Electronic Supplementary Information (ESI)

Naphtho[1,2-*b*:5,6-*b′*]dithiophene-based conjugated polymer as a new electron donor for bulk heterojunction organic solar cells

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1. General Instrumentations

^{1}H and ^{13}C NMR spectra were recorded on a JEOL FT-NMR (400 MHz) spectrophotometer using $CDCl_3$ as a solvent. Chemical shifts were reported as δ values (ppm) relative to the internal standard tetramethylsilane (TMS). Elemental analyses were carried out using CE Instruments Flash EA 1112 series. Number-average (M_n) and weight-average (M_w) molecular weights of the polymer were determined via gel permeation chromatography (GPC) with a Waters 1515 gel permeation chromatograph (GPC) with a refractive index detector. The calibration curve was constructed with a series of monodisperse polystyrene standards (Shodex). GPC analysis was performed with polymer/THF (HPLC grade) solution at a flow rate of 1 mL/min at 25 ^{o}C. The UV–Vis absorption spectra were obtained using a Shimadzu UV-2550 spectrophotometer. Photoluminescence (PL) spectra of films or solutions in chlorobenzene were obtained using a FP-6500 (JASCO). Thermogravimetric analysis (TGA) was carried out with a TA Instrument Q-50 at a scanning rate of 20 ^{o}C min^{-1} under a nitrogen atmosphere. The temperature of degradation (T_d) corresponded to a 5% weight loss. Differential scanning calorimetry (DSC) experiments were performed on a TA Instrument (DSC 2910) at a heating rate of 15 ^{o}C min^{-1} under a nitrogen atmosphere. Cyclic voltammetry (CV) measurements were performed on a VersaSTAT3 (METEK), using a solution of tetrabutylammonium hexafluorophosphate (n-Bu_4NPF_6) (0.10M) in chloroform, under argon, at a scan rate of 50 mVs^{-1} at room temperature. A Pt wire and Ag/AgCl were used as the counter and reference electrodes, respectively. The surface morphology was measured using a Digital Instruments Multimode atomic force microscope (AFM) controlled by a Nanoscope IIIa scanning probe microscope 20 controller.

2. Material Synthesis

All chemicals and solvents were reagent grades and purchased from Aldrich, Fluka, TCI, Lancaster Chemical Co. Toluene, Chlorobenzene, Tetrahydrofuran, and diethyl ether were distilled over sodium/benzophenone to keep anhydrous before use. Chloroform was purified by refluxing with calcium hydride and then distilled. 2-bromo-3-hexadecylthiophene, naphtho[1,2-*b*:5,6-*b*′]dithiophene[1] (**NDT**) (**5**), 2,3-bis-(4-octyloxyphenyl)-5,8-dibromo-quinoxalline[2] (**9**) were prepared according to literature procedures.

(i) Synthesis of 2,7-bis(trimethylstannyl)naphtho[1,2-*b*:5,6-*b'*]dithiophene (6)

To a solution of NDT, **5** (0.5 g, 2.08 mmol) in THF (20 mL), TMEDA (0.68 mL, 4.57 mmol) was added at -50 ˚C under stirring, and then 1.6 M *n*-butyllithium in hexane (4.57 mmol, 2.85 mL) was added dropwise at -78 ˚C. The solution was stirred at -78 ˚C for 30 minutes and subsequently refluxed for 2 h under N_2 atmosphere. Then the reaction mixture was cooled to -78 ˚C, and trimethyl tin chloride in THF (1.04 mL, 5.0 mmol) was added in one portion. The reaction mixture was warmed to room temperature and was stirred for 6 h. The reaction was quenched with 20 mL of water and the compound was extracted with dichloromethane. The organic layer was washed twice with 20 mL brine and dried with anhydrous $MgSO_4$. Finally the residue obtained after removing the solvent was recrystallized from acetone to yield 0.82 g (70 %) of **6** as white solid. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ: 7.56 (s, 2H, ArH), 7.92 (d, 2H, ArH), 8.05 (d, 2H, ArH). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm), 0.47 (s, 18H, $Sn(CH_3)$). δ: 143.3, 138.7, 138.5, 133.2, 125.4, 121.9, 121.4. **Elemental analysis**: Calculated for $C_{20}H_{24}S_2Sn_2$: C, 42.44 %; H, 4.27%; S, 11.33%. Found: C, 42.51 %; H, 4.19%; S, 11.39%.

(ii) Synthesis of 2,7-bis(3-hexadecylthiophene-2-yl)naphtho[1,2-*b*:5,6-*b′*]dithiophene (7)

