

Supplementary Information

Effect of Solvent Additive on Active Layer Morphologies and Photovoltaic Performance of Polymer Solar Cells Based on PBDTTT-C-T/PC₇₁BM

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Experimental Section

Materials

PC₇₁BM was purchased from NANO.C Inc. and used as received. PBDTTT-C-T was synthesized in our laboratory according to the procedures reported in our previous paper^[1]. Three solvent additives and the ultra dry solvents used in device

fabrication process were purchased from Alfa Aesar. The other chemicals are commercial available products and used without any further purification.

Measurements and Instruments

Absorption spectra were taken on a Hitachi U-3010 UV-vis spectrophotometer. The PBDTTT-C-T: PC₇₁BM blend films (1:1.5, w/w) for the UV-vis absorption measurements were prepared on quartz glass substrates using the same method as that for device fabrication. The atomic force microscopy (AFM) measurement of the surface morphology of samples was conducted on a Nanoscope III (DI, USA) in contacting mode with a 1 μm scanner. The PBDTTT-C-T: PC₇₁BM blend films (1:1.5, w/w) for AFM measurements were prepared on ITO/PEDOT: PSS substrates using the same method as that for device fabrication. The bright-field transmission electron microscopy (TEM) characterization was carried out on a TECNAI G20, FEI operating at 300 kV. The samples for the TEM measurements were prepared as follows: The thin active-layer (about 100 nm) films were spin-cast on ITO/PEDOT:PSS substrates, and the ITO glass with the active layers were submerged in deionized water (10 min) to make the active layers floated onto the air/water interface. Then the floated films were picked up on unsupported 200 mesh copper grids for the TEM measurement. The Samples for PFKPFM measurements were prepared as the same condition with device fabrication in glass substrate coated with ITO on Bruker's Multimode 8 Nanoscope V (Veeco) Atomic Force Microscopy. Conductive KPFM probes (Back side: 50nm Al coatings, Bruker) were used throughout the measurements. The WFD images were obtained on a typical area of $0.5\mu\text{m}\times 0.5\mu\text{m}$,

over which the average WFD were used. The water contact angle measurements were performed on a Krüss DSA 100 Contact Angle Measuring Instrument (Krüss Company, Ltd., Germany) at ambient temperature. X-ray photoelectron spectroscopy data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300W Al K α radiation.

GIWAXS experiment was performed at beamline 7.3.3^[2] at the Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA. Samples were prepared using identical blend solutions as those used in devices on a PSS pre-coated Si substrate. The 10 keV X-ray beam was incident at a grazing angle of 0.14°, which maximized the scattering intensity from the samples. The scattered intensity was detected with an Pilatus detector.

RSoXS transmission measurements were performed at beamline 11.0.1.2^[3] at the Advanced Light Source (ALS). Samples for R-SoXS measurements were first prepared on a PSS modified Si substrate under the same conditions as those used for devices fabrication, and then transferred to a 1 mm \times 1 mm, 100 nm thick Si₃N₄ membrane supported by a 5 mm \times 5 mm, 200 μ m thick Si frame (Norcada Inc.). 2-D scattering patterns were collected on an in-vacuum CCD camera (Princeton Instrument PI-MTE). The sample detector distance was measured from diffraction peaks of a triblock copolymer poly(isoprene-b-styrene-b-2-vinyl pyridine), which has a known spacing of 391 Å. The beam size at the sample is approximately 100 μ m by 200 μ m. Reference spectroscopy at beamline 5.3.2.2.

