Supporting Information for

Monodisperse Cooligomer Approach toward Nanostructured Films with Alternating Donor-Acceptor Lamellae

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General Methods

Preparative gel-permeation chromatography (PGPC) purification was carried out with a JAI LC-9104 recycling preparative high performance liquid chromatograph (JAIGEL 2H/3H column assembly) with toluene as eluent. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV 300-MHz spectrometer in $CDCl_3$ with trimethylsilane (TMS) as an internal standard. Elemental analysis was carried out on a FlashEA1112 elemental analysis system. MALDI-TOF mass spectra were recorded on a Bruker/AutoflexIII Smartbean MALDI Mass Spectrometer with anthracene-1,8,9-triol as the matrix. Cyclic voltammetry (CV) was performed on a CHI660a electrochemical analyzer with a three-electrode cell in a solution of 0.1 mole L^{-1} tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in anhydrous CH_2Cl_2 at a scanning rate of 50 mV s^{-1}. A platinum (Pt) electrode with a diameter of 2 mm, a Pt wire and a saturated calomel electrode (SCE) were used as the working, the counter and the reference electrodes, respectively. UV-vis absorption was recorded on a Shimadzu UV3600 spectrometer. Differential scanning calorimetry (DSC) measurements were performed on a TA Q100 thermal analyzer at scanning rate of 10 ^{o}C min^{-1}. Small angle X-ray scattering (SAXS) was recorded on a Bruker Nanostar instrument operated at 40KV and 35mA. Powders for SAXS measurements were collected with slow evaporation of cooligomers CH_2Cl_2 solution.

Transmission electron microscopy (TEM) characterization. To prepare cooligomer films for TEM observations, 50 nm poly (3, 4-ethylene dioxythiophene):poly(styrene sulphonate) (PEDOT:PSS) was first spin-cast on precleaned glass slides. After heating the substrates at 120

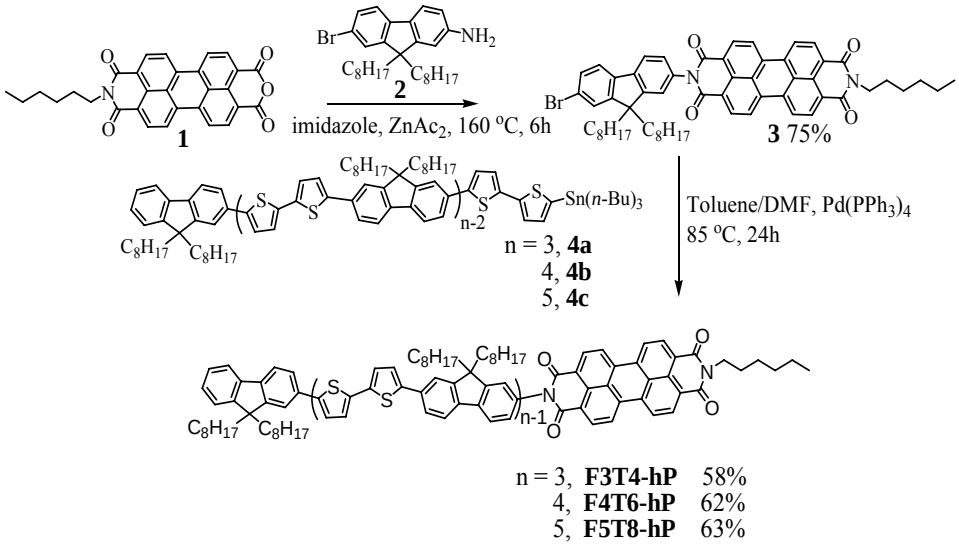
^{o}C for 30 min, 70 nm cooligomer layers were spin-coated from 16 mg/mL chlorobenzene solutions in N_2 filled glovebox. The films were then heated at 210 ^{o}C for two min or put in CH_2Cl_2 atmosphere for 20 min as noted. Finally, films were floated with water to micro grids and dried at ambient conditions. TEM was performed on a JEOL JEM-1011 transmission electron microscope operated at an acceleration voltage of 100 kV. Selected area electron diffractions (SAED) were taken with cameral length of 160 cm and Au (111) diffraction as the external standard.

