, *n*-BuLi (2.5 M in hexane, 30.50 mL, 76.27 mmol) was added dropwise to a solution of 2-octylthiophene (14.26 g, 72.76 mmol) in THF (13 mL) at 0 °C under a N_2 atmosphere. The reaction mixture was heated at 50 °C for 1 h and then cooled to room temperature (RT). A solution of 4,8-dehydrobenzo[1,2-*b*:4,5-*b*′]dithiophene-4,8-dione (4.00 g, 18.16 mmol) in THF (40 mL) was added slowly and then the mixture was kept for 2 h at 50 °C. After cooling to ambient temperature, $SnCl_2 \cdot 2H_2O$ (32.78 g, 145.28 mmol) in HCl (10%) was added and then the mixture was stirred for a further 2 h. The

mixture was poured into ice water and extracted three times with CH_2Cl_2. The organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified through column chromatography [SiO_2; CH_2Cl_2/hexane, 1:10 (v/v)] to obtain a yellow solid (6.72 g, 63.9%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64 (d, 2H), 7.44 (d, 2H), 7.28 (d, 2H), 6.90 (d, 2H), 2.91 (d, 4H), 1.76–1.56 (m, 4H), 1.46–1.30 (m, 20H), 0.92-0.83 (m, 6H).

2,6-Bis(trimethyltin)-4,8-bis(2-octyl-2-thienyl)benzo[1,2-*b*:4,5-*b*´]dithiophene (3)

Under a N_2 atmosphere, *n*-BuLi (2.5 M in hexane, 6.40 mL, 15.89 mmol) was added dropwise to a solution of **2** (4.00 g, 6.90 mmol) in dry THF (12 mL) at –78 °C. The reaction mixture was stirred at –78 °C for 2 h and then warmed to room temperature and stirred for 1 h. The reaction mixture was cooled again to –78 °C and then 1 M THF solution of trimethyltin chloride (17.27 mL, 17.27 mmol) was added drop-wise. The mixture was slowly warmed to room temperature and stirred overnight. Water was added to quench the reaction and then the aqueous phase was extracted three times with EtOAc. The combined organic phases were dried ($MgSO_4$) and concentrated under reduced pressure. Recrystallization of the residue from MeOH gave a pale yellow solid (4.40 g, 70.4%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68 (s, 2H), 7.31 (d, 2H), 6.91 (d, 2H), 2.93 (d, 4H), 1.79–1.74 (m, 2H), 1.59–1.28 (m, 20H), 0.89 (t, J=6.2 Hz, 6H), 0.39 (s, 18H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.79, 143.27, 142.24, 137.75, 137.31, 131.15, 127.62, 124.15, 122.39, 31.88, 31.56, 30.28, 29.38, 29.31, 29.72, 22.67, 14.11, –8.33. EIMS (*m*/*z*): calcd for $C_{40}H_{58}S_4Sn_2$ 906.14, found 906 [M^+].

3,4´-Dioctyl-2,2´-bithiophene-5-carbaldehyde (4)

$Pd(PPh_3)_4$ (2 mol %) was added to a solution of 5-bromo-4-octylthiophene-2-carbaldehyde (10.0 g, 33.0 mmol) and trimethyl(4-octylthien-2-yl)stannane (14.2 g, 39.6 mmol) in toluene (100 mL) under N_2 and then the mixture was heated under reflux overnight. After pouring the mixture into

water (200 mL), the organic phase was extracted with CH_2Cl_2; the combined extracts were washed three times with distilled water, dried ($MgSO_4$), and concentrated. The residue was purified through column chromatography (SiO_2; hexanes/CH_2Cl_2, 6:1) to provide a yellow solid (10.9 g, 79.3%). ^{1}H NMR (300 MHz, $CDCl_3$): 9.81 (s, 1H), 7.57 (s, 1H), 7.10 (s, 1H), 7.00 (s, 1H), 2.78 (t, J = 7.8 Hz, 2H), 2.60 (t, J = 7.6 Hz, 2H), 1.68–1.57 (m, 4H), 1.27 (m, 20H), 0.88 (t, J = 6.6 Hz, 6H). EIMS (m/z): calcd for $C_{25}H_{38}OS_2$ 418.23, found 419 [M^+].

5′-Bromo-3,4′-dioctyl-2,2′-bithiophene-5-carbaldehyde (5)

Under a N_2 atmosphere and protection from light, *N*-bromosuccinimide (NBS, 4.70 g, 26.3 mmol) was added portionwise to a solution of **4** (10.0 g, 23.9 mmol) in $CHCl_3$ (80 mL) and AcOH (80 mL) at 0 °C. The mixture was stirred for 4 h at room temperature and then water was added to quench the reaction. The aqueous phase was extracted three times with CH_2Cl_2; the combined extracts were washed sequentially with $NaHCO_3$ solution, brine, and water, dried ($MgSO_4$), and then concentrated under reduced pressure. The residue was purified through column chromatography (SiO_2; hexane/CH_2Cl_2, 6:1) to afford a yellow oil (8.5 g, 71.5%). ^{1}H NMR (300 MHz, $CDCl_3$): 9.82 (s, 1H), 7.57 (s, 1H), 6.97 (s, 1H), 2.74 (t, J = 7.8 Hz, 2H), 2.57 (t, J = 7.6 Hz, 2H), 1.61–1.55 (m, 4H), 1.30–1.55 (m, 20H), 0.88 (t, J = 6.6 Hz, 6H). EIMS (m/z): calcd for $C_{25}H_{38}OS_2Br$ 496.214, found 497 [M^+].

3,4′,4′′-Trioctyl-2,2′:5′,2′′-terthiophene-5-carbaldehyde (6)

Compound **6** was prepared from **5** (5.00 g, 10.0 mmol), trimethyl(4-octylthien-2-yl)stannane (4.33 g, 12.1 mmol), and $Pd(PPh_3)_4$ (2 mol %) using the procedure described for the preparation of **4**; purification through column chromatography (SiO_2; hexane/CH_2Cl_2, 4:1) gave a yellow oil (4.98 g, 81.2%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.81 (s, 1H), 7.58 (s, 1H), 7.10 (s, 1H), 6.99 (s, 1H), 6.93 (s, 1H), 2.81 (t, J = 8.4 Hz, 2H), 2.74 (t, J = 7.8 Hz, 2H), 2.59 (t, J = 7.5 Hz, 2H),

1.70–1.58 (m, 6H), 1.32–1.27 (m, 30H), 0.89–0.85 (m, 9H). EIMS (*m*/*z*): calcd for $C_{37}H_{56}OS_3$ 612.34, found 613 [M^+].

