

Electronic Supplementary Information for

Acceptor-Donor-Acceptor Based Small Molecules with Varied Crystallinity: Processing Additive Induced Nanofibril in Blend Film for Photovoltaic Application

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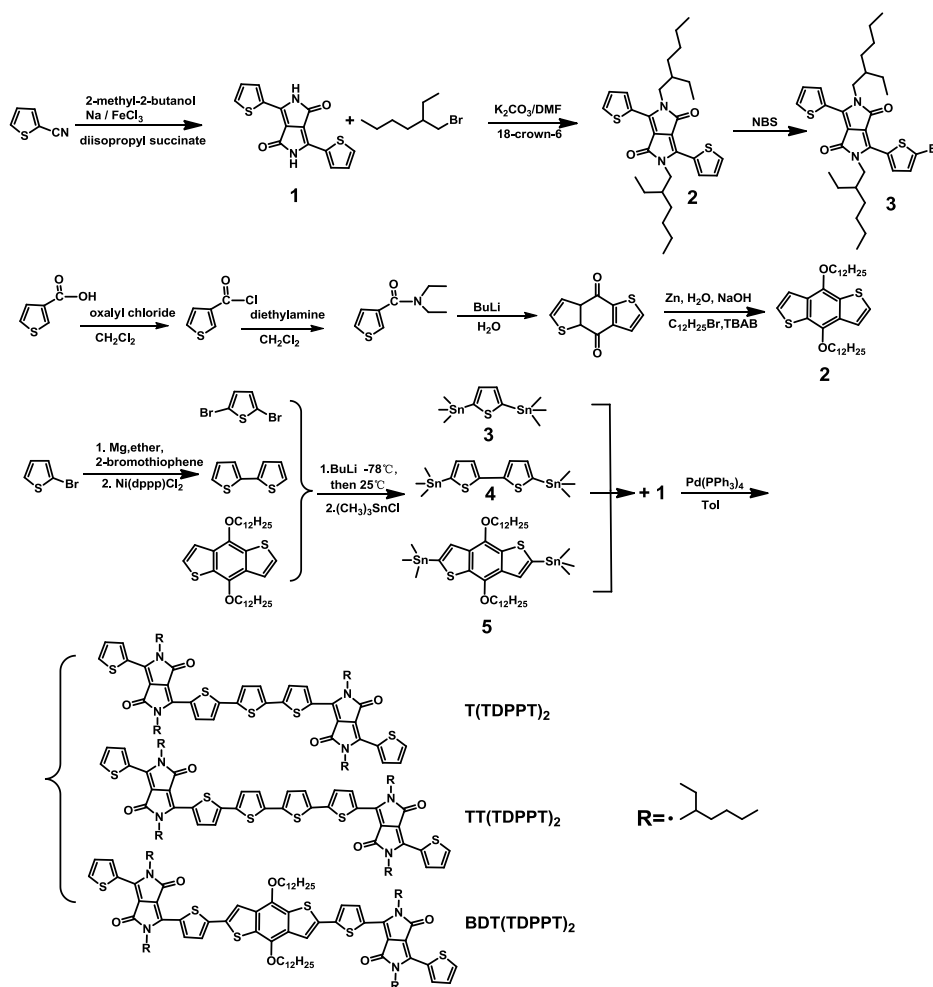
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Synthesis



Scheme 1 molecular structures and synthesis of T(TDPPT)₂, TT(TDPPT)₂ and BDT(TDPPT)₂.

3,6-dithiophene-2-yl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**1**)

Sodium (0.26 g, 11.3 mmol) and iron(III) chloride (~10 mg) was added to 6mL of 2-methyl-2-butanol and the mixture was heated to reflux until full consumption of the sodium was observed (~3h). The solution was cooled to 85°C and thiophene-2-carbonitrile (0.82 g, 7.5 mmol) was added, followed by diisopropyl succinate (0.60 g, 3.0 mmol). After stirring for 2hr, the reaction was cooled to 50 °C, and methanol (10 mL) was added. The reaction was quenched by addition of glacial acetic acid (3 mL) and refluxed for 0.5h. The reaction mixture was filtered and washed with water (2 x 50 mL), hot methanol

(2 x 50 mL), acetone (2 x 25mL) and hexane (25mL) to afford the product as a dark blue solid (0.68 g, 75 %), which was used without further purification.