In a 50 mL flame-dried two neck flask fitted with condenser, 2,7-bis(trimethylstannyl)naphtho[1,2-*b*:5,6-*b'*]dithiophene (**6**) (2.0 g, 3.53 mmol), 2-bromo-3-hexadecylthiophene (3.41 g, 8.82 mmol, 2.5 eq.), and dichlorobis-(triphenylphosphine)palladium(II) (118 mg, 0.17 mmol) were added and subjected to three vacuum/argon fill cycles. Argon degassed chlorobenzene (20 mL) were added and the mixture was stirred for 20 min under argon. The reaction mixture was heated to reflux for 24 h and was monitored by TLC. After completion of the reaction, the reaction was quenched with 20 mL of water and the compound was extracted with dichloromethane. The organic layer was washed twice with 20 mL brine and dried with anhydrous $MgSO_4$. Dichloromethane was removed under reduced pressure. The resulting crude product was purified by column chromatography eluting with hexane to afford compound **7** (2.1 g, 70 %). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ: 8.01 (d, 2H, ArH), 7.88 (d, 2H, ArH), 7.47 (s, 2H, ArH), 7.26 (s, 2H, ArH), 7.08 (d, 2H, ArH), 2.92 (t, 4H), 1.74 (m, 4H), 1.44-1.24 (m, 28 H), 0.88 (t, 6H). **^{13}C NMR** ($CDCl_3$, 100 MHz, ppm) δ: 140.95, 138.60, 137.77, 135.95, 130.44, 125.81, 124.89, 123.67, 122.72, 121.54, 32.13, 31.13, 30.96, 29.85, 29.83, 29.75, 29.69, 29.56, 22.89, 14.32. **Elemental analysis**: Calculated for $C_{54}H_{76}S_4$, C, 76.00%; H, 8.98%; S, 15.03%. Found: C, 76.06%; H, 8.91%; S, 15.07%.

(iii) Synthesis of 2,7-bis(3-hexadecylthiophene-2-yl)naphtho[1,2-*b*:5,6-*b'*]dithiophene distannane (8)

2,7-bis(3-decylthiophene-2-yl)naphtho[1,2-*b*:5,6-*b'*]dithiophene distannane (**8**) was prepared similar to the method reported for the compound **6**. Briefly, to a solution of **7** (2.0 g, 2.34 mmol) in THF (20 mL), TMEDA (0.77 mL, 5.15 mmol) was added at -50 ˚C under stirring, and then 1.6 M *n*-butyllithium in hexane (5.61 mmol, 3.15 mL) was added dropwise at -78 ˚C under N_2 atmosphere. After 30 min, the solution was refluxed for 2 h. The reaction mixture was cooled to -78 ˚C, and 1.0 M solution of trimethyltin chloride (5.85 mmol, 5.85 ml) was added in one portion. The reaction mixture was warmed to room temperature and was stirred for 6 h. The reaction was quenched with 20 mL of water and the compound was extracted with dichloromethane. The residue obtained after removing the solvent was recrystallized from acetone to yield 2.0 g (72%) of **8** as yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ: 7.96 (d, 2H, ArH), 7.86 (d, 2H, ArH), 7.45 (s, 2H, ArH), 7.06 (s, 2H, ArH), 2.93 (t, 4H), 1.77-1.67 (m, 4H), 1.43-1.23 (m, 28 H), 0.89 (t, 6H), 0.50 (s, 18H, $Sn(CH_3)$). **^{13}C NMR** ($CDCl_3$, 100 MHz, ppm) δ: 141.77, 138.52, 138.26, 137.67, 137.58, 136.22, 135.98, 125.52, 123.40, 122.80, 122.42, 121.23, 31.91, 30.87, 30.73, 29.70, 29.62, 29.46, 29.36, 29.24, 29.69, 22.69, 14.12. **Elemental analysis**: Calculated for $C_{60}H_{92}S_4Sn_2$, C, 61.12%; H, 7.86%; S, 10.88%. Found: C, 61.23%; H, 7.71%; S, 10.80%.

(iv) Synthesis of 2,3-bis-(4-octyloxyphenyl)-5,8-dithiophen-2-yl-quinoxaline (10):

A mixture of compound **9** (8.21 g, 11.8 mmol), 2-(tributylstannyl)thiophene (9.2 g, 24.6 mmol), dichlorobis-(triphenylphosphine)palladium(II) (320 mg, 0.46 mmol), were added to a 250 mL Schlenk flask and subjected to three vacuum/argon fill cycles. Argon degassed toluene (100 mL) was added and three more vacuum/argon cycles were repeated to make sure oxygen was excluded, and the mixture was stirred for 20 min under argon. The reaction mixture was heated to reflux for 24 h and was monitored by TLC. After completion of the reaction, toluene was removed under reduced pressure and the residue was crystallized from petroleum ether. The product was purified by passing it through a short column of silica gel using CH_2Cl_2 as eluent to afford compound **10** (4.0 g, 49.9%). **^{1}H NMR** (300 MHz, $CDCl_3$, ppm) δ: 8.11 (s, 2H), 7.88 (d, 2H, J = 3.6 Hz), 7.75 (d, 4H, J = 8.6 Hz), 7.54 (d, 2H, J = 5.1 Hz), 7.28-7.18 (m, 2H), 6.94 (d, 4H, J = 8.6 Hz), 4.0 (t, 4H), 1.8 (q, 4H), 1.5-1.2 (m, 20 H), 0.94 (t, 6H).**^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ: 160.19, 151.50, 139.15, 137.18, 132.08, 131.36, 131.22, 128.92, 126.73, 126.40, 114.43, 68.28, 32.05, 29.60, 29.48, 26.30, 22.89, 14.34. **Elemental analysis**: Calculated for $C_{44}H_{50}N_2O_2S_2$, C, 75.17; H, 7.17; N, 3.98; S, 9.12 ; found : C, 75.20; H, 7.15; N, 3.92; S, 9.15.