5´´-Bromo-3,4´,4´´-trioctyl-2,2´:5´,2´´-terthiophene-5-carbaldehyde (7)

Compound **7** was prepared from **6** (4.00 g, 6.52 mmol) and NBS (1.27 g, 7.17 mmol) using the same procedure as that described for the preparation of **5**; purification through column chromatography (SiO_2; hexane/CH_2Cl_2, 4:1) gave a yellow oil (3.85 g, 85.3%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.82 (s, 1H), 7.58 (s, 1H), 7.09 (s, 1H), 6.84 (s, 1H), 2.80 (t, *J* = 8.1 Hz, 2H), 2.74 (t, *J* = 7.8 Hz, 2H), 2.59 (t, *J* = 7.5 Hz, 2H), 1.64–1.58 (m, 6H), 1.33–1.27 (m, 30H), 0.88–0.86 (m, 9H). EIMS (*m*/*z*): calcd for $C_{37}H_{55}OS_2Br$ 690.25, found 691 [M^+].

Synthesis of 5'',5''''-(4,8-bis(5-octylthiophen-2-yl)benzo[1,2-b:5,4-b']dithiophene-2,6-diyl)bis(3,4',4''-trioctyl-[2,2':5',2''-terthiophene]-5-carbaldehyde) TBT6OT(CHO)2 (8)

A clean and dry 25-mL two-neck flask was charged with **3** (1.00 g, 1.10 mmol), **7** (1.76 g, 2.54 mmol), and $Pd(PPh_3)_4$ (5 mol %) and subjected to three successive cycles of vacuum followed by refilling with N_2. Anhydrous toluene (30 mL) was added via syringe and then the reaction mixture was heated under reflux for 36 h. The cooled reaction mixture was filtered through Celite to remove the metal catalyst and then washed with CH_2Cl_2. The solvent was evaporated under reduced pressure and the crude product purified through column chromatography (Hexane and CH_2Cl_2= 4:1) and then washed with acetone to afford a dark solid (1.26 g, 63.3%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.74 (s, 2H) 7.63 (s, 2H), 7.51 (s, 2H), 7.28 (d, 2H), 7.05 (s, 2H), 6.94 (s, 2H), 6.85 (d, 2H), 2.85–2.83 (m, 4H), 2.78–2.70 (m, 12H), 1.71–1.52 (m, 16H), 1.33–1.20 (m, 80H), 0.89–0.86 (m, 24H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 182.49, 147.32, 141.08, 141.51, 141.16, 140.40, 140.31, 140.06, 139.03, 136.93, 136.70, 132.70, 132.48, 131.35, 130. 45, 129.30, 129.05, 127.81, 124.33, 123.31, 121.63, 31.90, 31.84, 31.62, 30.65, 30.42, 30.29, 30.23, 29.76,

29.62, 29.57, 29.43, 29.36, 29.26, 29.21, 22.65, 14.08. Anal. Calcd for $C_{108}H_{150}O_2S_{10}$: C, 72.02; H, 8.39; O, 1.78; S, 17.80; found C, 72.23; H, 8. 29.

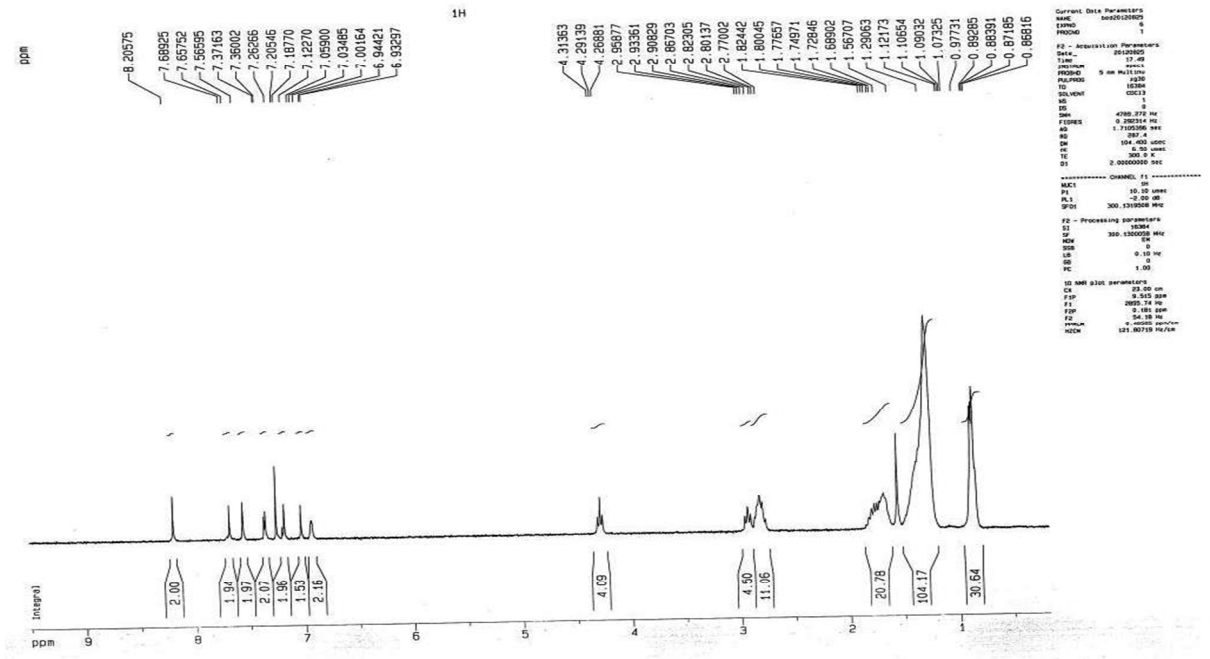
Synthesis of (2Z,2'E)-dioctyl 3,3'-(5'',5''''-(4,8-bis(5-octylthiophen-2-yl)benzo[1,2-b:5,4-b']dithiophene-2,6-diyl)bis(3,4',4''-trioctyl-[2,2':5',2''-terthiophene]-5'',5-diyl))bis(2-cyanoacrylate) (TBTCNR)