Solar cell fabrication and measurement. Cooligomer films were prepared in the same way as those for TEM observation, except for that indium-tin-oxide (ITO) glass instead of glass slides were used as the substrates. After the preparation of cooligomers films or **OFbT**/**epPDI** blend films, N,N'-bis(1-ethylpropyl)-3,4,9,10-perylenetetracarboxyl diimide (**epPDI**) hole blocking-layer (3 nm), LiF (1 nm) and Al electrode (100 nm) were thermal evaporated successively in vacum. The active area of the unit cell is 3.14 mm^2. The current-voltage measurements of devices were conducted under AM 1.5G solar simulation at 100 mW cm^{-2} using a computer-controlled Keithley 2400 source meter. The external quantum efficiency (EQE) was measured with a lock-in amplifier after illumination with monochromatic light from a xenon lamp, and was calibrated against a multicrystalline Si solar cell with a known spectral response.

Synthesis and characterization

Toluene was distilled over sodium/benzophenone. N, N-dimethyl formamide (DMF) was distilled over CaH_2 under reduced pressure. Compounds N,N'-bis(1-ethylpropyl)-3,4,9,10-perylenetetracarboxyl diimide (**epPDI**),[1] **1**,[1] **2**[2], **4**[3], **F4Th6**[3] and **F5Th8**[3] were synthesized according to the procedures reported in the literatures. Other reagents were obtained from commercial resources and used without further purification.

Scheme S1. Synthetic route of **F3T4-hP, F4T6-hP and F5T8-hP.**



Compound 3. A mixture of N-hexylperylene-3,4:9,10-tetracarboxylic 3,4-anhydride 9,10-imide (**1**, 0.48 g, 1.00 mmol), (9,9-dioctylfluoren-2-yl)amine (**2**, 0.73 g, 1.50mmol), imidazole (20 g) and zinc acetate (0.20 mg) were stirred at 160 ^{o}C for 4 hours under argon. After cooling to room temperature, the mixture was washed with water, 10% HCl and then diluted KOH aqueous solution. The crude product was dried at 80 ^{o}C under vacuum, and then purified with column chromatography on silica gel with CH_2Cl_2 as eluent to yield 0.72 g (75 %) product as a dark-red solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.70 (d, J = 8.01H_Z, 2H), 8.63 (d, J = 8.01H_Z, 2H), 8.54 (m, 4H), 7.85 (d, *J* = 8.22 Hz, 1H), 7.62 (d, J = 8.67H_Z, 2H), 7.51-7.49 (m, 2H), 7.37-7.35 (m, 2H), 4.23-4.18 (m, 2H), 1.97 (m, 4H), 1.76 (m, 2H), 1.41-1.36 (m, 6H), 1.26-1.10 (m, 20H), 0.91 (t, *J* = 7.04 Hz, 3H) 0.84 (t, *J* = 6.93 Hz, 6H), 0.73(m, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.5, 16.3, 153.9, 151.8, 140.8, 139.9, 134.6, 134.2, 131.5, 131.1,

130.5, 128.0, 126.7, 126.1, 124.1, 123.8, 123.5, 123.1, 121.8, 120.8, 56.1, 41.1, 40.4, 32.2, 31.9, 30.4, 29.6, 28.4, 27.3, 24.2, 23.0, 14.5 ppm. Elemental analysis (%) calcd for $C_{59}H_{61}BrN_2O_4$ (940.38): C 75.22, H 6.53, found: C 74.95, H 6.30. MS (MALDI-TOF, reflection mode): *m/z* 941.37 $[M+H]^+$.

Preparation of cooligomers F3T4-hP, F4T6-hP, F5T8-hP.