3,6-dithien-2-yl-2,5-di(2-ethylhexyl)-pyrrolo[3,4-c]pyrrole-1,4-dione (2)

A solution of 3-(bromomethyl)heptane (4.2 g, 21.7 mmol) in anhydrous DMF (20 mL) was added dropwise to a mixture of 3,6-dithiene -2-yl-2,5-dihydropyrrolo[3,4-c] pyrrole-1,4- dione (2.8 g, 9.4 mmol), K₂CO₃ (3.0 g, 21.6 mmol) in anhydrous DMF (55 mL). The mixture was maintained at 120°C overnight. The reaction was cooled to room temperature and poured into water (100 mL). The compound was extracted in CHCl₃, washed with brine, dried over MgSO₄. The solvent was evaporated under reduced pressure. The crude product was purified by chromatography on silica with 30% dichloromethane in hexane as eluent. Isolated yield 5.1 g as a dark red powder (yield 55%) ¹H NMR (400 MHz, CDCl₃ δppm): 2.7 (d, J=3 Hz, 2H), 7.64 (d, J=4.76Hz, 2H), 7.29 (t, 2H), 4.09 (t, 4H), 1.76 (m, 4H), 1.26-1.43 (m, 20H), 0.89 (t, 6H).

3-(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (3)

N-Bromosuccinimide (NBS, 0.63g, 3.08 mmol) was added slowly to a solution of 3,6-dithien-2-yl-2,5-di(2-ethylhexyl)-pyrrolo[3,4-c]pyrrole-1,4-dione (3 g, 3.08 mmol) in CHCl₃(100 mL). The solution was protected from light and stirred at room temperature for 48 h. The reaction mixture was poured into water (100 mL) and extracted in CHCl₃. The organic layer was dried over MgSO₄ and the solvent was evaporated under reduced pressure. The crude product was purified by chromatography on silica with 50% dichloromethane in hexane as eluent. Isolated yield = 1.1 g (61%) as a dark red powder. ¹H NMR (400 MHz, CDCl₃: δppm 8.92 (d, J=3.2 Hz, 1H), 8.86 (d, J=3.0 Hz, 1H), 7.64 (d, J=4.7Hz, 1H), 7.52 (d, J=4.6Hz, 1H), 7.29 (t, 2H), 4.09 (t, 4H), 1.76 (t, 4H), 1.26-1.43 (m, 20H), 0.89 (t, 6H).

2,5-bis{5-(2,5-bis(2-ethylhexyl)-6-(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione-3-yl)-(thiophene-2-yl)}thiophene T(TDPPT)₂

0.31g, 0.51 mmol compound 1, 0.095g 0.23mmol of 2,5-bis(trimethylstannyl) thiophene 3, and 5 mL of toluene were put into a flask with oil bath. The solution was flushed with argon for 10 min, and then 5 mg of Pd(PPh₃)₄ was added into the flask. The solution was flushed again for 20 min. The oil bath was heated to 110 °C carefully, and the reactant was stirred for 48 h at this temperature under an argon atmosphere. Then, the reactant was cooled to room temperature. The solution was poured into distilled water and extracted with chloroform. The organic phase was washed with water, dried over anhydrous MgSO₄. The solvent was removed by a rotate evaporator and the residue was purified by silica-gel chromatography, the obtained material was further purified by redissolving in chloroform and deposited in 100 mL of methanol. The solid was dried under vacuum for 1 day to get the final product 0.19g. The yield of the coupling reaction was 73%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) ¹H NMR (400 MHz, CDCl₃) δ 8.94 (d, J = 3.9 Hz, 2H), 8.91 (d, J = 3.4 Hz, 2H), 7.63 (d, J = 4.3 Hz, 2H), 7.35 (d, J = 4.0 Hz, 2H), 7.28 (s, 4H), 4.04 (t, J = 6.7 Hz, 8H), 1.87 (s, 4H), 1.47 – 1.14 (m, 32H), 0.95 – 0.83 (m, 24H). MALDI-TOF MS: Calcd for C₆₄H₈₀N₄O₄S₅: 1128.35; Found: 1128.4.

