

[\[Supplementary Information\]](#)

**Strong Addition Effect of Charge-Bridging Polymer in Polymer:Fullerene Solar Cells with Low Fullerene Contents**

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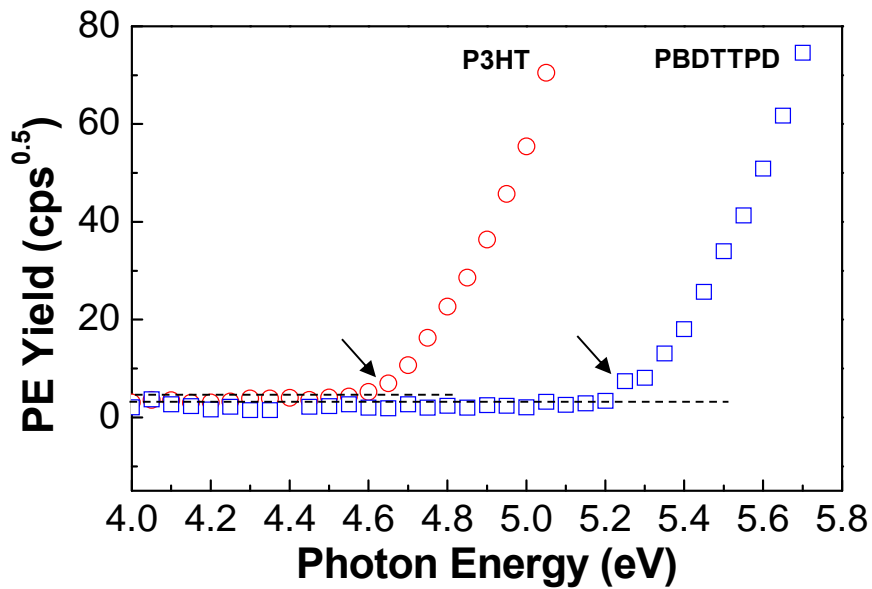
This ESI contains summary of solar cell performance, d-spacings for pristine and BHJ films, photoelectron (PE) yield spectra of P3HT and PBDTTPD films, semi-logarithmic J-V curves of devices, dark J-V curves of devices, light J-V curves of two binary BHJ devices, thickness-normalized PL spectra of P3HT and PBDTTPD films, and enlarged TEM images.

**Table S1.** Summary of solar cell performances according to the PBDTTPD content. All data were taken from the light J-V curves in Figure 1.

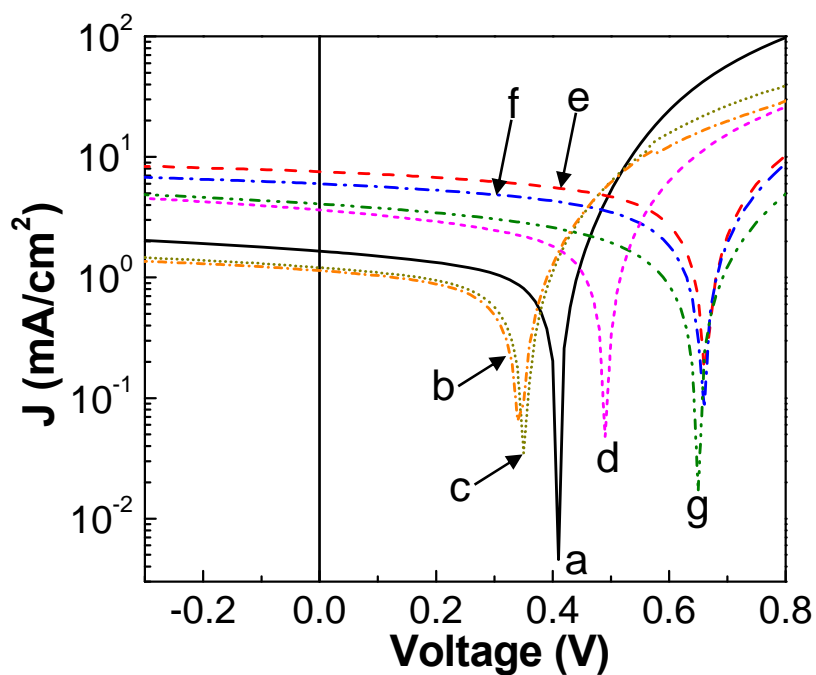
PBDTTPD (wt.%)	0	1	5	10	20	40	60
$J_{SC}$ (mA/cm <sup>2</sup> )	1.655	1.142	1.210	3.638	7.551	5.985	4.074
$V_{OC}$ (V)	0.40	0.34	0.35	0.49	0.66	0.65	0.64
FF (%)	48.7	48.5	48.2	43.2	47.3	45.7	40.1
PCE (%)	0.322	0.188	0.204	0.770	2.358	1.779	1.045
$R_S$ (k $\Omega$ cm <sup>2</sup> )	0.59	0.77	0.71	0.32	0.21	0.30	0.58
$R_{SH}$ (k $\Omega$ cm <sup>2</sup> )	8.0	13.2	12.1	3.7	3.4	3.2	3.9

