A novel benzo[1,2-b:4,5-b′]dithiophene-based conjugated polymer with a pendant diketopyrrolopyrrole unit for high-performance solar cells

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1. General considerations for characterization

Measurements: Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DRX 400 spectrometer using tetramethylsilane as a reference in deuterated chloroform solution at 298 K. MALDI-TOF mass spectrometric measurements were performed on Bruker Bifiex III MALDI-TOF. Molecular weight was determined using a Waters GPC 2410 in THF via a calibration curve of polystyrene as standard. Thermogravimetric analysis (TGA) was conducted under a dry nitrogen gas flow at a heating rate of 20 °C min^{-1} on a Perkin-Elmer TGA 7. The FT-IR spectra were recorded on a Perkin–Elmer Spectrum One Fourier transform infrared spectrometer by incorporating samples in KBr discs. UV-Vis absorption spectra were recorded on a HP-8453 UV visible system. Cyclic voltammetry was carried out on a CHI660A electrochemical work station in a three-electrode cell dipped in a 0.1M tetrabutyl-ammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution under nitrogen protection at a scan rate of 100 mV/s and room temperature (RT). In this three-electrode cell, a platinum rod, platinum wire and saturated calomel electrode were used as a working electrode, counter electrode and reference electrode, respectively. The morphology of the polymer/PCBM blend film was investigated by an atomic force microscopy (AFM) on a Veeco, DI Multimode NS-3D apparatus in a trapping mode under normal air condition at RT.

2. Device fabrication and characterization

Device Fabrication: Polymer solar cells were fabricated using indium tin oxide (ITO) glass as an anode, LiF/Al as a cathode, and a blend film of the polymer and PCBM as a photosensitive layer. After a 30 nm buffer layer of poly-(3,4-ethylenedioxythiophene) and polystyrene sulfonic acid (PEDOT:PSS) was spin-coated onto the precleaned ITO substrate, the photosensitive layer was subsequently prepared by spin-coating a solution of the polymer and PCBM (1:1.3, w/w) in chlorobenzene on the PEDOT:PSS layer with a typical concentration of 20 mg mL^{-1}, followed by annealing at 120 °C for 10 minutes to remove chlorobenzene. LiF (0.7 nm) and Al (100 nm) were successively deposited on the photosensitive

layer in vacuum and used as top electrodes. The current–voltage (*I–V*) characterization of the devices was carried out on a computer-controlled Keithley 236 source measurement system. A solar simulator was used as the light source and the light intensity was monitored by a standard Si solar cell. The active area was 7×10^{-2} cm^2 for each cell. The thicknesses of the spun-cast films were recorded by a profilometer (Alpha-Step 200, Tencor Instruments). The incident photon-to-current conversion efficiency (IPCE) spectrum was measured by a Stanford research systems model SR830 DSP lock-in amplifier coupled with WDG3 monochromator and a 500 W xenon lamp.

Hole mobility of the PBDT-TDPP-S/$PC_{71}BM$(w:w, 1:1.3) blend film was measured according to a similar method described in the literature [1-2], using a diode configuration of ITO/PEDOT:PSS(40nm)/active layer/ MoO_3/Al(100 nm) by taking current-voltage current in the range of 0-4 V and fitting the results to a space charge limited form, where the space charge limited current (SCLC) is described by $J = 9\varepsilon_0\varepsilon_r\mu_h V^2/8L^3$, where J is the current density, L is the film thickness of active layer, μ_h is the hole mobility, ε_r is the relative dielectric constant of the transport medium, ε_0 is the permittivity of free space (8.85×10^{-12} F m^{-1}), V is the internal voltage in the device and $V = V_{appl}-V_a-V_{bi}$, where V_{appl} is the applied voltage to the device, V_a is the voltage drop due to contact resistance and series resistance across the electrodes, and V_{bi} is the built-in voltage due to the relative work function difference of the two electrodes.

Electron mobility measurements of the PBDT-TDPP-S/$PC_{71}BM$(w:w, 1:1.3) blend film were done using a similar method described in the literature with the following diode structures: ITO/Al(30 nm)/active layer/Ca(5nm)/Al(100 nm).[1-2] The charge carrier mobilities were calculated using the space-charge limited current (SCLC) model as describe above.

