

### **Supplementary Information**

### Synthesis of pyridine-capped diketopyrrolopyrrole and its use as a building block of low band-gap polymer for efficient polymer solar cells

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#### Synthesis and Characterization of PyDPP and PBTPyDPP

3,6-bis(5-bromopyridin-2-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-Synthesis of 1,4(2H,5H)-dione (PyDPP): In a dry 150 mL round bottom flask, 150 mL of t-amyl alcohol was added to a mixture of sodium pieces (0.45 g, 19.6 mmol) and 10 mg of FeCl<sub>3</sub>. After fully dissolving sodium by heating the solution at 90 °C for 3 h, 5-bromo-2-pyridinecarbonitrile (3g, 16.4 mmol) and dimethyl succinate (804 mg, 5.5 mmol) were rapidly added to the solution, and then the solution was refluxed for 1 h. The solution was then cooled to room temperature, and then the solution was poured into 200 mL of cold MeOH. After the precipitates were filtered, which is intermediate of 3,6-bis(5-bromopyridin-2-yl)pyrrolo[3,4c]pyrrole-1,4-(2H,5H)-dione, the dark red solid (assuming 5.5 mmol) was mixed with K<sub>2</sub>CO<sub>3</sub> (2.0 g, 14.5 mmol) and 2-octyldodecyl bromide (4.7 g, 13 mmol) in 150 mL of DMF. The mixture was poured into 200 mL of water after refluxing the solution for 30 min. The organic phase was extracted with dichloromethane and washed with brine. After solvent was evaporated, crude solid was purified by column chromatography using dichloromethane as an eluent yielding pure product as a dark red solid (2.25 g, 41% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 8.93 (d, 2H, Ar H), 8.74 (d, 2H, ArH), 8.00 (dd, 2H, ArH), 4.28 (d, 4H), 3.53 (d, 2H), 1.10–1.60 (m, 64H), 0.87 (t, 12H) ; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 165.5, 155.1, 153.5,

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114.0, 113.3, 113.0, 120.7, 49.5, 35.5, 31.8, 30.0, 28.2, 26.5, 22.6, 14.5. Anal. Calcd for C<sub>56</sub>H<sub>88</sub>Br<sub>2</sub>N<sub>4</sub>O<sub>2</sub>: C 66.65, H 8.79, N 5.55. Found: C 66.62, H 8.82, N 5.57.

*Synthesis of PBTPyDPP*: To a mixture of 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (98.4 mg, 0.200 mmol) and 3,6-bis(5-bromopyridin-2-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dion (201.8 mg, 0.200 mmol), a small amount of Pd<sub>2</sub>(dba)<sub>3</sub> and P(*o*-tolyl)<sub>3</sub> were rapidly added under N<sub>2</sub> atmosphere. After 6 mL of anhydrous toluene was added, the solution was refluxed for 24 h under nitrogen, followed by end-capping using 2-bromothiophene and 2-tributyltinthiophene successively. After cooling down to room temperature, the solution was precipitated in methanol. The solid (precipitate) was further purified by Soxhlet extraction successively with methanol, acetone, hexane, and then chloroform. Finally the chloroform fraction was concentrated, and then precipitated in methanol. The dark purple solid was obtained after filtering by PTFE filter in 81% yield.

*Characterization*: <sup>1</sup>H NMR and <sup>13</sup>C NMR (300 MHz) spectra were obtained from a Brucker Avance DPX 300 NMR spectrometer using deuterated chloroform as a solvent. Size exclusion chromatography was performed on Agilent 1200 GPC System (eluted with CHCl<sub>3</sub>). The solution for GPC analysis was stirred at 50 °C for 12 h, and then at room temperature for 1 h. Before injection, the solution was filtered with PTFE 0.45 µm syringe filter. The molecular weights were calculated according to relative calibration with polystyrene standards and toluene was used as a flow marker. Thermogravimetric analysis was performed using a TA Instrument Q500 at a heating rate of 20 °C/min. UV-Vis absorption spectra were obtained from a Lambda 25 (Perkin Elmer) spectrometer. Cyclic voltammetry experiments were carried out on a potentiostat/galvanostat (VMP3, Biologic) in an electrolyte solution of 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile for thin film state or in methylenechloride for solution state, respectively. Platinum wire and gold electrode were used as a counter and a working electrode, respectively, and silver/silver ion (Ag in 0.1 M AgNO<sub>3</sub> solution) was used as a reference electrode. Morphology of the active layer was observed Electronic Supplementary Material (ESI) for Chemical Communications This journal is © The Royal Society of Chemistry 2013

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using transmission electron microscopy (TEM) (JEM1010, JEOL) operating at 80 kV of acceleration voltage. For TEM, the solar cell device was immersed in deionized water and then the active layer was floated onto Cu grid. Grazing incidence X-ray scattering characterization was performed at the Stanford Synchrotron Radiation Light Source on beam 11-3. The scattering signal was recorded on a 2-D image plate (MAR-345) with a pixel size of 150 µm. The samples were 15 mm long in the direction of the beam path, and the detector was located at a distance of 450 mm from the sample center (distance calibrated using a lanthanum hexaboride standard). The incidence angle of 0.1° was chosen which gave the optimized signal-to-background ratio. The beam size was 150 µm by 150 µm, which resulted in a beam exposure on the sample of 150 µm wide over the entire length of the sample. The data was processed and analyzed using WxDiff software package.<sup>[1]</sup>