5,5'-bis{5-(2,5-bis(2-ethylhexyl)-6-(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione-3-yl)-(thiophene-2-yl)}-2,2'-bithiophene **TT(TDPPT)₂**

This compound was prepared with the same procedure as T(TDPPT)₂. ¹H NMR (400 MHz, CDCl₃): δ (ppm) ¹H NMR (400 MHz, CDCl₃) δ 8.99 – 8.92 (m, 2H), 8.90 (d, J = 3.5 Hz, 2H), 7.66 – 7.58 (m, 2H), 7.31 (s, 2H), 7.28 (s, 1H), 7.24 (s, 2H), 7.14 (d, J = 19.9 Hz, 2H), 4.11- 3.97 (m, 8H), 1.87 (s, 4H), 1.47-1.14 (m, 32H), 0.95-0.83 (m, 24H). MALDI-TOF MS: Calcd for C₆₈H₈₂N₄O₄S₆: 1210.55; Found: 1210.47.

4,8-bis(dodecyloxy)-2,6-bis{5-(2,5-bis(2-ethylhexyl)-6-(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione-3-yl)-(thiophene-2-yl)}benzo[1,2-b:4,5-b']dithiophene **BDT(TDPPT)₂**

This compound was prepared with the same procedure as T(TDPPT)₂. ¹H NMR (400 MHz, CDCl₃) : δ (ppm) ¹H NMR (400 MHz, CDCl₃) δ 8.97 (s, 2H), 8.93 (s, 2H), 7.59 (s, 4H), 7.42 (s, 2H), 7.26 (s, 2H), 4.32 (d, J = 6.4 Hz, 4H), 4.04 (s, 8H), 1.93 (s, 8H), 1.60 (s, 4H), 1.26 (s, 64H), 1.01-0.79 (m, 30H). MALDI-TOF MS: Calcd for C₉₄H₁₃₀N₄O₄S₆: 1602.68; Found: 1602.83.

Measurements and characterizations.

Differential scanning calorimetry (DSC) was performed under nitrogen flushing at a heating rate of 10 °C/min with a NETZSCH (DSC-204) instrument. Thermal gravimetric analysis (TGA) was carried out on a Perkin-Elmer Pyris 6, with a heating rate of 10 °C/min under nitrogen flow. Electrochemical measurements of these derivatives were performed with a Bioanalytical Systems BAS100 B/W electrochemical workstation. The cyclic voltammetry (CV) diagrams of the fullerene derivatives were obtained by using n-Bu₄NPF₆ as supporting electrolyte in acetonitrile solution with a glass carbon working electrode, a platinum wire counter electrode and a Ag/AgNO₃ reference electrode under N₂ atmosphere. Ferrocene was used as the internal standard. The redox potential of Fc/Fc⁺ which has an absolute energy level of -4.8 eV relative to the vacuum level for calibration is located at 0.09 V in 0.1 M n-Bu₄NPF₆/acetonitrile solution. ¹H NMR spectra were measured using a Varian Mercury-400 NMR. Time-of-flight mass spectra were recorded with a Kratos MALDI-TOF mass system. UV-visible absorption spectra were measured using a Shimadzu UV-3100 spectrophotometer. Atomic force Microscopy (AFM) images were recorded under ambient conditions, using a Park XE-120 microscope (Park Systems Corp., Suwon, Korea) operating in the tapping mode regime. The samples were prepared by spin-coating onto silica at 1000 rpm from sample solutions. X-ray diffraction (XRD) analysis was performed on an X'Pert-Pro MPD diffractometer with a Cu K radiation source at room temperature. The transmission electron microscopy (TEM) measurements were conducted on a Tecnai G2 F20 S-Twin transmission electron microscope operated at 200 kV.

Device Fabrication and Characterization.

