Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

Donor-acceptor conjugated polymers based on a pentacyclic aromatic lactam acceptor unit for polymer solar cells

Qiaogan Liao,‡[a,b] Jiamin Cao,‡[b] Zuo Xiao,[b] Jianhe Liao,*[a] and Liming Ding*[b]

[a] *College of Materials and Chemical Engineering, Hainan University, Haikou 570228, China; E-mail: jhlhn@sina.com*

[b] *National Center for Nanoscience and Technology, Beijing 100190, China; E-mail: opv.china@yahoo.com*

‡ These authors contributed equally to this work.

Content

1. General characterization

^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance-400 spectrometer. Absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Gel permeation chromatography (GPC) measurements were performed on a Waters 1515 series GPC coupled with UV-vis detector using tetrahydrofuran as eluent and polystyrenes as standards. Thermogravimetric analysis was measured by a Perkin-Elmer Diamond TG/DTA thermal analyzer. Cyclic voltammetry was conducted on a Shanghai Chenhua CHI620 voltammetric analyzer under argon in an anhydrous acetonitrile solution of tetra-n-butylammonium hexafluorophosphate (0.1 M). A glassy-carbon electrode was used as the working electrode, a platinum-wire was used as the counter electrode, and a Ag/Ag$^+$ electrode was used as the reference electrode. Polymers were coated on the surface of glassy-carbon electrode and all potentials were corrected against Fc/Fc$^+$. AFM was performed on a Multimode 8 microscope (Veeco). The thickness of the active layer was measured by using a KLA Tencor D-120 profilometer.

2. Device fabrication and measurements

2.1. Solar cell fabrication and characterization

Patterned ITO glass with a sheet resistance of 15 Ω sq^{-1} was ultrasonically cleaned using detergent, distilled water, acetone, isopropanol sequentially and then given UV-ozone treatment. A 30 nm thick poly(3,4-ethylenedioxythiophene)/polystyrenesulfonate (PEDOT:PSS, Clevios^{TM} P VP Al 4083) layer was formed on ITO substrates by spin coating an aqueous dispersion onto ITO glass (4000 rpm for 30 s). PEDOT:PSS coated substrates were dried at 150 °C for 10 min. A **P1**/PC$_{71}$BM blend (1:1.6 w/w, 16 mg/mL) in ODCB with 5 vol% DIO was spin-coated onto PEDOT:PSS layer (800 rpm for 60 s). Finally, Ca (~10 nm) and Al (~100 nm) were thermally evaporated under a shadow mask (pressure ca. 10^{-4} Pa). The effective area for the devices is 4 mm^2. **P2-P4** cells were fabricated through the same procedure. It should be noted that the active layers were spin-coated using chloroform solution. *J-V* curves were measured with a computerized Keithley 2420 SourceMeter. Device characterization was done in air using a Xenon-lamp-based solar simulator (Newport, Oriel 91159A, 150 W, AM 1.5G, 100 mW/cm^2). The illumination intensity of solar simulator was determined using a monocrystalline silicon solar cell (Oriel 91150 Mode, 2 × 2 cm) calibrated by NREL. The external quantum efficiency (EQE) was measured by a QE-R3011 measurement system (Enli Technology, Inc.).

2.2. Hole-only devices

The structure of hole-only devices is ITO/PEDOT:PSS/active layer/MoO_3/Al. A 30 nm thick PEDOT:PSS layer was formed on ITO substrates by spin coating an aqueous dispersion onto ITO glass (4000 rpm for 30 s). PEDOT:PSS coated substrates were dried at 150 °C for 10 min. A **P1**/$PC_{71}BM$ blend (1:1.6 w/w, 16 mg/mL) in ODCB with 5 vol% DIO was spin-coated onto PEDOT:PSS layer (800 rpm for 60 s). Finally, MoO_3 (~6 nm) and Al (~100 nm) were successively evaporated onto the active layer under a shadow mask (pressure ca. 10^{-4} Pa). **P2-P4** devices were fabricated through the same procedure. *J*-*V* curves were measured with a computerized Keithley 2420 SourceMeter in the dark.

