

ADVANCED MATERIALS

Supporting Information

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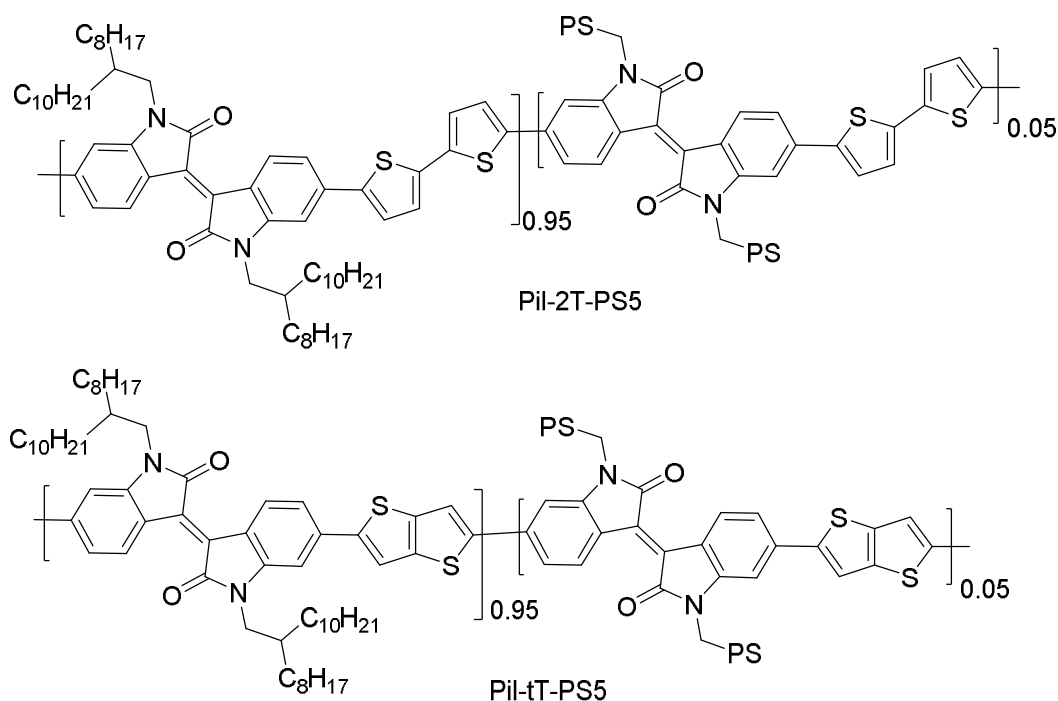
High Performance All-Polymer Solar Cell via Polymer Side-Chain Engineering

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Supporting Information

Title High Performance All-Polymer Solar Cell via Polymer Side-Chain Engineering

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Scheme S1. Polystyrene modified polymer donor.^[22]

Table S1. Opto-physical characteristics of the donors and acceptor. The optical band gaps were calculated from the onset of the absorption of neat polymer films on ZnO covered glass. The HOMO and LUMO levels were obtained by UPS and IPES measurement under vacuum. The molecular weight and PDI of all polymers were measured by high temperature GPC with 1,2,4-trichlorobenzene as the solvent and polystyrenes as the calibration standards at 160 °C.

polymers	$E_{g,opt}/\text{eV}$	E_{HOMO}/eV	E_{LUMO}/eV	$\lambda_{max, em}/\text{nm}$	$\lambda_{max, abs}/\text{nm}$	PDI	M_n/kD
PiI-2T	1.65	-5.41	-3.76	800	701,635	2.89	12.1
PiI-tT	1.61	-5.30	-3.74	825	722,658	2.68	18.1
PiI-BDT	1.70	-5.45	-3.65	740,800	673,612	2.21	16.3
PiI-2F	1.61	-5.32	-3.72	820	711,646	1.66	28.8
P(TP)	1.80	-5.60	-3.80	760	565	2.10	20.5

Table S2. The d-spacing of the pure polymer films measured by GIXRD. The films were prepared by spin-coating on ZnO covered silicon substrates.

	PiI-2T	PiI-BDT	PiI-tT	PiI-2F	PiI-2T-PS5	PiI-tT-PS5
$d_{lamella}/\text{\AA}$	19.72	19.84	20.98	19.56	19.34	21.54
$d_{\pi-\pi}/\text{\AA}$	3.67	3.51	3.50	3.65	3.69	3.50

Table S3. The hole and electron mobilities of the donor and acceptor polymers, respectively.