Octyl cyanoacetate (1.45 mL, 1.66 mmol) was added to a solution of **8** (0.30 g, 0.16 mmol) and piperidine (3 drops) in dry $CHCl_3$ (50 mL) and then the solution was stirred for 36 h under N_2 at room temperature. Water was added and the reaction mixture was extracted with CH_2Cl_2, the combined extracts were washed three times with water and then dried ($MgSO_4$). The solvent was evaporated under reduced pressure and the crude product further purified through column chromatography (hexane/CH_2Cl_2, 4:1) and subsequently washed with hexane and acetone to afford a dark powder (0.305 g, 84.7%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.20 (s, 2H), 7.65 (s, 2H), 7.56 (s, 2H), 7.46 (d, 2H), 7.12 (s, 2H), 7.00 (s, 2H), 6.93 (d, 2H), 4.29 (t, *J* = 6.6 Hz, 4H), 2.93 (t, *J*= 7.5 Hz, 4H), 2.82–2.77 (m, 12H), 1.82–1.68 (m, 20H), 1.29–1.07 (m, 100H), 0.89–0.86 (m, 30H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.16, 147.32, 146.00, 141.88, 141.55, 140.96, 140.57, 140.40, 136.32, 134.45, 133.23, 132.76, 132.35, 121.47, 130. 85, 129.35, 127.82, 124.32, 123.32, 121.64, 116.03, 97.51, 66.52, 31.90, 31.87, 31.75, 31.62, 30.64, 30.47, 30.30, 30.10, 29.63, 29.54, 29.54, 29.44, 29.35, 29.26, 29.21, 29.16, 29.13, 28.55, 25.79, 22.63, 14.08. MALDI-TOF MS (*m*/*z*): $C_{130}H_{188}N_2O_4S_{10}$ $[M]^+$ 2161.778, found 2161.72. Anal. Calcd for $C_{130}H_{188}N_2O_4S_{10}$: C, 72.17; H, 8.76; N, 1.29; Found C, 72.35, H, 8.59, N, 1.28.

Synthesis of 2,2'-((5'',5''''-(4,8-bis(5-octylthiophen-2-yl)benzo[1,2-b:5,4-b']dithiophene-2,6-diyl)bis(3,4',4''-trioctyl-[2,2':5',2''-terthiophene]-5'',5-diyl))bis(methanylylidene))dimalononitrile (TBTCN)

Malononitrile (0.220 g, 3.33 mmol) was added to a solution of **8** (0.300 g, 0.16 mmol) and piperidine (3 drops) in dry $CHCl_3$ (70 mL) and then the resulting solution was stirred for 36 h under N_2 at room temperature. Water was added and the reaction mixture was extracted with CH_2Cl_2; the combined extracts were washed three times with water, dried ($MgSO_4$), and then concentrated under reduced pressure. The crude product was purified through column chromatography (SiO_2; hexane/CH_2Cl_2, 2:1) and subsequently washed with hexane and acetone to afford a dark powder (0.230 g, 72.8%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.06 (s, 2H), 7.44 (s, 2H), 7.28 (s, 2H), 7.18 (d, J = 2 Hz, 2H), 7.13 (s, 2H), 6.96 (s, 2H), 6.85 (s, 2H), 2.85–2.76 (m, 4H), 2.75–2.66 (m, 12H), 1.73–1.56 (m, 16H), 1.54–1.20 (m, 80H), 0.80–0.79 (m, 24H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.85, 147.38, 143.95, 141.81, 141.63, 140.77, 140.66, 140.07, 139.01, 136.94, 136.64, 134.23, 132.00, 131.79, 131. 74, 131.45, 129.56, 129.23, 128.95, 127.84, 124.33, 123.36, 121.75, 114.43, 113.50, 111.86, 31.91, 31.86, 31.62, 31.55, 30.65, 30.45, 30.30, 29.99, 29.69, 29.63, 29.58, 29.53, 29.45, 29.42, 29.36, 29.26, 29.20, 25.28, 22.65, 14.10. MALDI-TOF MS (*m*/*z*): calcd for $C_{114}H_{150}N_4S_{10}$ $[M]^+$ 1894.907, found 1894.97. Anal. Calcd for $C_{114}H_{150}N_4S_{10}$: C, 72.17; H, 7.97; N, 2.95; Found: C, 72.38; H, 7.89; N, 2.91.

(a)



(b)

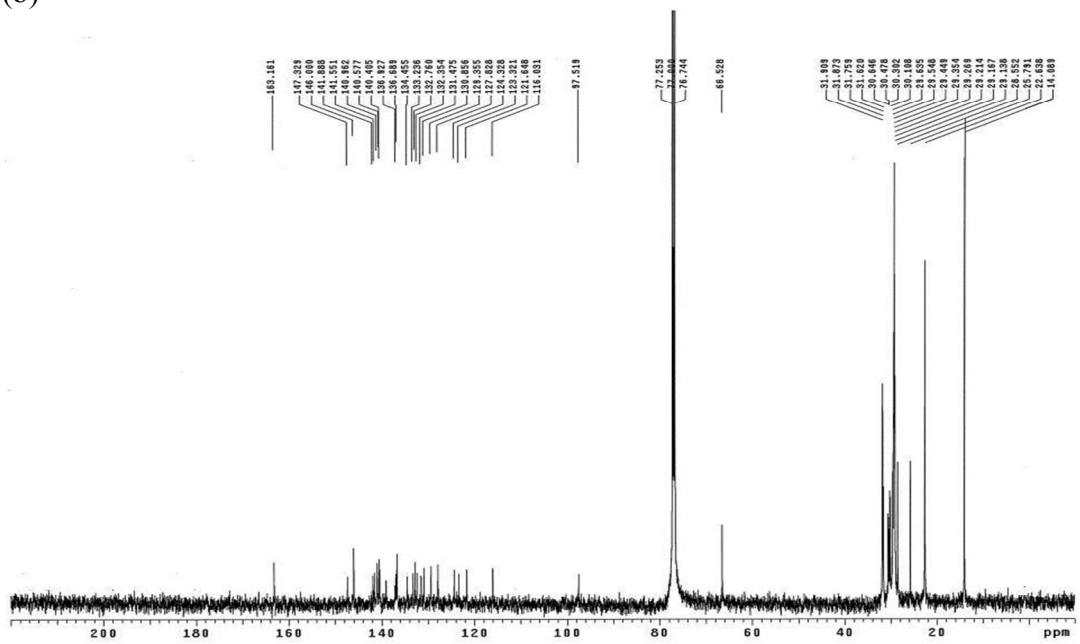
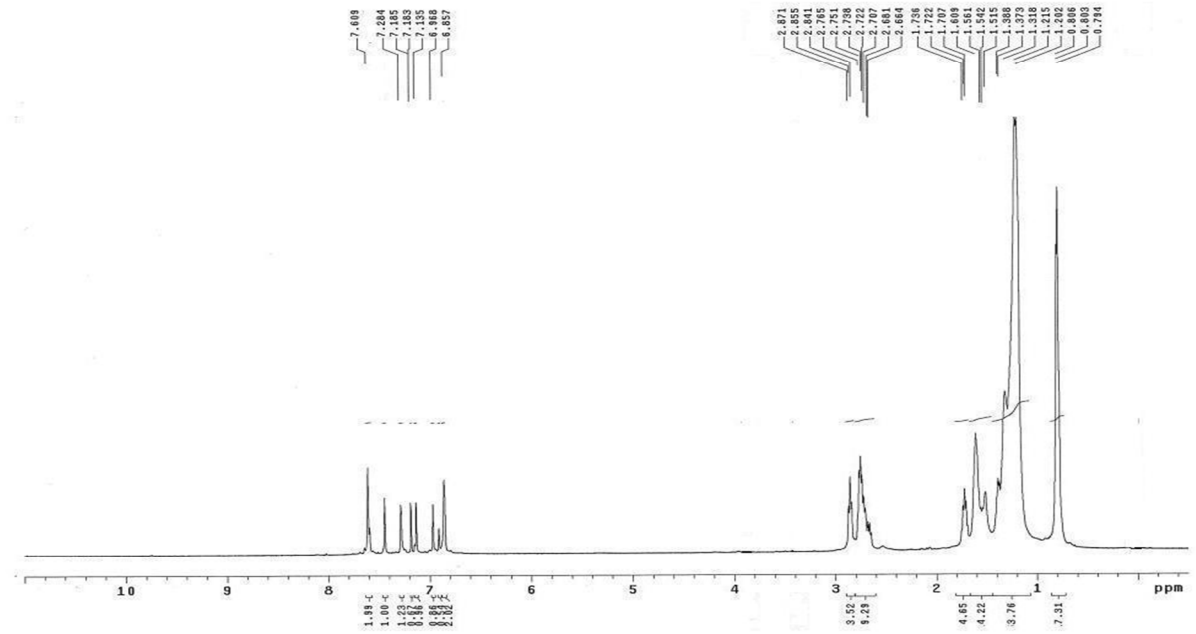