General procedure for the synthesis of these cooligomers is exemplified by the synthesis of **F3T4-hP**: In absence of light, a solution of compound **3** (0.49 g, 0.52 mmol), compound **4a** (0.73 g, 0.52 mmol), and $Pd(PPh_3)_4$ (3.0 mg, 2.6 x 10^{-6} mol) in anhydrous DMF/toluene (5 mL, v/v=1:4) was stirred at 85 ^oC for 24 hours. The mixture was cooled to room temperature and then poured into a large amount of ethanol. The precipitate was collected by vacuum filtration and then purified with column chromatography on silica gel with dichloromethane as eluent and further purified with PGPC to afford a dark-red solid (0.60g, 58 %). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.70 (d, *J* = 7.89 Hz, 2H), 8.62 (d, *J* = 7.92 Hz, 2H), 8.53-8.50 (m, 4H), 7.89 (d, *J* = 8.76 Hz, 1H), 7.77 (d, *J* = 7.92 Hz, 1H), 7.71-7.66 (m, 4H), 7.63-7.57 (m, 8H), 7.38-7.31 (m, 9H), 7.23-7.20 (m, 4H), 4.24-4.19 (m, 2H), 2.03 (m, 12H), 1.78 (m, 2H), 1.47-1.38 (m, 6H), 1.20-1.09 (m, 60H), 0.91 (t, *J* = 7.01 Hz, 3H), 0.85-0.78 (m, 18H), 0.69(m, 12H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.6,163.2, 152.6, 152.3, 152.0, 151.3, 144.3, 144.2, 141.3, 141.0, 140.7, 137.0, 136.8, 134.4, 133.6, 133.4, 133.2, 131.5, 131.0, 129.7, 129.1, 128.0, 127.6, 127.3, 126.1, 125.1, 124.9, 123.9, 123.4, 123.3, 120.6, 120.5, 120.2, 55.9, 55.8, 55.6, 40.8, 32.3, 32.2, 32.0, 30.5, 30.4, 29.6, 28.5, 27.3, 24.2, 23.0, 14.5, 14.4 ppm. Elemental analysis (%) calcd for $C_{133}H_{150}N_2O_4S_4$ (1967.05): C 81.13, H 7.68, found: C 81.49, H 8.05. MS (MALDI-TOF, reflection mode): *m/z*: 1967.05 $[M]^+$.

F4T6-hP: Dark-red solid in a yield of 62%. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.72-8.62 (m, 8H), 7.86 (d, J = 8.61 H_Z, 1H), 7.74-7.56 (m, 19H), 7.32 (m, 11H), 7.21 (m, 6H), 4.23-4.18 (m, 2H), 2.01 (m, 16H), 1.78 (m, 2H), 1.47-1.36 (m, 6H), 1.20-1.09 (m, 80H), 0.91 (m, 3H), 0.85-0.78 (m, 24H), 0.69(m, 16H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.3,162.0, 151.2, 150.8, 149.9, 142.8, 139.9, 135.6, 133.3, 133.0, 129.9, 126.5, 126.2, 125.9, 124.9, 123.7, 123.5,

122.7, 122.2, 121.9, 119.3, 118.7, 54.4, 54.2, 39.4, 30.8, 30.6, 29.0, 28.2, 27.1, 25.9, 22.8, 21.6, 13.1 ppm. Elemental analysis (%) calcd for $C_{170}H_{194}N_2O_4S_6$ (2519.34): C 80.97, H 7.75, found: C 80.65, H 8.23. MS (MALDI-TOF, reflection mode): *m/z* 2519.35 $[M]^+$.

F5T8-hP: Dark-red solid in a yield of 63%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.78-8.65 (m, 8H), 7.88 (d, J = 8.46 H_Z, 1H), 7.78-7.57 (m, 26H), 7.34 (m, 13H), 7.23 (m, 8H), 4.25-4.20 (m, 2H), 2.03 (m, 20H), 1.78 (m, 2H), 1.47-1.36 (m, 6H), 1.20-1.09 (m, 100H), 0.91 (m, 3H), 0.85-0.78 (m, 30H), 0.71(m, 20H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.3,162.0, 151.2, 150.8, 150.6, 149.9, 142.8, 139.9, 139.6, 139.2, 135.5, 132.2, 131.9, 131.8, 130.4, 120.0, 126.2, 125.9, 123.7, 123.5, 122.7, 122.2, 121.9, 119.3, 119.1, 118.7, 54.4, 54.4, 54.2, 39.4, 30.8, 30.6, 29.0, 28.2, 27.1, 25.9, 22.8, 21.6, 13.1 ppm. Elemental analysis (%) calcd for $C_{207}H_{218}N_2O_4S_8$ (3071.52): C 80.86, H 7.80, found: C 80.55, H 8.30. MS (MALDI-TOF, reflection mode): *m/z* 3071.63 $[M]^+$.