3. The GPC elution curve of PBDT-TDPP-S

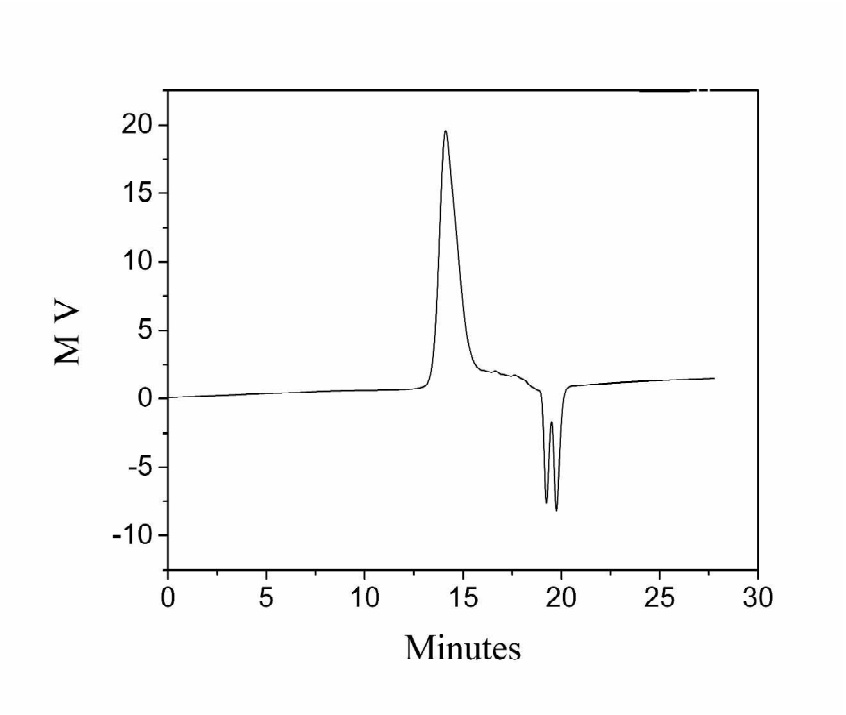


Figure S1. The GPC elution curve of PBDT-TDPP-S

4. TGA measurement

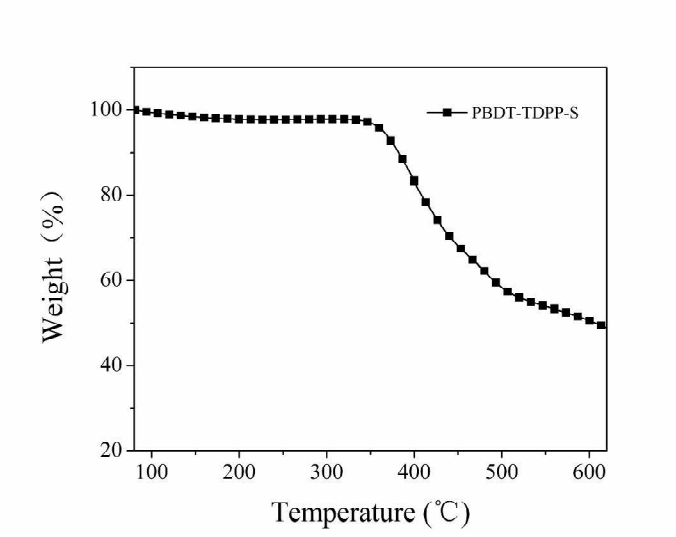


Figure S2. TGA curve of PBDT-TDPP-S at a scan rate of 20 ^{o}C/min under nitrogen atmosphere

