Supporting Information

TPD-Based Polythiophene Derivatives with Higher V_{oc} for Polymer Solar Cells

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Experimental Section

I. Measurements

^{1}H NMR and ^{13}C NMR spectra of the monomers and the polymers were measured on a Bruker ARX-400 spectrometer. UV-vis absorption spectra were taken on an Agilent Technologies Cary Series UV-Vis-NIR Spectrophotometer. The electrochemical cyclic voltammetry (CV) was conducted on a Zahner Ennium Electrochemical Workstation with glassy carbon disk, Pt wire, and Ag/Ag^{+} electrode as working electrode, counter electrode, and reference electrode respectively in a 0.1 mol L^{-1} tetrabutylammonium

hexafluorophosphate (Bu_4NPF_6) acetonitrile solution at a scan rate of 50 mV s^{-1}. The thermo-gravimetric analysis (TGA) was carried out on a TA Instruments, Inc., discovery instrument under purified nitrogen gas flow with a 10 °C min^{-1} heating rate. Differential scanning calorimeter (DSC) was carried out on a TA Instruments, Inc., Q200 instrument under purified nitrogen gas flow with a 5 °C min^{-1} heating rate. GPC measurement was performed on Agilent Technologies, PL-GPC 220 High Temperature Chromatograph using 1,2,4-trichlorobenzene as the eluent at 160 ^{o}C. X-ray diffraction (XRD) of the polymers were carried out on a X'Pert-Pro MRD diffractomer from PANalytical B.V. Transmission electron microscopy (TEM) was performed using a Tecnai G2 F20 S-Twin instrument at 200 kV accelerating voltage. Atomic force microscope (AFM) was performed using a Veeco Dimension 3100 instrument.

II. **Device fabrication and characterization**

Polymer solar cells (PSCs) were fabricated by routine methods, the details of the device fabrication and characterization were described in the following:

PSCs with the structure of ITO/PEDOT: PSS/polymer: $PC_{71}BM$/buller layer/Al were fabricated under the conditions as follows: patterned indium tin oxide (ITO)-coated glass with a sheet resistance of 10-15 ohm/square was cleaned by a surfactant scrub and then underwent a wet-cleaning process inside an ultrasonic bath, beginning with deionized water followed by acetone and isopropanol. After oxygen plasma cleaning for 10 min, a 30 nm thick poly(3, 4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) (Bayer Baytron 4083) anode buffer layer was

spin-cast onto the ITO substrate and then dried by baking in an oven at 150 ^{o}C for 15 min. The active layer was then deposited on top of the PEDOT: PSS layer by spin-coating a 10 mg ml^{-1} *o*-dichlorobenzene blend solution of polymer and $PC_{71}BM$. The thickness of the active layer was controlled by changing the spin speed during the spin-coating process and measured on an Ambios Tech. XP-2 profilometer. Finally, 20 nm Ca and 80 nm Al layer were successively deposited in vacuum onto the active layer at a pressure of ca. 4×10^{-4} Pa. The overlapping area between the cathode and anode defined a pixel size of 4 mm^2. Except for the deposition of the PEDOT: PSS layers, all the fabrication processes were carried out inside a dry box containing less than 5 ppm oxygen and moisture.

The current density-voltage (*J-V*) curves of the PSCs were measured with a Keithley 236 Source Measure unit, under the illumination of AM 1.5G, 100 mW cm^{-2} using a xenon-lamp- based solar simulator (SAN-EI ELECTRIC CO., LTD.). The external quantum efficiency (EQE) was measured by Solar Cell Spectral Response Measurement System QE-R3011 (Enli Technology CO., Ltd.). The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell.