Fabrication and characterization of the PSCs

The PSCs were fabricated in the configuration of the traditional sandwich structure with an indium tin oxide (ITO) glass positive electrode and a metal negative electrode. Patterned ITO glass with a sheet resistance of $10 \Omega/\square$ was purchased from CSG HOLDING Co., LTD. (China). The ITO glass was cleaned by sequential ultrasonic treatment in detergent, deionized water, acetone, and isopropanol, and then treated in an ultraviolet-ozone chamber (Ultraviolet Ozone Cleaner, Jelight Company, USA) for 15 min. Then PEDOT: PSS (poly (3,4-ethylene dioxythiophene): poly(styrene sulfonate)) (Clevios P VP AI 4083 H. C. Stark, Germany) was filtered through a $0.45 \mu\text{m}$ PVDF filter and spin coated at 2000 rpm for 60 s on the ITO electrode. Subsequently, the PEDOT: PSS film was baked at $150 \text{ }^\circ\text{C}$ for 30 min in the air and then transferred into a nitrogen glove box for subsequent procedures. The thickness of the film was around 40 nm. PBDTTT-C-T:PC₇₁BM (1:1.5, w/w) were prepared in *ortho*-dichlorobenzene at a concentration of 10 mg/ml for PBDTTT-C-T and were heated to $60 \text{ }^\circ\text{C}$ and stirred 3-5h for complete dissolution, and then the needing amounts of different additives were added to the blend solutions before spin coating. The blend solution of PBDTTT-C-T and PC₇₁BM in *ortho*-dichlorobenzene (DCB) (1:1.5, w/w, 10 mg/ml for PBDTTT-C-T) was spin-coated on top of the PEDOT: PSS layer at 900 rpm for 90 s. The thickness of the photoactive layer is measured by Ambios Technology XP-2 profilometer. Then, the negative electrode consisted of Ca (~20 nm) capped with Al (~100 nm) was thermally evaporated on the active layer under a shadow mask in a base pressure of *ca.* 1×10^{-4} Pa. The mobility was measured by the space charge limited current (SCLC) method by a hole-only

device with a structure of ITO/PEDOT: PSS/Active layer/Au or an electron-only device with a structure of ITO/Al/Active layer/Al and estimated through the Mott-Gurney equation. The $J-V$ curves were measured under the illumination of AM 1.5G, 100 mW/cm^2 using a XES-70S1 (SAN-EI Electric Co., Ltd.) solar simulator (AAA grade, $70 \text{ mm} \times 70 \text{ mm}$ photo-beam size). $2 \times 2 \text{ cm}^2$ Monocrystalline silicon reference cell (SRC-1000-TC-QZ) was purchased from VLSI Standards Inc. EQE measurements were performed at Solar Cell Spectral Response Measurement System QE-R3011 (Enli Technololy Co. Ltd).

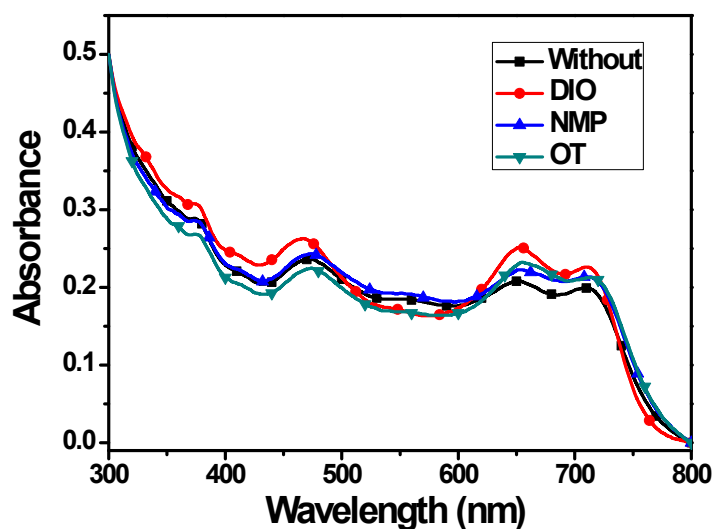


Figure S1. Absorption spectra of the blend film of PBDTTT-C-T: PC₇₁BM (1:1.5, w/w) without or with different additives

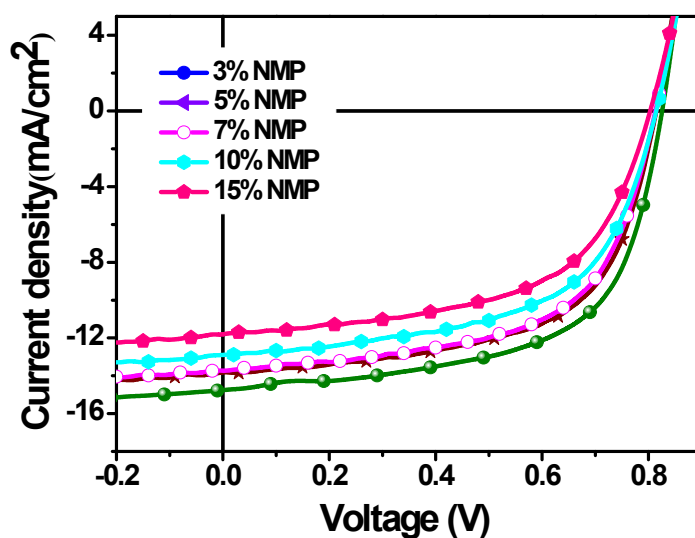


Figure S2. J - V curves of the PSCs based on PBDTTT-C-T: PC₇₁BM(1:1.5, w/w) with NMP additive under illumination of AM1.5G, 100 mW/cm²

