Bithienopyrroledione vs Thienopyrroledione Based Copolymers: Dramatic Increasement of Power Conversion Efficiency in Bulk Heterojunction Solar Cells

General

Absorption spectra were measured on a U-3900 UV-vis spectrophotometer. Cyclic voltammetric measurements were carried out in a conventional three electrode cell using a platinum working electrode, a platinum wire counter electrode, and a saturated calomel electrode (SCE) reference electrode on a computer-controlled CHI610D instrument. The reference electrode was calibrated using a ferrocene/ferrocenium redox couple as internal standard, whose HOMO energy level is set as -4.8 eV. The HOMO energy levels of the polymers were obtained from the equation: $E_{\text{HOMO}}(eV) = -(E_{\text{ox}}^{\text{onset}}-E_{\text{ox}}^{\text{Ferrocene}}+4.8)$. AFM images were recorded on an Agilent 5400 in tapping mode. TEM images were obtained on a Hitachi H-7650 transmission electron microscope at an accelerating voltage of 100 kV. 2D-GIXD was carried out at Shanghai Synchrotron Radiation Facility. The *J-V* curves of hole-only and electron-only devices were measured by a Keithley 2420 source meter.

Experimental section

Polymer syntheses

Compounds 1, 2, 3, 4 and polymer P3 were synthesized according to the literatures. [1-2]



Scheme S1.Synthetic route of P1, P2, and P4.

Synthesis of **P1**. A reaction mixture of compound **1** (0.259 g, 0.20 mmol), compound **4** (0.093 g, 0.20 mmol), Pd₂(dba)₃ (0.0009 g, 0.01mmol) and P(*o*-tolyl)₃ (0.012 g, 0.04 mmol) in toluene (15 mL) was heated to 100 \mathbb{C} under nitrogen for 50 hours. After cooling to room temperature, the reaction mixture was slowly dropped into 300 mL methanol(containing 10 mL concentrated HCl). The precipitate was filtered and successively extracted by the Soxhlet with methanol, acetone, petroleum ether, dichloromethane, chloroform, and chlorobenzene. Then, the chlorobenzene solution was concentrated to about 20 mL and poured into 200 mL methanol. The precipitate was filtered off and dried in vacuum at 50 \mathbb{C} overnight to afford **P1** (0.220 g, yield: 85.9 %). GPC (1,2,4-tricholorobenzene, 150 \mathbb{C}): M_n = 82.9 kDa, PDI = 2.87. Anal. Calcd. for C₇₄H₁₀₆N₂O₄S₆: C, 69.43; H, 8.35; N, 2.19 %; Found: C, 69.61; H, 8.43; N, 2.04 %.

Synthesis of **P2**. A reaction mixture of compound **2** (0.25 g, 0.164 mmol), compound **4** (0.0764 g, 0.164 mmol), $Pd_2(dba)_3$ (0.0075 g, 0.0082 mmol) and $P(o-tolyl)_3$ (0.01 g, 0.033 mmol) in toluene (25 mL) was heated to 100 °C for 50 hours under nitrogen. After cooling to room temperature, the reaction mixture was slowly dropped into 200 mL methanol. The precipitate was filtered and successively extracted by the Soxhlet with methanol, acetone, petroleum ether, dichloromethane, chloroform, and chlorobenzene. Then, the chlorobenzene solution was concentrated to about 20 mL and was poured into 200 mL methanol. The precipitate was filtered off and dried in vacuum at 50 °C overnight to afford **P2** (0.137 g, yield: 55.6%). GPC (1,2,4-tricholorobenzene, 150 °C): M_n = 53.3 kDa, PDI = 2.29. Anal. Calcd. for C₉₀H₁₃₈N₂O₄S₆: C, 71.85; H, 9.25; N, 1.86 %; Found: C, 71.38; H, 9.16; N, 1.77 %.

Synthesis of P4. A reaction mixture of compound **3** (1.47 g, 1.8 mmol), compound **4** (0.84 g, 1.8 mmol), Pd₂(dba)₃ (0.082 g, 0.09 mmol) and P(*o*-tolyl)₃ (0.054 g, 0.18 mmol) in toluene (25 mL)was heated to 110 \mathbb{C} for 2 hours under nitrogen. After cooling to room temperature, the reaction mixture was slowly dropped into 200 mL methanol. The precipitate was filtered and successively extracted by the Soxhlet with methanol, acetone, petroleum ether, dichloromethane, chloroform and chlorobenzene. After Soxhlet extraction, large amount of unsolvable powder was remained. The chlorobenzene solution was concentrated to about 20 mL and was poured into 200 mL methanol. The precipitate was filtered off and dried in vacuum at 50 \mathbb{C} overnight to afford P4 (0.07 g). GPC (1,2,4-tricholorobenzene, 150 \mathbb{C}): M_n = 7.1 kDa, PDI = 2.83.