5. Cyclic voltammetry curve measurement

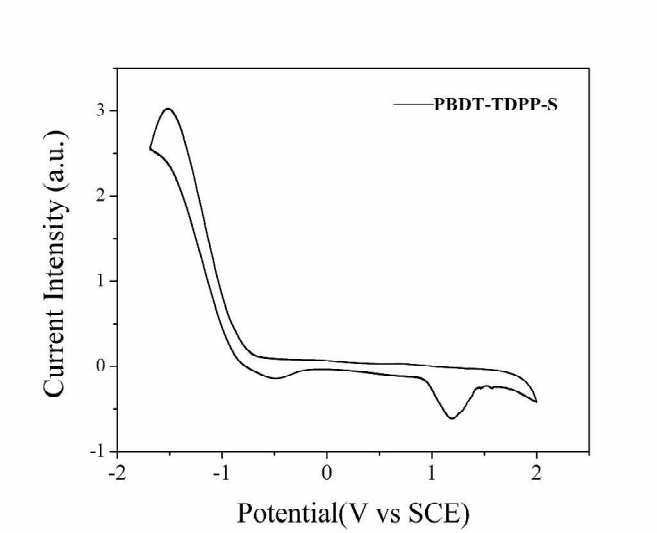


Figure S3. Electrochemical cyclic voltammetry curve of PBDT-TDPP-S

6. Photovoltaic Properties of the PBDT-TDPP-S-based PSCs at different conditions

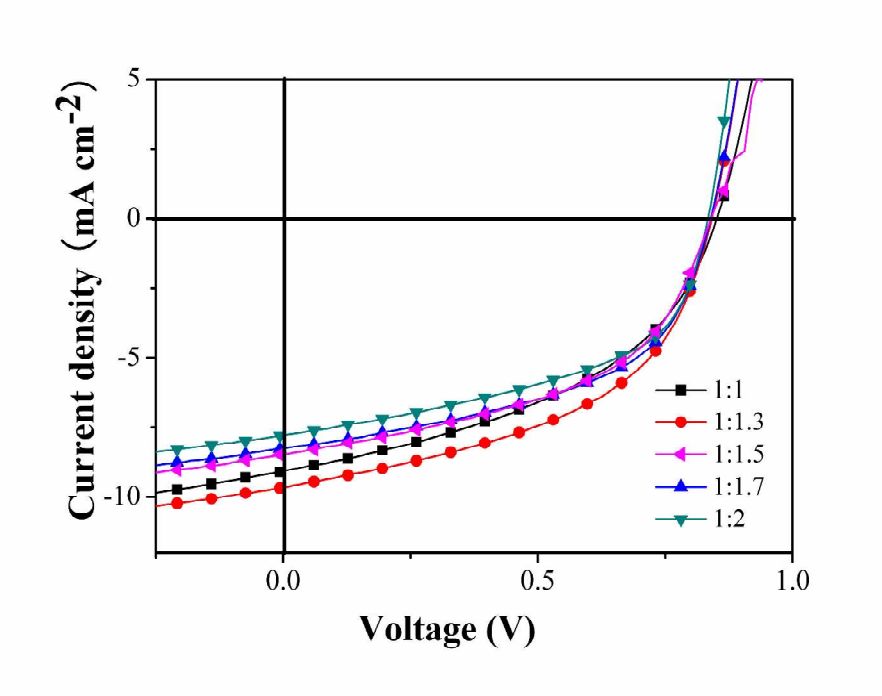


Figure S4. *J-V* curves of the PBDT-TDPP-S:$PC_{71}BM$ PSCs with different blend ratios (w/w) at thickness of 80 nm and thermal annealing temperature of 90°C

Table S1. Photovoltaic properties of the PBDT-TDPP-S:$PC_{71}BM$ PSCs with different blend ratios (w/w) at thickness of 80 nm and thermal annealing temperature of 90°C

D/A Ratio	J_{sc} / mA cm^{-2}	V_{oc} / V	FF / %	PCE_{max} / %
1:1	9.07	0.85	45	3.58
1:1.3	9.65	0.84	49	4.15
1:1.5	8.26	0.84	51	3.70
1:1.7	7.77	0.83	51	3.41
1:2	7.45	0.84	49	3.19