(v) Synthesis of 2,3-bis-(4-octyloxyphenyl)-5,8-bis(5-bromothiophene-2-yl)- quinoxaline (11)

A solution of 2,3-bis-(4-octyloxyphenyl)-5,8-dithien-2-ly-quinoxaline (3.5 g, 4.98 mmol) in $CHCl_3$ and protected from light was cooled to 0 °C. N-bromosuccinimide (1.79 g, 9.96 mmol) was added in small portions over 20 min, and then the reaction was stirred for 3 h. The mixture was poured into water (100 mL) and was extracted with $CHCl_3$. The organic layer was dried over anhydrous $MgSO_4$, and the solvent was removed by rotary evaporation. The crude product was purified by crystallization from MeOH to yield compound **11** as a red-yellow solid (4.0 g, 93%). **^{1}H NMR** ($CDCl_3$, 300 MHz, ppm) δ: 7.91 (s, 2H), 7.65 (d, 4H, J = 8.6 Hz), 7.48 (d, 2H, J = 3.8 Hz), 7.07 (d, 2H, J = 4.2 Hz), 6.91 (d, 4H, J = 8.6 Hz), 4.00 (t, 4H), 1.81 (m, 4H), 1.48-1.30 (m, 20H), 0.89 (t, 6H).**^{13}C NMR** ($CDCl_3$, 100 MHz, ppm) δ: 160.14, 151.76, 139.74, 136.35, 131.91, 130.63, 130.29, 129.02, 125.31, 125.17, 116.94, 114.26, 68.11, 31.83, 29.40, 29.30, 29.26, 26.09, 22.68, 14.12.**Elemental analysis**: Calculated for $C_{44}H_{48}Br_2N_2O_2S_2$, C, 61.39; H, 5.62; N, 3.25; S, 7.45 ; found : C, 61.31; H, 5.67; N, 3.23; S, 7.63.

(vi) Synthesis of poly[2,7-bis(3-hexadecylthiophene-2-yl)naphtho[1,2-*b*:5,6-*b*′]dithiophene-5,5′-diyl-*alt*-2,3-bis-(4-octyloxyphenyl)-5,8-dithiophen-2-yl quinoxaline-5,5′-diyl] (PTNDTT-QX).

2,7-bis(3-hexadecylthiophene-2-yl)naphtho[1,2-*b*:5,6-*b*′]dithiophene distannane (**8**) (648 mg, 0.55 mmol; 1.1 eq.) and 2,3-bis-(4-octyloxyphenyl)-5,8-dithien-2-ly-quinoxaline (**11**) (431 mg, 0.5 mmol; 1.0 eq) were dissolved in chlorobenzene (20 mL). The solution was flushed with argon for 10 min, and then Pd_2dba_3 (23 mg, 5 mol% with respect to monomer) and P(*o*-tolyl)$_3$ (15 mg, 10 mol%) were added to the flask. The flask was purged three times with successive vacuum and argon fill cycles. The reaction mixture was heated to 110 °C for 24 h under an argon atmosphere. The resulting polymer was cooled to room temperature and was slowly poured into

150 mL of well stirred methanol containing 15 mL of hydrochloric acid. The dark precipitate was collected on a membrane filter and was subjected to sequential Soxhlet extraction with methanol, acetone, and hexane to remove the low molecular weight fraction of the material. The residue was then collected through extraction with chloroform. The extract was then concentrated and precipitated into methanol to yield the polymer as a black colored solid (71%). **^{1}H NMR** (300 MHz, $CDCl_3$, ppm) δ: 8.0-7.25 (m, br, 8H), 7.2-6.5 (m, br, 12H), 3.9 (br, 4H), 2.9 (m, br, 4H), 1.9-0.5 (m, br, 92 H). **GPC** (THF) M_n = 12.3 kD; M_w = 78 kD; PDI = 6.32

3. OFET device fabrication and characterization

Thin-film transistors devices were fabricated on silicon wafers in a bottom-contact geometry (channel length, $L = 12$ μm, width, $W = 120$ μm). A heavily n-doped silicon wafer with a 300 nm thermal silicon dioxide (SiO_2) layer was used as the substrate/gate electrode, with the top SiO_2 layer serving as the gate dielectric. The SiO_2 surface of the wafer substrate was first cleaned with piranha solution (H_2O_2/H_2SO_4) at 130 °C for 20 min, and the cleaned wafer was immersed in a solution of 1.0 mM octyltrichlorosilane (OTS-8) in toluene at room temperature for 2 h under nitrogen. The semiconductor layer was spin-coated at 2000 rpm from a 0.5 wt% chlorobenzene solution, to a thickness of 70 nm. Subsequently, a series of gold source/drain electrode pairs were deposited by vacuum evaporation through a shadow mask. Silicon oxide on the backside of the silicon wafer of the TFT device was removed with HF to provide a conductive gate contact. All device fabrication procedures and measurements were carried out in air at room temperature.

4. Photovoltaic device fabrication and characterization

Organic photovoltaic cells, with a structure of Glass/ITO/PEDOT:PSS/**PTNDTT-QX**:$PC_{71}BM$/LiF/Al, were prepared on commercial ITO-coated glass substrates with a sheet resistance of 7 Ohms/sq. Prior to use, the substrates were cleaned with deionized water. Sonication of the substrate in acetone followed by isopropanol was done to obtain clean substrates. A thin film of PEDOT:PSS (35 nm) (AI 4083, H. C. Starck) was spin-coated (3000 rpm, 40 s) onto the substrate and was dried at 140 °C for 20 min. The active layer was prepared, with a thickness of about 55-70 nm onto the surface of PEDOT:PSS, using spin coating with different **PTNDTT-QX** to $PC_{71}BM$ (Nano-C, USA) ratios (from 1:1 to 1:4 w/w) in *o*-dichlorobenzene (ODCB) and was dried at RT for 3 hr in glove box under nitrogen. The devices were completed by deposition of a 0.5 nm layer of LiF and a 150 nm layer of Al. These layers were thermally evaporated at a pressure of 1×10^{-6} Torr at room temperature. The active area was $0.09\ cm^2$. The current–voltage (I–V) characteristics of the photovoltaic devices in the dark and under white light illumination were measured at AM 1.5 G solar simulator (Newport) and $100mW/cm^2$ conditions, adjusted with a standard PV reference cell (2 cm × 2 cm), a mono-crystalline silicon solar cell, (calibrated at NREL, Colorado, USA) with a Keithley 2400 source-measure unit. The external quantum efficiency (EQE) was performed using a Polaronix K3100 spectrometer.