References

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(2) a) W. E. Kuhn, *Org. Syn.*, **1943**, *Coll. Vol. 2,* p.447; b) C. J. Kelley, A. Ghiorghis, J. M. Kauffman, *J. Chem. Research (S)*, **1997**, 446-447; c) G. Saroja, P. Z. Zhang, N. P. Ernsting, J. Liebscher, *J. Org. Chem.*, **2004**, *69,* 987- 990.

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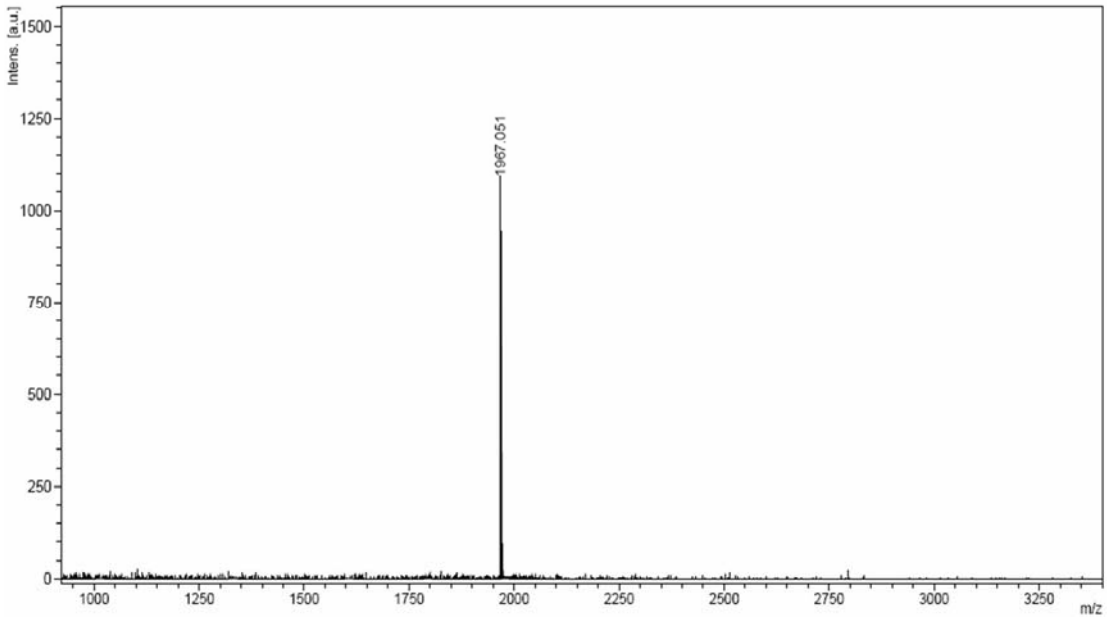

Figure S1. MALDI-TOF mass spectrum of **F3T4-hP**.