Figure S1. (a) ^{1}H and (b) ^{13}C NMR spectra of TBDTCNR.

(a)



(b)

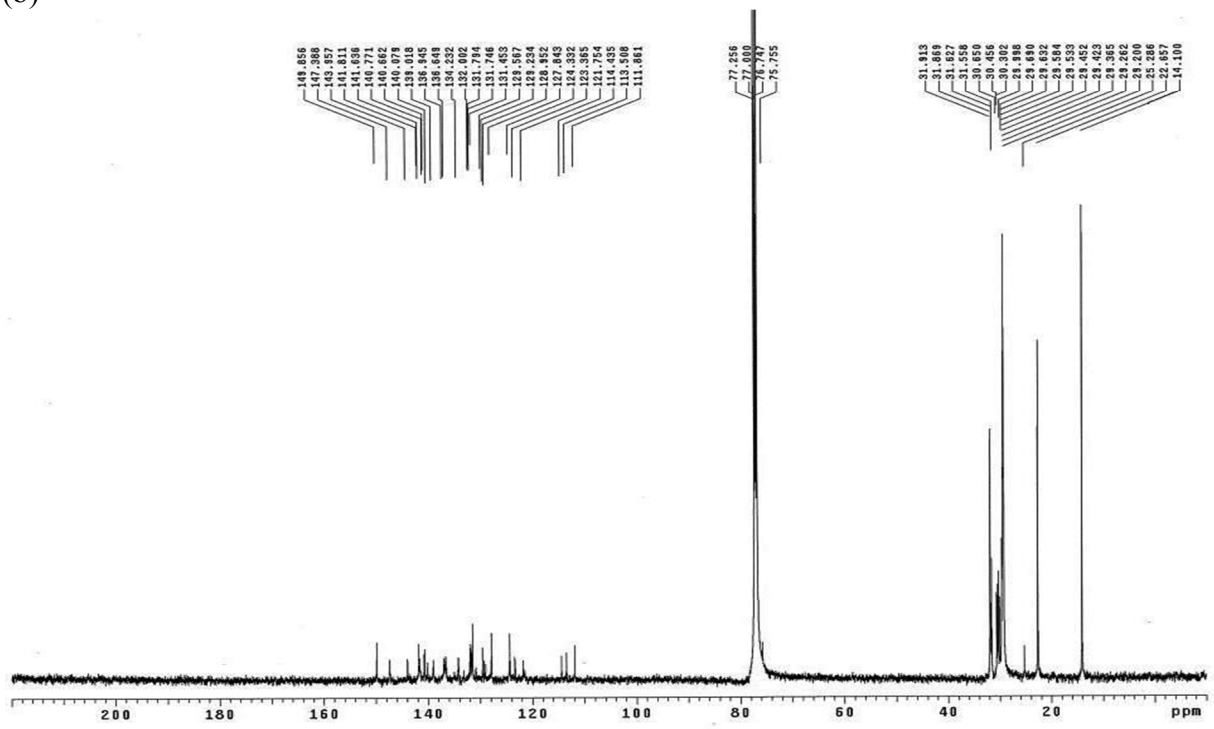


Figure S2. (a) ^{1}H and (b) ^{13}C NMR spectra of TBDTCN.