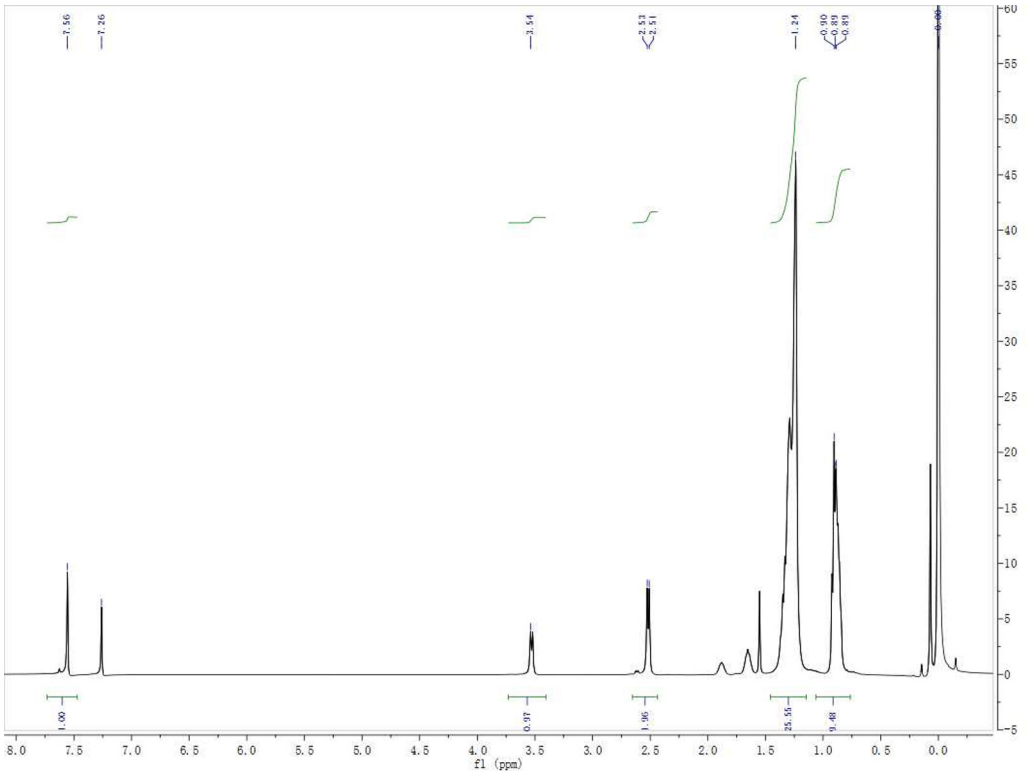

Fig. S1. ^{1}H NMR spectrum of monomer **TPD**

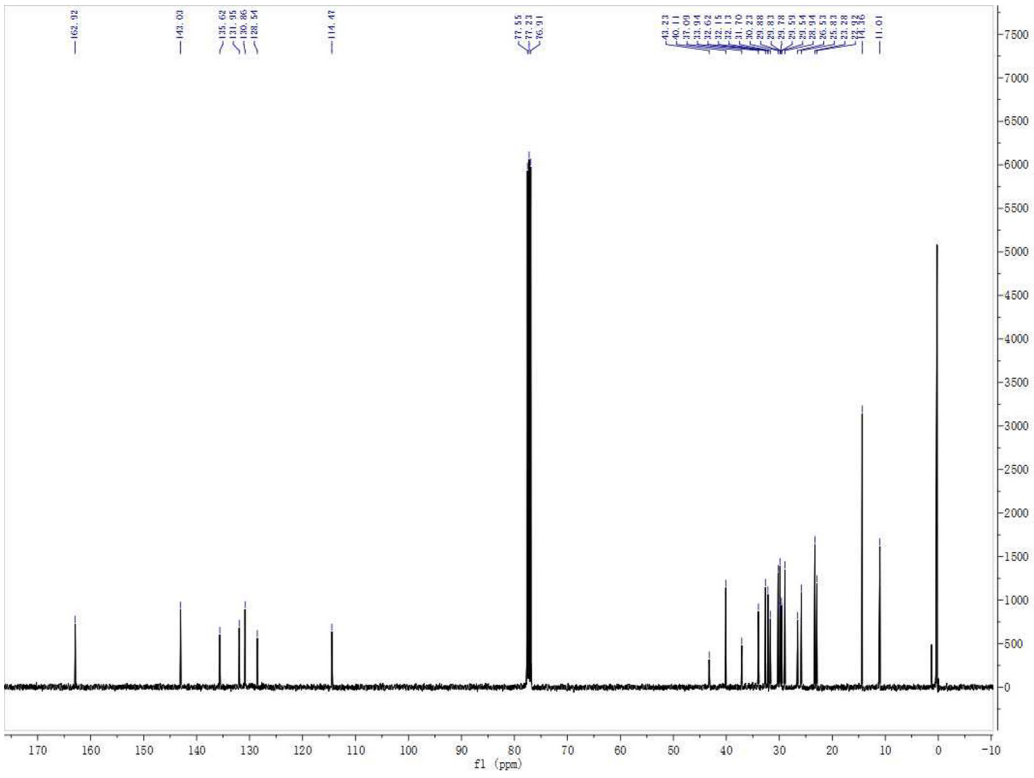

Fig. S2. ^{13}C NMR spectrum of monomer **TPD**

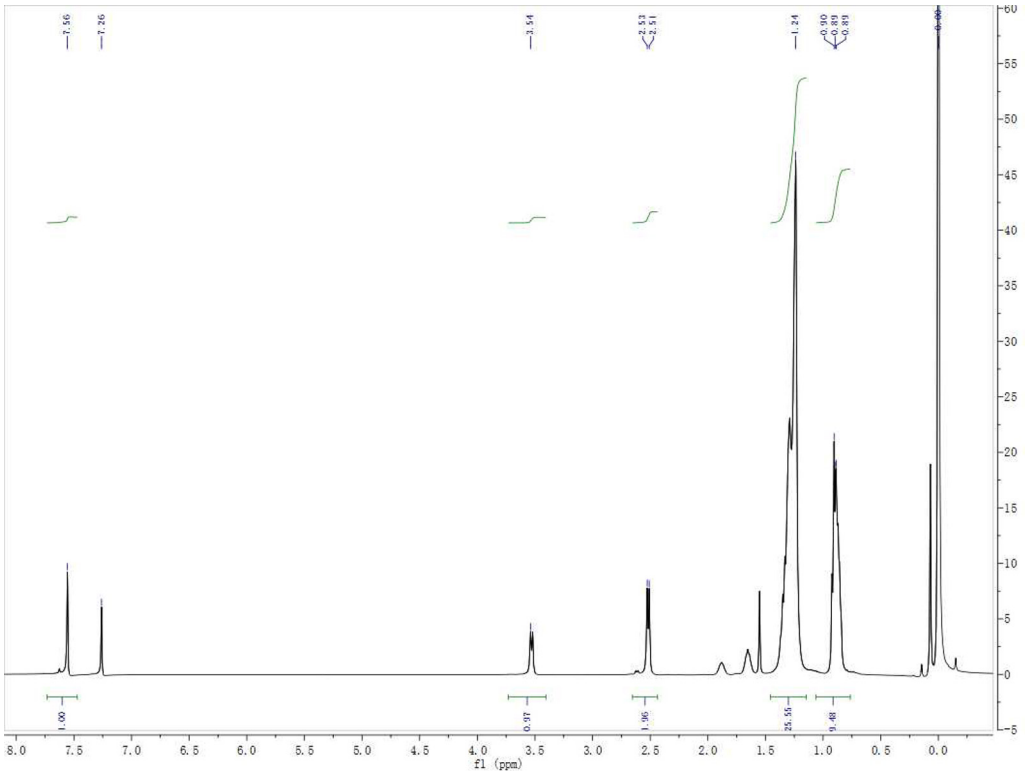

Fig. S3. ^{1}H NMR spectrum of monomer **DT**

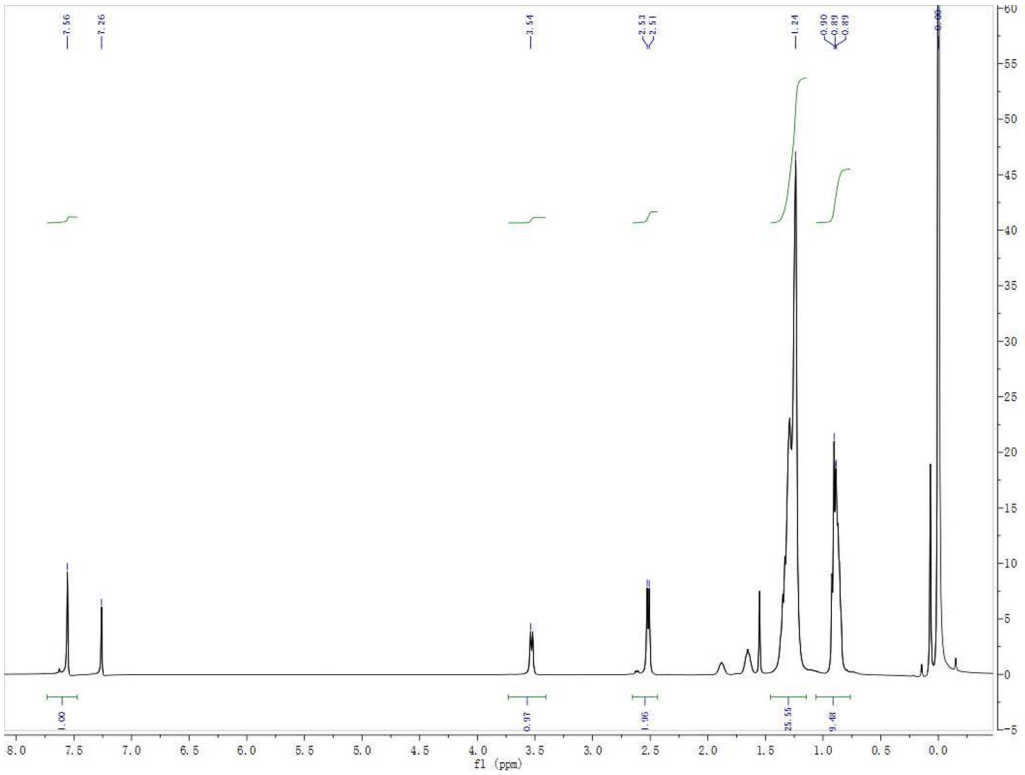

Fig. S4. ^{1}H NMR spectrum of monomer **DFDT**

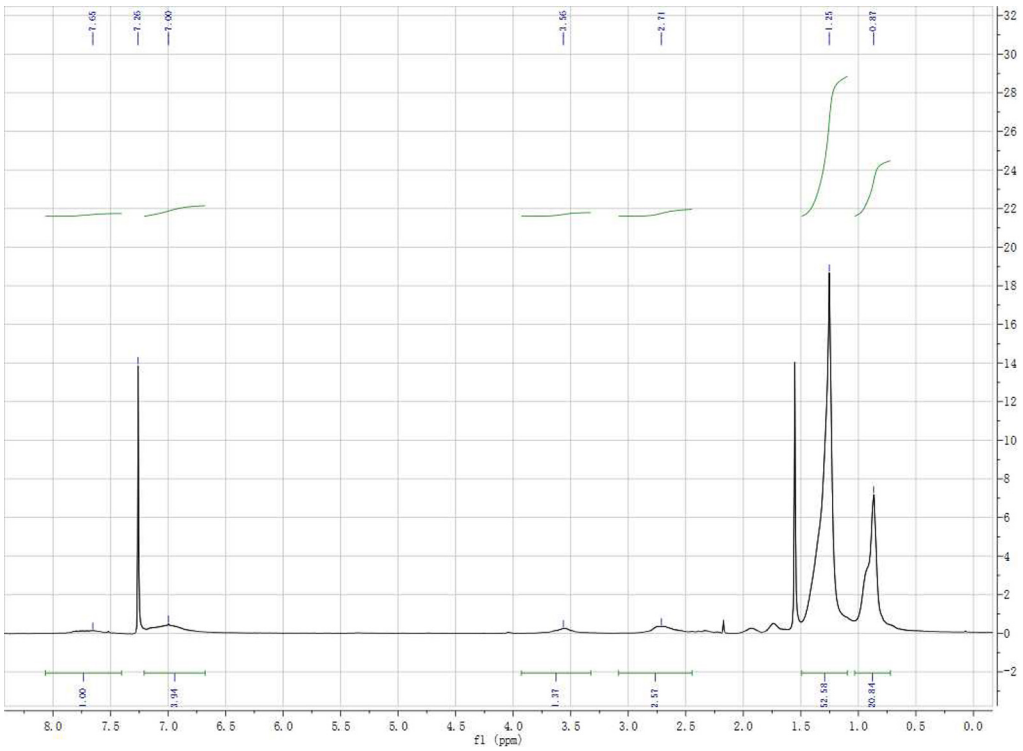