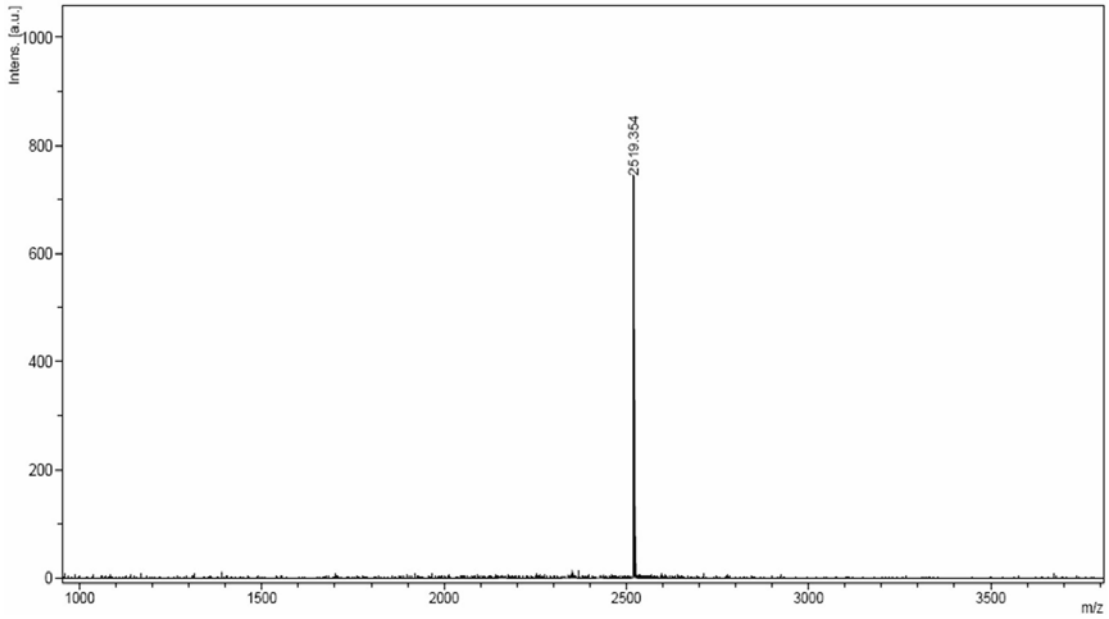

Figure S2. MALDI-TOF mass spectrum of **F4T6-hP**.

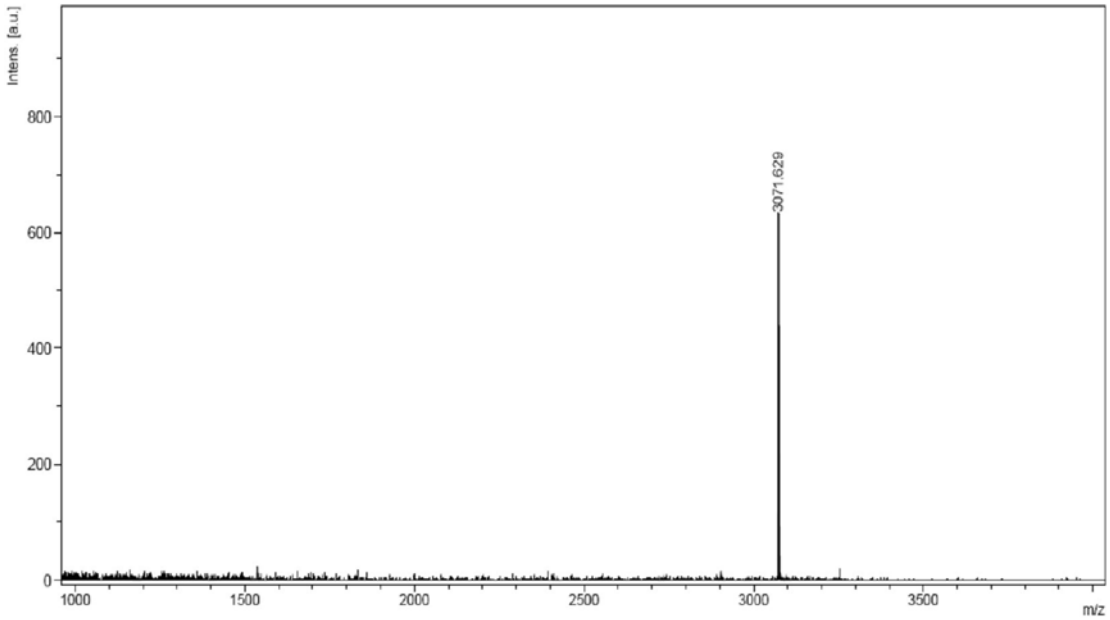

Figure S3. MALDI-TOF mass spectrum of **F5T8-hP**.

