

Supporting Information

Low band-gap copolymer composed of thienyl substituted anthracene and diketopyrrolopyrrole compatible with multiple electron acceptors for high efficiency polymer solar cells

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Characterization

¹H NMR spectra were obtained from Bruker Avance 300MHz NMR spectrometer with deuterated chloroform as a solvent. Size exclusion chromatography was performed at room temperature on Agilent 1200 GPC System (eluted with CHCl₃). The molecular weights were calculated according to relative calibration with polystyrene standards. UV-Vis absorption spectra were measured with 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 using gold electrodes as a counter and a working electrode, respectively, and silver/silver ion (Ag in 0.1 M AgNO₃ solution) was used as a reference electrode. The thin film morphology was observed by transmission electron microscopy (TEM) (JEM1010) operating at 80 kV of acceleration voltage. The crystallinities of the films were investigated by X-ray diffractometer (M18XHF-SRA). To characterize charge transport characteristics of the copolymers, thin film transistors (bottom-gate top-contact device geometry) were fabricated. On the heavily n-doped SiO₂/Si substrate, the spin-coated films (thickness of 50 nm) of PTATDPP or PTAFDPP were coated from chloroform solution. Surface of the substrate was treated by octadecyltrichlorosilane to make hydrophobic dielectric surface. Au was then thermally evaporated (60 nm) as source and drain electrodes with channel width and length of 1500 μm and 30 μm, respectively. All the devices were fabricated in this study were clearly isolated to

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achieve negligible gate leakage current. All the field effect mobilities were extracted in the saturation regime using the relationship $\mu_{\text{sat}} = (2 \cdot I_{\text{DS}} \cdot L) / (W \cdot C (V_{\text{G}} - V_{\text{th}})^2)$, where I_{DS} is saturation drain current, C is capacitance of SiO_2 dielectric, V_{G} is gate bias, and V_{th} is threshold voltage. The device performance was evaluated under N_2 atmosphere using 4200-SCS semiconductor characterization system.

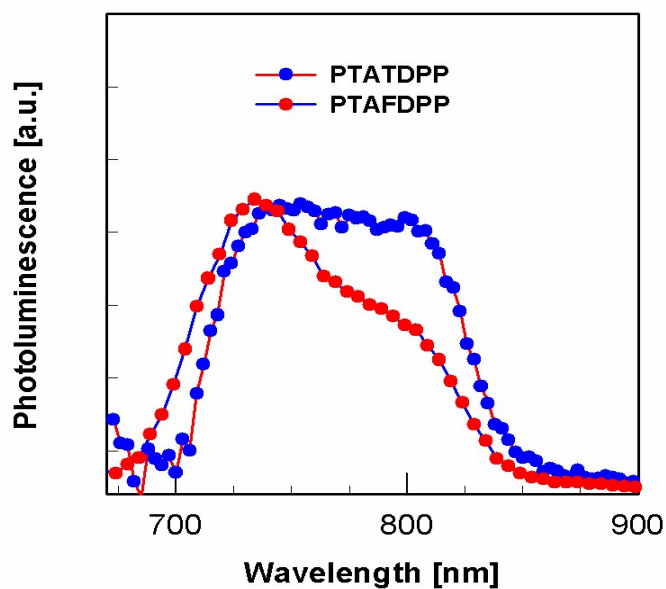


Figure S1. Photoluminescence spectra of PTATDPP and PTAFDPP films on glass substrates (excited at 600 nm).