*Fabrication and characterization of photovoltaic cells:* Photovoltaic cells were fabricated with a conventional structure of ITO/PEDOT:PSS/PBTPyDPP:PC<sub>70</sub>BM/Ca/AI. The patterned indium tin oxide (ITO) glass was cleaned in an ultrasonic bath of acetone and isopropanol, and treated in ultraviolet-ozone chamber for 30 min. Thin layer (40 nm) of poly(3,4-thylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS, Baytron P) was spin-coated onto the ITO glass and baked at 150 °C for 30 min. An *o*-dichlorobenzene solution of PBTPyDPP and PC<sub>71</sub>BM with or without processing additive was subsequently spin-coated on the top of PEDOT:PSS coated ITO glass as an active layer (ca. 90–100 nm thickness) After drying the active layer, calcium (20 nm) and aluminium (100 nm) were thermally evaporated under high vacuum (10–6 Pa) as a metal cathode. The active area of device was 4 mm<sup>2</sup>. The PSC device was characterized in N<sub>2</sub> under 100 mW·cm<sup>-2</sup> (AM1.5G) irradiation using an Oriel Xe arc lamp coupled with a Keithley 4200 source measurement unit. The solar simulator light intensity was calibrated with an NREL certified Si photodiode with a KG5 optical filter. The hole mobility of the active layer was determined by fitting the dark current to the model of a single carrier SCLC, which was described by the equation

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 $J = (9/8)\varepsilon_0\varepsilon_r\mu_h(V^2/d^3)$ , where J is the current density,  $\mu h$  is the zero-field mobility,  $\varepsilon_0$  is the permittivity of free space,  $\varepsilon_r$  is the relative permittivity of the material, V is the effective voltage, and d is the thickness of polymer layer.

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**Figure S1.** Cyclic voltammetry of PBTPyDPP thin film and solution states as compared to ferrocene.





**Figure S2.** Electrostatic potential maps PBTPyDPP at HOMO and LUMO levels computed using DFT at B3LYP/6-31G\* level.



**Figure S3.** Current density–voltage curves of the PSC devices based on PBTPyDPP and  $PC_{71}BM$  with different blend ratios of PBTPyDPP to  $PC_{71}BM$  in DCB under the illumination of AM 1.5G, 100 mW/cm<sup>2</sup>.

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**Figure S4.** Current density–voltage curves of the PSC devices based on PBTPyDPP and PC<sub>71</sub>BM from CHCl<sub>3</sub> and mixture of CHCl<sub>3</sub> and DCB under the illumination of AM 1.5G, 100 mW/cm<sup>2</sup>.

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**Figure S5.** TEM images of active layer thin films of PBTPyDPP:PC<sub>71</sub>BM cast from different solvent mixture.



**Figure S6.** Dark current density–effective voltage curves from SCLC hole-only device based on PBTPyDPP:PC<sub>71</sub>BM blend films cast from different solvent mixture.

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**Figure S7.** IPCE spectrum of solar cell device made of PBTPyDPP:PC<sub>71</sub>BM cast from *o*-DCB with 5.0 vol% CN. The integrated JSC from IPCE spectrum yielded 7.62 mA/cm<sup>2</sup>.

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Blend ratio (PBTPyDPP:PC <sub>71</sub> BM)	Solvent	V <sub>OC</sub> (V)	J <sub>SC</sub> (mA/cm²)	FF (%)	PCE <sub>Max</sub> (%)	PCE <sub>Average</sub> <sup>a</sup> (%)	
1:1	DCB	0.91	4.79	62.4	2.72	2.66	
1:2	DCB	0.91	6.57	61.5	3.68	3.54	
1:3	DCB	0.90	6.41	60.8	3.51	3.48	
1:2	CF	0.73	3.14	50.1	1.15	1.08	
1:2	CF/DCB (1:4 v/v)	0.77	3.43	56.9	1.50	1.32	
1:2	DCB + 1.0 vol% DIO	0.86	6.61	58.8	3.34	3.25	
1:2	DCB + 2.0 vol% DIO	0.82	7.18	56.1	3.31	3.18	
1:2	DCB + 2.5 vol% CN	0.89	6.61	59.1	3.48	3.41	
1:2	DCB + 5.0 vol% CN	0.92	7.96	65.8	4.88	4.72	
1:2	DCB + 7.5 vol% CN	0.90	7.63	57.8	3.97	3.90	

### Table S1. Photovoltaic properties of PBTPyDPP and PC71BM

<sup>a</sup> solar cell devices were fabricated more than 8 cells in each condition

#### Table S2. Structural details of PBTPyDPP and PBTPyDPP:PC71BM films

film	<i>q</i> (Å <sup>−1</sup> )	d Z,100 (Å)	L <sub>Z,100</sub> (nm)	<i>q</i> (Å <sup>−1</sup> )	d Z,010 (Å)	q (Å⁻¹)	d <sub>XY,100</sub> (Å)	L <sub>XY,100</sub> (nm)	q (Å <sup>-1</sup> )	d Z,010 (Å)
PBTPyDPP	0.326	19.3	12.2	1.78	3.53	0.312	20.1	14.6	1.76	3.57
PBTPyDPP:PC71BM	0.331	19.0	12.2	1.78	3.53	0.317	19.9	22.5	1.76	3.57

#### Reference

1. S. C. B. Mannsfeld, M. L. Tang and Z. Bao, Adv. Mater., 2011, 23, 127.