**Table S2.** d-spacing values for the pristine (P3HT and PBDTTPD) and bulk heterojunction (BHJ) films with different PBDTTPD contents. All data are taken from the GIXD profiles from Figure 7.

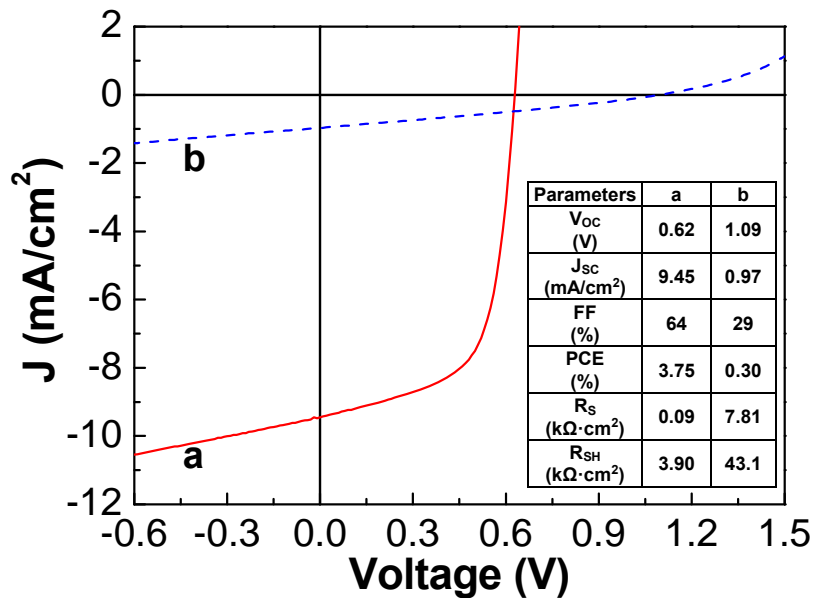
Films	Constituent	Direction	d-spacing (Å)
Pristine	P3HT	OOP, IP	16.42
Pristine	PBDTTPD	OOP, IP	18.75
BHJ PBDTTPD (wt.%) = 0 wt.%	P3HT	OOP	16.74
	PBDTTPD	IP	16.57
BHJ PBDTTPD (wt.%) = 20 wt.%	P3HT	OOP	N/M
	PBDTTPD	OOP	18.53
	P3HT	IP	16.49
	PBDTTPD	IP	18.35
BHJ PBDTTPD (wt.%) = 40 wt.%	P3HT	OOP	N/M
	PBDTTPD	OOP	18.70
	P3HT	IP	16.74
	PBDTTPD	IP	18.70



