Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information

Conformational locking strategy in linked-acceptor type polymers for organic solar cells

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Experiment Section

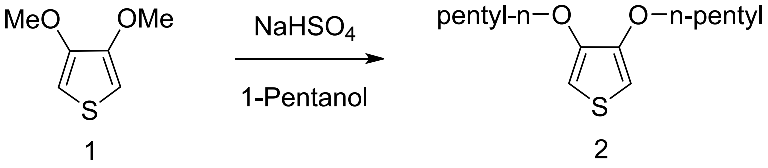
^{1}H NMR (400 MHz) and ^{13}C NMR (400 MHz) spectra were obtained using a Bruker DMX-400 NMR spectrometer with tetramethylsilane as an internal standard. MS spectra (MALDI-TOF-MS) were determined by a Micromass GCT-MS spectrometer. UV–vis spectra were identified with a JASCO-V570 spectrophotometer. Electrochemical CV was conducted on an electrochemical workstation (VMP3 Biologic, France) with a Pt disk coated with a molecular film, a Pt plate, and an Ag^+/Ag electrode acting as the working, counter, and reference electrodes, respectively, in a 0.1 mol L^{-1} tetrabutylammonium phosphorus hexafluoride (Bu_4NPF_6) acetonitrile solution. The AFM images of the neat and blend films were captured on a Nanoscope Ia AFM (Digital Instruments) in tapping mode. The GIWAXS samples were prepared on PEDOT:PSS coated on (indium tin oxide) ITO substrates following the same preparation conditions as those for devices. The data were obtained with an area pilatus 100k detector that had a resolution of 195 × 487 pixels (0.172 mm × 0.172 mm) at an in-house X-ray scattering facility (Xenocs WAXS/SAXS system). The X-ray wavelength was 1.54 Å, and the incidence angle was 0.2°. The thickness of the active layer was measured by a Kla-Tencor D120 profilometer. The *J–V* curves were determined by a Keithley 2420 source-measure unit. The photocurrent was measured under illumination with an Oriel Newport 150 W solar simulator (AM 1.5 G), and the light intensity was calibrated with a Newport reference detector (Oriel PN 91150V). The EQEs of the devices were measured in air with an Oriel Newport system (Model 66902). The mobility of the pristine and blend films were determined using a hole-only SCLC method with the following diode structures for holes ITO/PEDOT:PSS/active layer/Au. *J*–*V* curves were assumed to be in the range of 0–5 V and the results were fitted to a space-charge-limited form.

The ground-state geometries of the oligomers with four repeat units were optimized according to density functional theory (DFT) at the B3LYP/6-31G (d, p) level. For calculation, the alkyl groups were replaced by hydrogen and methyl groups. All of the calculations were performed in the gas phase with the Gaussian 09 program. Given that the combination of electron-rich and electron-deficient moieties in these oligomers is expected to generate a charge-transfer characteristic in the low-lying excitations, the low-lying, optical excited states were evaluated by time-dependent DFT with the long-range corrected functional ωB97x and 6-31G (d, p) basis set. The ω values for this functional were optimized according to the method reported by Stein et al. The optimized ω values were equal to 0.09 and 0.11 bohr^{-1} for the PBDTT-TPD and PBDTT-LTPD tetrameters, respectively. Optical absorption spectra were simulated through a Gaussian broadening of the vertical transition energies and the associated oscillator strengths. The full width at half maximum was set to 0.1 eV.

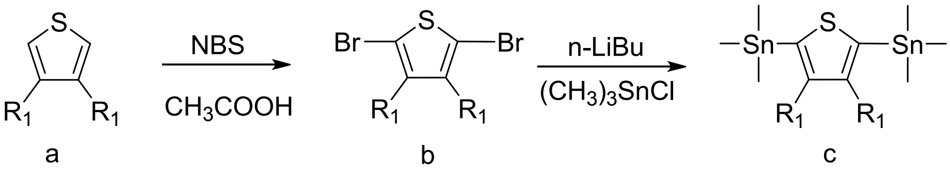
PSC with the structure of (ITO)/(PEDOT:PSS)/polymer:PCBM/Ca/Al were fabricated as follows: A 40 nm layer of PEDOT:PSS was spin-coated onto a cleaned ITO-coated glass substrate. The additive DIO was added prior to the spin-coating process. The thickness of the active layer was controlled by altering the spin speed during this process. The devices were finished by evaporating metal electrodes with an area of 4 mm^2. These areas were defined by masks. Furthermore, the layers were thermally evaporated at a pressure of 2×10^{-6} Torr.

To optimize device performance, D/A weight ratios, and additive ratios (v/v) were applied during device fabrication.