3. Synthetic procedures and spectra data

All reactions dealing with air- or moisture-sensitive compounds were carried out using standard Schlenk technique. All reagents were purchased from Alfa Aesar Co., Aladdin Co., J&K Co., Aldrich Chemical Co., Solarmer Materials Inc., and other commercial suppliers. 2,8-Dibromo-4,10-bis(2-hexyldecyl)thieno[2',3':5,6]pyrido[3,4-*g*]thieno[3,2-*c*]isoquinoline-5,11(4*H*,10*H*)-dione (**4a**) was synthesized according to our previous report.[1] *N*-(2-ethylhexyl)thiophen-3-amine (**1b**), 2,6-bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b′*]dithiophene (BDT) and 4,4-bis(2-ethylhexyl)-2,6-bis(trimethyltin)-dithieno[3,2-*b*:2′,3′-*d*]silole (DTS) were synthesized according to literatures.[2-4]

2,5-Dibromo-*N*^{1},*N*^{4}-bis(2-ethylhexyl)-*N*^{1},*N*^{4}-di(thiophen-3-yl)terephthalamide (2b). To a solution of 2,5-dibromoterephthalic acid (0.65 g, 2.0 mmol) in dry CH_2Cl_2 (50 mL) were added oxalyl chloride (2 mL, 22.8 mmol) and 2 drops of DMF. The mixture was stirred at room temperature overnight. The solvent was removed under vacuum to obtain 2,5-dibromoterephthaloyl dichloride, which was used in next step without purification. To the solution of 2,5-dibromoterephthaloyl dichloride in dry CH_2Cl_2 (20 mL) was slowly added a solution of compound **1b** (1.0 g, 4.7 mmol) and Et_3N (1.3 mL) in dry CH_2Cl_2 (20 mL) at 0 °C. The mixture was stirred at room temperature overnight. Then, the mixture was poured into water and extracted with $CHCl_3$ three times. The organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent, the crude product was purified through a silica gel column with CH_2Cl_2 to give compound **2b** as a yellow oil (1.01 g, 71%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.13 (dd, *J* = 4.9, 3.3 Hz, 2H), 7.09 (s, 2H), 6.85 (s, 2H), 6.77 (d, *J* = 5.1 Hz, 2H), 3.76 (br, 4H), 1.55-1.49 (m, 2H), 1.44-1.19 (m, 16H), 0.88-0.83 (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 166.69, 140.29, 139.58, 131.92, 125.69, 125.40, 120.80, 117.88, 51.92, 37.40, 30.23, 28.48, 23.56, 23.04, 14.07, 10.42.

4,10-Bis(2-ethylhexyl)thieno[2',3':5,6]pyrido[3,4-*g*]thieno[3,2-*c*]isoquinoline-5,11(4*H*,10*H*)-dione (3b). To a solution of compound **2b** (0.31 g, 0.44 mmol) in N,N-dimethylacetamide (50 mL) were added $PCy_3{\cdot}HBF_4$ (330 mg, 0.90 mmol), Cs_2CO_3 (1.3 g, 3.99 mmol) and $Pd(OAc)_2$ (100 mg, 0.45 mmol) under Ar. The mixture was stirred at 120 °C overnight and then cooled to room temperature. The mixture was poured into water and extracted with $CHCl_3$ three times. The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified through a silica gel column with petroleum ether/CH_2Cl_2 (1:4) as eluent to give **3b** as a yellow solid (186 mg, 77%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.89 (s, 2H), 7.49 (d, *J* = 5.4 Hz, 2H), 7.10 (d, *J* = 5.4 Hz, 2H), 4.34-4.17 (m, 4H), 2.02-1.95 (m, 2H), 1.52-1.26 (m, 16H), 0.95 (t, *J* = 7.4 Hz, 6H), 0.88 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 161.55, 139.38, 129.93, 126.74, 126.11, 123.55, 117.92, 117.67, 49.27, 38.45, 30.70, 28.84, 24.00, 23.02, 14.03, 10.74. TOF-MS ES+(m/e): 549.2 (M^+, 100%).