Table S1. Photovoltaic performance of the devices based on PBDTTT-C-T: PC₇₁BM (1:1.5, w/w) with NMP as additive under the illumination of AM1.5G, 100 mW/cm²

Additive	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	PCE (%)
3% NMP	0.83	14.8	0.61	7.44
5% NMP	0.82	13.8	0.60	6.83
7% NMP	0.82	13.7	0.60	6.74
10% NMP	0.81	12.9	0.58	6.06
15% NMP	0.80	11.8	0.57	5.38

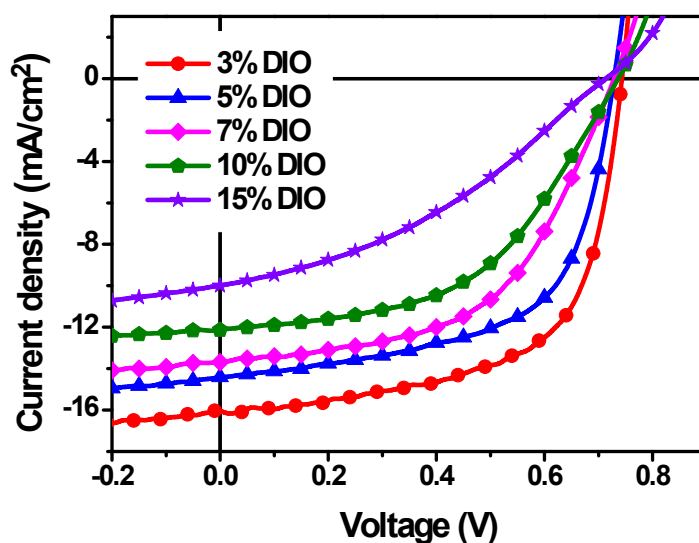
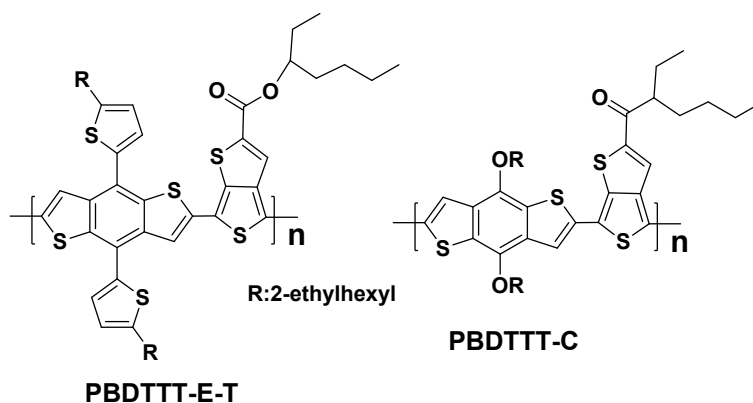


Figure S3. J - V curves of the PSCs based on PBDTTT-C-T: PC₇₁BM(1:1.5, w/w) with DIO additive under illumination of AM1.5G, 100 mW/cm²

Table S2. Photovoltaic performance of the devices based on PBDTTT-C-T: PC₇₁BM (1:1.5, w/w) with DIO as additive under the illumination of AM1.5G, 100 mW/cm²

Additive	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	PCE (%)
3% DIO	0.75	15.6	0.63	7.37
5% DIO	0.73	14.1	0.61	6.28
7% DIO	0.73	13.7	0.53	5.34
10% DIO	0.72	12.1	0.50	4.36
15% DIO	0.71	10.0	0.36	2.56