Materials and synthesis. All reagents and chemicals were purchased from Aldrich, Alfa and used as received. Solvents and other common reagents were obtained from the Beijing Chemical Plant. Toluene, chloroform and tetrahydrofuran were freshly distilled prior to use. The other materials were used without further purification. 3,4-dimethoxythiophene (1), n-pentanol, thiophene-3,4-dicarboxylic acid was purchased from Aldrich and used as received. 5-octyl-thieno[3,4-*c*]pyrrole-4,6-dione, 2,6-Bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b*]dithiophene (BDTT-Sn),[1] 1-bromo-5-octyl-thieno[3,4-*c*]pyrrole-4,6-dione (d)[2] were prepared according to the literature procedures.



Compound (2). 3,4-dimethoxythiophene (1) (7.2 g, 50 mmol), n-pentanol (17.6 g, 200 mmol), Anhydrous $NaHSO_4$ (0.6 g, 5mmol) were dissolved in a 100 mL argon purged flask with 25 mL toluene. The reaction was stirred for 5 h at 110 ^{o}C under nitrogen. The reactant was cooled down to room temperature and the solvent was removed under reduced pressure. The crude product was purified by column chromatography using hexanes/ethyl acetate (100:1 ratio) to get the product as colorless liquid. (9.6 g, yield: 75%). MS (EI): m/z = 256. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 6.16 (s, 2H), 3.99-3.96 (t, 4H), 1.86-1.79 (m, 4H), 1.47-1.34 (m, 8H), 0.95-0.92 (t, 6H).



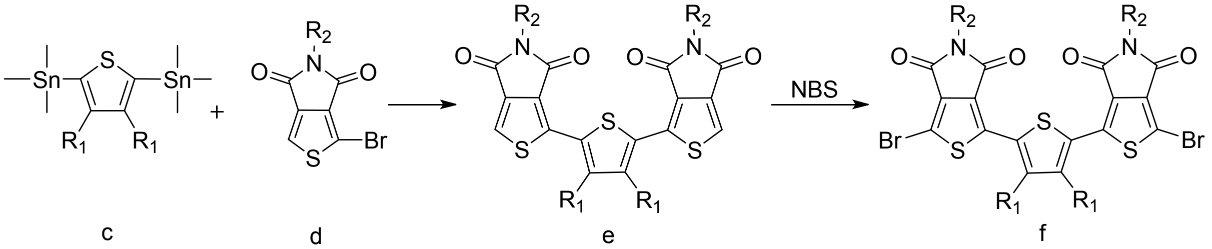
Compound (b). 3,4-dimethoxythiophene (a) (1.2 g, 8.0 mmol) was dissolved in a mixture of chloroform and acetic acid (90 mL) (ratio 10:1). N-bromosuccinimide (NBS) (3.2 g, 18 mmol) was added to the solution in one portion. The reaction was stirred at ambient temperature for 3 h. The reaction solution was poured into water and extracted three times with chloroform. The organic phases were combined and the solvent was removed under reduced pressure. The crude product was purified by column chromatography using hexane as the eluent to afford the product as a colorless liquid (2.1 g, yield: 90%). MS (MALDI-TOF-MS): m/z = 301.8. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 3.82 (s, 6H).

3,4-dipentyloxy-2,5-dibromothiophene was synthesized according the same procedure. 3,4-dipentyloxythiophene (a) (2.0 g, 8.0 mmol) was dissolved in a mixture of chloroform and acetic acid (90 mL) (ratio 10:1). N-bromosuccinimide (NBS) (3.2 g, 18 mmol) was added to the solution in one portion. The reaction was stirred at ambient temperature for 3 h. The reaction solution was poured into water and extracted three times with chloroform. The organic phases were combined and the solvent was removed under reduced pressure. The crude product was purified by column chromatography using hexane as the eluent to afford the product as a colorless liquid (3.1 g, yield: 95%). MS (MALDI-TOF-MS): m/z = 413.9. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 4.06–4.03 (t, 4H), 1.76–1.70 (m, 4H), 1.48–1.32 (m, 8H), 0.92 (t, 6H).

Compound (c). 3,4-dimethoxy-2,5-dibromothiophene (b) (0.72 g, 2.4 mmol) was poured into a 100 mL argon purged flask with 30 mL THF at –78 ^oC, and then *n*-butyllithium (2.4 M, 2.2

mL, 5.3 mmol) was added within 30 min. After the reaction was stirred for 3h at –78^{o}C, chlorotrimethylstannane (1.0 M in THF, 6 mL, 6 mmol) was added and the mixture was stirred for an additional 1 h at –78 ^{o}C. Then the mixture was stirred overnight at ambient temperature. The mixture was poured into water and extracted three times with hexane. The organic phases were combined and the solvent was removed under reduced pressure to obtain the compound as yellow liquid. The crude product was used for the next step without any purification.