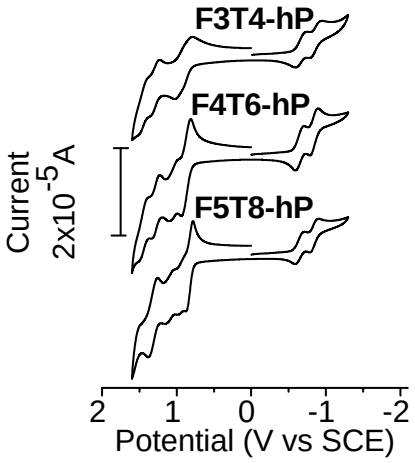

Figure S4. Cyclic voltammograms of three cooligomers (10^{-3} M) in CH_2Cl_2 solution. Redox waves at positive and negative potentials are attributed to **OFbT** and **PDI** blocks, respectively. Calculated from the redox onset potentials, the LUMO energy levels of **PDI** blocks were 3.90 eV for **F3T4-hP**, 3.91eV for **F4T6-hP** and 3.91eV for **F5T8-hP**, and HOMO energy levels of **OFbT** blocks were 5.27 eV for **F3T4-hP**, 5.27 eV for **F4T6-hP** and 5.26 eV for **F5T8-hP**.

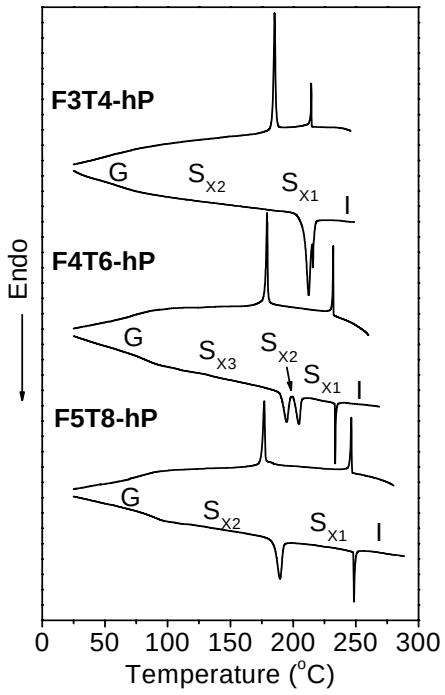

Figure S5. DSC curves of **F3T4-hP**, **F4T6-hP** and **F5T8-hP** at scanning rate of 10 °C/min in N_2.

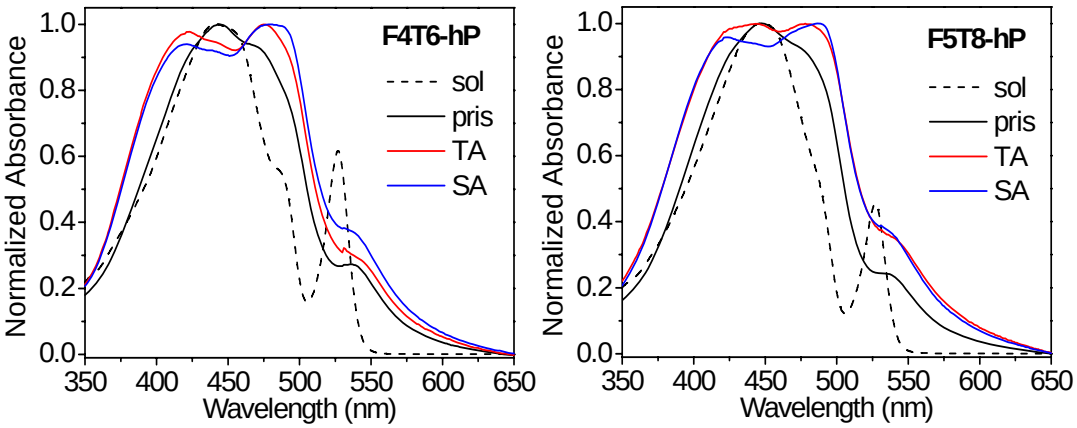

Figure S6. UV-vis absorption spectra of **F4T6-hP** and **F5T8-hP**: solution in chloroform (4 x 10^{-6} M) (sol), pristine film (pris), thermal annealed film (TA) and solvent-vapor annealed film (SA). Films were spin-coated from 16 mg/mL chlorobenzene solutions on quartz with thickness of ~70 nm. Thermal and solvent-vapor annealings were conducted in the same way as those for TEM observation and solar cell preparation.