The mobilities were measured by SCLC diode, and calculated from equation S1. The hole mobilities were measured by hole only diode with structure of ITO/PEDOT:PSS/blend film/MoO₃/Ag, and the electron mobility was measured by electron only diode with structure of ITO/ZnO/Blend film/LiF/Al.

	PiI-2T	PiI-BDT	PiI-tT	PiI-2F	PiI-2T-PS5	P(TP) ^a
mobility/ $\times 10^{-4} \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$	1.8	1.3	1.8	2.0	1.4	0.2

a. Electron mobility.

$$J = \frac{9\epsilon_r\epsilon_0\mu V^2}{8l^3}$$

Equation S1

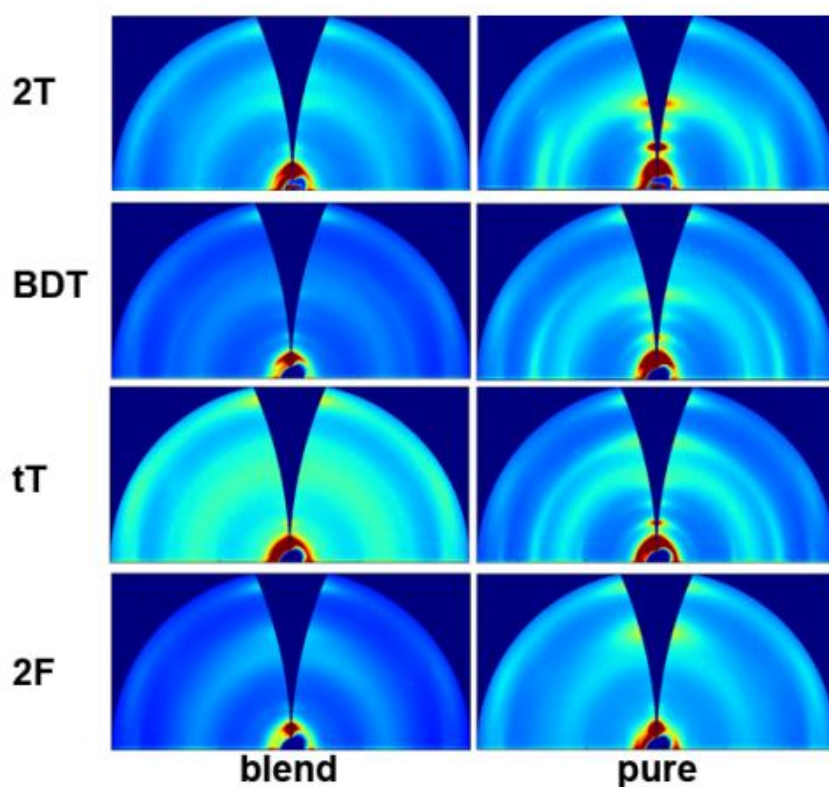


Figure S1. GIXRD patterns of the neat donor films and the blends films with P(TP). All the scattering intensities with the same donor were shown in the same scale bars for comparison.

We evaluated the BHJ blend morphology by GIXRD. Only the scattering signals from the donor polymers were visible. All the BHJ films still showed strong lamellar patterns from the donor polymer. The d-spacing did not change between the neat films and blend films, for both the lamellar distance and the π - π distance, but the intensities of those diffraction patterns were notably lower. This indicates that the crystallinity of the donor polymers was reduced by blending with the acceptor polymer, but the orientation of the crystalline regions remains unchanged.

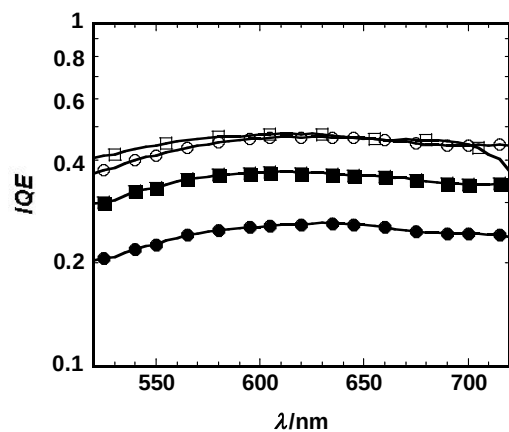


Figure S2. IQE spectra of the all polymer solar cell. PiI-2T(empty circle), PiI-BDT(empty square), filled squares(PiI-2F) and filled circle(PiI-tT).

