

## **Supporting Information**

### **Conjugated Polymers Containing Sulfonic Acid Fluorene Unit for Achieving Multiple Interfacial Modifications in Fullerene-free Organic Solar Cells**

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## Experimental Section

### Device fabrication

*Devices D1-D3, E1-E2, F1-F3 were fabricated taking PFS, PFSF and PFB as anode interlayers (AIL) and cathode interlayers (CIL) simultaneously.*

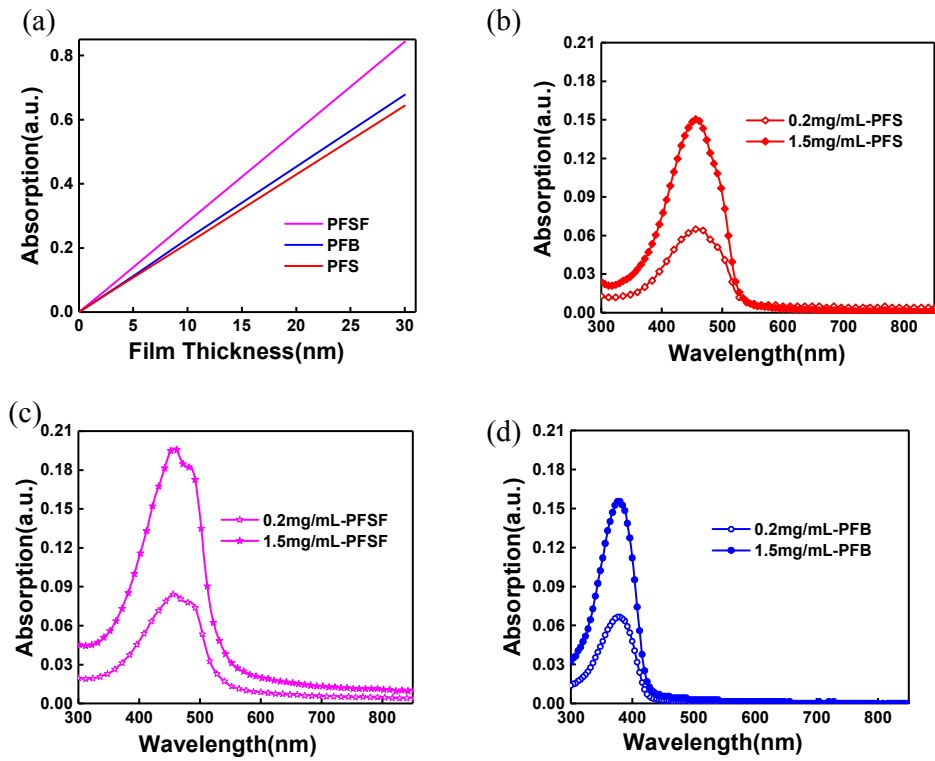
The devices structure of D-type (ITO/interlayer/J52-2F: ITM/Interlayer/Al), E-type (ITO/interlayer/PBDTTTEFT: IEICO-4F/Interlayer/Al) and F-type (ITO/interlayer/PBDB-T: ITIC/Interlayer/Al) were fabricated according to the following conditions:

The pre-cleaned ITO-coated glass substrates were UV/ozone-treated for 20 min. PFS and PFSF were dissolved in methanol with the optimal concentration of 1.5mg/ml and spin-coated on the ITO-electrode according to the devices A-1 mentioned above. All the photoactive materials J52-2F: ITM (D/A1:1), PBDTTTEFT: IEICO-4F (D/A 1:2) and PBDB-T: ITIC (D/A 1:1) were dissolved in CB at the polymer concentration of 10 mg/mL. To dissolve the polymers fully, active layer solution PBDB-T: ITIC was stirred at 40 °C, PBDTTTEFT: IEICO-4F and J52-2F: IT-M at 60 °C for 2 h at least. Before spin-coating, 1, 8-iodooctane (0.5%, v/v) was added to the active layers solution J52-2F: IT-M and PBDB-T: ITIC. In addition, chloronaphthalene (3%, v/v) was added to PBDTTTEFT: IEICO-4F. For the cathode interlayer, PFN-Br was dissolved in methanol with the concentration of 0.5 mg/mL, and 0.2mg/ml PFS, PFSF were prepared to be spin-coated (3000rpm/min, 30s) on the

photoactive layer. At last, Al was evaporated on the substrate as cathode under high vacuum.