2,8-Dibromo-4,10-bis(2-ethylhexyl)thieno[2',3':5,6]pyrido[3,4-*g*]thieno[3,2-*c*]isoquinoline-5,11(4*H*,10*H*)-dione (4b). To a solution of **3b** (200 mg, 0.36 mmol) in a solvent mixture of $CHCl_3$ (20 mL) and DMF (20 mL) was added NBS (142 mg, 0.80 mmol) under Ar. The mixture was stirred at room temperature for 24 h and then poured into 150 mL methanol. The precipitate was filtered and purified through a silica gel column with petroleum ether/CH_2Cl_2 (1:3) as eluent to give **4b** as a yellow solid (198 mg, 77%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.69 (s, 2H), 7.07 (s, 2H), 4.24-4.09 (m, 4H), 1.97-1.91 (m, 2H), 1.43-1.25 (m, 16H), 0.95 (t, *J* = 7.4 Hz, 6H), 0.89 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR spectrum for **4b** is not obtained due to its low solubility. TOF-MS ES+(m/e): 705.0 (M^+, 100%).

Poly{2,6-(4,8-bis(2-ethylhexyloxy))benzo[1,2-*b*:4,5-*b'*]dithiophene-alt-2,8-(4,10-bis(2-hexyldecyl))thieno[2',3':5,6]pyrido[3,4-*g*]thieno[3,2-*c*]isoquinoline-5,11(4*H*,10*H*)-dione} (P1). **4a** (85 mg, 0.09 mmol) and BDT (71 mg, 0.09 mmol) were dissolved in 20 mL toluene. The solution was flushed with argon for 15 min. Then, $Pd(PPh_3)_4$ (7 mg) was added into the solution. The mixture was flushed again with argon for 20 min and heated to reflux for 24 h. The reaction mixture was cooled to room temperature and added dropwise to 150 mL methanol. The precipitate was collected and further purified by Soxhlet extraction with methanol, hexane, and chloroform in sequence. The chloroform fraction was concentrated and added dropwise into methanol. The precipitates were collected and dried under vacuum overnight to get **P1** as a purple-red solid (103 mg, 93%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.15-6.65 (br, 6H), 4.98-3.88 (br, 8H), 1.81-1.25 (br, 68H), 0.96-0.82 (br, 24H). Elemental analysis (%) calcd for $C_{74}H_{106}N_2O_4S_4$: C 73.10, H 8.79, N 2.30. Found: C 72.39, H 8.70, N 2.25.

Poly{2,6-(4,8-bis(2-ethylhexyloxy))benzo[1,2-*b*:4,5-*b'*]dithiophene-alt-2,8-(4,10-bis(2-ethylhexyl))thieno[2',3':5,6]pyrido[3,4-*g*]thieno[3,2-*c*]isoquinoline-5,11(4*H*,10*H*)-dione} (P2). **P2** was synthesized by following the same procedures for **P1**. **4b** (76 mg, 0.11 mmol) and BDT (81 mg, 0.11 mmol) were used as starting materials. **P2** was obtained as a purple-red solid (101 mg, 92%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.46-6.40 (br, 6H), 4.20 (br, 8H), 1.56-1.21 (br, 36H), 1.11-0.88 (br, 24H). Elemental analysis (%) calcd for $C_{58}H_{74}N_2O_4S_4$: C 70.26, H 7.52, N 2.83. Found: C 68.67, H 7.48, N 2.51.