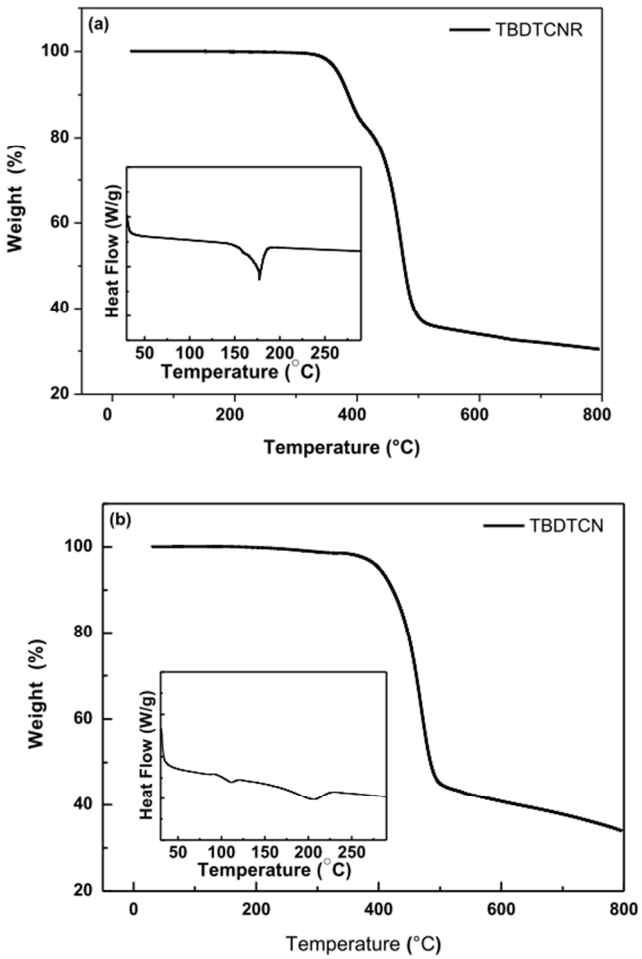


Figure S3. TGA and (inset) DSC plots of (a) TBDTCNR and (b) TBDTCN, recorded under N_2 at a heating rate of 10 °C min^{-1}.

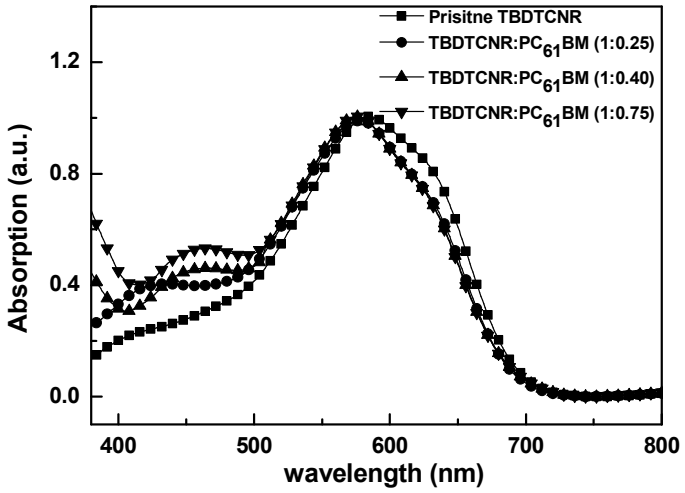


Figure S4. Absorption spectra of pristine TBDTCNR (1 wt%), TBDTCNR/$PC_{61}BM$ (1:0.25, w/w), TBDTCNR/$PC_{61}BM$ (1:0.40, w/w), and TBDTCNR/$PC_{61}BM$ (1:0.75, w/w) spin-coated from $CHCl_3$ onto glass substrates.

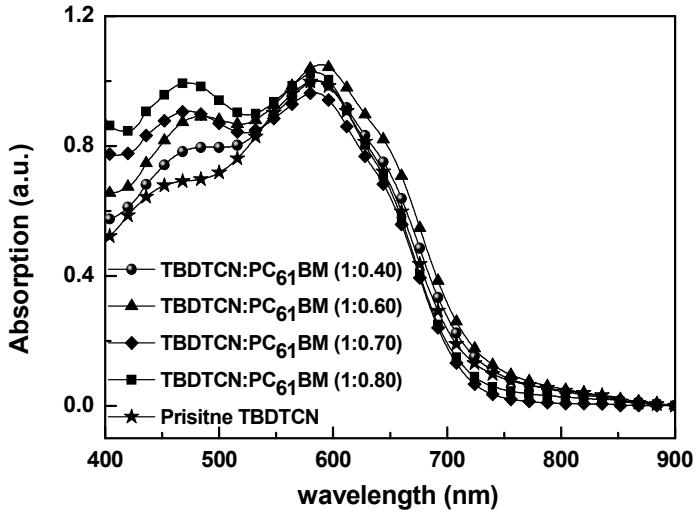
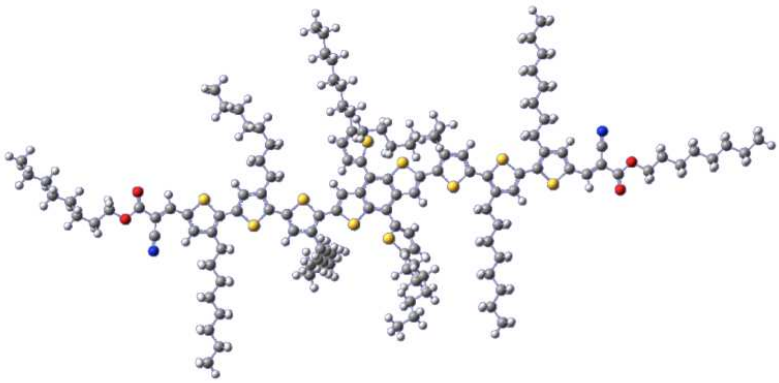
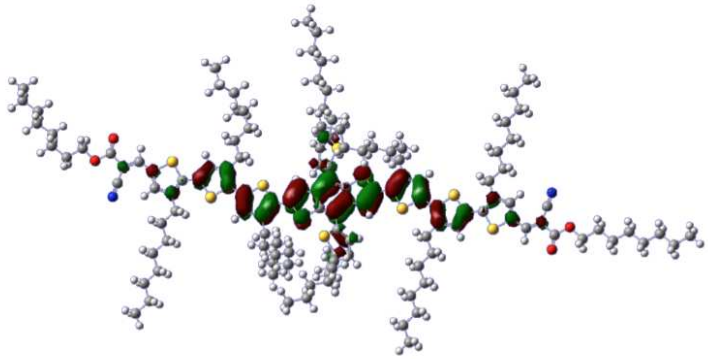


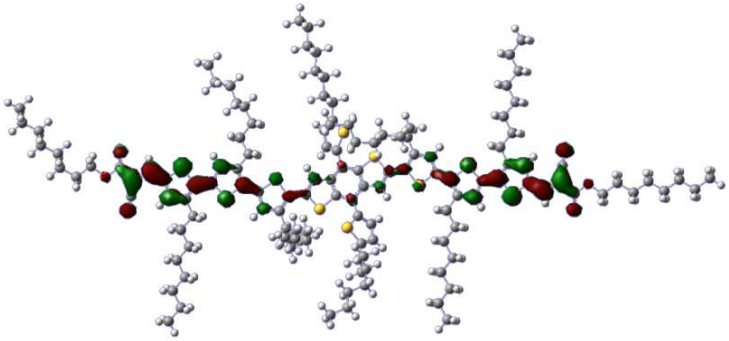
Figure S5. Absorption spectra of TBDTCN/$PC_{61}BM$ (1:0.50, w/w), TBDTCN/$PC_{61}BM$ (1:0.60, w/w), TBDTCN/$PC_{61}BM$ (1:0.70, w/w), TBDTCN/$PC_{61}BM$ (1:0.75, w/w), and pristine TBDTCN (1 wt%) spin-coated from $CHCl_3$ onto glass substrates.