Scheme S1. Molecular structures of **PBDTTT-E-T** and **PBDTTT-C**

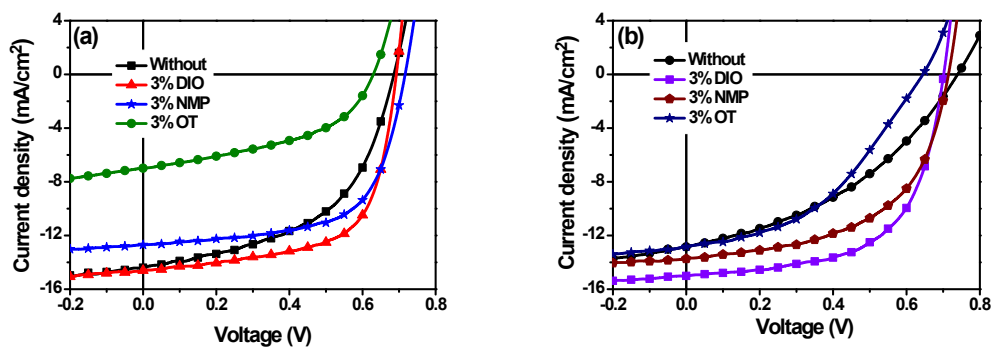


Figure S4. J - V curves of the PSCs based on (a) PBDTTT-E-T: PC₇₁BM (1:1.5, w/w) and (b) PBDTTT-C: PC₇₁BM (1:1.5, w/w) without additive or with different additives under the illumination of AM 1.5G, 100 mW/cm².

Table S3. Photovoltaic performance of the devices based on PBDTTT-E-T: PC₇₁BM (1:1.5, w/w) and PBDTTT-C: PC₇₁BM (1:1.5, w/w) with or with different additives under the illumination of AM1.5G, 100 mW/cm²

Donor	Additive	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	PCE (%)
PBDTTT-E-T	Without	0.69	14.4	0.52	5.16
	DIO	0.69	14.6	0.63	6.34
	NMP	0.72	12.7	0.63	5.76
	OT	0.63	7.0	0.47	2.07
PBDTTT-C	Without	0.74	12.8	0.40	3.79
	DIO	0.70	15.0	0.61	6.41
	NMP	0.72	13.7	0.55	5.43
	OT	0.64	12.8	0.43	3.52

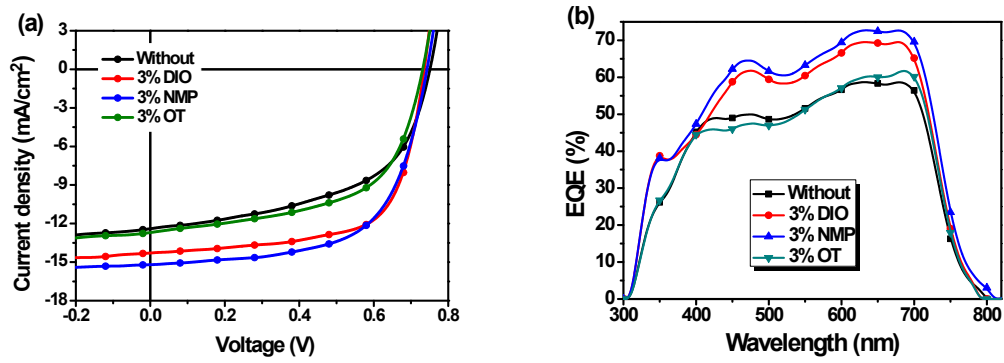


Figure S5. (a) J - V curves and (b) EQE of the PSCs based on PTB7: PC₇₁BM: ICBA (1:1.125:0.225, w/w) without additive or with different additives under the illumination of AM 1.5G, 100 mW/cm².

Table S4. Photovoltaic performance of the devices based on PTB7: PC₇₁BM: ICBA (1:1.125:0.225, w/w) without or with different additives under the illumination of AM1.5G, 100 mW/cm²

Additive	V_{oc} (V)	$J_{sc}^{[a]}$ (mA/cm ²)	FF	PCE (%)
Without	0.75	12.4 (12.2)	0.54	5.02
DIO	0.74	14.3 (14.0)	0.67	7.09
NMP	0.74	15.2 (14.8)	0.62	6.97
OT	0.73	12.7 (12.3)	0.57	5.28

[a]: calculated J_{sc} values from the EQE spectra.

