

## Supporting Information

Fluorinated D1<sub>(0.5)</sub>-A-D2<sub>(0.5)</sub>-A model terpolymer: ultrafast charge separation kinetics and electron transfer at fluorinated D/A interface for power conversion

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## Experiment Section

### Instrument and measurements

The thermal property of the polymers were measured by thermogravimetric analysis (TGA) in a nitrogen atmosphere at a heating rate of 10 °C min<sup>-1</sup>. UV-vis absorption spectra were performed on Lambda 25 spectrophotometer. Cyclic voltammetry (CV) measurements were taken on a CHI660D electrochemical workstation. The CV experiments were carried out at room temperature with a conventional three-electrode system using a glassy carbon electrode as working electrode, Pt wire as the counter electrode, and saturated calomel electrode as the reference electrode. Tetrabutylammonium phosphorus hexafluoride (Bu<sub>4</sub>NPF<sub>6</sub>, 0.1 M) in acetonitrile solution was used as the supporting electrolyte, and the scan rate was 100 mV/s. Ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) was used as the internal standard. Atomic force microscopy (AFM) was recorded in tapping mode under ambient conditions using an Agilent 5400 instrument. Transmission electron microscopy (TEM) images were acquired using a HITACHI H-7650 electron microscope operating at an acceleration voltage of 100 kV.

### Materials and synthesis

The polymer of PBTA-PS was synthesized according to the literature.<sup>[1]</sup> The monomers BDTPS and BDTPSF were previous synthesized in our laboratory,<sup>[2,3]</sup> monomer 4,7-bis(5-bromothiophen-2-yl)-5,6-difluoro-2-(2-hexyldecyl)-2H-benzo[d][1,2,3]triazole was purchased from Derthon Photoelectric Material Technology Co., LTD. Tetrahydrofuran and toluene need to be dried over Na/benzophenone and freshly distilled prior to use. Other chemicals were commercial and can be used as received.

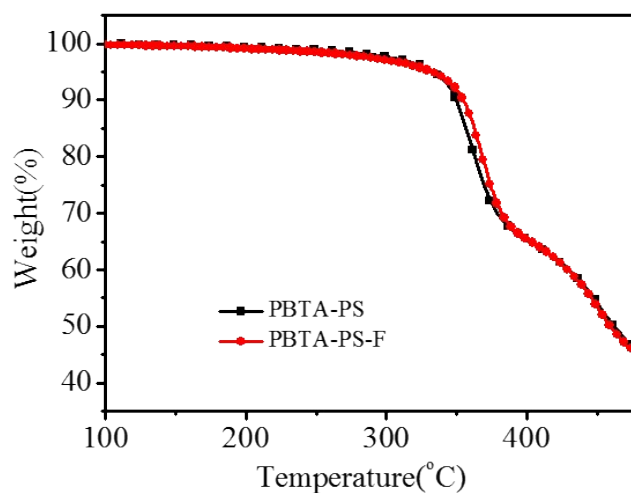
### Synthesis of polymer PBTA-PS-F

Compound BDTPS (59.05 mg, 0.05 mmol), BDTPSF (60.85 mg, 0.05 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (1.8 mg, 0.002 mmol), and P(o-tol)<sub>3</sub> (3.6 mg, 0.012 mmol) were added into a flask. The flask was subjected to three successive cycles of vacuum followed by refilling with argon, and then 5 mL