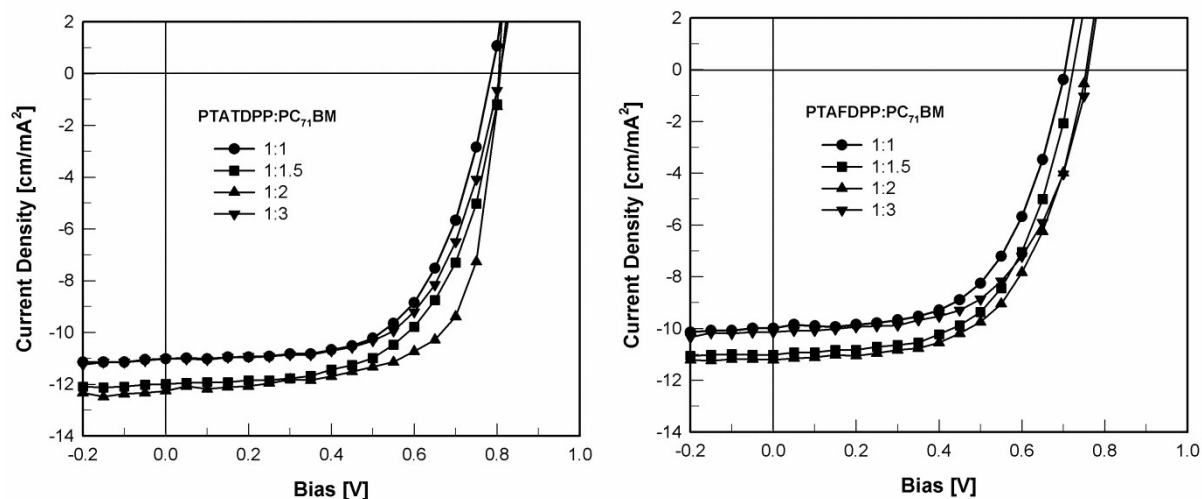


Figure S2. Current density–voltage curves of the PSC devices based on PTATDPP:PC₇₁BM blend with different blend ratios (left) and PTAFDPP:PC₇₁BM blend with different blend ratios (right) under the illumination of AM 1.5G, 100 mW/cm^2 .

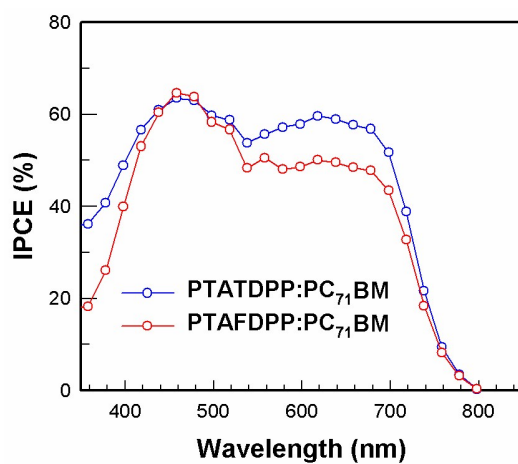


Fig. S3. Incident photon to current efficiencies of PSC devices made of PTATDPP:PC₇₁BM blend and PTAFDPP:PC₇₁BM blend films.

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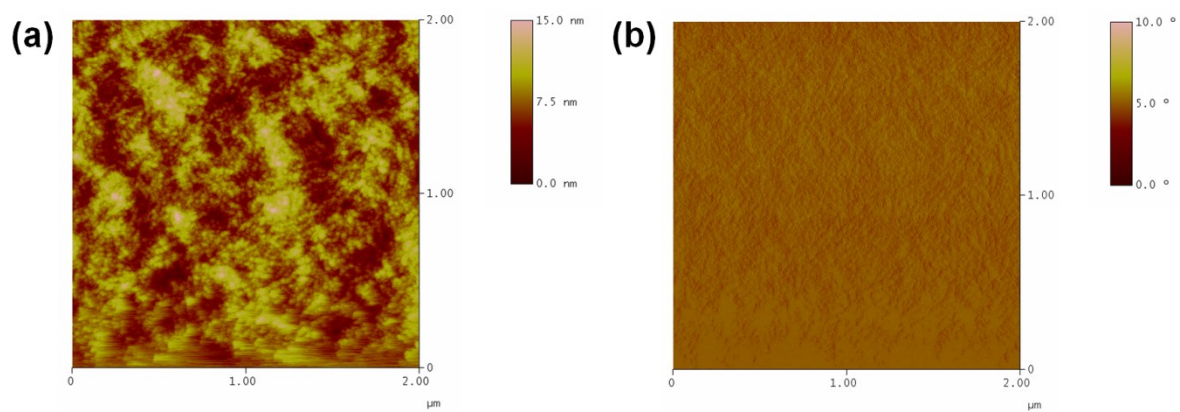


Fig. S4. (a) Height and (b) phase images of PTATDPP:di-PBI observed from AFM.