Poly{2,6-(4,4-bis(2-ethylhexyl))dithieno[3,2-b:2’,3’-d]silole-alt-2,8-(4,10-bis(2-hexyldecyl))thieno[2',3':5,6]pyrido[3,4-*g*]thieno[3,2-*c*]isoquinoline-5,11(4*H*,10*H*)-dione} (P3). **P3** was synthesized by following the same procedures for **P1**. **4a** (160 mg, 0.17 mmol) and DTS (128 mg, 0.17 mmol) were used as starting materials. **P3** was obtained as a purple solid (95 mg, 47%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.71-6.65 (br, 6H), 4.76-3.54 (br, 4H), 2.56-1.18 (br, 72H), 0.95-0.60 (br, 24H). Elemental analysis (%) calcd for $C_{72}H_{106}N_2O_2S_4Si$: C 72.79, H 8.99, N 2.36. Found: C 71.33, H 8.80, N 2.37.

Poly{2,6-(4,4-bis(2-ethylhexyl))dithieno[3,2-*b*:2′,3′-*d*]silole-alt-2,8-(4,10-bis(2-ethylhexyl))thieno[2',3':5,6]pyrido[3,4-*g*]thieno[3,2-*c*]isoquinoline-5,11(4*H*,10*H*)-dione} (P4). **P4** was synthesized by following the same procedures for **P1**. **4b** (89 mg, 0.13 mmol) and DTS (94 mg, 0.13 mmol) were used as starting materials. **P4** was obtained as a purple solid (77 mg, 64%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.76-6.72 (br, 6H), 4.78-3.68 (br, 4H), 2.52-1.21 (br, 40H), 1.01-0.64 (br, 24H). Elemental analysis (%) calcd for $C_{56}H_{74}N_2O_2S_4Si$: C 69.80, H 7.74, N 2.91. Found: C 69.31, H 7.96, N 2.76.

4. TGA measurements for P1-P4

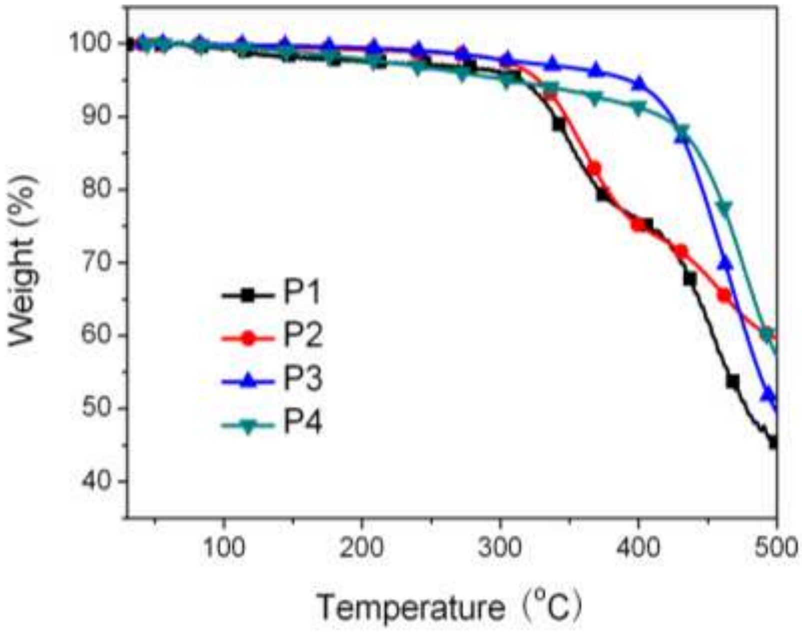

Fig. S1 TGA curves for **P1-P4**.