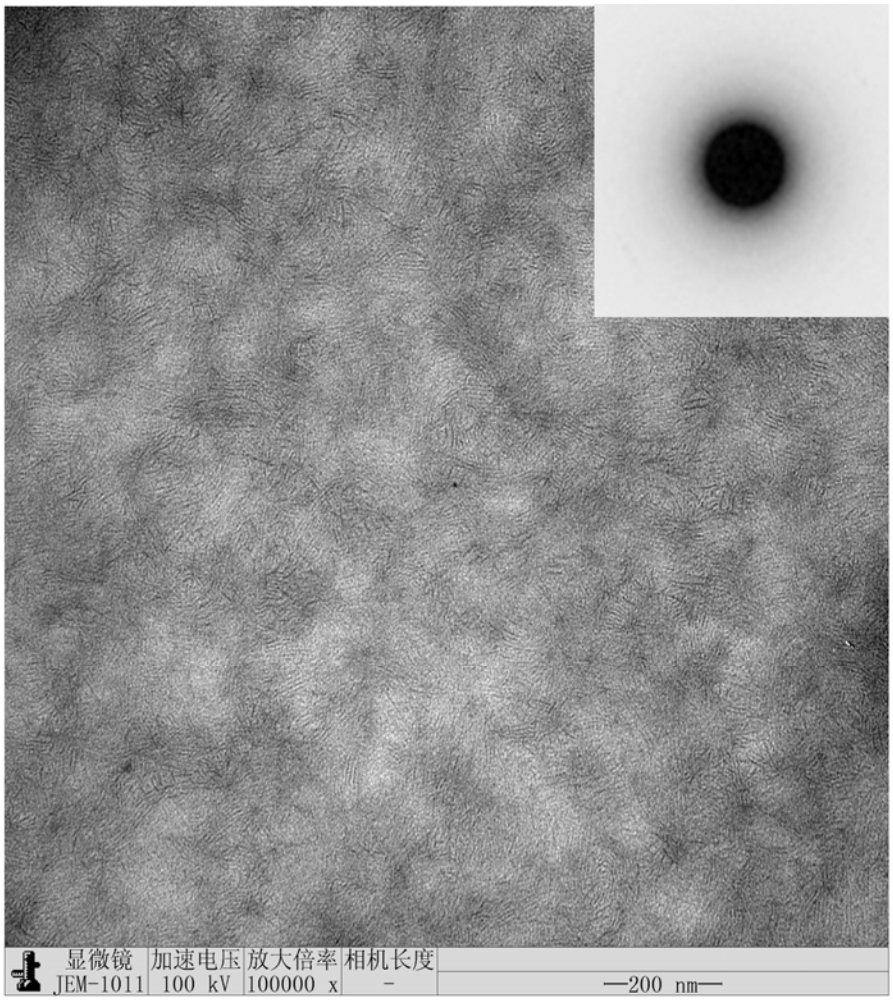

Figure S7. TEM image of **F5T8-hP** pristine film with thickness of ~70 nm, which was cast from 16 mg/mL chlorobenzene solution on 50 nm PEDOT:PSS coated glass then floated with water to micro grid. Inset is the corresponding SAED.

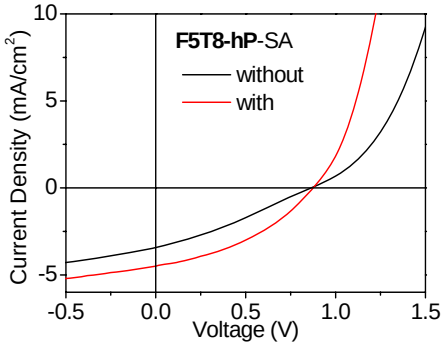

Figure S8. I-V characteristics of photovoltaic devices with or without **epPDI** hole blocking layer based on **F5T8-hP** solvent-vapor annealed films.