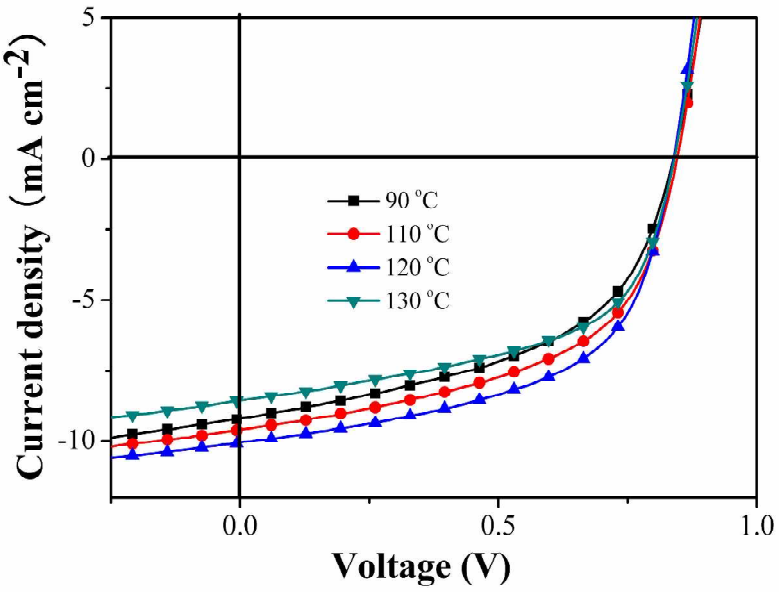


Figure S5. *J-V* curves of the PBDT-TDPP-S:$PC_{71}BM$ PSCs with a thickness of 80 nm and a PBDT-TDPP-S/$PC_{71}BM$ ratio of 1:1.3 at different pre-thermal annealing temperatures.

Table S2. Photovoltaic properties of the PBDT-TDPP-S:$PC_{71}BM$ PSCs with a thickness of 80 nm and a PBDT-TDPP-S/$PC_{71}BM$ ratio of 1:1.3 at different pre-thermal annealing temperatures

Temperatures (°C)	J_{sc} / mA cm^{-2}	V_{oc} / V	FF / %	PCE_{max} / %
90	9.20	0.84	50	4.04
110	9.59	0.84	53	4.47
120	10.04	0.84	56	4.89
130	8.56	0.84	55	4.10

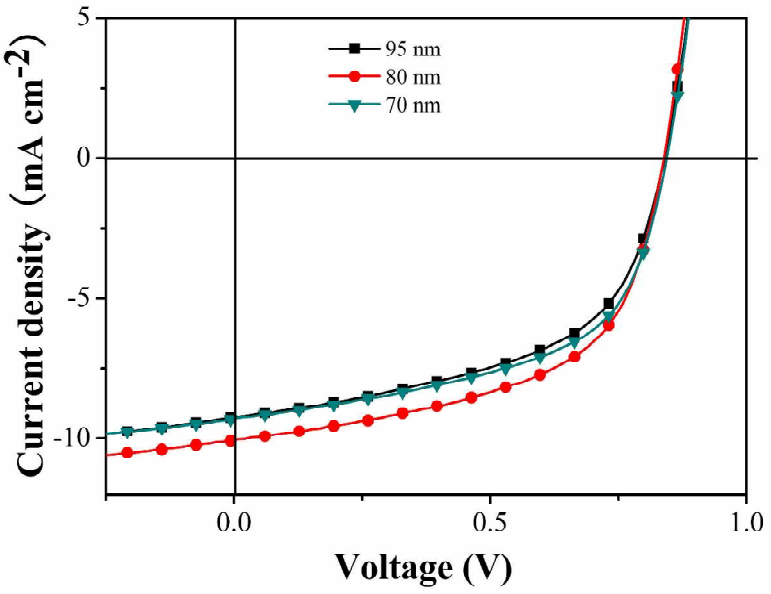
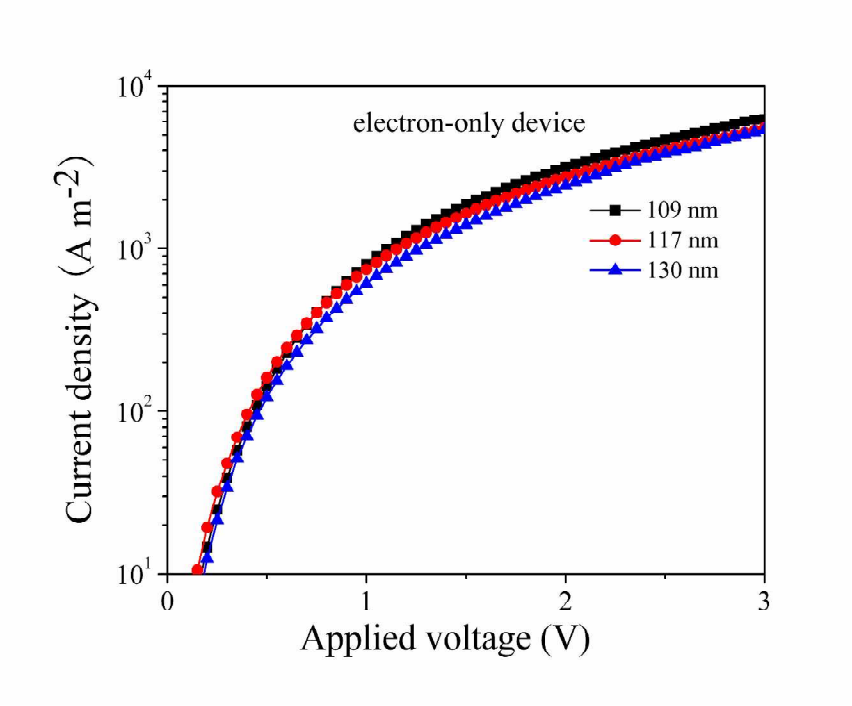