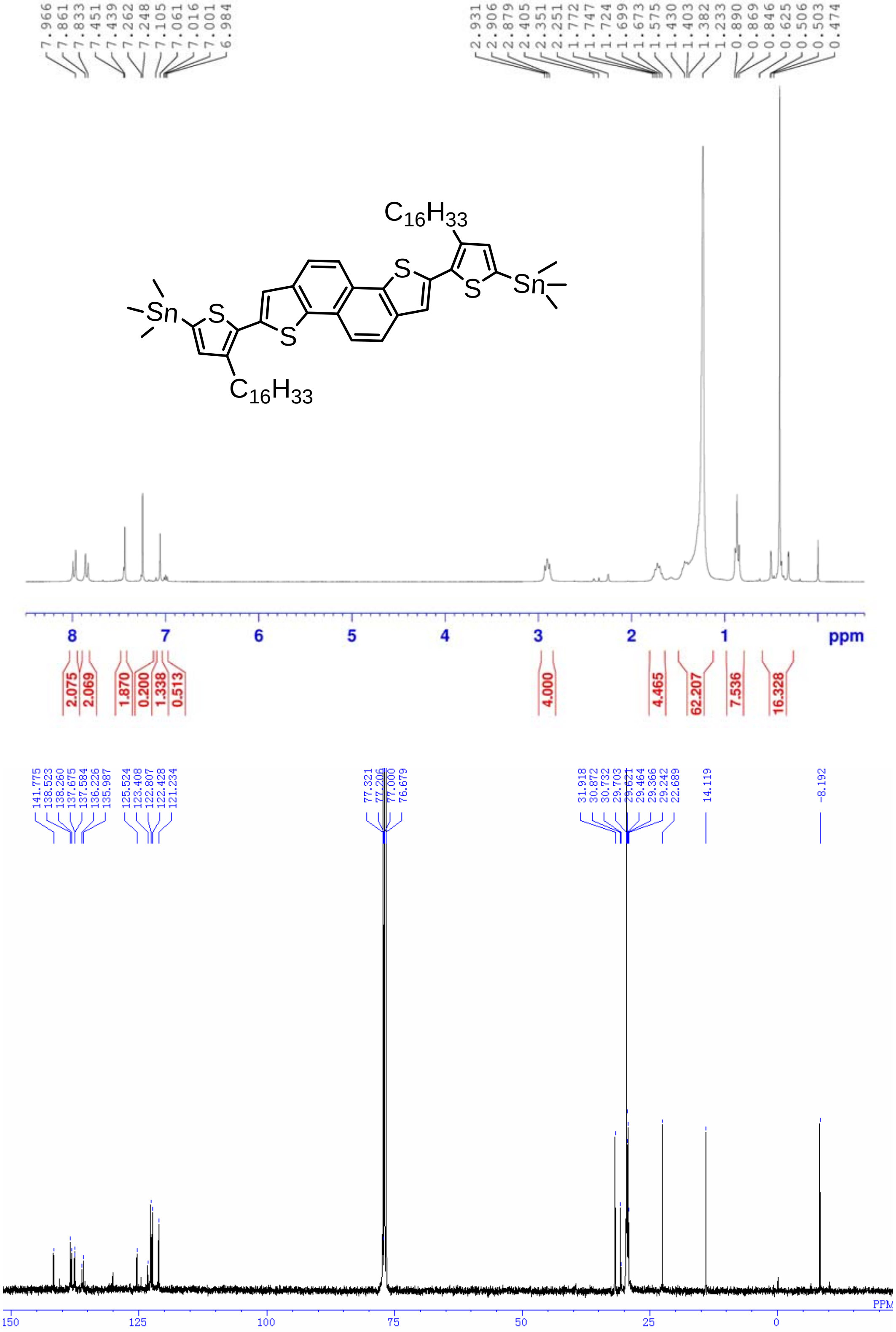


Fig. S1 ^{1}H-NMR and ^{13}C NMR spectra of compound **8**