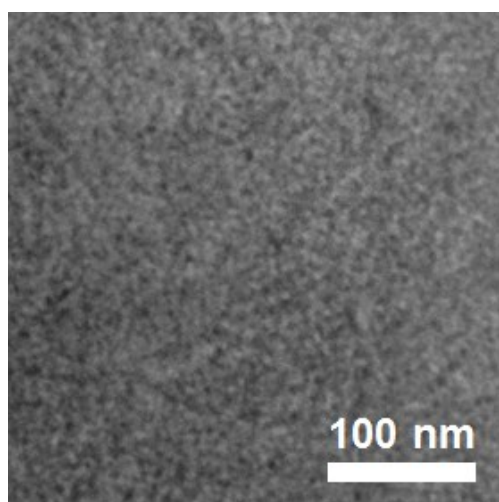


Fig. S5. TEM image of PTATDPP:di-PBI blend film.

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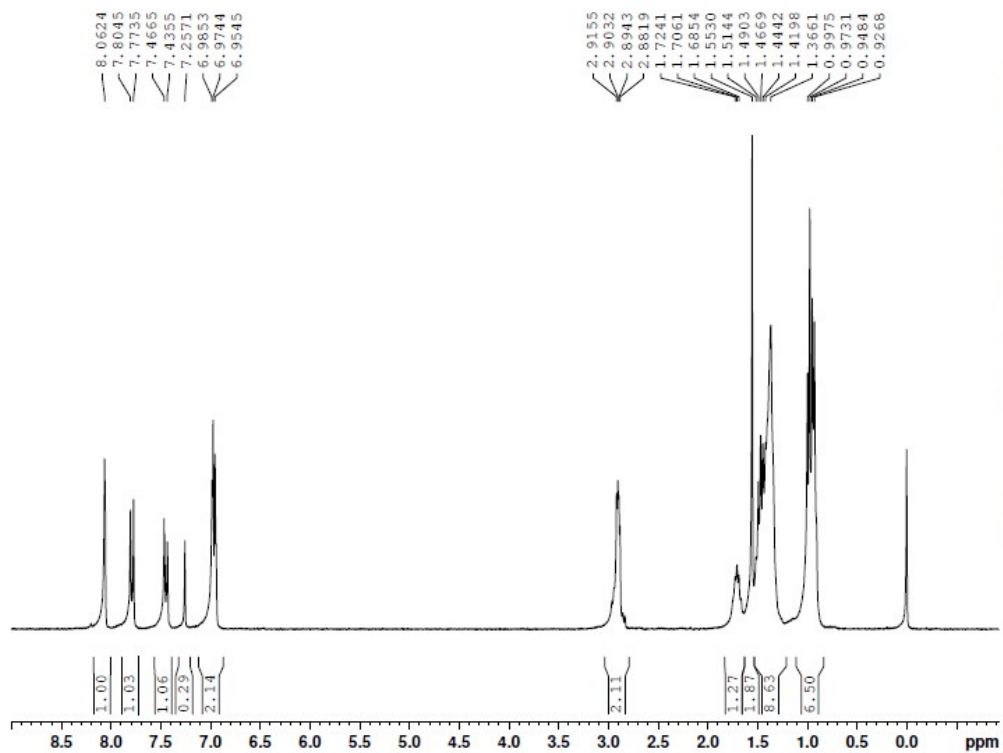


Fig. S6. ¹H NMR spectrum of M1.