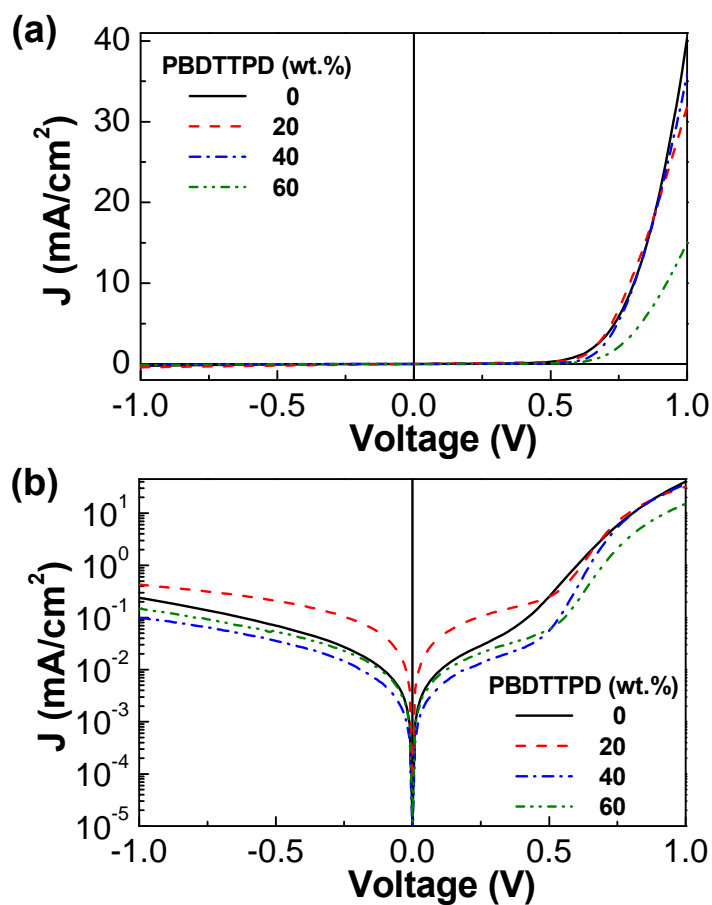
**Fig. S1.** Photoelectron (PE) yield spectra of the pristine polymer films (P3HT and PBDTTPD) coated on the ITO-glass substrates. Arrows denote the onset points for each film.



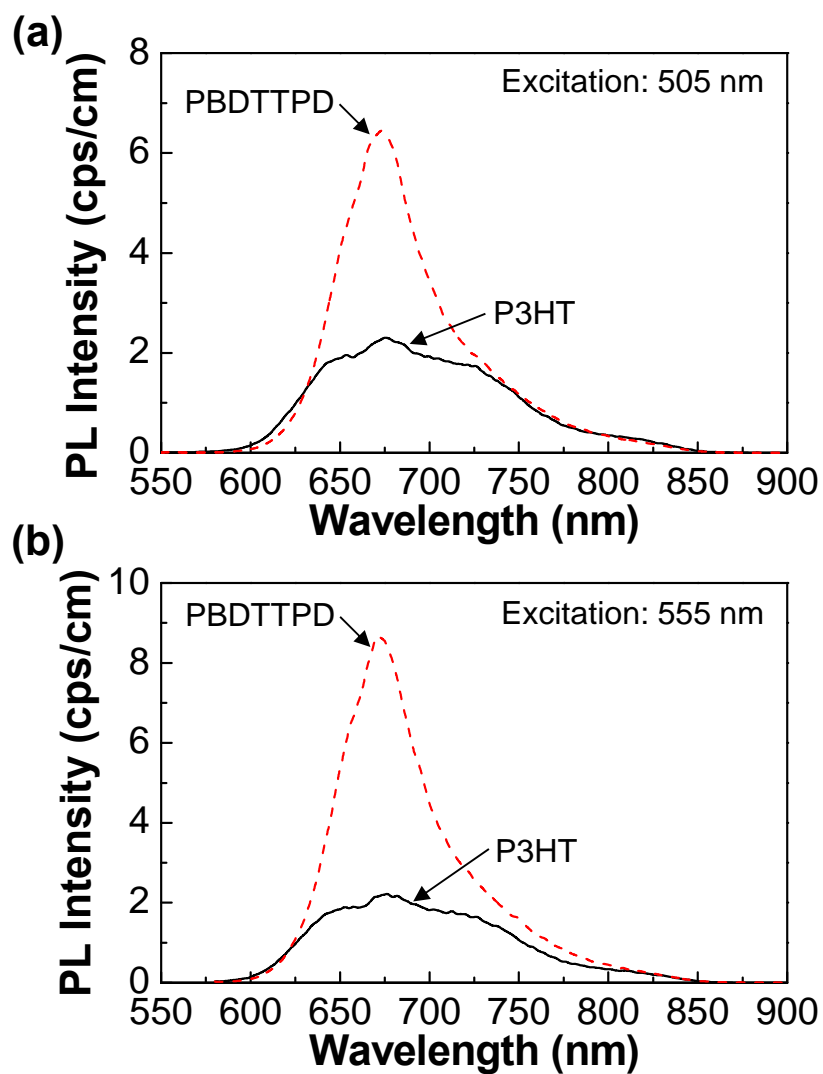
**Fig. S2.** Semi-logarithmic light ( $100 \text{ mW/cm}^2$ ) J-V curves of devices according to the PBDTTPD content: (a) 0, (b) 1, (c) 5, (d) 10, (e) 20, (f) 40 wt.%.