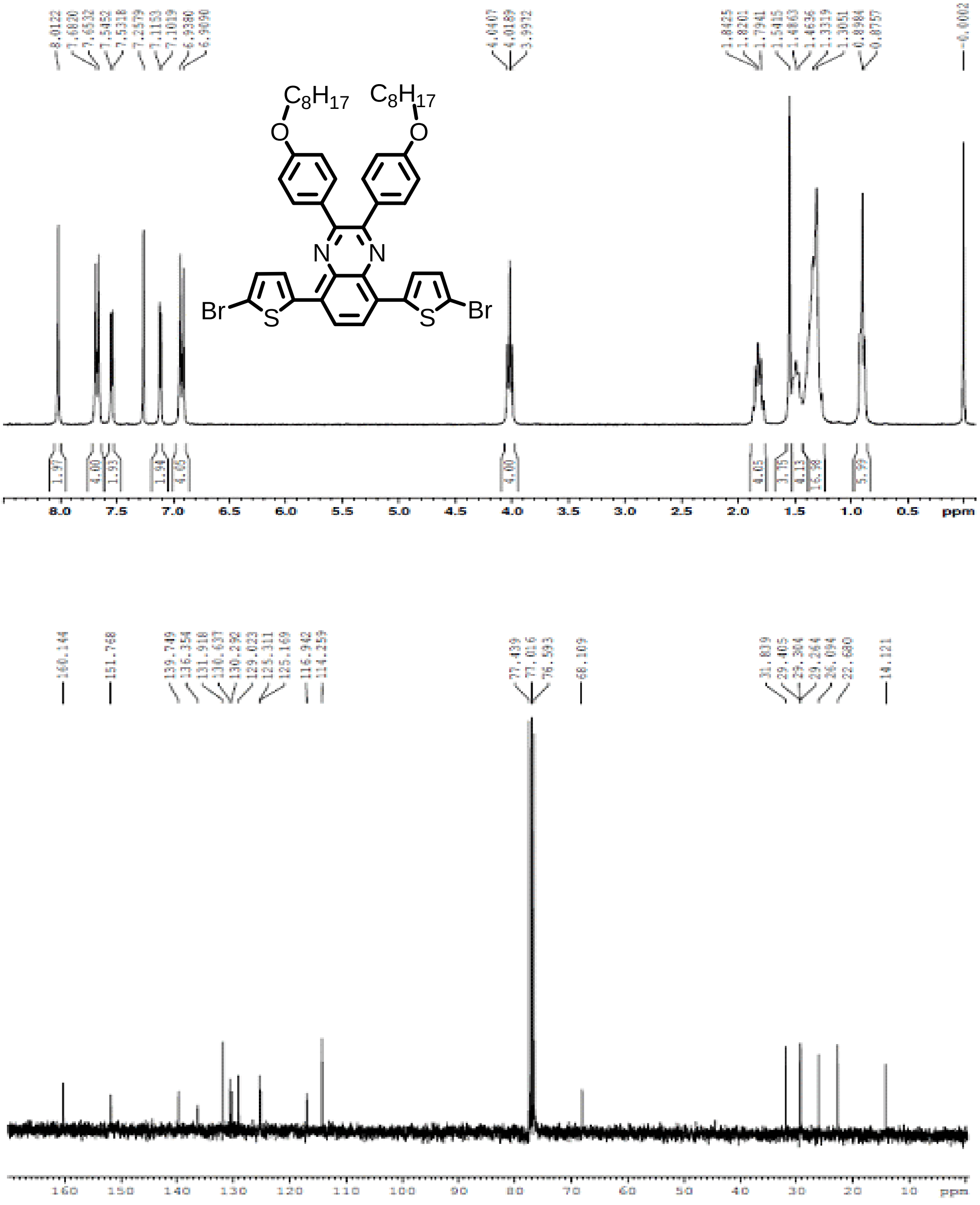


Fig. S2. ^{1}H and ^{13}C NMR spectra of compound **11**.