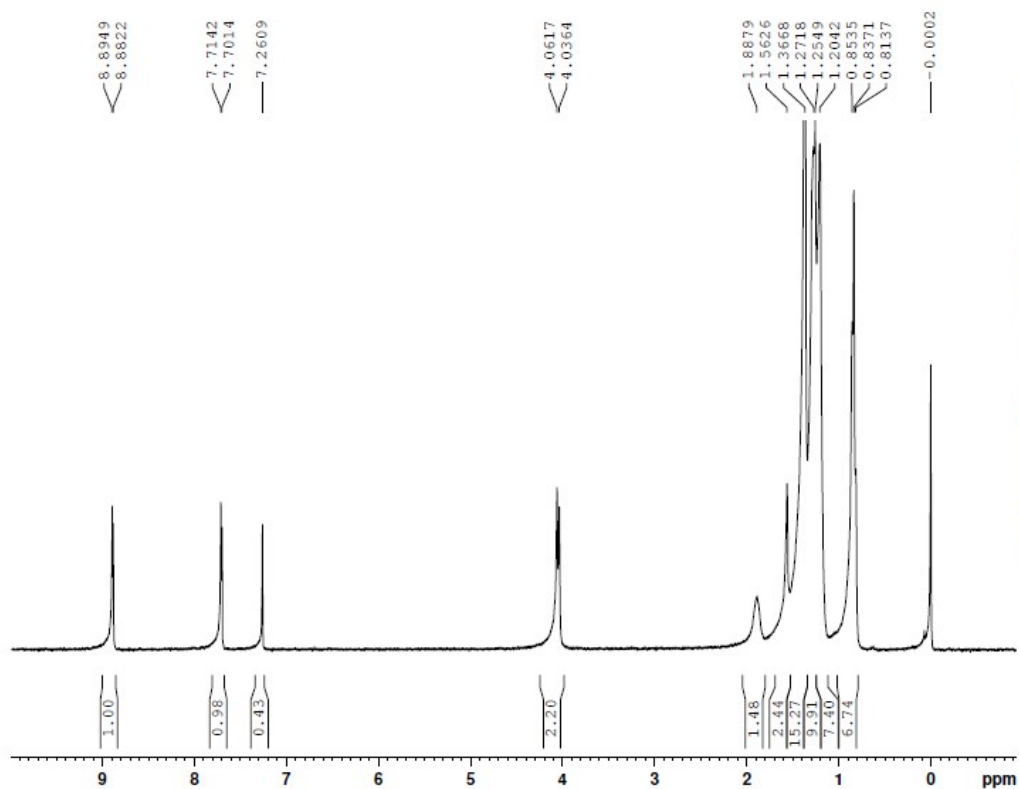


Fig. S7. ¹H NMR spectrum of M2.

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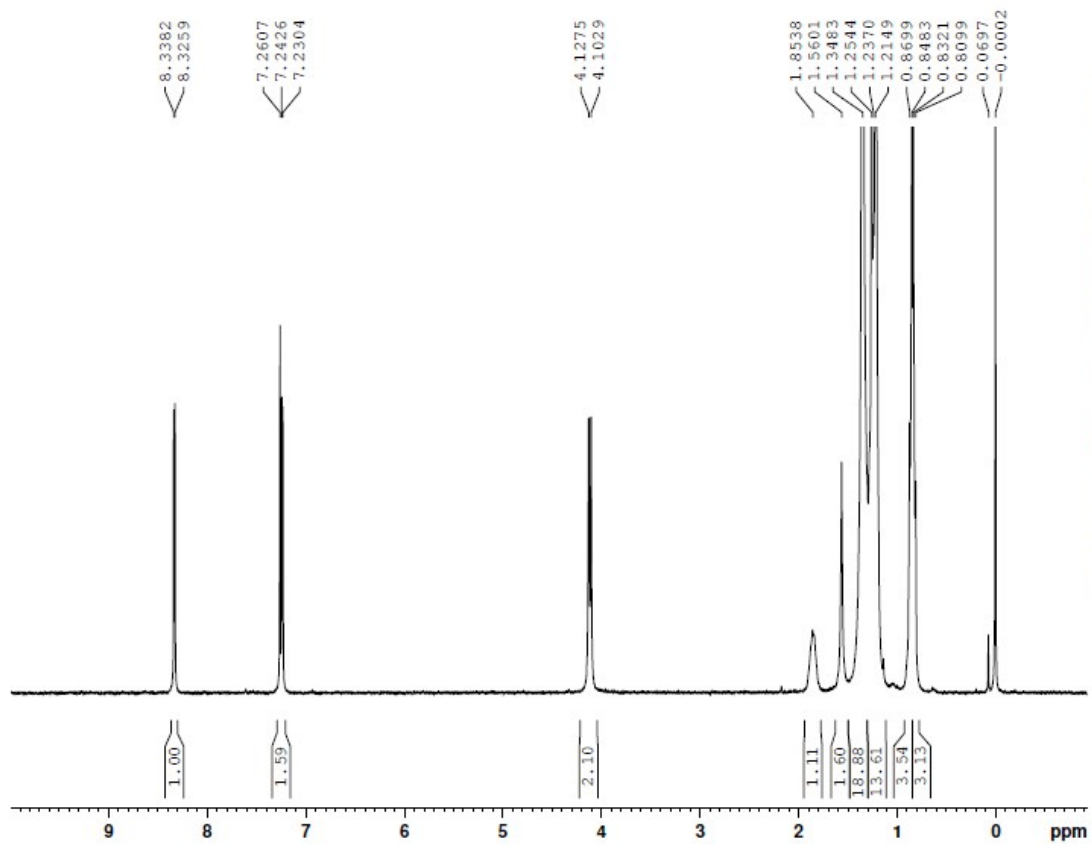