3,4-dipentyloxy-2,5-bis-trimethylstannanyl-thiophene was synthesized according the same procedure. 3,4-dipentyloxy-2,5-dibromothiophene (b) (1.0 g, 2.4 mmol) was poured into a 100 mL argon purged flask with 30 mL THF at –78 ^{o}C, and then *n*-butyllithium (2.4 M, 2.2 mL, 5.3 mmol) was added within 30 min. After the reaction was stirred for 3h at –78^{o}C, chlorotrimethylstannane (1.0 M in THF, 6 mL, 6 mmol) was added and the mixture was stirred for an additional 1 h at –78 ^{o}C. Then the mixture was stirred overnight at ambient temperature. The mixture was poured into water and extracted three times with hexane. The organic phases were combined and the solvent was removed under reduced pressure to obtain the compound as yellow liquid. The crude product was used for the next step without any purification.



Compound (e). 3,4-dimethoxy-2,5-bis-trimethylstannanyl-thiophene (c) (705.0 mg, 1.5 mmol) and 1-bromo-5-octyl-thieno[3,4-*c*]pyrrole-4,6-dione (d) (1.03 g, 3.0 mmol) and dry toluene

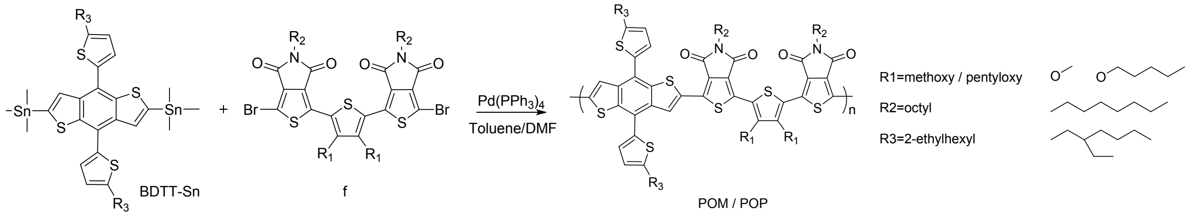
(100 mL) were added to a 250 mL double-neck round-bottom flask. The solution was flushed with argon for 10 min. The flask was purged three times with successive vacuum and argon filling cycles and then $Pd(PPh_3)_4$ (30 mg) was added. The reaction was stirred overnight at 95 ^oC under nitrogen. The reactant was cooled down to room temperature and the solvent was removed under reduced pressure. The crude product was purified by column chromatography using dichloromethane/hexanes (5:1 ratio) to get the product as yellow solid (804.4 mg, yield: 80%). MS (MALDI-TOF-MS): m/z = 670.2. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.74 (s, 2H), 4.03 (s, 6H), 3.69-3.65 (t, 4H), 1.72-1.65 (m, 4H), 1.29-1.18 (m, 20H), 0.89-0.86 (t, 6H).

2,5-Bis(5-octyl-thieno[3,4-c]pyrrole-4,6-dione-1-yl)3,4-dipentyloxythiophene was synthesized according the same procedure. 3,4-dipentyloxy-2,5-bis-trimethylstannanyl-thiophene (c) (873.0 mg, 1.5 mmol) and 1-bromo-5-octyl-thieno[3,4-*c*]pyrrole-4,6-dione (d) (1.03 g, 3.0 mmol) and dry toluene (100 mL) were added to a 250 mL double-neck round-bottom flask. The solution was flushed with argon for 10 min. The flask was purged three times with successive vacuum and argon filling cycles and then $Pd(PPh_3)_4$ (30 mg) was added. The reaction was stirred overnight at 95 ^oC under nitrogen. The reactant was cooled down to room temperature and the solvent was removed under reduced pressure. The crude product was purified by column chromatography using dichloromethane/hexanes (5:1 ratio) to get the product as yellow solid (1.0 g, yield: 85%). MS (MALDI-TOF-MS): m/z = 782.3. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ:7.73 (s, 2H), 4.19-4.15 (t, 4H), 3.69-3.65 (t, 4H), 1.93-1.86 (t,4H), 1.72-1.65 (m, 4H), 1.51-1.37 (m,8H), 1.35-1.18 (m,20H), 0.96-0.93 (t, 6H), 0.89-0.86 (t, 6H).

Compound (f). 2,5-bis(5-octyl-thieno[3,4-*c*]pyrrole-4,6-dione-1-yl)3,4-dimethoxythiophene (e) (429 mg, 0.64 mmol) was dissolved in trifluoroacetic acid (30 mL). NBS (249.6 mg, 1.41

mmol) was added in one portion to the solution and the reaction mixture was stirred at room temperature for 4 h. Then the brown-red solution was diluted with water (100 mL). The mixture was extracted with dichloromethane. The organic phases were combined and the solvent was removed under reduced pressure. The crude product was purified by column chromatography using dichloromethane/hexanes (3:1 ratio) to get the product as yellow solid (519.2 mg, yield: 98%). MS (MALDI-TOF-MS): m/z = 828.0. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 4.03 (s, 6H), 3.69-3.65 (t, 4H), 1.72-1.65 (m, 4H), 1.35-1.23 (m, 20H), 0.89-0.86 (t, 6H).