Fig. S5. ^{1}H NMR spectrum of **PTPD-DT**

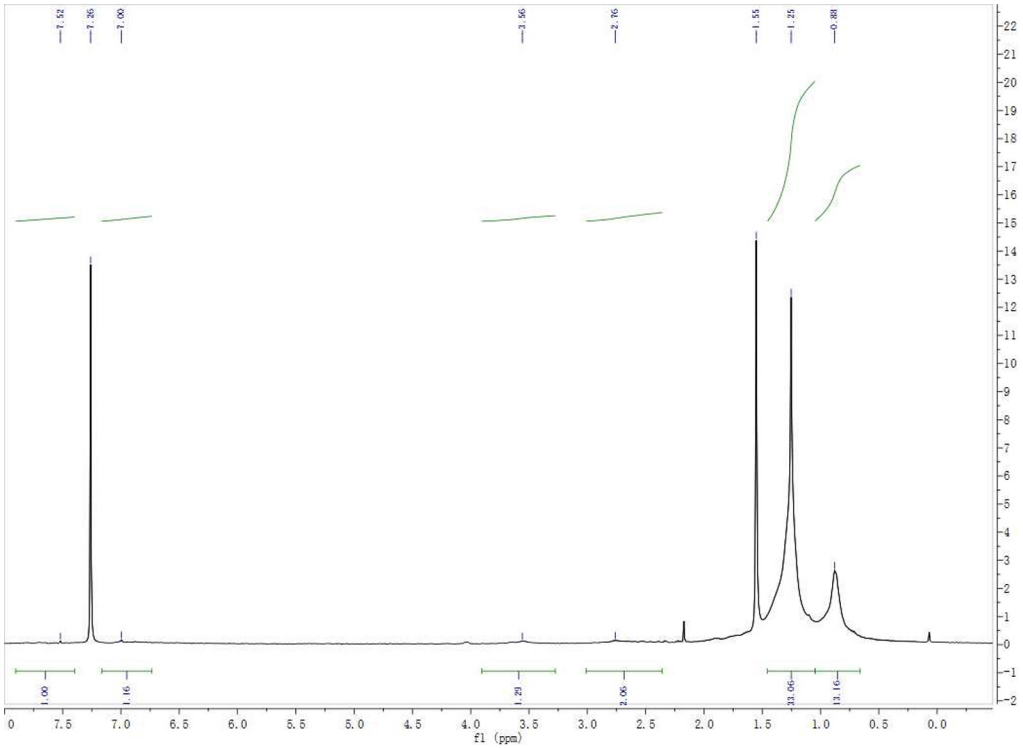

Fig. S6. ^{1}H NMR spectrum of **PTPD-DFDT**

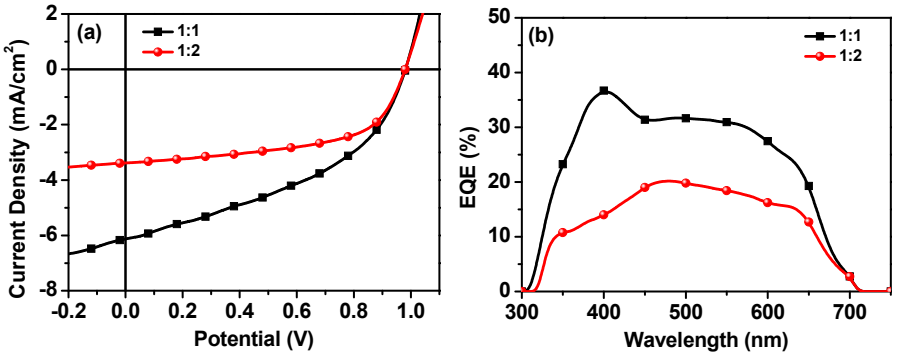

Fig. S7 (a) *J–V* characteristics, (b) EQE curves of devices based on **PTPD-DFDT**: $PC_{71}BM$ blend film with D/A weight ratios of 1:1 and 1:2.

Table S1. Photovoltaic performance parameters of the PSCs based on **PTPD-DFDT** as donor and $PC_{71}BM$ as acceptor with D/A weight ratios of 1:1 and 1:2 under illumination of AM 1.5 G, 100 mW cm^{-2}.

D/A ratio	V_{oc} (V)	J_{sc} (mA cm^{-2})	J_{sc} (mA cm^{-2}) [a]	FF (%)	PCE (%)
1:1	0.98	6.12	5.68	42.6	2.56
1:2	0.98	3.38	3.24	57.2	1.90

[a] Integrated from EQE,

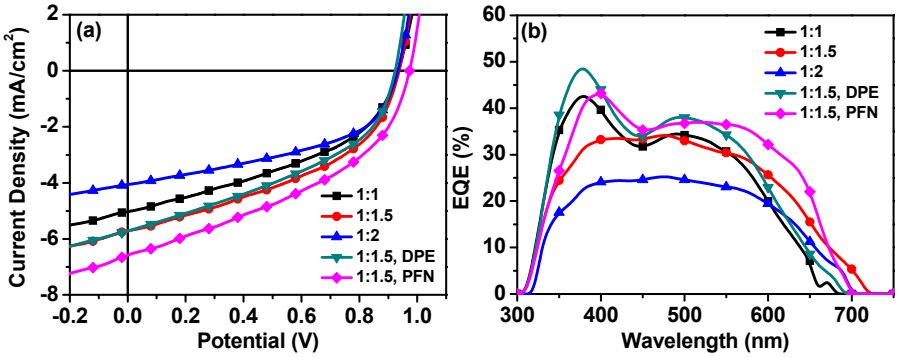

Fig. S8 (a) *J–V* characteristics, (b) EQE curves of devices based on **PTPD-DT**: $PC_{71}BM$ blend film with different conditions.

Table S2. Photovoltaic performance parameters of the PSCs based on **PTPD-DT** as donor and $PC_{71}BM$ as acceptor with different conditions under illumination of AM 1.5 G, 100 mW cm^{-2}.

D/A ratio	V_{oc} (V)	J_{sc} (mA cm^{-2})	J_{sc} (mA cm^{-2}) [a]	FF (%)	PCE (%)
1:1	0.94	5.02	4.71	42.0	1.97
1:1.5	0.94	5.72	5.25	43.3	2.32
1:2	0.93	4.06	3.86	47.4	1.79
1:1.5[b]	0.92	5.72	5.32	41.3	2.18
1:.5[c]	0.93	6.15	6.12	43.3	2.48

[a] Integrated from EQE, [b] with 3% DPE as solvent additive, [c] with PFN as buffer layer.

Table S3. Photovoltaic performance parameters of the PSCs based on **PTPD-DT** as donor and $PC_{71}BM$ as acceptor with different additives (w/w, 1:1.5) under illumination of AM 1.5 G, 100 mW cm^{-2}.