### **Characterization and Measurement.**

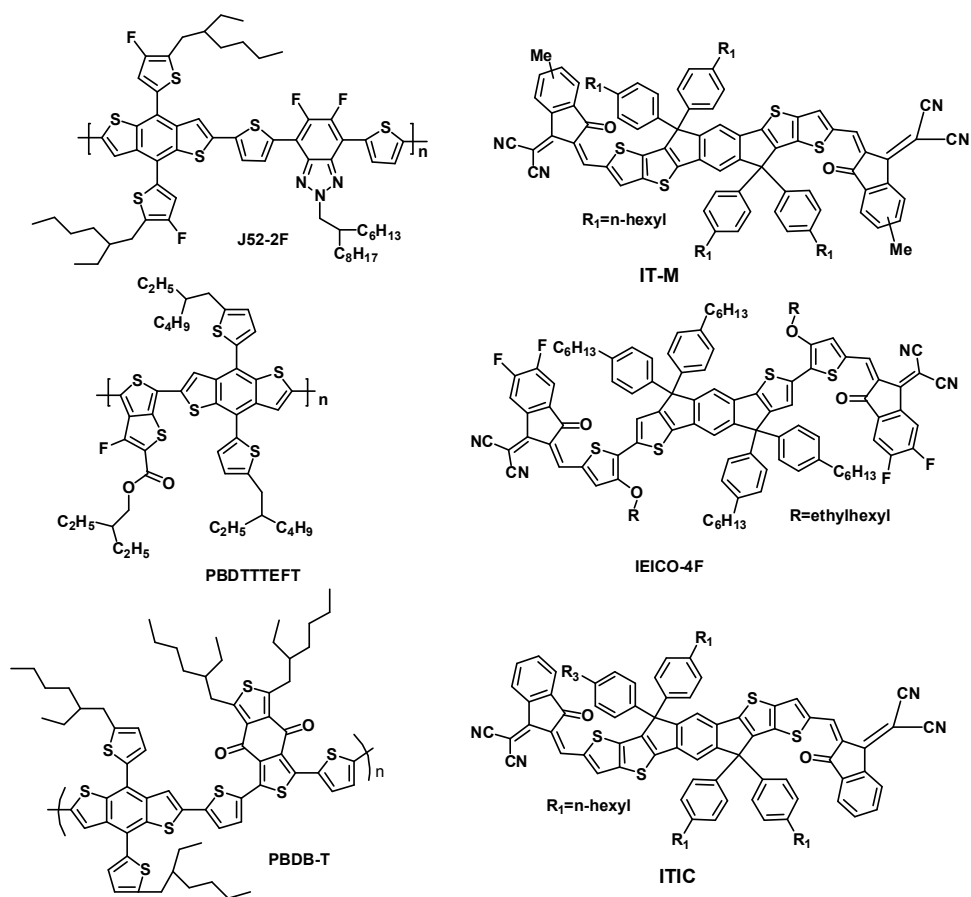
The PCE of devices were measured under  $100 \text{ mW/cm}^2$  AM1.5G light source, using an AAA solar simulator. Standard silicon reference cell was purchased from Enli Technology Co., Ltd. The effective area of the device calibrated by microscope is  $3.7 \text{ mm}^2$ . The EQE spectrum was measured by a Solar Cell Spectral Response Measurement System QE-R3011 from Enli Technology Co., Ltd.



**Figure S1.** (a) The relationship curves of film thickness and UV-vis absorption, (b) the UV-vis absorption curve of PFS, PFSF and PFB with concentration of 0.2mg/mL and 1.5mg/mL.