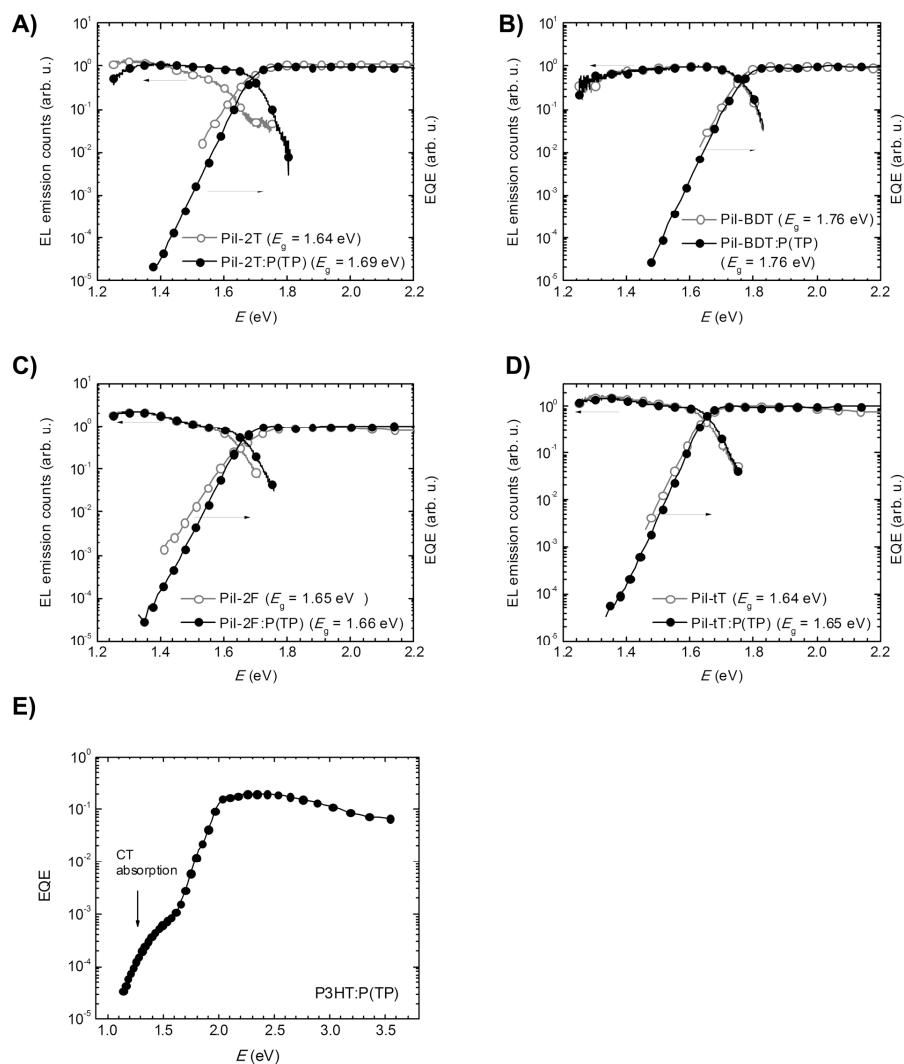


Figure S3. The high sensitive EQE spectra and electro-luminescence spectra of the pure polymer donors and the blends with P(TP).(A~D). High sensitive EQE spectrum of the blends with P(TP) and P3HT.

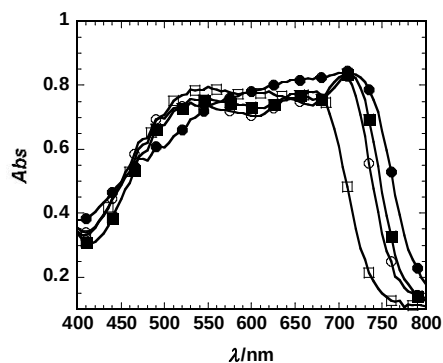


Figure S4. Double pass absorption of the devices. PiI-2T(empty circle), PiI-BDT(empty square), filled squares(PiI-2F) and filled circle(PiI-tT).