2,5-Bis(3-bromo-5-octyl-thieno[3,4-c]pyrrole-4,6-dione-1-yl)3,4-dipentyloxythiophene was synthesized according the same procedure. 2,5-bis(5-octyl-thieno[3,4-*c*]pyrrole-4,6-dione-1-yl)3,4-dipentyloxythiophene (e) (500 mg, 0.64 mmol) was dissolved in trifluoroacetic acid (30 mL). NBS (249.6 mg, 1.41 mmol) was added in one portion to the solution and the reaction mixture was stirred at room temperature for 4 h. Then the brown-red solution was diluted with water (100 mL). The mixture was extracted with dichloromethane. The organic phases were combined and the solvent was removed under reduced pressure. The crude product was purified by column chromatography using dichloromethane/hexanes (3:1 ratio) to get the product as yellow solid (541.0, yield: 90%). (MALDI-TOF-MS): m/z = 940.1. ^{1}H NMR (400 MHz, CDCl3, ppm) δ: 4.19-4.15 (t, 4H), 3.69-3.65 (t, 4H), 1.93-1.86 (m, 4H), 1.72-1.65 (m, 4H), 1.49-1.37 (m, 8H), 1.35-1.18 (m, 20H), 0.96-0.93 (t, 6H), 0.89-0.86 (t, 6H).



Synthesis of POM. 2,5-bis(3-bromo-5-octyl-thieno[3,4-*c*]pyrrole-4,6-dione)3,4-dimethoxythiophene (f) (82.8 mg, 0.1 mmol) and 2,6-bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b*]dithiophene (BDTT-Sn) (90.4 mg, 0.1 mmol) were dissolved in o-dichlorobenzene (10 mL) and dimethylformamide (DMF 2 mL). The solution was flushed with argon for 10 min, and then Pd $(PPh_3)_4$ (11.5 mg, 0.01 mmol, 10% with respect to the monomer) and the flask was purged three times with successive vacuum and argon filling cycles. The polymerization reaction was heated to 110 °C and stirred for 5 h under argon atmosphere. The mixture was cooled to room temperature and poured slowly in methanol (200 mL). The solid was filtered through 0.45 μm PTFE filter. The polymer was further purified by column chromatography using chloroform as the eluent. Then the polymer solution was poured in methanol (200 mL). The solid was filtered through 0.45 μm PTFE filter and a dark red solid was obtained. The solid was dried under vacuum overnight (80.9 mg, yield: 65%), M_n = 12.1 kDa, PDI = 2.39, ^1H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.74-7.35 (r, 4H), 6.94-6.90 (r, 2H), 4.02-4.00 (r, 6H), 3.61-3.53 (r, 4H), 2.92-2.73 (r, 4H), 1.78-1.63 (r, 10H), 1.25-1.33 (r, 32H), 0.90-0.86 (r, 18H).

POP was synthesized according the same procedure. 2,5-bis(3-bromo-5-octyl-thieno[3,4-*c*]pyrrole-4,6-dione)3,4-dimethoxythiophene (f) (94.0 mg, 0.1 mmol) and 2,6-bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b*]dithiophene (BDTT-Sn) (90.4 mg, 0.1 mmol) were dissolved in o-dichlorobenzene (10 mL) and dimethylformamide (DMF 2 mL). The solution was flushed with argon for 10 min, and then Pd $(PPh_3)_4$ (11.5 mg, 0.01 mmol, 10% with respect to the monomer) and the flask was purged three times with successive vacuum and argon filling cycles. The polymerization reaction was heated to 110 °C and stirred for 6 h under argon atmosphere. The mixture was cooled to room temperature and poured slowly in methanol (200 mL). The solid was filtered through 0.45 μm PTFE filter. The polymer was further purified by column chromatography using chloroform as the eluent. Then the polymer solution was poured in methanol (200 mL). The solid was filtered through 0.45 μm PTFE filter and a dark red solid was obtained. The solid was dried under vacuum overnight (95.1 mg, yield: 70%). M_n = 50.4 kDa, PDI = 2.77, ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.74-7.35 (r, 4H), 6.94-6.90 (r, 2H), 4.02-4.00 (r, 4H), 3.61-3.53 (r, 4H), 2.92-2.73 (r, 4H), 1.78-1.63 (r, 14H), 1.25-1.39 (r, 40H), 0.90-0.86 (r, 24H).