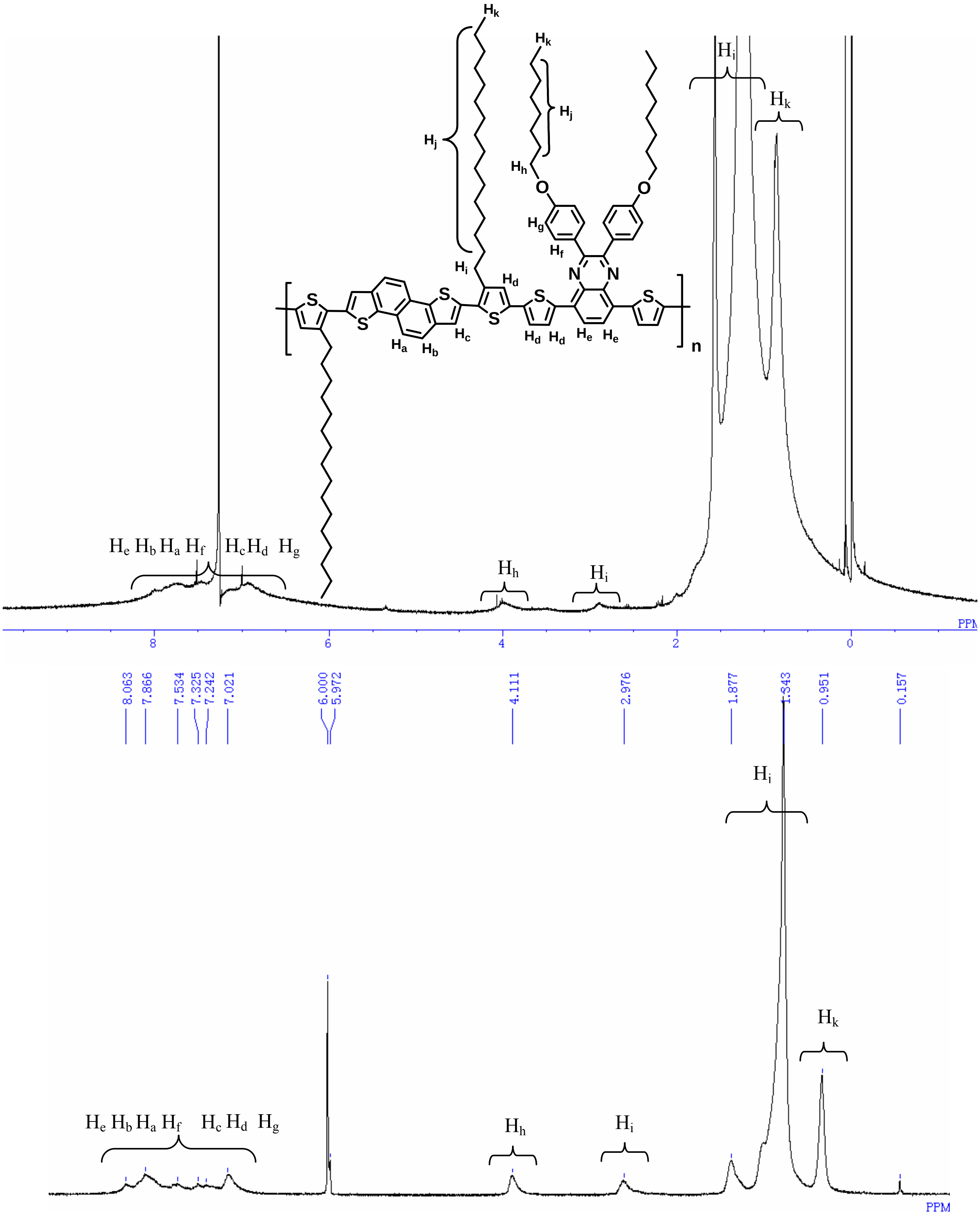
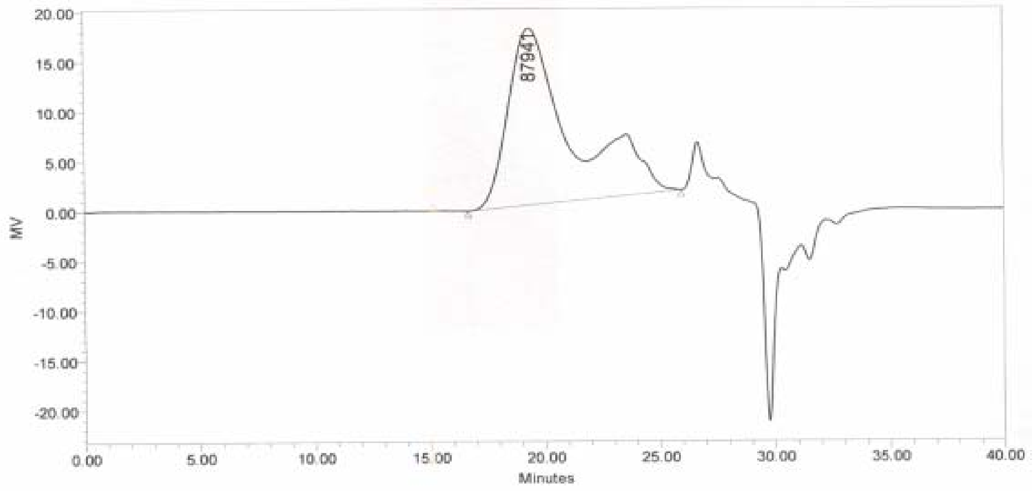


Fig. S3. (a) ^{1}H-NMR spectra of **PTNDTT-QX** in $CDCl_3$; (b) ^{1}H-NMR spectra of **PTNDTT-QX** in **$CDCl_2CDCl_2$** at 127 °C.



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		12355	78046	87941	174323	275354		6.317177		

Fig. S4. Gel permeation chromatogram of **PTNDTT-QX** in tetrahydrofuran (THF).

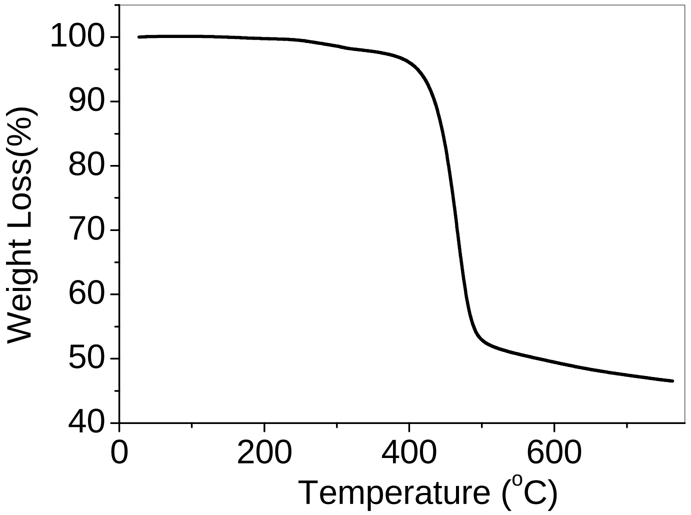


Fig. S5. TGA curve of **PTNDTT-QX** with a heating rate of 20˚C/min.