Fig. S8. ¹H NMR spectrum of M3.

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Table S1. Photovoltaic parameters of PSC devices based on PTATDPP:PC₇₁BM blend
PTAFDPP:PC₇₁BM blend with different blend ratios

Polymer	Ratio to :PC ₇₁ BM	V _{oc} (V)	J _{sc} (mA/cm ²)	FF	PCE (%) ^a
PTATDPP	1:1	0.80 (0.80 ± 0.01)	11.0 (10.6 ± 0.4)	0.62 (0.60 ± 0.02)	5.42 (5.11 ± 0.30)
	1:1.5	0.81 (0.80 ± 0.01)	11.1 (10.8 ± 0.3)	0.61 (0.60 ± 0.01)	5.47 (5.25 ± 0.21)
	1:2	0.80 (0.80 ± 0.01)	12.3 (11.4 ± 0.9)	0.68 (0.65 ± 0.03)	6.69 (6.45 ± 0.24)
	1:3	0.81 (0.80 ± 0.01)	11.0 (10.2 ± 0.7)	0.63 (0.59 ± 0.03)	6.00 (5.60 ± 0.40)
PTAFDPP	1:1	0.71 (0.71 ± 0.01)	10.0 (9.4 ± 0.6)	0.59 (0.57 ± 0.02)	4.14 (3.88 ± 0.25)
	1:1.5	0.73 (0.72 ± 0.01)	11.0 (10.6 ± 0.3)	0.60 (0.57 ± 0.02)	4.71 (4.50 ± 0.21)
	1:2	0.76 (0.75 ± 0.01)	11.2 (10.1 ± 1.1)	0.59 (0.57 ± 0.02)	5.02 (4.68 ± 0.34)
	1:3	0.77 (0.76 ± 0.01)	10.1 (9.6 ± 0.4)	0.59 (0.55 ± 0.04)	4.59 (4.43 ± 0.16)

^aMore than 20 devices were fabricated in each condition.

Table S2. Photovoltaic parameters of optimized devices based on PTATDPP and PTAFDPP.

Polymer	Ratio to PC ₇₁ BM	Device architecture	V _{oc} (V)	J _{sc} (mA/cm ²)	FF	PCE (%) ^a
PTATDPP	1:2	conventional	0.80 (0.80 ± 0.01)	12.3 (11.4 ± 0.9)	0.68 (0.65 ± 0.03)	6.69 (6.45 ± 0.24)
		inverted	0.80 (0.80 ± 0.01)	13.1 (12.5 ± 0.6)	0.67 (0.64 ± 0.03)	7.02 (6.75 ± 0.27)
PTAFDPP	1:2	conventional	0.76 (0.75 ± 0.01)	11.2 (10.1 ± 1.1)	0.59 (0.57 ± 0.02)	5.02 (4.68 ± 0.34)
		inverted	0.75 (0.75 ± 0.01)	11.4 (10.6 ± 0.5)	0.61 (0.57 ± 0.03)	5.22 (4.87 ± 0.35)

^aMore than 20 devices were fabricated in each condition.

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Reference

1. L. Dou, J. Gao, E. Richard, J. You, C.-C. Chen, K. C. Cha, Y. He, G. Li and Y. Yang, *J. Am. Chem. Soc.*, 2012, **134**, 10071
2. L. Dou, W.-H. Chang, J. Gao, C.-C. Chen, J. You, Y. Yang, *Adv. Mater.*, 2013, **25**, 825