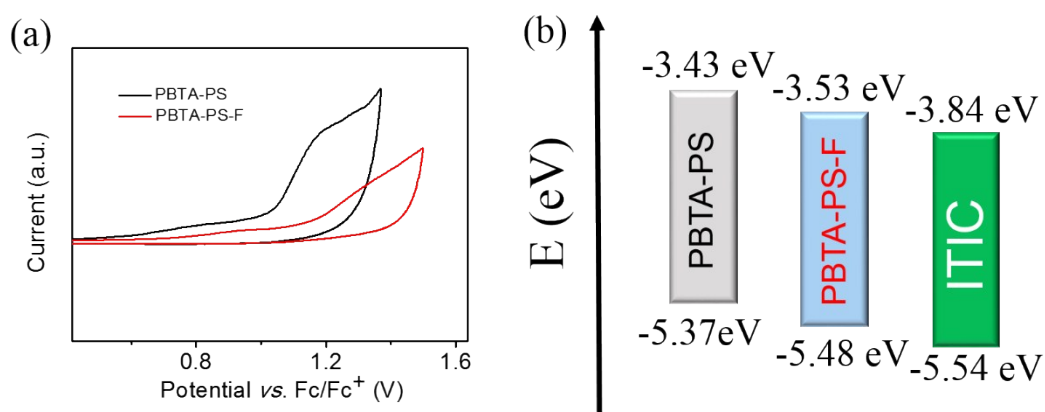
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of dry toluene was added. The reaction mixture was heated to 110 °C carefully for 6 h under argon protection. Then the mixture was cooled to room temperature, and the polymer was precipitated by addition of methanol, filtered, and purified by Soxhlet extraction with methanol, chloroform, and chlorobenzene, respectively. The CB solution was concentrated by evaporation and then precipitated into methanol. The purple solid was filtered to yield the desired polymer PBTA-PS-F (60% yield). PBTA-PS and PBTA-PS-F had number-average molecular weights ( $M_n$ ) of 47.0 and 41.5 KDa, and polydispersity index (PDI) of 2.4 and 2.3, respectively.

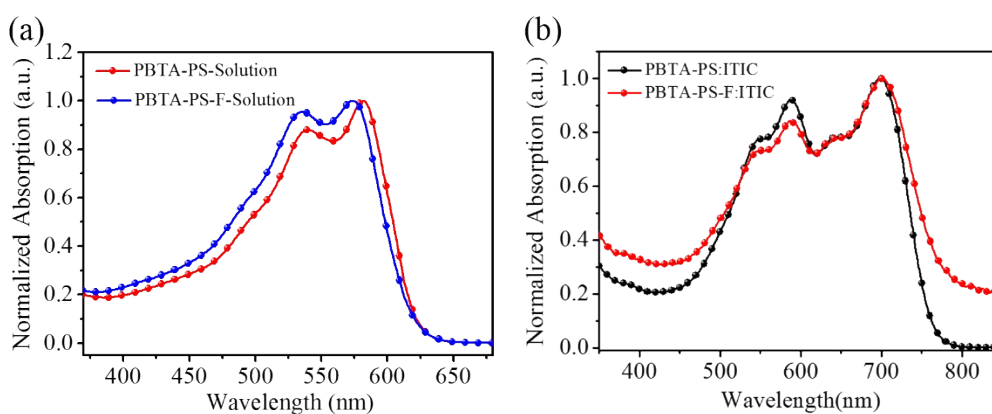
Device Fabrication Process: The devices were fabricated with a conventional architecture of ITO/PEDOT:PSS/polymers:ITIC/PDINO/Al. The ITO-coated glass substrates were washed ultrasonically in water/detergent, water, acetone, water and isopropanol in sequence for 13 min, and then the substrates were treated in UV-ozone for 6 min. The PEDOT:PSS were spin-coated on the substrates and annealed at 160 °C for 20 min in the air, the substrates were transferred into a nitrogen-filled glove box. Optimized devices were prepared under the following conditions. The PBTA-PS-F:ITIC(1:1, w/w) blend was dissolved in chlorobenzene (CB) with a concentration of 10 mg/ml (for polymer), with 0.5% DPE. The solution was stirred for 5 hours at 50 °C and then spin-coated on the surface of PEDOT:PSS layer in nitrogen-based atmosphere glove box, 110 °C thermal annealing 10 min, and the optimal film of the active layer is ca. 100-120 nm. Subsequently, an ultrathin layer of PDINO (1 mg mL<sup>-1</sup> in methanol) was cast on the active layer under 3000 rpm for 30 s. Then, Al (ca. 100 nm) metal top electrode was evaporated under  $2 \times 10^{-4}$  Pa.