Photovoltaic cells were fabricated with a structure of ITO/PEDOT:PSS/SM:PC₇₁BM/LiF/Al. Patterned ITO glass was cleaned with detergent water, deionized water, alcohol, acetone and isopropyl alcohol. After drying with N₂, the ITO glass was treated with air plasma. Then PEDOT:PSS was spin-coated on the ITO glass at 3500 rpm for 1 min and annealed at 120 °C for 25 min to obtain a 35 nm thick film. The active layer contained a blend of small molecule as electron donor and PC₇₁BM as electron acceptor, which was prepared from 1:1 weight ratios by solution (10 mg/mL of SMs) in chlorobenzene or chlorobenzene/DIO (99%/1% or 98%/2%). After spin coating the blend from solution at 1000 rpm (all three film thicknesses are about 90~95 nanometers measured by AFM), the devices were completed by evaporating a 0.8 nm LiF layer protected by 100 nm of Al at a base pressure of 4 × 10⁻⁴ Pa. The effective photovoltaic area defined by the geometrical overlap between the bottom ITO electrode and the top cathode was 12 mm². Current-voltage characteristics of the solar cells in the dark and under illumination of 100 mW/cm² white light from a Hg-Xe lamp filtered by a Newport 81094 Air Mass Filter, using a GWinstek SFG-1023 source meter. Monochromatic light from a Hg-Xe lamp (Newport 67005) in combination with monochromator (Oriel, Cornerstone 260) was modulated with a mechanical chopper. The response was recorded as the voltage over a 50 Ω resistance, using a lock-in amplifier (Newport 70104 Merlin). A calibrated Si cell was used as reference. All the measurements were performed under ambient atmosphere at room temperature.

We applied the method of space charge limited current (SCLC) to measure hole mobility and electron mobility. Hole-only and electron-only diodes were fabricated using the architectures: ITO/PEDOT:PSS/SM:PC₇₁BM/Au for holes and Al/ SM:PC₇₁BM/Al for electrons. The J-V curves of the devices were plotted as $\ln[Jd^3/(V_{\text{appl}} - V_{\text{bi}})^2]$ versus $[(V_{\text{appl}} - V_{\text{bi}})/d]^{0.5}$ using Eq. (1) for holes and $\ln(J)$ versus $\ln(V_{\text{appl}})$ using Eq. (2) for electrons.

$$\ln(Jd^3/V^2) \cong 0.89(1/E_o)(V/d)^{0.5} + \ln(9\varepsilon_r\varepsilon_o\mu_h/8) \quad (1)$$

Calculation of hole mobility using SCLC methods, $V = V_{\text{appl}} - V_{\text{bi}}$, V_{appl} is the applied voltage, V_{bi} is the offset voltage (for this device architecture, V_{bi} is 0.2 V)

$$\ln(J) = 2 \ln(V) + \ln(9\epsilon_r\epsilon_0\mu_h/8d^3) \quad (2)$$

Calculation of electron mobility using SCLC methods, $V = V_{\text{appl}}$ (for this device architecture, V_{bi} is 0 V)

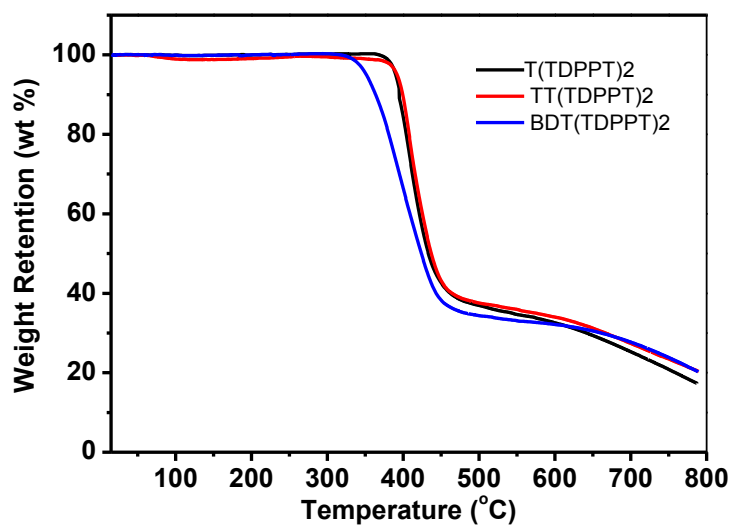


Fig. S1 TGA thermogram of SMs at a heating rate of 10 °C/min under N₂.