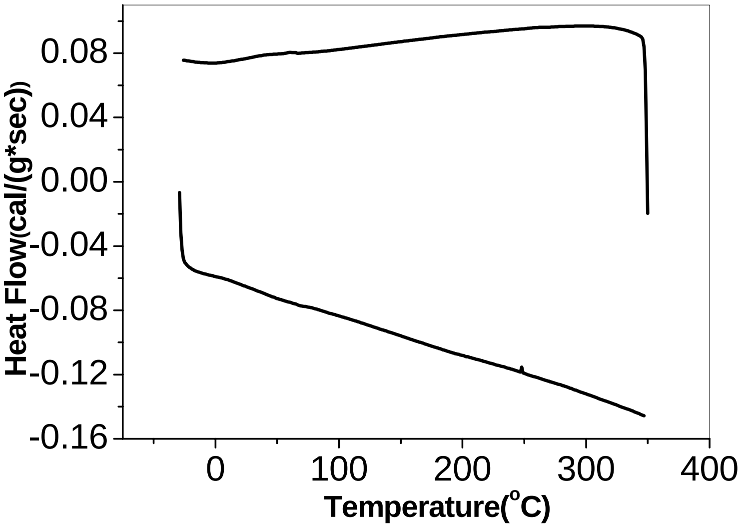


Fig. S6. DSC thermogram of **PTNDTT-QX** at a scanning rate of 20˚C/min.

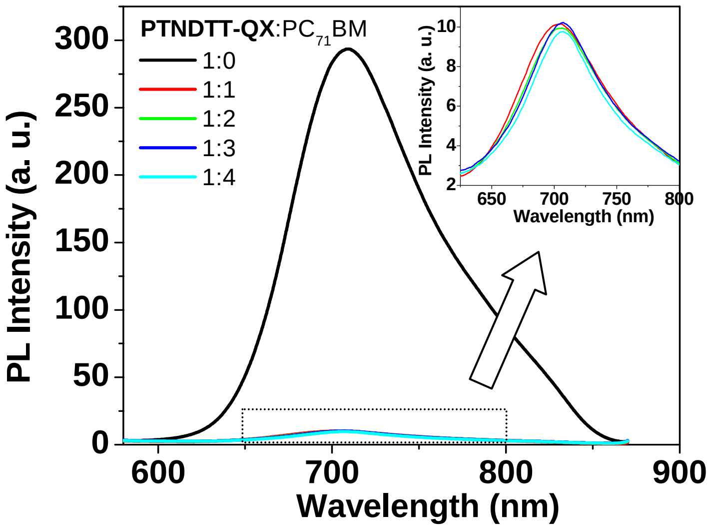


Fig. S7. PL spectra of **PTNDTT-QX** and **PTNDTT-QX**/PC$_{71}$BM-blended film

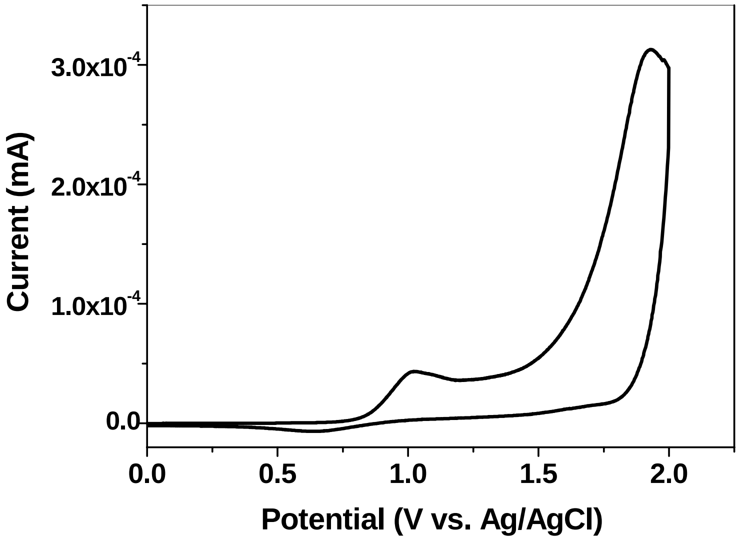


Fig. S8. Cyclic voltammogram of **PTNDTT-QX** film in a 0.1 molL^{-1} Bu_4NPF_6/CH_3CN solution.

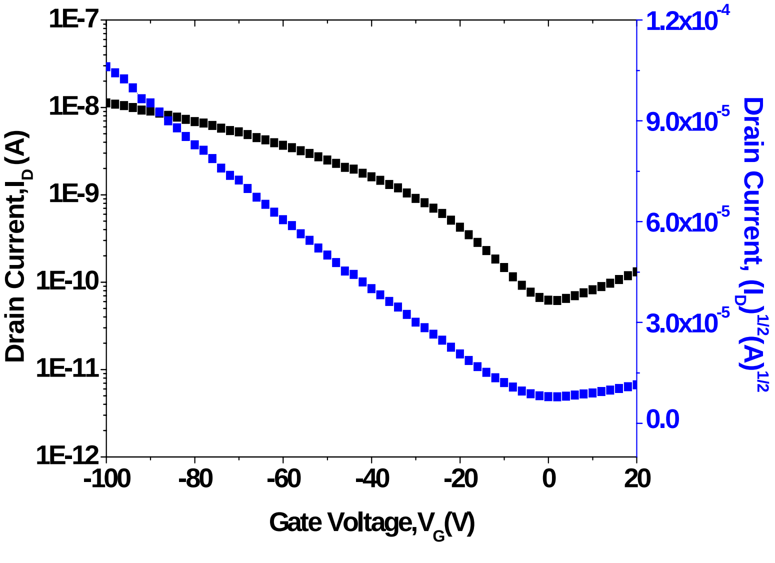


Fig. S9. Transfer characteristics curves at constant V_D = –60 V for an OFET device with **PTNDTT-QX**.