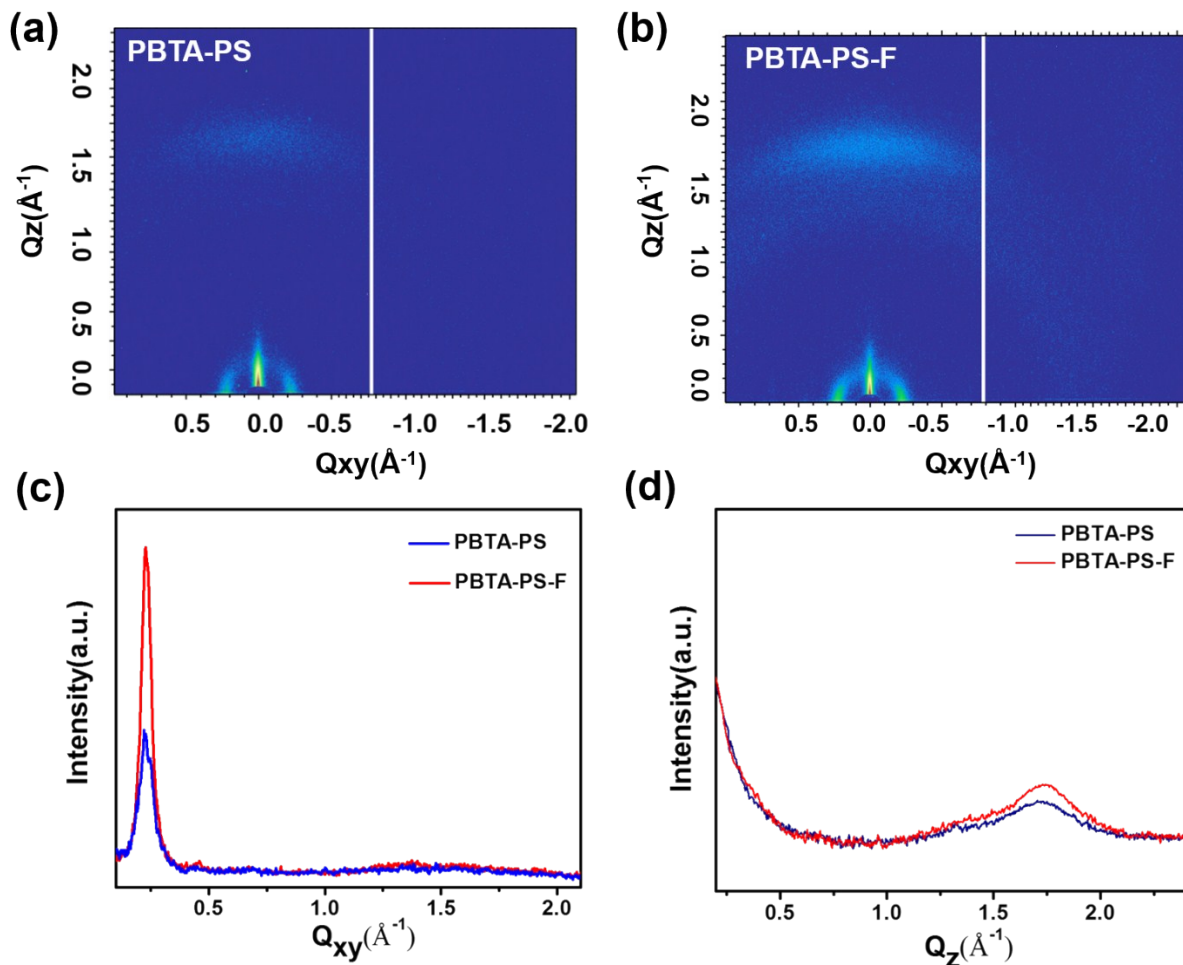
**Fig. S1.** TGA plots of polymers with a heating rate of 10 °C/min under an inert atmosphere.