Figure S6. *J-V* curves of the PBDT-TDPP-S: $PC_{71}BM$ PSCs with a PBDT-TDPP-S/$PC_{71}BM$ ratio of 1:1.3 under pre-thermal annealing temperature of 120 ^{o}C at different thicknesses

Table S3. Photovoltaic properties of the PBDT-TDPP-S: $PC_{71}BM$ PSCs with a PBDT-TDPP-S/$PC_{71}BM$ ratio of 1:1.3 under pre-thermal annealing temperature of 120 ^{o}C at different thicknesses

Donor	Acceptor	Thickness / nm	J_{sc} / mA cm^{-2}	V_{oc} / V	FF / %	PCE_{max} / %
PBDT-TDPP-S	$PC_{71}BM$	95	9.25	0.84	53	4.31
PBDT-TDPP-S	$PC_{71}BM$	80	10.04	0.84	56	4.89
PBDT-TDPP-S	$PC_{71}BM$	70	9.30	0.84	55	4.51

7. Electron mobility measurements (SCLC)



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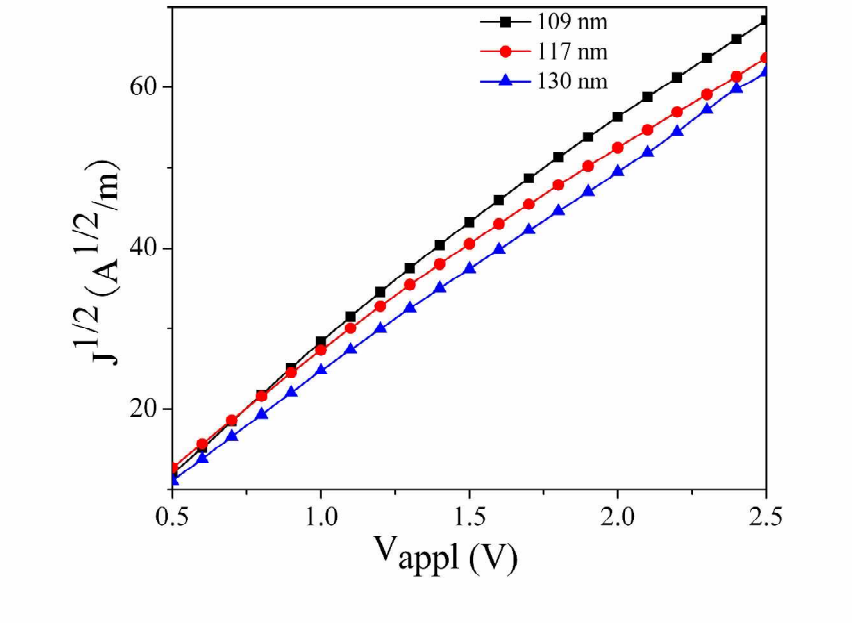
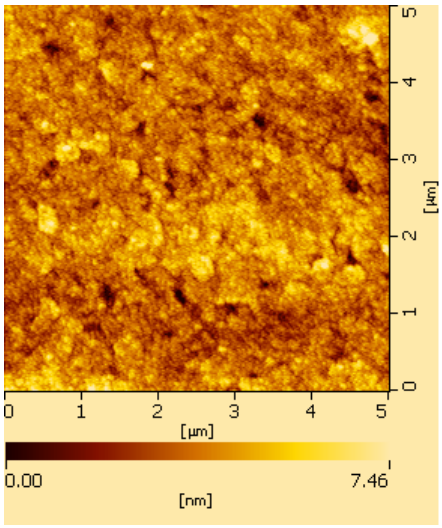