5. CV measurements for P1-P4

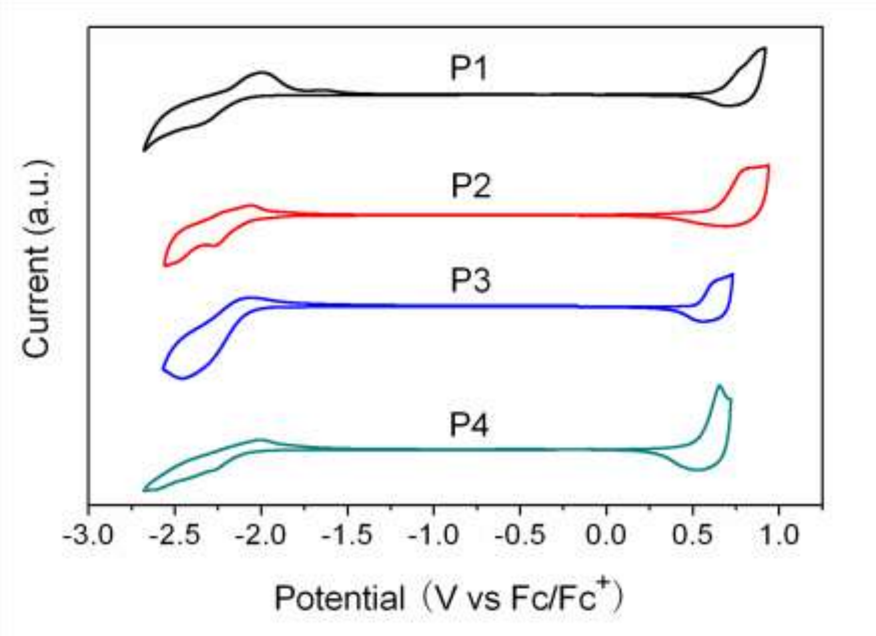

Fig. S2 Cyclic voltammograms for **P1-P4**.

Table S1 Optical and electrochemical properties of **P1-P4**.

Polymers	**λ_{sol} (nm)**	**λ_{film} (nm)**	**λ_{onset} (nm)**	**E_g^{opt} (eV)$^{a)}$**	**E_{ox} (eV)**	**E_{red} (eV)**	**HOMO (eV)**	**LUMO (eV)**	**E_g^{ec} (eV)$^{b)}$**
P1	529, 570	536, 580	612	2.03	0.65	-2.12	-5.45	-2.68	2.77
P2	534, 574	534, 577	613	2.02	0.63	-2.09	-5.43	-2.71	2.72
P3	556, 597	564, 609	670	1.85	0.53	-2.08	-5.33	-2.72	2.61
P4	557, 601	571, 616	666	1.86	0.54	-2.11	-5.34	-2.69	2.65

$^{a)}$ Calculated from the absorption edge of the films, $E_g^{opt} = 1240/\lambda_{onset}$; $^{b)}$ Calculated from E_g^{ec} = LUMO - HOMO.

6. Device optimization

Table S2 D/A ratio optimization.

Blend	**D/A Ratio [w/w]**	**V_{oc} [V]**	**J_{sc} [mA/cm^2]**	**FF [%]**	**PCE [%]**
P1:PC$_{71}$BM (3% DIO)	1/1.4	0.92	8.76	59.8	4.82
	1/1.6	0.87	8.92	63.2	4.90
	1/1.8	0.85	8.90	60.9	4.59
P2:PC$_{71}$BM (3% DIO)	1/0.8	0.91	9.94	43.2	3.91
	1/1	0.84	9.79	49.5	4.07
	1/1.2	0.83	10.12	46.9	3.94
P3:PC$_{71}$BM (3% DIO)	1/1	0.86	7.20	52.4	3.24
	1/1.2	0.87	7.62	54.9	3.64
	1/1.4	0.86	7.32	53.8	3.39
P4:PC$_{71}$BM (3% DIO)	1/0.8	0.80	10.07	38.1	3.07
	1/1	0.83	10.44	36.9	3.20
	1/1.2	0.82	10.30	37.4	3.16

Table S3 Additive content optimization.