Additive (3%)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
without	0.94	5.72	43.3	2.32
DIO	0.92	3.20	46.5	1.36
CN	0.93	5.30	41.8	2.05
NMP	0.91	4.05	41.3	1.52
DPE	0.92	5.72	41.3	2.18

Table S4. Photovoltaic performance parameters of the PSCs based on **PTPD-DFDT** as donor and $PC_{71}BM$ as acceptor with different additives (w/w, 1:1.5) under illumination of AM 1.5 G, 100 mW cm^{-2}.

Additive (3%)	V_{oc} **(V)**	J_{sc} **(mA** cm^{-2}**)**	**FF (%)**	**PCE (%)**
without	0.98	6.03	47.4	2.80
DIO	0.97	7.54	47.6	3.47
CN	0.96	8.11	50.5	3.94
NMP	0.93	9.54	47.3	4.20
DPE	0.96	10.25	54.0	5.31

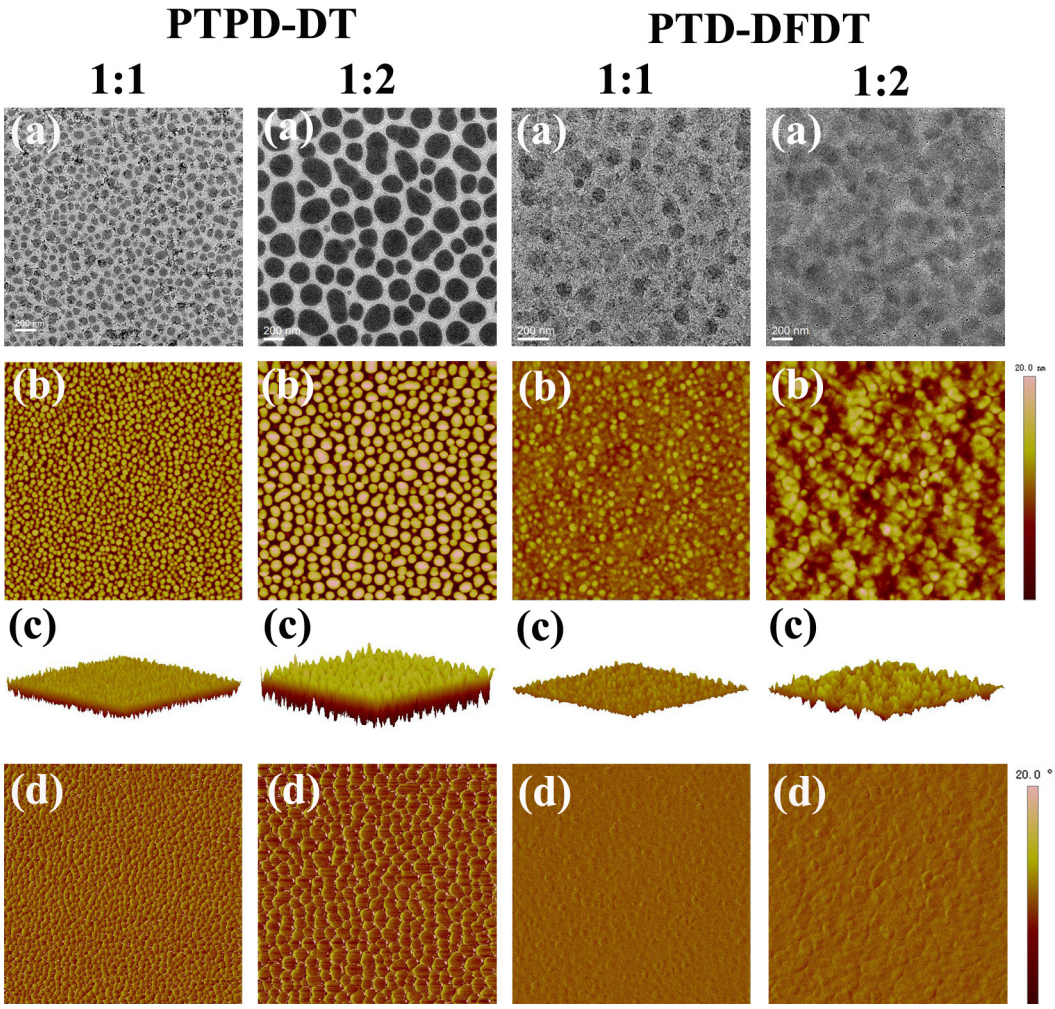