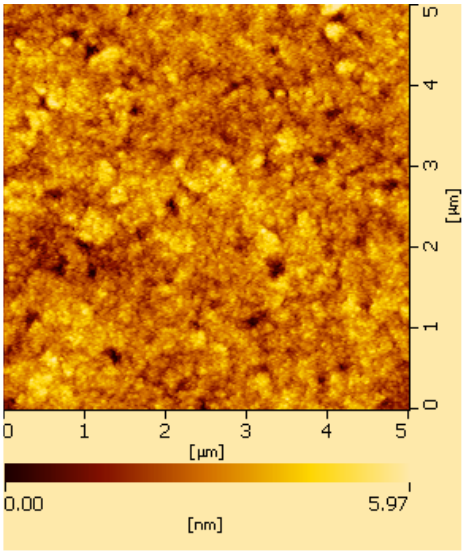
(b)

Figure S7. (a) *J-V* characteristics, (b) $J^{1/2}$-*V* characteristics of PBDT-TDPP-S electron-only devices with different thicknesses measured at ambient temperature

8. Impact of thermal annealing on film morphologies



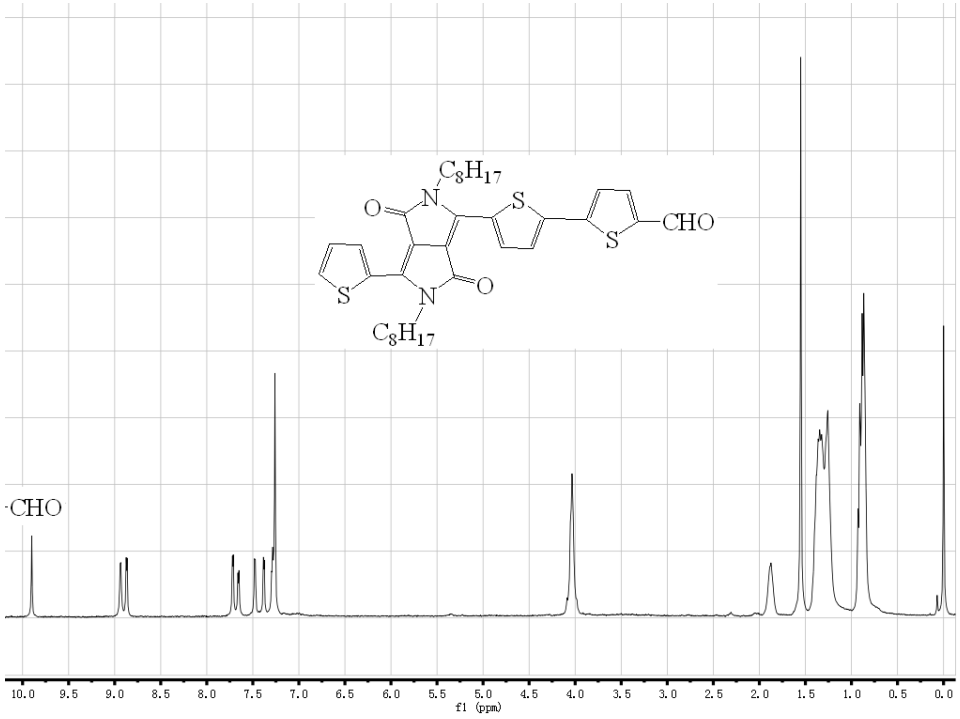
(a)