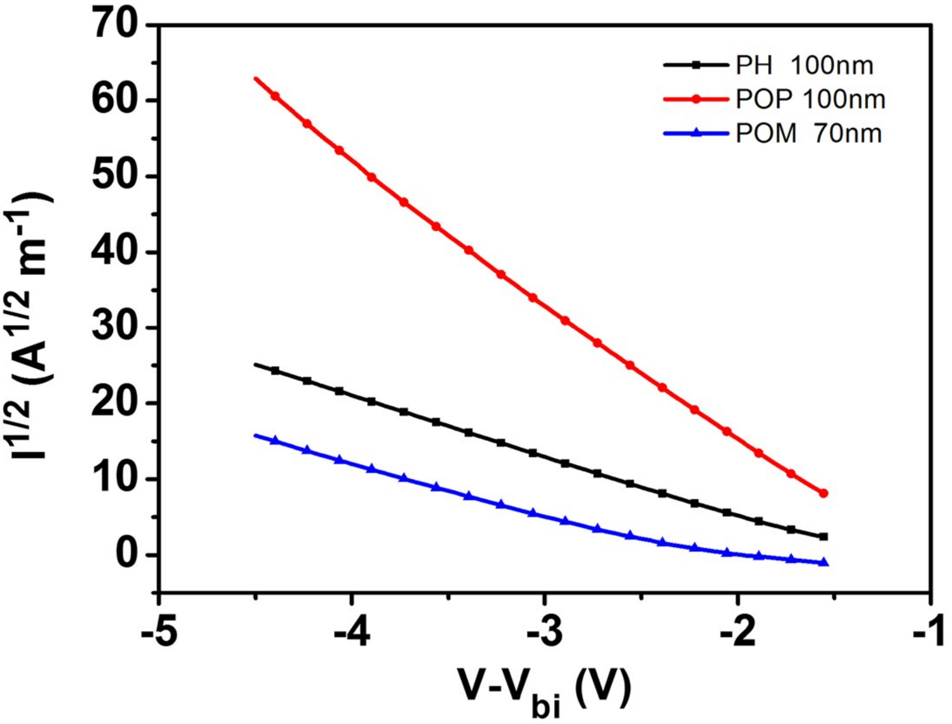


Figure S1. Dark current densities for hole-only devices composed of PH, POP, and POM neat films.

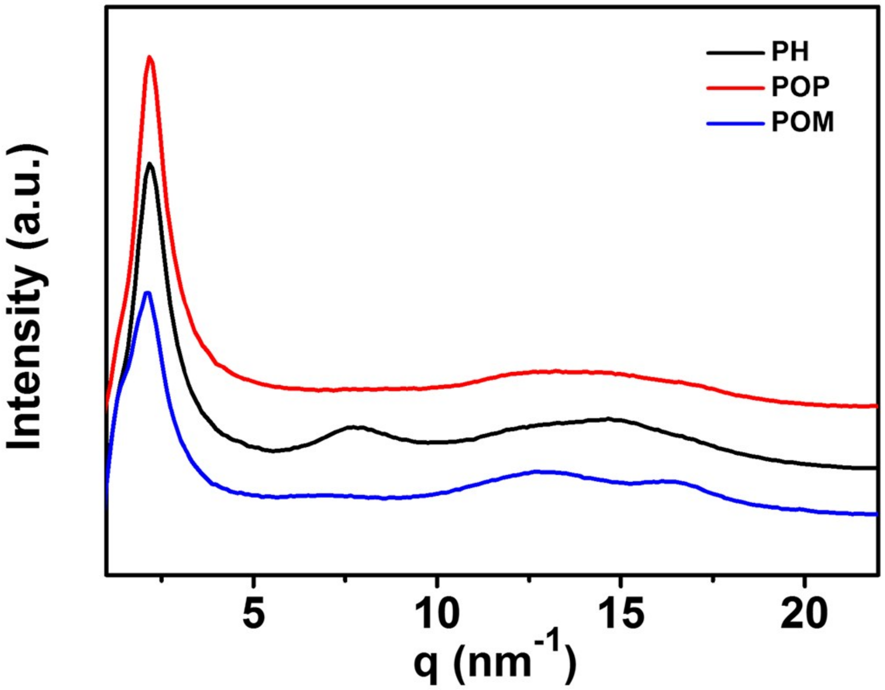


Figure S2. GIWAXS patterns of PH, POP and POM in powder state.