Blend	**DIO [vol%]**	**V_{oc} [V]**	**J_{sc} [mA/cm^2]**	**FF [%]**	**PCE [%]**
P1:PC$_{71}$BM (1:1.6)	0	0.96	6.47	53.8	3.34
	1	0.89	8.85	62.1	4.89
	3	0.87	8.92	63.2	4.90
	5	0.90	9.26	63.6	5.30
	7	0.85	8.23	61.4	4.30
P2:PC$_{71}$BM (1:1)	0	0.95	4.16	58.2	2.30
	0.5	0.91	9.60	55.8	4.87
	1	0.86	10.96	44.0	4.15
	3	0.84	9.79	49.5	4.07
	5	0.81	10.09	43.9	3.59
P3:PC$_{71}$BM (1:1.2)	0	0.90	1.75	63.2	1.00
	0.5	0.90	4.27	54.1	2.08
	1	0.93	4.58	54.0	2.30
	3	0.87	7.62	54.9	3.64
	5	0.88	5.86	48.4	2.49
P4:PC$_{71}$BM (1:1)	0	0.87	3.19	53.9	1.50
	0.5	0.83	8.99	40.5	3.02
	1	0.80	10.31	42.2	3.48
	3	0.83	10.44	36.9	3.20
	5	0.78	9.98	40.5	3.15

7. Space charge limited current (SCLC) measurements

Charge carrier mobility was measured by SCLC method. The mobility was determined by fitting the dark current to the following formula:

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu\frac{V^2}{d^3}$$

where J is the current density, μ is the zero-field mobility of holes, ε_0 is the permittivity of the vacuum, ε_r is the relative permittivity of the material, d is the thickness of the blend film, and V is the effective voltage, $V = V_{appl} - V_{bi}$, where V_{appl} is the applied voltage, and V_{bi} is the built-in potential determined by electrode workfunction difference. Figure S3 shows J-V curves for the hole-only devices. The mobility was calculated from the slope of $J^{1/2}$-V curves.

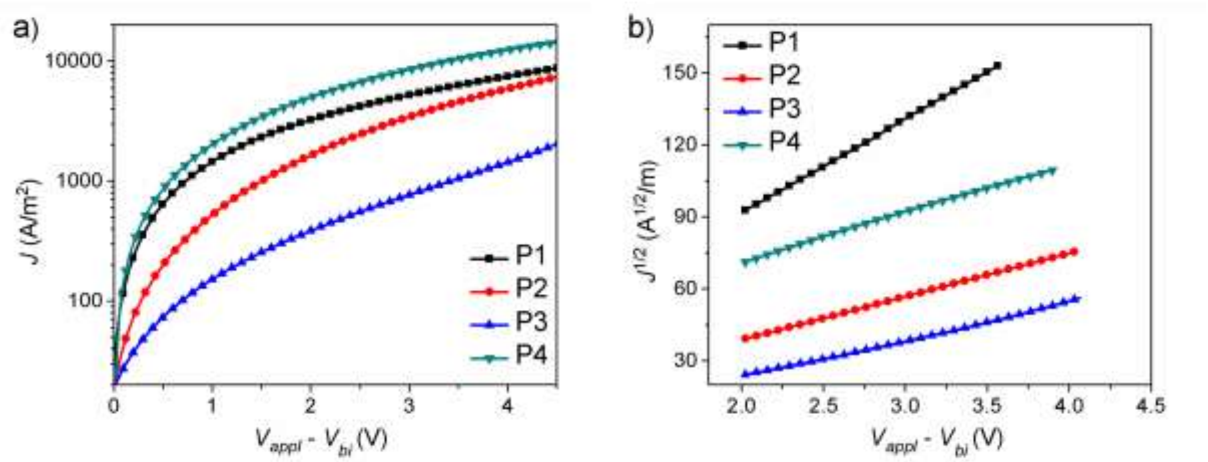

Fig. S3 J-V curves (a) and the corresponding $J^{1/2}$-V curves (b) for hole-only devices (in dark). The thicknesses of the blend films are 95 nm, 107 nm, 100 nm, and 97 nm, respectively.

Table S4 Hole mobilities for the blends.