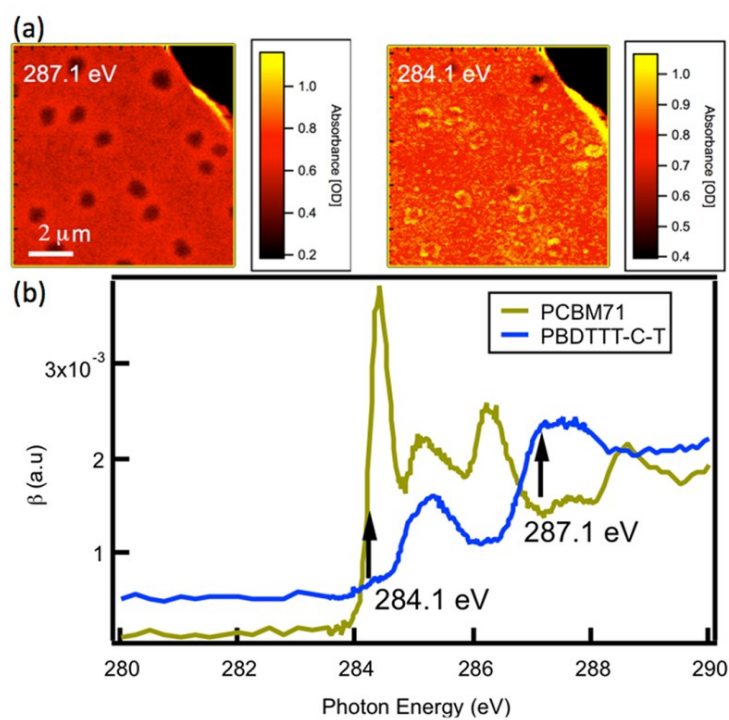


Figure S6. (a) STXM image obtained at photon energies of 287.1 eV and 284.1 eV (b) Absorption spectra of PCBM and PBDTTT-C-T

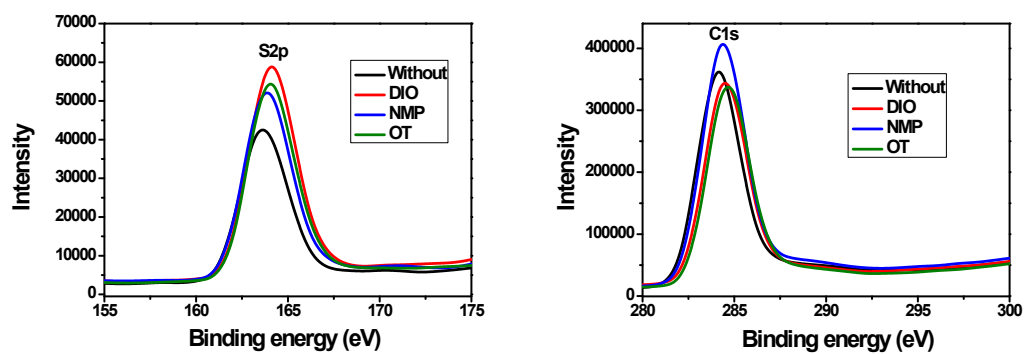


Figure S7. XPS survey of the top surfaces of PBDTTT-C-T: PC₇₁BM blend films (1:1.5, w/w) without or with additives.

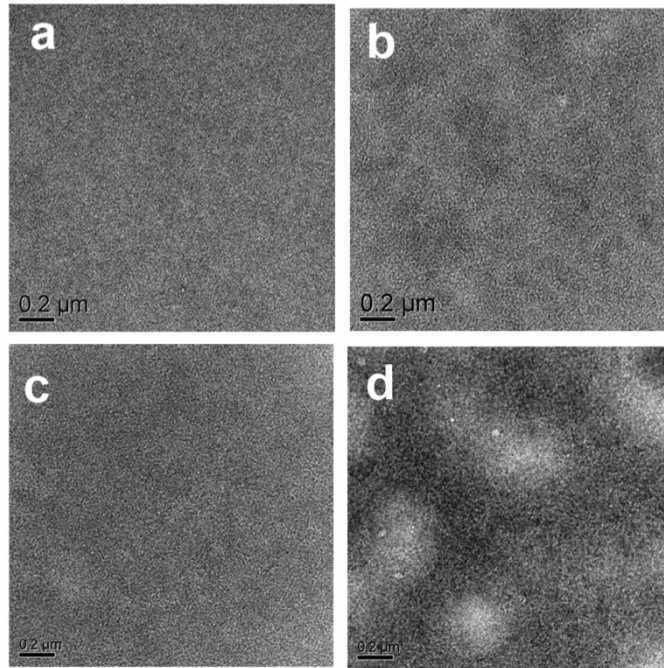


Figure S8. TEM images of PBDTTT-C:T:PC₇₁BM blend films (1:1.5, w/w); (a) processed with pure *o*-DCB; (b) processed with 3% DIO; (c) processed with 3% NMP; (d) processed with 3% OT.