Fig. S9. TEM images and Tapping-mode AFM images of **PTPD-DT or PTPD-DFDT**: $PC_{71}BM$ blend films. TEM images (a), AFM (all 5 × 5 μm) height images (b), three-dimensional height images (c) and topography images (d) of the blend films with D/A ratio of 1:1 and 1:2. The R_q of the blend films are 3.35 nm for **PTPD-DT** with D/A of 1:1; 7.30 nm for **PTPD-DT** with D/A of 1:2; 1.49 nm for **PTPD-DFDT** with D/A of 1:1 and 2.99 nm for **PTPD-DFDT** with D/A of 1:2, respectively.

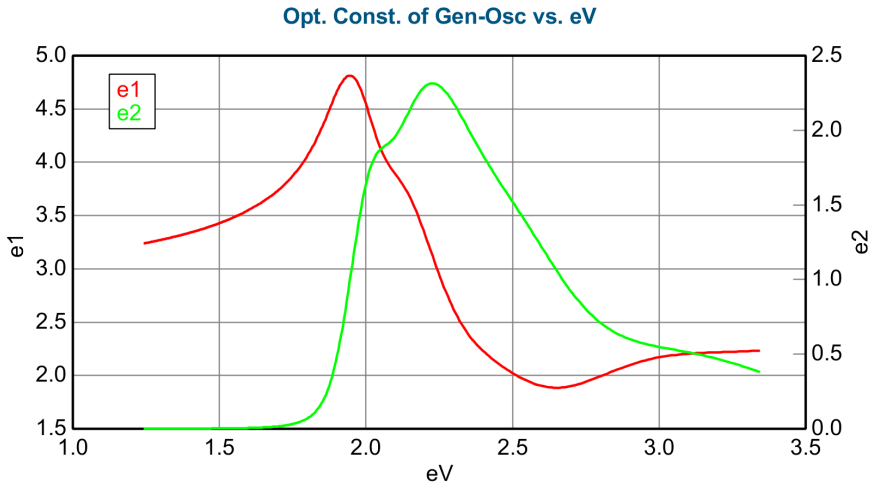

Fig. S10. Dielectric constant of PTPD-DT

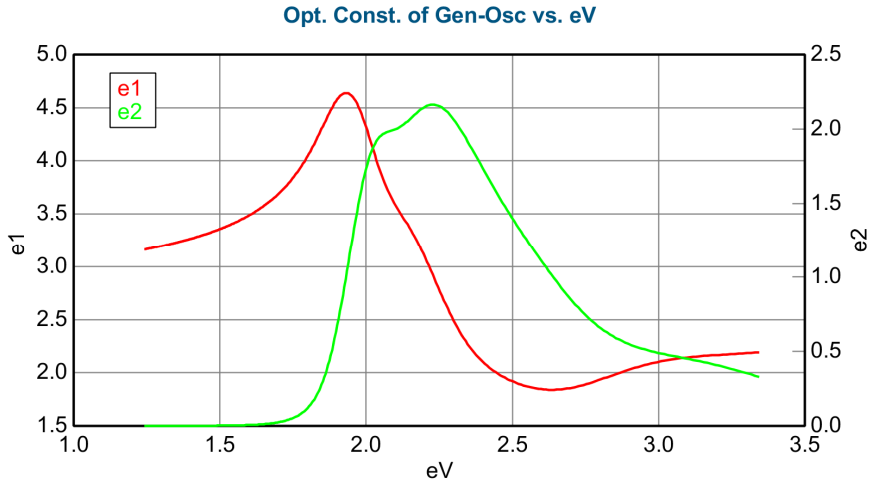

Fig. S11. Dielectric constant of PTPD-DFDT