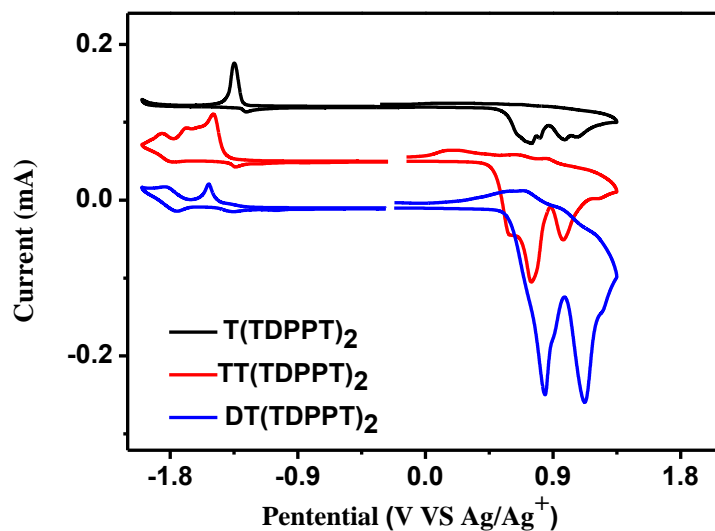


Fig. S2 Cyclic voltammograms scans of SMs in CH₃CN/0.1 M Bu₄NClO₄ at 50 mV/s.

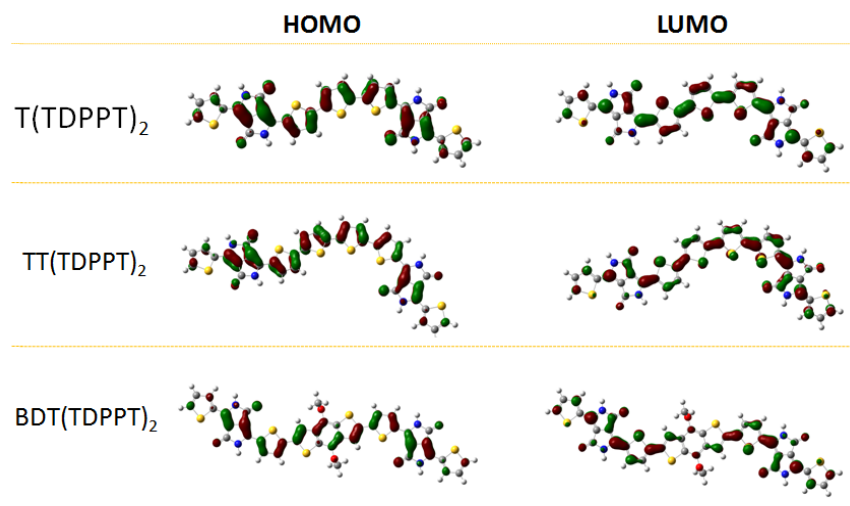


Fig. S3 Molecular orbital surfaces of the HOMO and LUMO of comonomer model obtained at B3 LYP/6-31G* level.