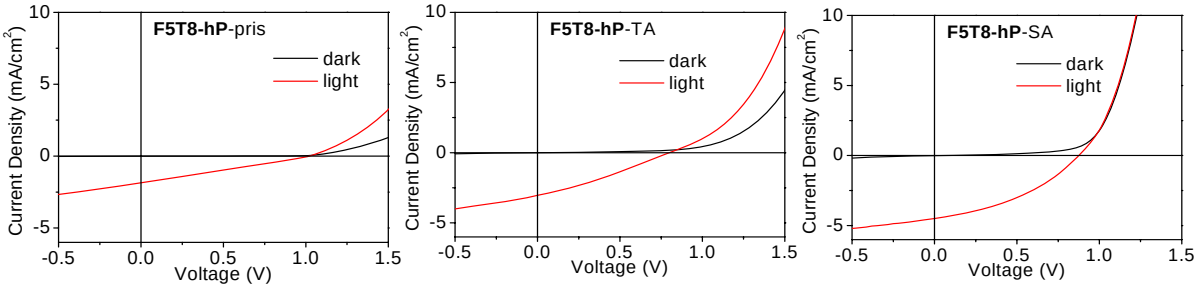

Figure S9. I-V characteristics of photovoltaic devices constructed from pristine (pris), thermal annealed (TA) and solvent-vapor annealed (SA) **F5T8-hP** films.

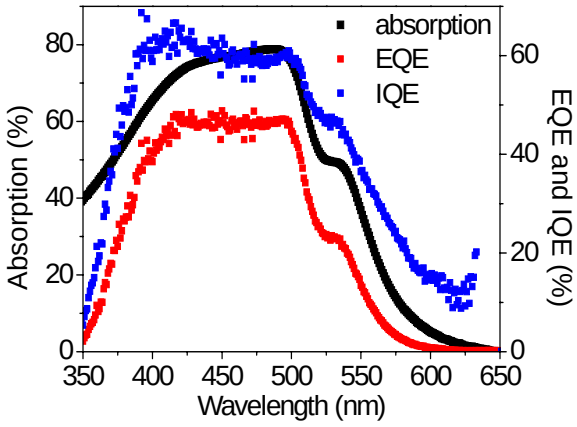

Figure S10. Absorption spectrum of a 70 nm solvent-vapor annealed (SA) **F5T8-hP** film covered with 3 nm **epPDI** and 100 nm Al as measured in the reflection mode, and external quantum efficiency (EQE) and internal quantum efficiency (IQE) curves of the corresponding solar cell.

Table S1. Device data of **F3T4-hP**, **F4T6-hP**, **F5T8-hP** and **OFbT**/**PDI** blends with a device structure of ITO/PEDOT:PSS (50 nm)/sample (70 nm)/**epPDI** (3 nm)/LiF (1 nm)/Al (100 nm).

		V_{OC} (V)	J_{SC} (mA/cm^2)	FF	PCE (%)
F3T4-hP	pris	0.92	0.91	0.18	0.15
		0.92	0.86	0.19	0.15
		0.94	0.96	0.18	0.16
	TA	0.84	2.80	0.23	0.54
		0.82	2.77	0.24	0.54
		0.82	3.02	0.25	0.61
	SA	0.90	3.16	0.25	0.70
		0.86	3.02	0.24	0.62
		0.86	3.13	0.25	0.67
F4T6-hP	pris	0.96	1.51	0.23	0.33
		0.98	1.64	0.23	0.37
		0.94	1.68	0.23	0.36
	TA	0.78	2.71	0.28	0.59
		0.76	2.57	0.28	0.56
		0.80	2.92	0.29	0.68
	SA	0.86	4.05	0.34	1.18
		0.88	3.86	0.31	1.04
		0.85	4.19	0.32	1.14
F5T8-hP	pris	1.01	1.95	0.26	0.51
		1.02	1.85	0.26	0.49
		1.02	1.95	0.26	0.52
	TA	0.80	3.05	0.29	0.71
		0.74	2.97	0.30	0.66
		0.78	3.76	0.28	0.82
	SA	0.87	4.49	0.38	1.50
		0.87	4.32	0.38	1.44
		0.85	4.44	0.38	1.43
F4Th6/epPDI blend	pris	0.88	0.50	0.24	0.11
	TA	0.84	0.56	0.38	0.18
	SA	0.86	0.53	0.41	0.18
F5Th8/epPDI blend	pris	0.80	0.55	0.22	0.10

Note: **epPDI** always formed micrometer-sized crystals upon thermal annealing (TA) or solvent-vapor annealing (SA), consequently, no obvious improvement of device performance was observed after these treatments.