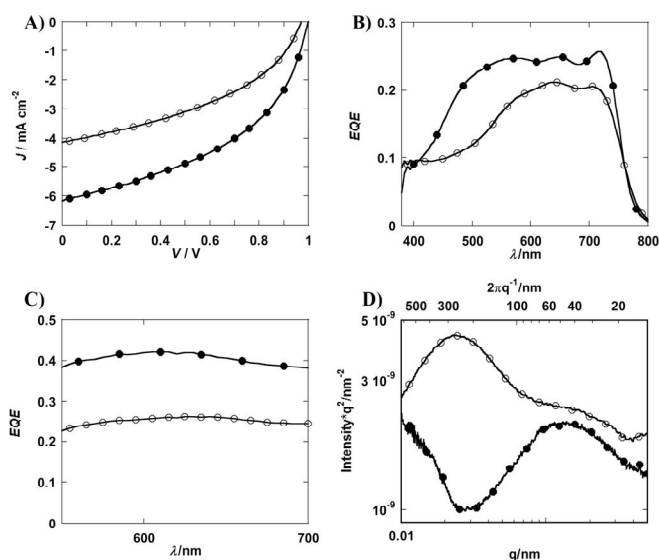


Figure S5. J - V curves(A), EQE spectra(B), IQE spectra(C) and RSoXS scattering features of solar cell made by PiI-tT/P(TP) (circles) and PiI-tT-PS5/P(TP) (filled circles).

We evaluate the recombination mechanisms of the charge carriers in the all polymer solar cell to better understand the device characteristics and to further optimize the performance. We thus tested the J - V curves under different light intensities. As shown in figure S6a and S6b, the J_{SC} followed power relationship with the incident light intensity ($J_{SC} \propto L.I.^{\alpha}$), with PiI-2T/P(TP) and PiI-BDT/P(TP) having a power index(α) of

0.92 to 0.94, while PiI-2F/P(TP) and PiI-tT/P(TP) had power index of 0.88 and 0.84, respectively. The deviations of powers from 1 indicated that even at the J_{SC} condition, bimolecular recombination was significant in these devices. The low power index of the PiI-2F and PiI-tT with respectively lower J_{SC} confirmed the severe free-charge recombination in those films. As shown in figure 4b, the V_{OC} followed different trends, with PiI-2T, PiI-BDT and PiI-2F, the slope was around $1.1kT/q$, indicating bimolecular recombination's dominance in this condition. And in PiI-tT films, the index was larger than $2kT/q$, which showed that severe monomolecular recombination occurred even in the V_{OC} region. Such monomolecular recombination most probably is caused by the large phase separation in the polymers blends.

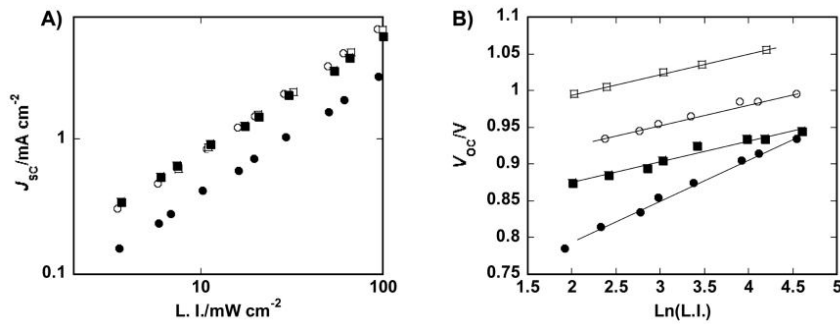


Figure S6. A) J_{SC} vs the incident light intensity(L.I.) and B) V_{OC} vs the $\ln(L.I.)$.

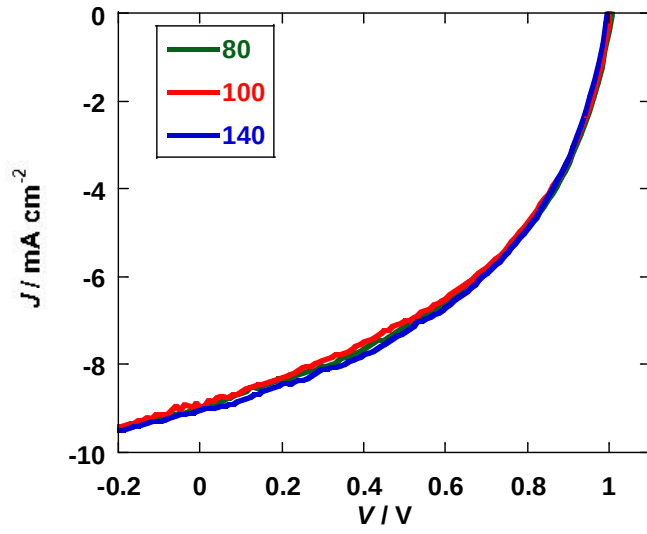


Figure S7. J - V curves of PiI-2T-PS5/P(TP) under different annealing conditions prior the deposition of the electrodes.