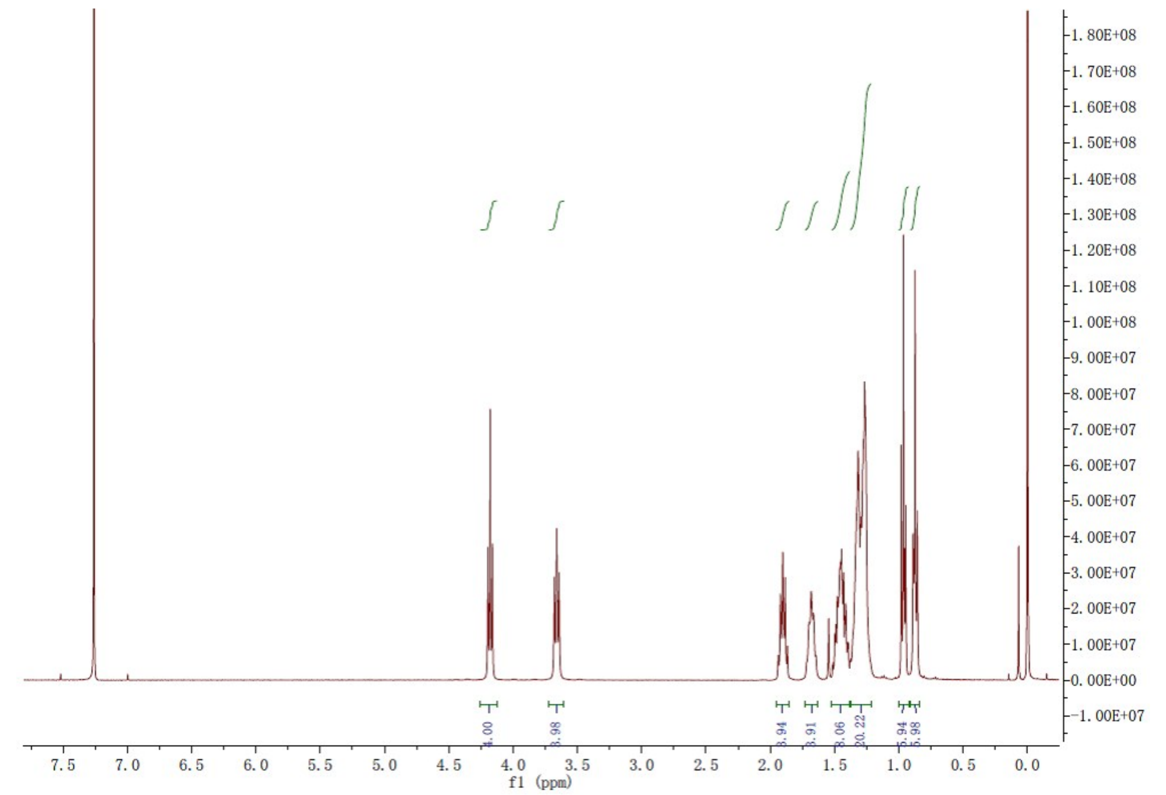


Figure S3. ^{1}H NMR spectra of monomer M1.

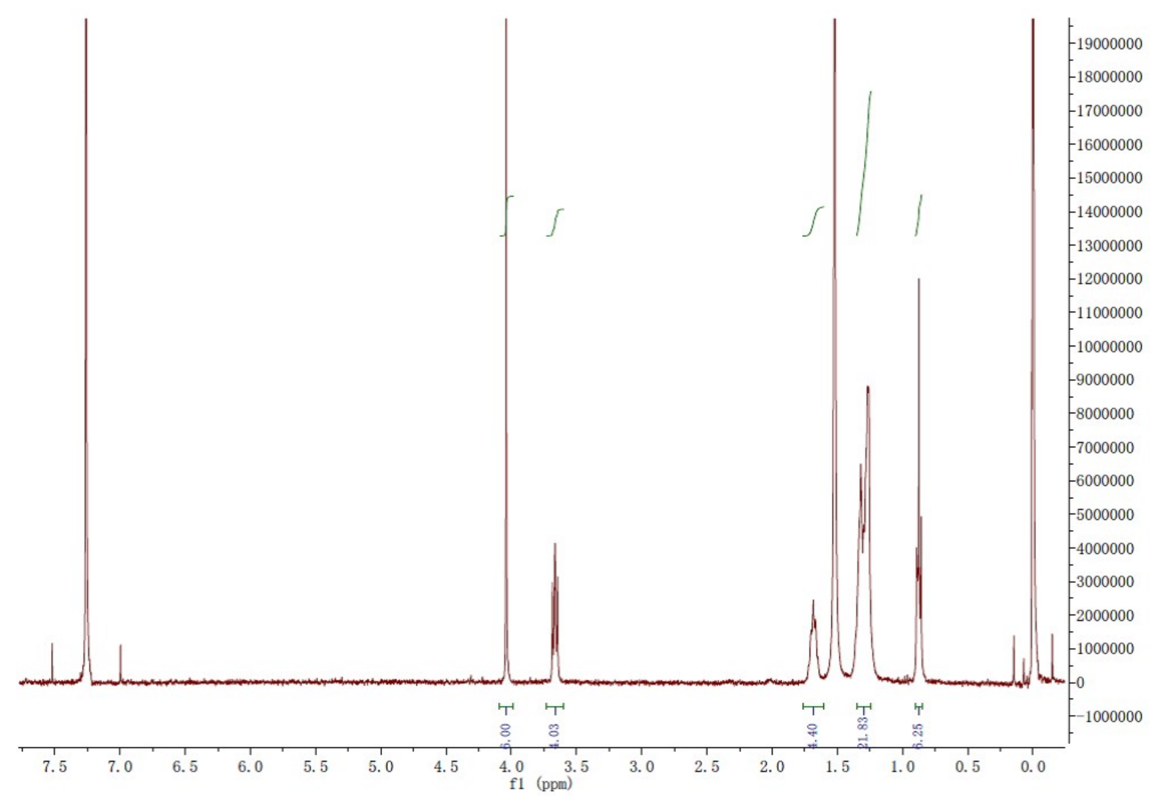


Figure S4. ^{1}H NMR spectra of monomer M2.