Devices Fabrication and Characterization:

Polymer solar cells were fabricated with the device structure ITO/PEDOT:PSS/ Polymer:PC₇₁BM/Ca/Al. Patterned ITO-coated glasses were cleaned according to the reported procedure.^[3] PEDOT:PSS (Baytron PVP Al 4083) about 35 nm was spin-coated onto the ITO-coated glass substrates and then annealed at 160 °C for 30 minutes. Subsequently, the substrates were transferred to the nitrogen-filled glove box. The *o*-DCB solutions of Polymer:PC₇₁BM (8 mg / mL for **P1**, 5 mg / mL for **P2**, and 8 mg / mL for **P3**, calculated by the weight of polymers) with different weight ratios were heated at 90 °C for 30 min and then stirred overnight at room temperature. The solutions were heated at 90 °C for 30 min before spin coating. Finally, Ca (10 nm) and Al (100 nm) were deposited in high vacuum via a mask to define the active area of 0.10 cm². Over 10 devices were fabricated under the same condition.PCE was estimated from *J-V* curves recorded with a Keithley 2420 source meter under illumination of 100 mW cm⁻² (AM 1.5G). The light intensity was calibrated with a standard silicon photodiode. EQEs of solar cells were analyzed by using a certified Newport incident photon conversion efficiency (IPCE) measurement system. The hole and electron mobilities were calculated according to the reported equation.^[4]

References

[1]X. Qiao, Q. Wu, H. Wu, D. Wang and H, Li, *Polym. Chem.*, 2016, **7**, 807.

[2] Q. Wu, M. Wang, X. Qiao, Y. Xiong, Y. Huang, X. Gao and H. Li, Macromolecules, 2013, 46, 3887.

[3] W. Chen, M. Xiao, L. Han, J. Zhang, H. Jiang, C. Gu,W. Shen and R. Yang, ACS Appl. Mater. Interfaces, 2016, 8, 19665.

[4] M. Wang, D. Cai, Z. Yin, S. C. Chen, C. F. Du and Q. Zheng, Adv. Mater., 2016, 28, 3359.



Figure S1. Cyclic voltammograms of P1 and P2 films on a platinum electrode. Bu₄NPF₆ was used as electrolyte, CH₃CN was used as solution, the scan rate was 50 mV s⁻¹.



Figure S2. *J-V* curves of PSCs based on **P1**:PC₇₁BM under AM 1.5G illumination (100 mWcm⁻²). (a) with different blend ratio; (b) with different DIO additives (the blend ratio of **P1** to PC₇₁BM is 1: 2).



Figure S3. *J-V* curves of PSCs based on **P2**:PC₇₁BM under AM 1.5G illumination (100 mWcm⁻²).(a) with different blend ratio; (b) with different DIO additives (the blend ratio of **P2** to PC₇₁BM is 1: 2).



Figure S4. *J-V* curves of PSCs based on **P3**:PC₇₁BM under AM 1.5G illumination (100 mWcm⁻²). (a) with different blend ratio; (b) with different DIO additives (the blend ratio of **P2** to PC₇₁BM is 1: 1.5).

Polymer ^{a)}	D:A ^{b)}	$V_{ m oc}$ (V)	$J_{\rm sc} ({\rm mAcm}^{-2})$	FF (%)	PCE (%) ^{c)}
P1	1:1.5	0.91	7.90	69.25	4.98 (4.72±0.26)
	1:2	0.91	10.11	67.29	6.19(6.05±0.14)
	1:2.5	0.90	7.59	65.65	4.48 (4.29±0.19)
P2	1:1.5	0.89	12.78	68.10	7.74 (7.50±0.24)
	1:2	0.89	13.92	71.34	8.84 (8.62±0.22)
	1:2.5	0.89	13.81	57.71	7.09 (6.94±0.15)
P3	1:1	0.69	10.13	56.76	3.97 (3.68±0.29)
	1:1.5	0.69	11.70	63.15	5.10 (4.89±0.21)
	1:2	0.68	9.06	54.22	3.34 (3.10±0.24)

Table S1. Photovoltaic parameters of PSCs based on polymer:PC₇₁BM with different blend ratios.

^{a)} The polymer:PC₇₁BM blends were dissolved in *o*-DCB; ^{b)} Blend ratios of polymer:PC₇₁BM (w/w); ^{c)} In parentheses are average values based on 10 devices.

Polymer	DIO (%)	$V_{\rm oc}\left({ m V} ight)$	$J_{\rm sc} ({\rm mAcm}^{-2})$	FF(%)	PCE(%)
P1	0	0.91	10.11	67.29	6.19(6.05±0.14)
	0.25	0.90	10.16	63.16	5.78 (5.58±0.20)
	0.5	0.91	11.17	64.21	6.53(6.29±0.24)
	1	0.91	13.45	67.18	8.22(8.02±0.20)
	2	0.91	11.84	66.08	7.12(6.85±0.27)
P2	0	0.89	13.92	71.34	8.84(8.62±0.22)
	0.25	0.89	14.15	72.13	9.08(8.92±0.16)
	0.5	0.89	12.97	70.09	8.09 (7.95±0.14)
	1	0.88	11.52	68.91	6.99 (6.77±0.22)
Р3	0	0.69	11.70	63.15	5.10(4.89±0.21)
	0.25	0.69	11.39	60.89	4.78(4.52±0.26)
	0.5	0.69	10.40	60.86	4.37 (4.07±0.30)
	1	0.68	9.51	58.75	3.80 (3.55±0.25)

Table S2. Photovoltaic parameters of PSCs based on polymer:PC₇₁BM with DIO.



Figure S5. AFM images $(4 \times 4 \ \mu m)$ of polymer:PC₇₁BM films. (a) **P1**:PC₇₁BM (1:2) with 1% DIO; (b) **P2**:PC₇₁BM (1:2) with 0.25% DIO; (c) **P3**:PC₇₁BM (1:1.5) without DIO.



Figure S6. *J-V* curves of vertical diodes with the device structures of ITO/PEDOT:PSS / polymer:PC₇₁BM / Au for hole only devices, and ITO/ZnO/ polymer:PC₇₁BM/Ca/Al for electron only devices.