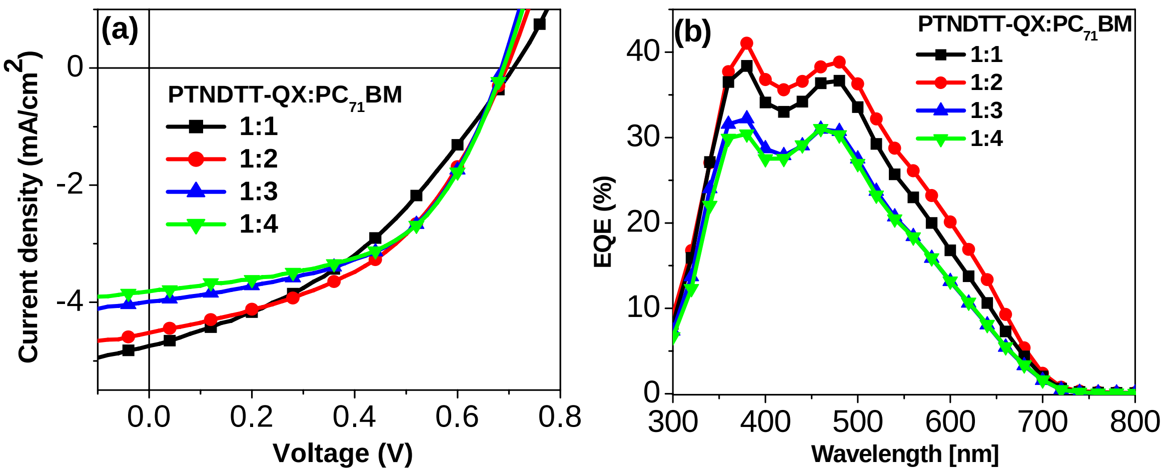


Fig. S10. *J-V* curve for **PTNDTT-QX**:PC$_{71}$BM solar cell devices at various ratios in ODCB under an illumination of AM 1.5G, 100 mW/cm^2.

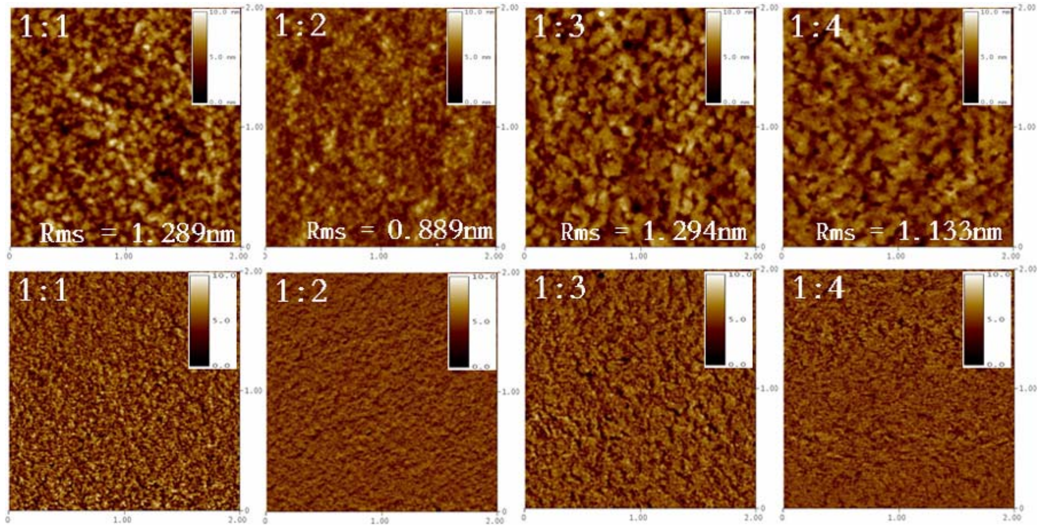


Fig. S11. AFM images (2 μm x 2 μm) (first row: height image; second row: phase image) of blend films spin-coated from ODCB at different **PTNDTT-QX**:PC$_{71}$BM ratios (1:1 to 1:4 w/w).

TABLE S1. The optical and electrochemical properties of **PTNDTT-QX**

Polymer	λ_{max} (nm), ODCB		$^{a}E_g^{opt}$ (eV)	$^{b}E_{ox}$/$^{c}E_{HOMO}$ (eV)	$^{d}E_{LUMO}$ (eV)
	Soln.	film			
PTNDTT-QX	430, 544	443, 575	1.77	0.84/-5.24	-3.47

$^{a}E_g^{opt}$ = 1240/$(\lambda_{onset})_{film}$. ^{b}Potential determined by cyclic voltammetry in 0.10 M Bu_4NPF_6-CH_3CN vs Ag/AgCl. $^{c}E_{HOMO}$ = -e(4.4 + E^{ox}_{onset}) (eV). $^{d}E_{LUMO}$ = E_g^{opt} + HOMO.

TABLE S2. Photovoltaic properties of **PTNDTT-QX**:$PC_{71}BM$ solar cell devices at various ratios in ODCB.

PTNDTT-QX:$PC_{71}BM$	**J_{sc} (mAcm^{-2})**	**V_{oc} (V)**	**FF**	**PCE (%)**
1:1	4.74	0.71	0.38	1.28
1:2	4.52	0.69	0.46	1.44
1:3	3.99	0.69	0.51	1.41
1:4	3.81	0.69	0.53	1.41

References

(1) S. Shinamura, E. Miyazaki and K. Takimiya, *J. Org. Chem.*, 2010, **75**, 1228.

(2) G. Zhang, Y. Fu, Q. Zhang and Z. Xie, *Polymer*, 2010, **51**, 2313.