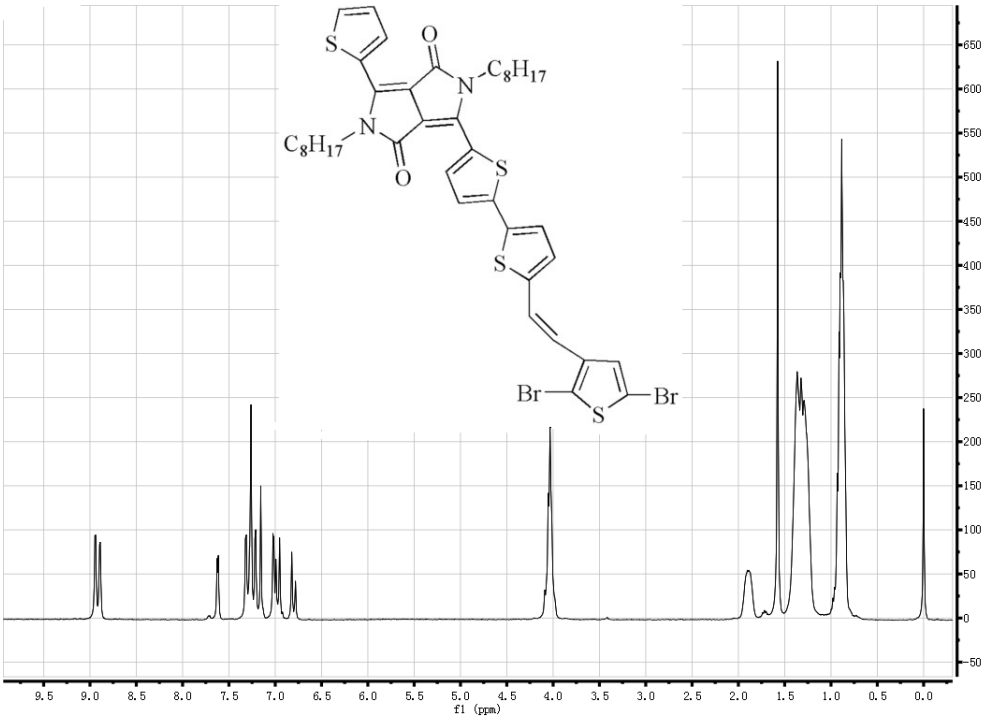


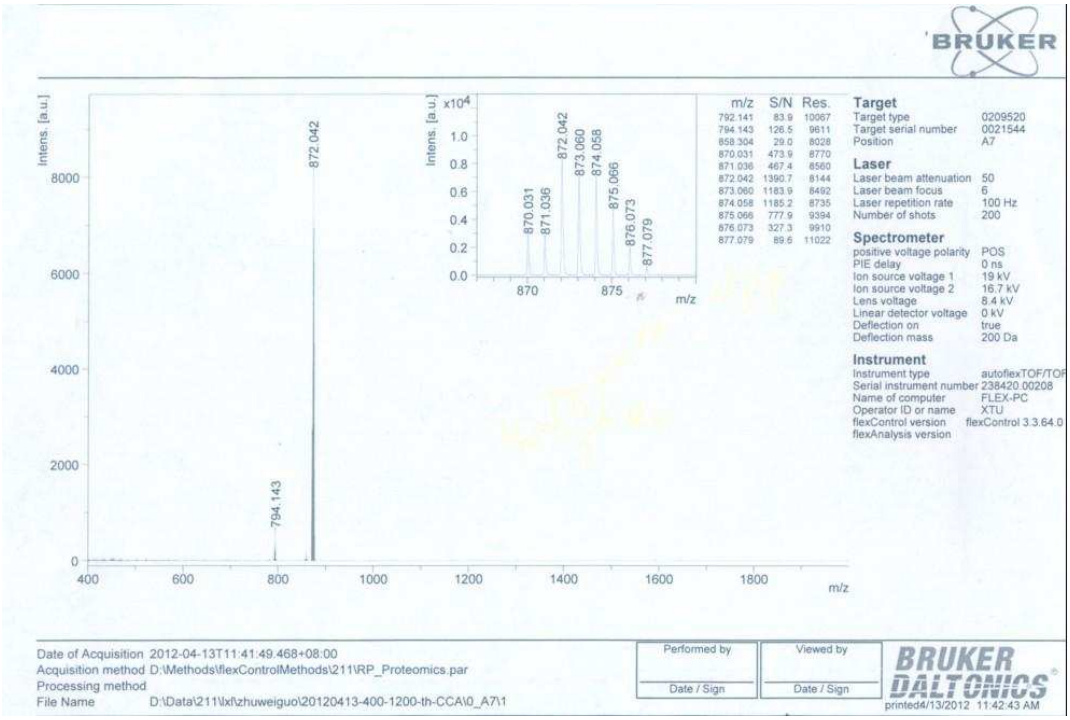
(b)

Figure S8. Tapping-mode AFM images of the PBDT-TDPP-S:$PC_{71}BM$ film (a) in unannealed condition and (b) in annealed condition at 120 °C on glass/ITO/PEDOT:PSS substrate.