TBDTCNR Relaxed Molecular Structure



TBDTCNR HOMO



TBDTCNR LUMO

Figure S6. Relaxed molecular structure (upper panel), electron density of the HOMO (middle panel), and electron density of the LUMO (lower panel) of TBDTCNR, determined through DFT calculations.

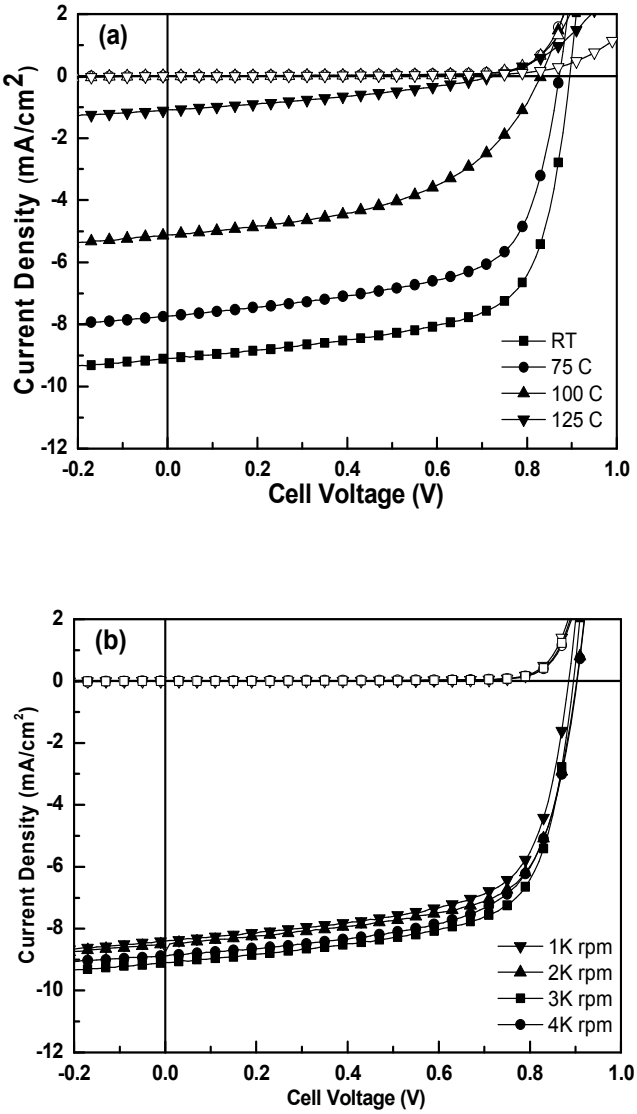


Figure S7. *J–V* curves of BHJ solar cell devices incorporating TBDTCNR:$PC_{61}BM$ after (a) pre-annealing thermal treatment and (b) optimizing the film thickness of the active layer.

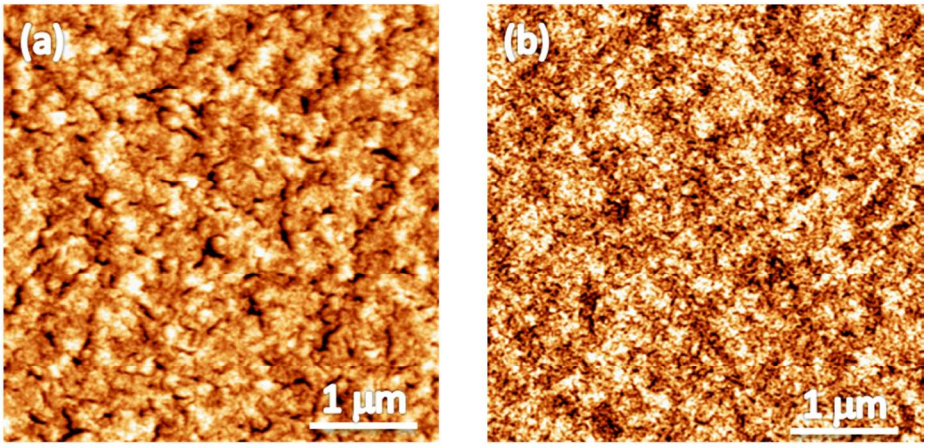


Figure S8. AFM phase images of TBDTCNR:$PC_{61}BM$ film spin-coated from $CHCl_3$ solutions at blend ratios of (a) 1:0.25 and (b) 1:0.75; root mean square roughnesses (R_{rms}): (a) 2.23 and (b) 0.92 nm.

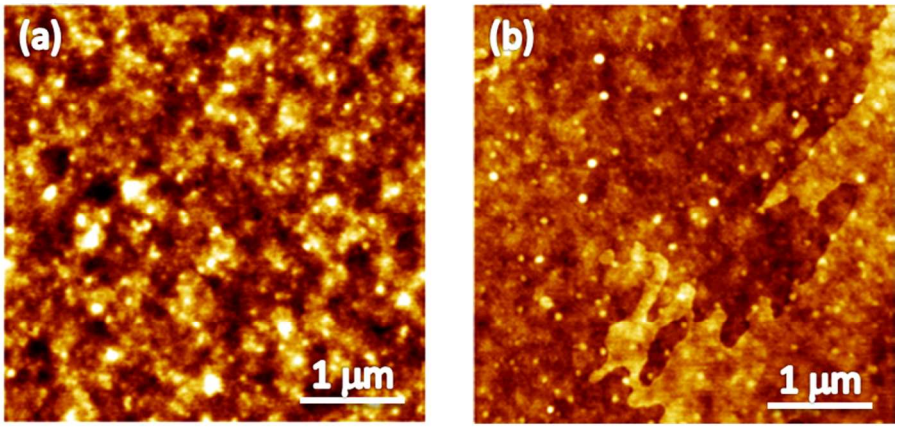


Figure S9. AFM phase images of TBDTCN:$PC_{61}BM$ films spin-coated from $CHCl_3$ solutions at blend ratios of (a) 1:0.40 and (b) 1:0.70; root mean square roughnesses (R_{rms}): (a) 1.05 and (b) 0.58 nm.