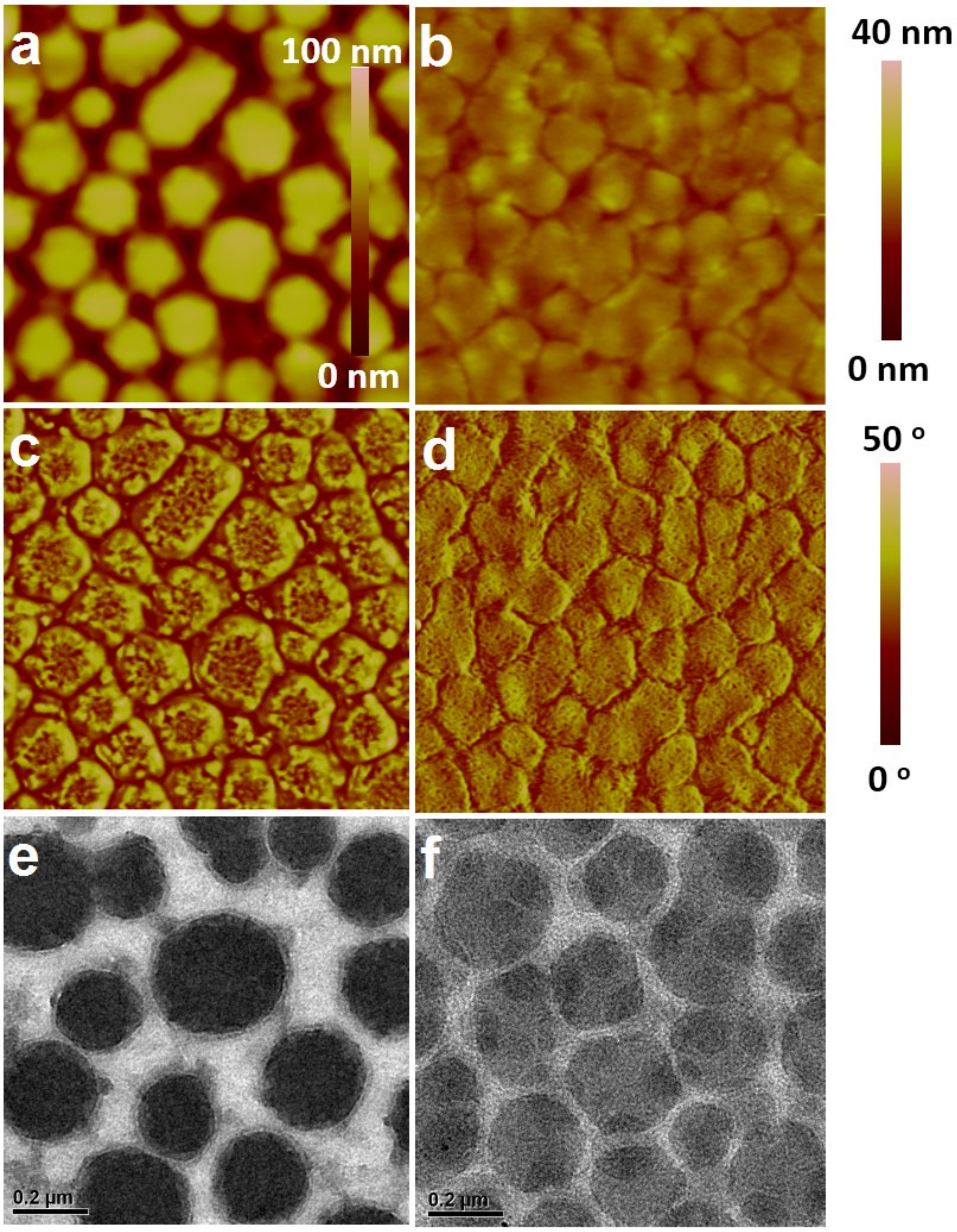


Figure S5. AFM topography images obtained in tapping mode: (a) POM:PC$_{71}$BM (1:1 without DIO) blend film. (b) POP:PC$_{71}$BM (1:1.7 without DIO) blend film. AFM phase images: (c) POM:PC$_{71}$BM (1:1 without DIO) blend film. (d) POP:PC$_{71}$BM (1:1.7 without DIO) blend film. Respective TEM images (e) and (f).