**Fig. S3.** Light J-V curves for two binary BHJ devices with the glass/ITO/PEDOT:PSS/ active layer/LiF/Al structure. The active layer was (a) P3HT:PC<sub>61</sub>BM (1:1 by weight) and (b) P3HT:PBDTTPD (1:0.7 by weight).

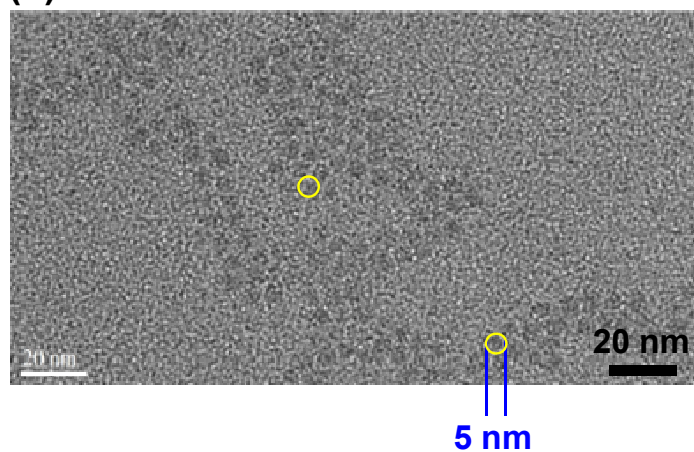


**Fig. S4.** Dark J-V curves of devices according to the PBDTTPD content: (a) linear plot, (b) semi-logarithmic plot.

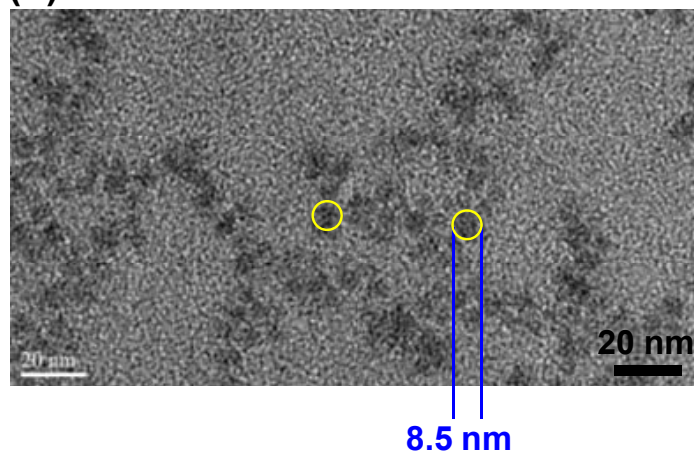


**Fig. S5.** Thickness-normalized PL spectra of the pristine films (P3HT and PBDTTPD). The excitation wavelength was (a) 505 nm and (b) 555 nm.

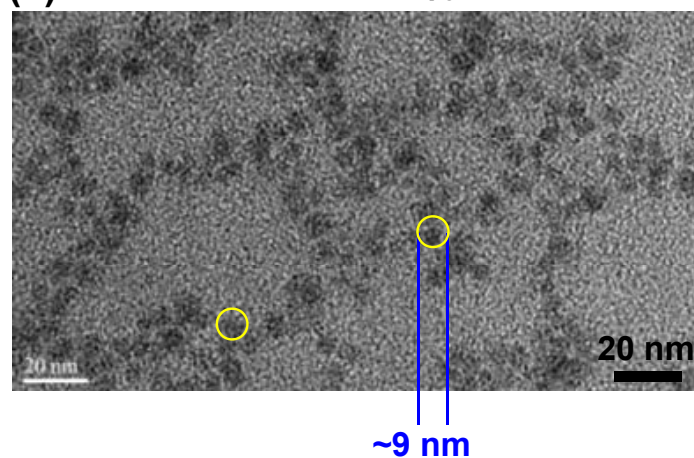
(a) PBDTTPD = 0 wt.%



(b) PBDTTPD = 20 wt.%



(c) PBDTTPD = 40 wt.%



**Fig. S6.** Enlarged TEM images of the bulk heterojunction films according to the PBDTTPPD content. The approximate size of PC<sub>61</sub>BM aggregates is displayed in each image.