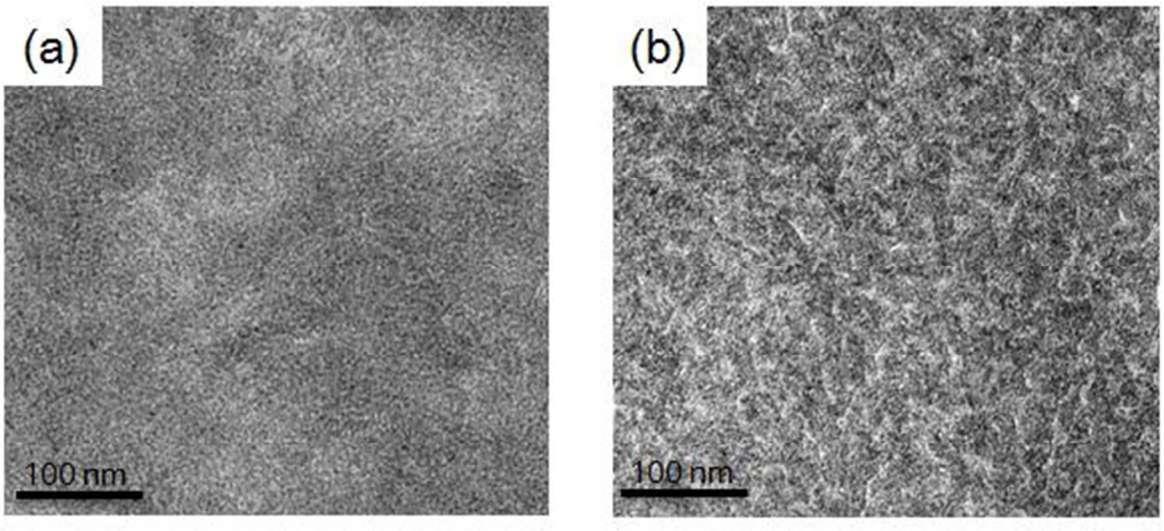


Figure S10. TEM image of blend films cast from $CHCl_3$ solutions for TBDTCNR:$PC_{61}BM$ at weight ratios of (a) 1:0 and (b) 1:0.4.

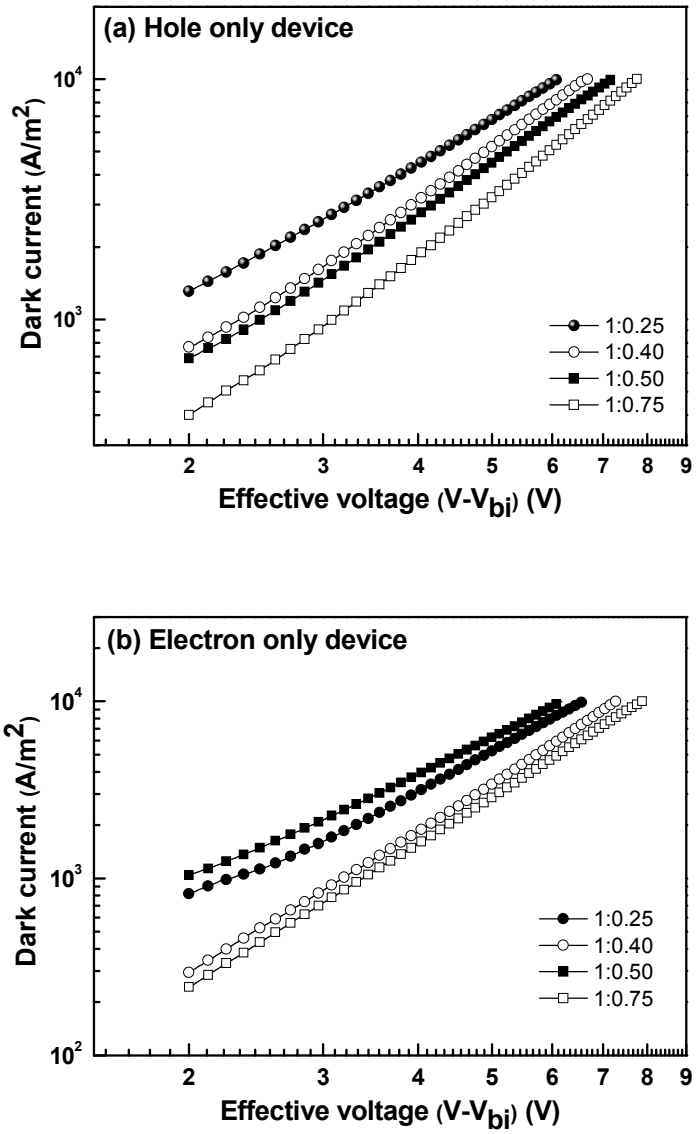


Figure S11. *J–V* curves of (a) hole and (b) electron mobility devices based on TBDTCNR:$PC_{61}BM$ films of various weight ratios.