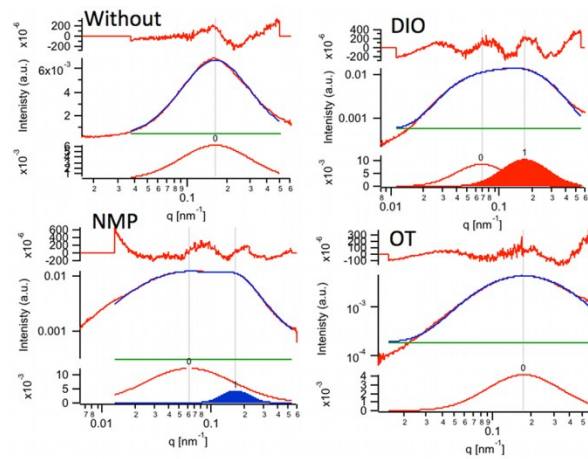


Figure S9. Fitted R-SoXS scattering profile with Lorentzian distributions of blend films without or with additives.

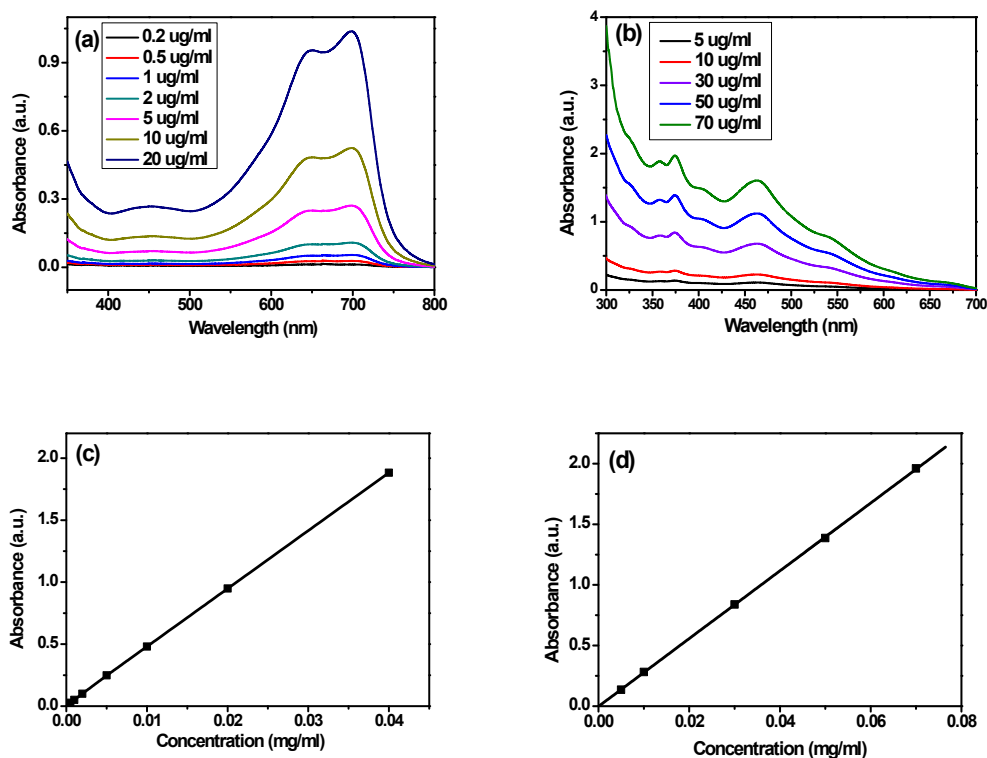


Figure S10: Calibration spectra used to calculate solubility. (a) and (b) Absorption spectra of standard solutions of PBDTTT-C-T and PC₇₁BM, respectively. (c) Plot of PBDTTT-C-T absorbance at 645 nm vs. concentration. (d) Plot of PC₇₁BM absorbance at 373 nm vs. concentration.

Reference

1. L. J. Huo, S. Q. Zhang, X. Guo, F. Xu, Y. F. Li, J. H. Hou, *Angew. Chem. Int. Ed.*, 2011, **50**, 9697.
2. A. Hexemer, W. Bras, J. Glossinger, E. Schaible, E. Gann, R. Kirian, A. MacDowell, M. Church, B. Rude, H. Padmore, *J. Phys. Conf. Ser.*, 2010, **247**, 012007.
3. E. Gann, A. T. Young, B. A. Collins, H. Yan, J. Nasiatka, H. A. Padmore, H. Ade, A. Hexemer, C. Wang, *Rev. Sci. Instrum.*, 2012, **83**, 045110.