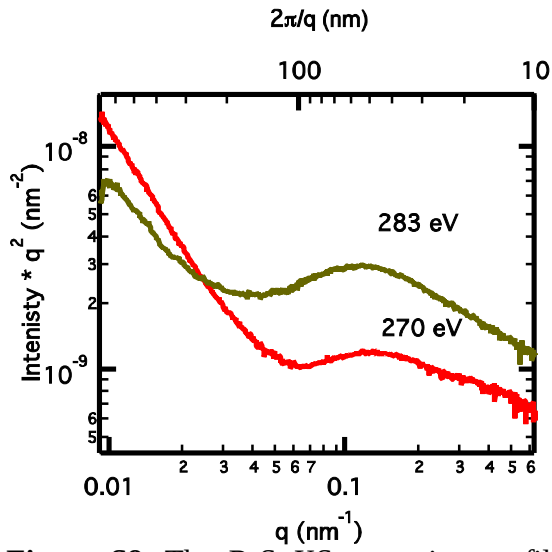


Figure S8. The R-SoXS scattering profiles at 270 eV and 283 eV for PiI-2T/P(TP) blends. At 270 eV, the vacuum/materials contrast dominates the scattering, and a weak peak is observed. At 283 eV, due the enhanced polymer-polymer contrast, the peak is more clear and intense.

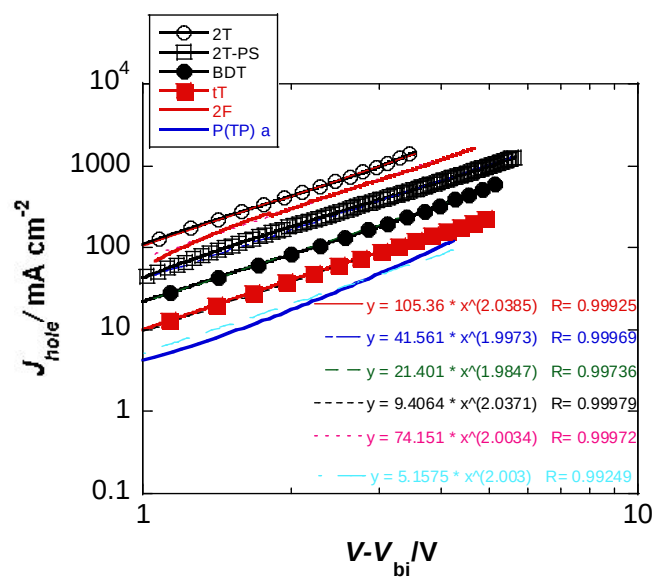


Figure 9. Raw SCLC data for the hole only and electron only diodes.

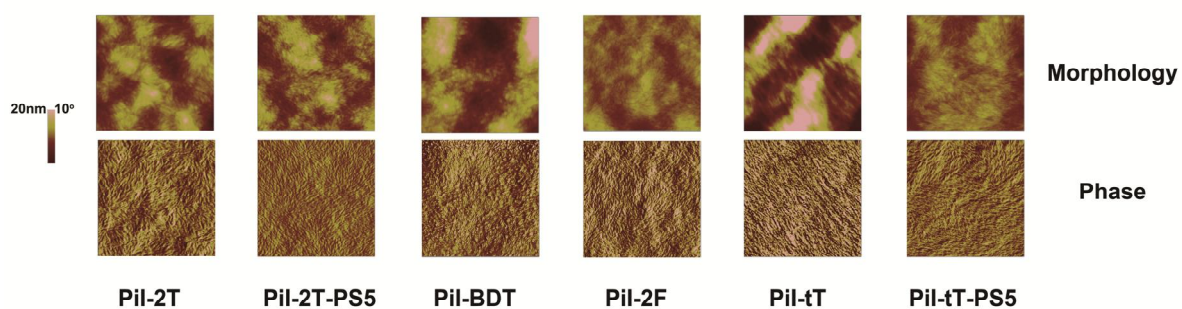


Figure 10. AFM images of the blend films. All the images are $1 \times 1 \mu\text{m}^2$.