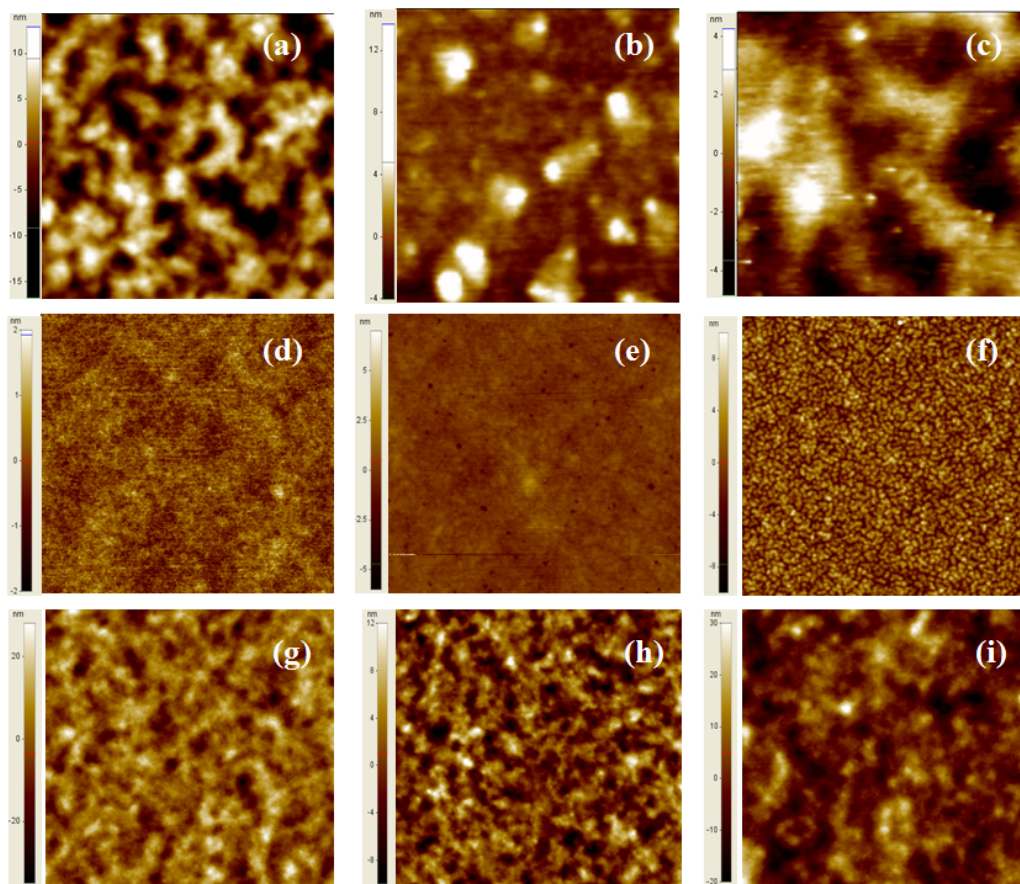


Fig. S4 Topography images of blend films: (a) T(TDPPT)₂ (b) TT(TDPPT)₂ (c) BDT(TDPPT)₂ (d) T(TDPPT)₂:PC₇₁BM; (e) TT(TDPPT)₂:PC₇₁BM (f) BDT(TDPPT)₂:PC₇₁BM; (g) T(TDPPT)₂:PC₇₁BM+DIO; (h) TT(TDPPT)₂:PC₇₁BM +DIO; (i) BDT(TDPPT)₂:PC₇₁BM +DIO.

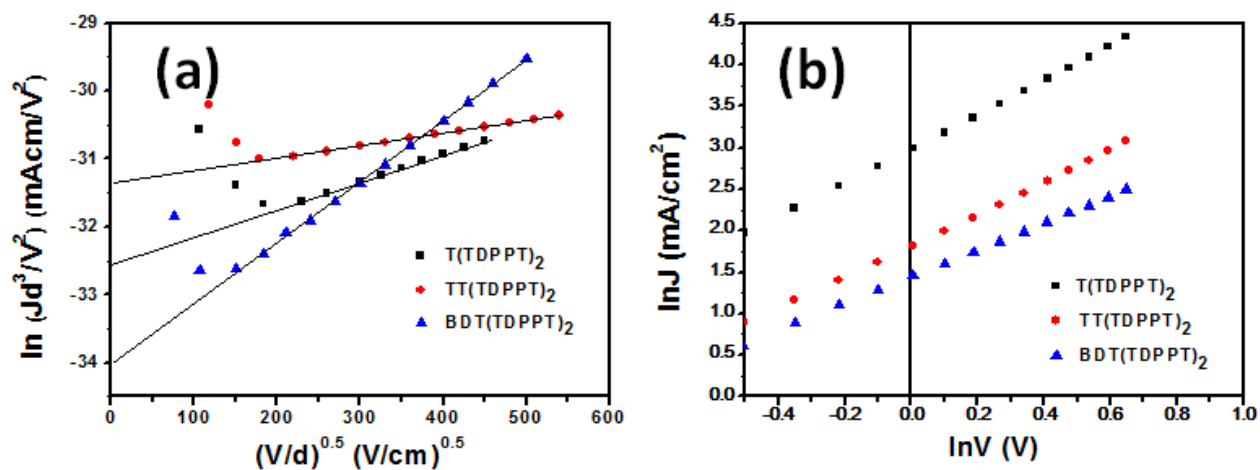


Fig. S5 Plots of $\ln(Jd^3/V^2)$ versus $(V/d)^{0.5}$ of the device ITO/PEDOT: PSS/SMs:PC₇₁BM/Au for the measurement of hole mobility and $\ln J$ versus $\ln V$ of the device Al/ SMs:PC₇₁BM/Al for the measurement of electron mobility.