**Table S1.** The parameters of thickness and absorption relations.

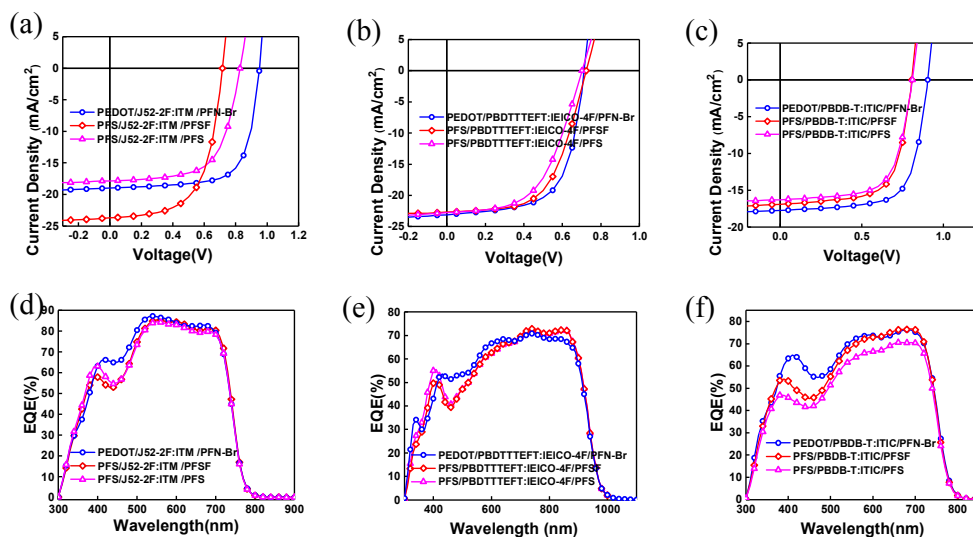
interlayers	concentrations (mg/mL)	absorption peak intensity	thickness (nm)
PFS	0.2	0.065	3
	1.5	0.150	7
PFSF	0.2	0.084	3
	1.5	0.197	7
PFB	0.2	0.067	3
	1.5	0.157	7



**Figure S2.** Chemical structures of photoactive layer materials for D-type device

J52-2F: IT-M, E-type device PBDTTTTEFT: IEICO-4F and F-type device PBDB-T:

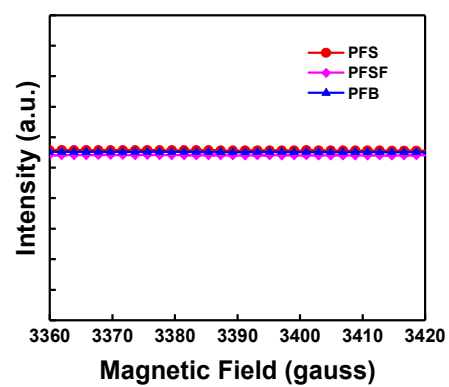
ITIC.



**Figure S3.** The J-V curves of (a) D-type devices: AIL/J52-2F:ITM/CIL, (b) E-type devices: AIL/ PBDTTTTEFT: IEICO-4F /CIL and (c) F-type devices: AIL/ PBDB-T: ITIC /CIL. The corresponding EQE curves of (d) D-type devices, (e) E-type devices and (f) F-type devices.

**Table S2.** Photovoltaic parameters of the devices D1-D3, E1-E3 and F1-F3.

Num.	device structures	$V_{oc}$	$J_{sc}$	$J_{cal}$	FF	PCE
		(V)	(mA/cm <sup>2</sup> )	(mA/cm <sup>2</sup> )		(%)
D1	PEDOT/ BHJ /PFN-Br	0.951	19.0	18.3	70.1	12.7
D2	PFS/ BHJ /PFS	0.828	17.9	17.5	63.7	9.43
D3	PFS/ BHJ /PFSF	0.917	18.1	17.7	63.2	10.4
E1	PEDOT/ BHJ /PFN-Br	0.713	23.1	22.2	64.0	10.6
E2	PFS/ BHJ /PFS	0.702	22.8	21.9	54.1	8.65
E3	PFS/ BHJ /PFSF	0.723	22.7	21.7	58.5	9.61
F1	PEDOT/ BHJ /PFN-Br	0.905	17.7	16.5	69.1	11.1
F2	PFS/ BHJ /PFS	0.812	16.3	14.4	66.6	8.78
F3	PFS/ BHJ /PFSF	0.807	16.9	15.8	67.4	9.20



**Figure S4.** Electron Paramagnetic Resonance (EPR) curves of PFS, PFSF, and PFB.