9. ^{1}H NMR data of compound 2, **M**2, PBDT-TDPP-S, and MS data of **M**2, and the infrared spectrum of PBDT-TDPP-S



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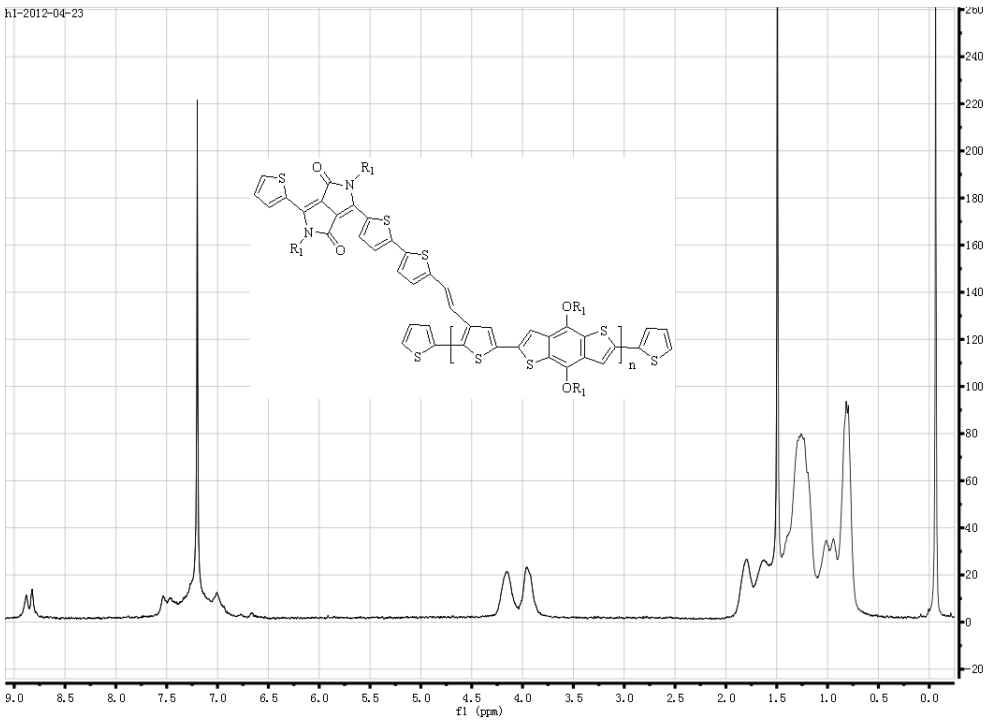
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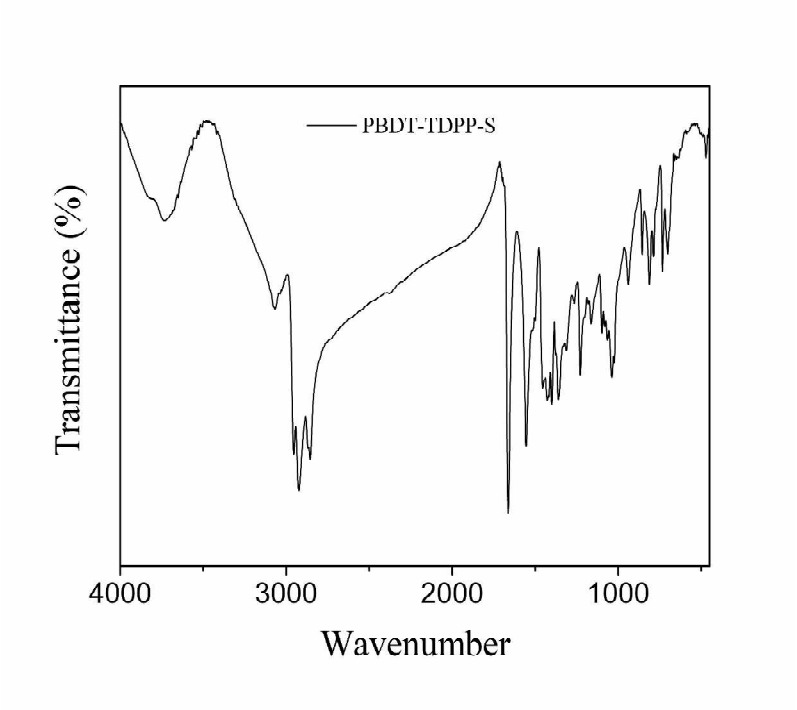

Reference

1. Wang, M.; Hu, X. W.; Liu, P.; Li, W.; Gong, X.; Huang, F.; Cao, Yong J. Am. Chem. Soc. **2011,**133, 9638-9641.

2. He, Z. C.; Zhong, C. M.; Huang, X.; Wong, W. –Y.; Wu, H. B.; Chen, L. X.; Cao, Y. Adv. Mater. **2011,** 23, 4636-4643.