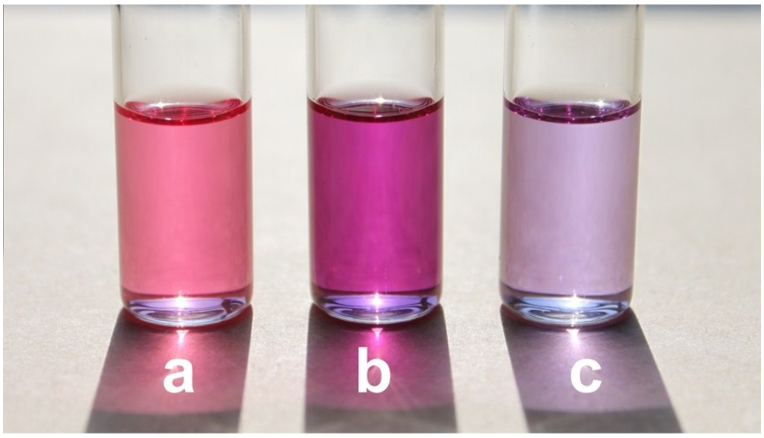


Figure S6. Solution of PH (a), POP (b) and POM (c) in chloroform.

Table S1. Device parameters for varied conditions based on POP, POM and PH.

Polymer	D:A [w/w]	DIO [v/v]	Jsc [mA cm^{-2}]	Voc [V]	FF [%]	PCE [%]
POP	1:2	1.4%	12.89	0.98	59.3	7.67
POP	1:2	1.4%	13.50	0.98	57.1	7.71
POP	1:2	1.4%	13.69	0.98	57.4	7.91
POP	1:2	1.4%	13.63	0.98	57.8	7.90
POP	1:2	1.4%	14.52	0.97	50.1	7.23
POP	1:1.8	1.2%	12.54	0.97	56.8	7.07
POP	1:1.8	1.2%	11.84	0.97	59.7	7.00
POP	1:1.8	1.4%	11.54	0.96	61.3	6.93
POP	1:1.8	1.4%	13.41	0.97	57.9	7.70
POP	1:1.8	1.4%	13.20	0.98	58.1	7.65
POP	1:1.8	1.6%	12.69	0.98	60.6	7.69
POP	1:1.8	1.6%	13.61	0.96	60.4	8.11
POP	1:1.8	1.6%	12.48	0.97	58.4	7.18
POP	1:1.7	1.6%	13.81	0.98	57.5	7.94
POP	1:1.7	1.6%	14.48	0.97	56.7	8.18
POP	1:1.7	1.6%	14.41	0.98	56.2	8.12
POP	1:1.7	1.6%	14.10	0.98	57.1	8.05
POP	1:1.7	1.4%	14.15	0.97	57.9	8.11
POP	1:1.7	1.4%	12.73	0.97	63.1	7.94
POP	1:1.7	1.4%	14.08	0.97	57.3	7.99
POP	1:1.7	1.4%	13.55	0.97	59.0	7.94
POP	1:1.6	1.6%	14.38	0.97	55.0	7.88
POP	1:1.6	1.6%	13.88	0.97	56.5	7.81
POP	1:1.6	1.6%	13.95	0.97	57.2	7.95
POP	1:1.6	1.6%	14.01	0.97	57.3	7.95
POP	1:1.6	1.5%	14.70	0.97	55.5	8.13
POP	1:1.6	1.5%	14.49	0.96	53.0	7.56
POP	1:1.6	1.5%	14.67	0.97	53.7	7.80
POP	1:1.6	1.5%	14.68	0.96	53.3	7.68
POP	1:1.6	1.4%	13.25	0.97	59.7	7.87
POP	1:1.6	1.4%	14.55	0.97	53.3	7.72
POP	1:1.6	1.4%	14.48	0.96	50.3	7.18
POP	1:1.6	1.4%	14.41	0.97	51.3	7.36

POP	1:1.6	1.4%	13.00	0.98	59.5	7.73
POP	1:1.6	1.4%	12.90	0.97	61.0	7.83
POP	1:1.5	1.8%	13.73	0.97	58.5	7.93
POP	1:1.5	1.6%	14.14	0.96	57.2	8.01
POP	1:1.5	1.6%	13.12	0.97	58.0	7.55
POM	1:1	1%	4.60	0.98	54.4	2.55
POM	1:1	1%	7.55	0.97	43.8	3.30
POM	1:1	1%	4.81	0.97	53.3	2.58
PH	1:1.5	1.5%	14.32	1.000	51.9	7.59

[1]. L. Huo, S. Zhang, X. Guo, F. Xu, Y. Li and J. Hou, *Angew. Chem. Int. Ed.*, 2011, **123**, 9871-9876.

[2]. B. Xia, K. Lu, Y. Zhao, J. Zhang, L. Yuan, L. Zhu, Y. Yi and Z. Wei, Adv. Sci., 2015, DOI: 10.1002/advs.201500021.