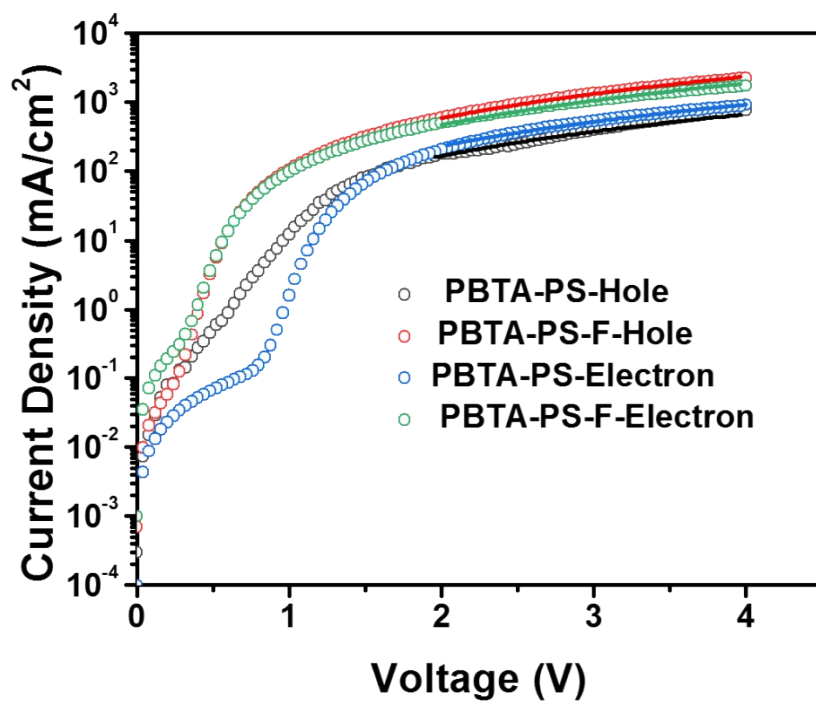
**Fig. S2.** (a) CV curves of PBTA-PS and PBTA-PS-F. (b) The energy level diagrams of polymer PBTA-PS, PBTA-PS-F and acceptor ITIC.



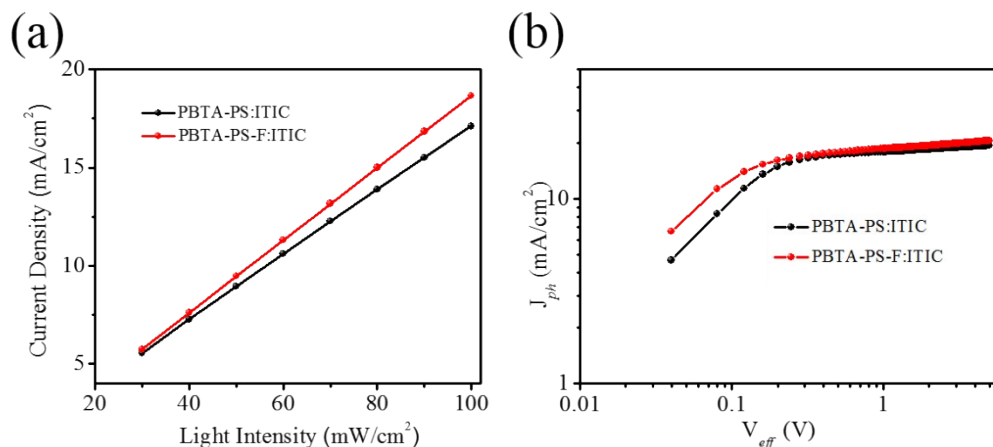
**Fig. S3.** (a) UV-vis absorption spectra of two polymers in chlorobenzene solution; (b) blend films with ITIC.