Blend	**DIO [vol%]**	**μ [cm^2 V^{-1} s^{-1}]**
P1:PC$_{71}$BM (1:1.6)	5	4.83×10^{-4}
P2:PC$_{71}$BM (1:1)	0.5	2.33×10^{-4}
P3:PC$_{71}$BM (1:1.2)	3	9.62×10^{-5}
P4:PC$_{71}$BM (1:1)	1	3.55×10^{-4}

8. AFM characterization

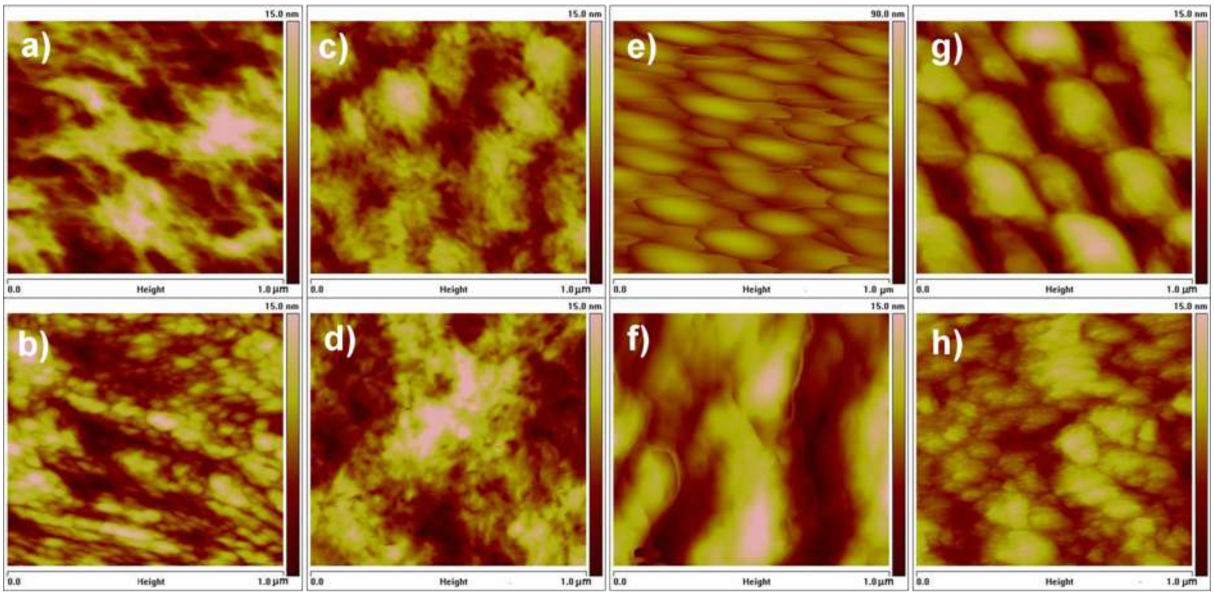

Fig. S4 AFM height images: **P1**:$PC_{71}BM$ blend films without DIO (a) and with 5% DIO (b); **P2**:$PC_{71}BM$ blend films without DIO (c) and with 0.5% DIO (d); **P3**:$PC_{71}BM$ blend films without DIO (e) and with 3% DIO (f); **P4**:$PC_{71}BM$ blend films without DIO (g) and with 1% DIO (h).

References

[1] J. Cao, Q. Liao, X. Du, J. Chen, Z. Xiao, Q. Zuo and L. Ding, *Energy Environ. Sci.*, 2013, DOI: 10.1039/c3ee41948g.

[2] (a) R. S. Ashraf, A. J. Kronemeijer, D. I. James, H. Sirringhaus and I. McCulloch, *Chem. Commun.*, 2012, **48**, 3939; (b) *US Pat.*, 20100297405.

[3] (a) J. Hou, M.-H. Park, S. Zhang, Y. Yao, L.-M. Chen, J.-H. Li and Y. Yang, *Macromolecules*, 2008, **41**, 6012; (b) G. Zhang, Y. Fu, Q. Zhang and Z. Xie, *Chem. Commun.*, 2010, **46**, 4997.

[4] L. Huo, J. Hou, H.-Y. Chen, S. Zhang, Y. Jiang, T. L. Chen and Y. Yang, *Macromolecules*, 2009, **42**, 6564.