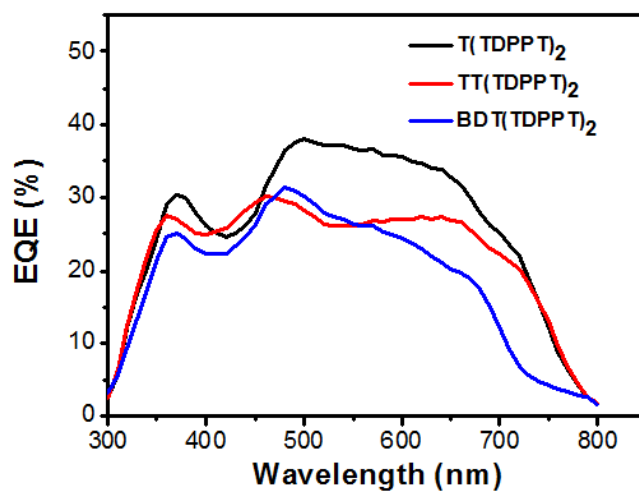


Fig. S6 The external quantum efficiencies (EQE) spectra of devices based on SM:PC₇₁BM with processing DIO.

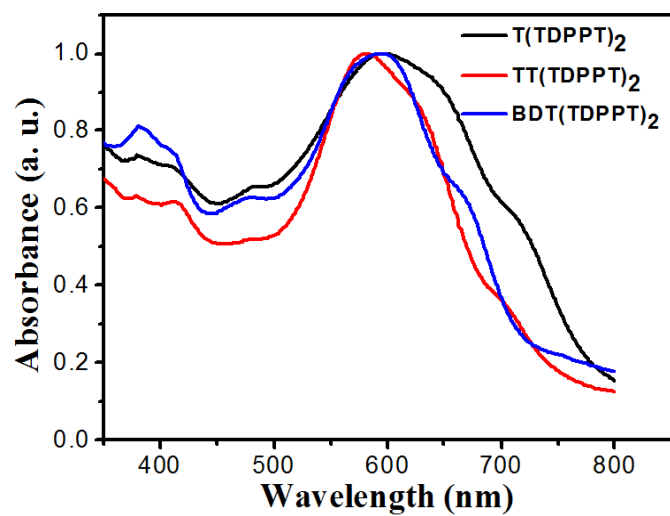


Fig. S7 UV-vis absorption spectra of SM:PC₇₁BM in films.

Table S1 optical and electrochemical properties of SMs.

SMs	In Solution ^a		In Film ^b			E_{ex}^{onset} (V) HOMO(eV)	E_{red}^{onset} (V) LUMO (eV)	Electrochem $E_{g,ec}$ (eV)	Optical ^c $E_{g,opt}$ (eV)
	λ_{max}^{obs} (nm)	λ_{edge} (nm)	λ_{edge} (nm)	λ_{edge} (nm)					
T(TDPPT) ₂	612(86800)	700	633	777	0.57/-5.29	-1.29/-3.43	1.86	1.60	
TT(TDPPT) ₂	616(86000)	690	623	764	0.48/-5.20	-1.42/-3.30	1.90	1.62	
BDT(TDPPT) ₂	616(98900)	673	610	726	0.58/-5.30	-1.28/-3.44	1.86	1.71	

^a 1×10^{-5} M in anhydrous chloroform. ^bSpin-coated from a 10mg/mL chloroform solution. ^cThe optical band gap ($E_{g,opt}$) was obtained from absorption edge.

Table S2 Photovoltaic Performances of SMs.

SM+DIO (V/V)	Voc (V)	Jsc (mA/cm ²)	FF (%)	PCE (%)	Rs (Ωcm^2)	Rsh (Ωcm^2)
T(TDPPT)2+0%	0.82	4.48	0.28	1.04	88	207
TT(TDPPT)2+0%	0.81	3.24	0.29	0.75	170	267
BDT(TDPPT)2+0%	0.80	2.83	0.47	1.05	52	597
T(TDPPT)2+2%	0.82	7.48	0.54	3.30	16.4	400
TT(TDPPT)2+1%	0.79	6.57	0.50	2.58	24.0	374
BDT(TDPPT)2+2%	0.76	5.22	0.55	2.19	21.8	571

Table S3 Electron and hole mobilities of SM:PC₇₁BM blend films cast under different conditions, estimated using the Mott-Gurney law.

SM+DIO(V/V)	Hole mobility ($\text{cm}^2\text{v}^{-1}\text{s}^{-1}$)	Electron mobility ($\text{cm}^2\text{v}^{-1}\text{s}^{-1}$)	μ_e/μ_h
T(TDPPT)2+2%	2.4×10^{-5}	4.8×10^{-5}	2.0
TT(TDPPT)2+1%	7.4×10^{-5}	1.5×10^{-5}	0.2
BDT(TDPPT)2+2%	5.9×10^{-6}	1.1×10^{-5}	1.9