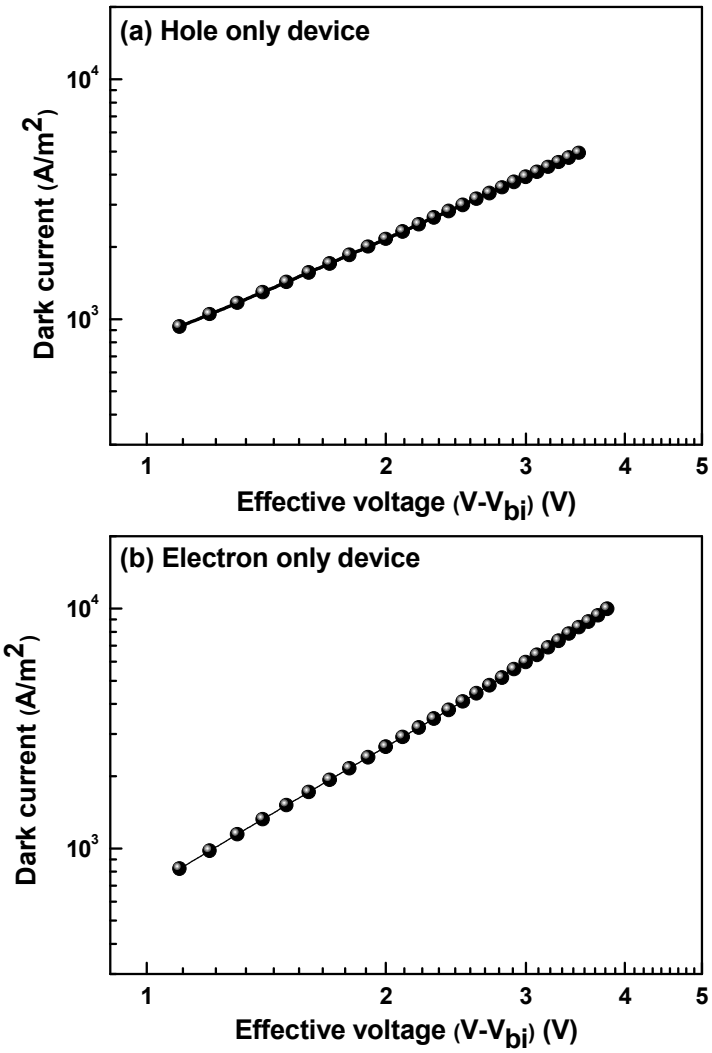


Figure S12. *J–V* curves of (a) hole and (b) electron mobility devices based on TBDTCN:$PC_{61}BM$ (1:0.6) films.

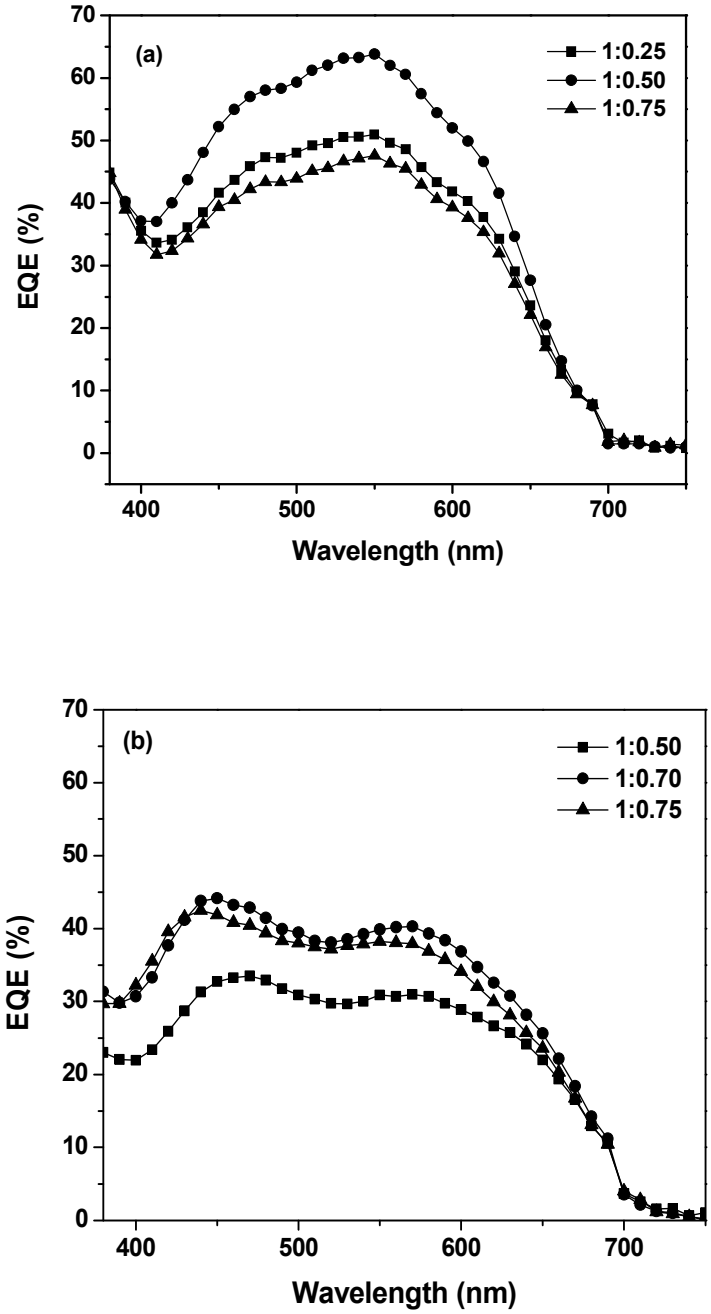


Figure S13. EQE curves of BHJ solar cells incorporating (a) TBDTCNR:$PC_{61}BM$ and (b) TBDTCN:$PC_{61}BM$ blends of various weight ratios.

Table S1. HOMO/LUMO Energy Levels and Theoretical Band Gaps Determined Through DFT Calculations

TBDTCNR	HOMO (eV)	LUMO (eV)	Theoretical band gap (eV)	Experimental band gap, E_g^{ec} (eV)
DFT (B3LYP)	–4.95	–2.91	2.04	
Experimental	–5.40	–3.63		1.77

Table S2. Performance of BHJ Photovoltaic Devices After Thermal Treatment and Optimization of the Film Thickness of the TBDTCNR:$PC_{61}BM$ Active Layer.

Annealing temperature (°C)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
Room temperature (25 °C)	0.90	9.08	0.66	5.42
75	0.89	7.72	0.63	4.29
100	0.83	5.11	0.50	2.11
125	0.73	1.09	0.33	0.25

TBDTCNR:$PC_{61}BM$ (weight ratio 1:0.4)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)
1000 rpm	0.89	8.40	0.65	4.84
2000 rpm	0.90	8.74	0.65	5.06
3000 rpm	0.90	9.08	0.66	5.42
4000 rpm	0.90	8.88	0.65	5.16

Table S3. Hole and Electron Mobilities in Films of TBDTCNR and TBDTCN Blended with $PC_{61}BM$.

SM:$PC_{61}BM$	Ratio	Hole mobility (μ_h, $cm^2\ V^{-1}\ s^{-1}$)	Electron mobility (μ_e, $cm^2\ V^{-1}\ s^{-1}$)	μ_e/μ_h
TBDTCNR	1:0.25	2.09×10^{-4}	1.37×10^{-4}	0.66
	1:0.40	1.72×10^{-4}	1.51×10^{-4}	0.88
	1:0.50	1.58×10^{-4}	1.81×10^{-4}	1.15
	1:0.75	1.02×10^{-4}	1.94×10^{-4}	1.90
TBDTCN	1:0.60	1.21×10^{-4}	9.73×10^{-5}	0.80

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