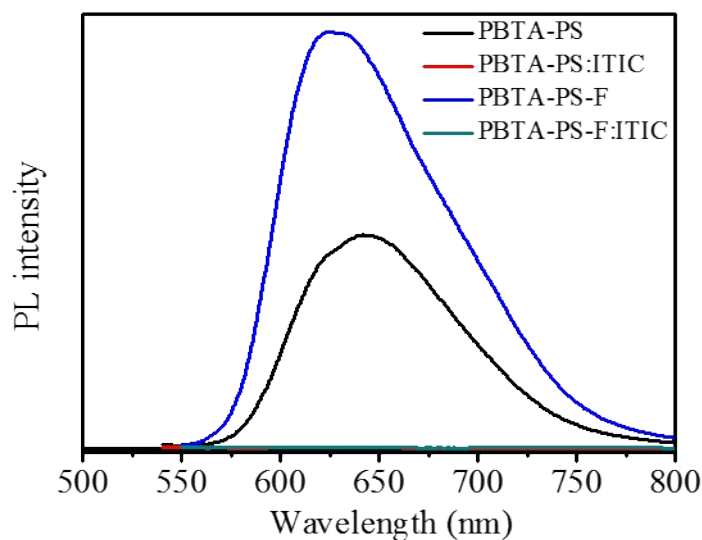
**Fig. S4.** a–b) GIXD scattering patterns of PBTA-PS, PBTA-PS-F, and the line profiles of GIXD c) in plane and d) out of plane.



**Fig. S5.** J–V characteristics of blend films based on the hole-only devices and electron-only devices.



**Fig. S6.** (a) light-intensity ( $P$ ) dependence of  $J_{SC}$  of the corresponding devices; (b) The curves of the photocurrent density ( $J_{ph}$ ) vs. the effective bias ( $V_{eff}$ ) for two solar cells;



**Fig. S7.** Photoluminescence spectra of pure PBTA-PS, PBTA-PS-F and the blend films of PBTA-PS:ITIC, PBTA-PS-F:ITIC (excited at 520 nm).

**Table S1.** The device parameters of the PBTA-PS-F: ITIC (1:1) with different additive ratio.

additive	$V_{oc}$	$J_{sc}$	FF	PCE
(v/v)	(V)	(mA cm <sup>-2</sup> )	(%)	(%)
0.25%DPE	0.98(0.97±0.01)	17.93(17.69±0.28)	68.85(66.15±2.43)	12.09(11.80±0.26)
0.5%DPE	0.97(0.97±0.01)	18.26(17.98±0.27)	71.03(69.31±2.42)	12.58(12.13±0.36)
1%DPE	0.96(0.96±0.01)	17.88(17.65±0.28)	67.78(65.66±2.94)	11.63(11.33±0.30)

The average parameters were calculated from more than 20 independent cells.

**Table S2.** The device parameters of the PBTA-PS-F: ITIC (1:1) with different thermal annealing temperature.

	Annealing temperature (°C)	$V_{oc}$ (V)	$J_{sc}$ (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
	no	0.98(0.97±0.01)	17.65(17.36±0.32)	68.64(66.50±2.12)	11.87(11.44±0.22)
PBTA-PS-F:	80	0.98(0.97±0.01)	17.70(17.40±0.38)	68.71(66.33±2.43)	11.92(11.62±0.26)
ITIC	100	0.98(0.97±0.01)	18.15(17.88±0.30)	71.78(68.63±2.13)	12.77(12.42±0.23)
	120	0.97(0.96±0.01)	18.07(17.88±0.25)	70.62(66.97±2.04)	12.37(12.03±0.25)
	140	0.96(0.95±0.01)	17.88(17.53±0.40)	67.97(64.66±2.25)	11.66(11.23±0.33)
	160	0.95(0.95±0.01)	17.66(17.22±0.32)	62.93(60.25±2.47)	10.56(10.27±0.21)

The average parameters were calculated from more than 20 independent cells.

## References

- [1] H. Jiang, X. Li, Z. Liang, G. Huang, W. Chen, N. Zheng, R. Yang, *J. Mater. Chem. A* **2019**, *7*, 7760.
- [2] X. Li, G. Huang, N. Zheng, Y. Li, X. Kang, S. Qiao, H. Jiang, W. Chen, R. Yang, *Solar RRL* **2019**, *3*, 1900005.
- [3] J. Zhang, G. Huang, H. Tan, H. Jiang, B. Wu, G. Lei, W. Chen, R. Yang, W. Zhu, *Polymer* **2018**, *145*, 108.