Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

Changing the π-bridge from thiophene to thieno[3,2-b]thiophene for D-π-A type polymer enables high performance fullerene-free organic solar cells

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Materials and Synthesis.

Materials. All Chemicals and solvents were reagent grades and purchased from Alfa, Aldrich, TCI, Beijing Chemical Plant or other chemical companies and used without further purification.

Measurements and characterizations

UV–vis spectra were identified with a Lambda 950 spectrophotometer. The J−V curves were measured in air with a Keithley 2420 source measure unit. The photocurrent was obtained under illumination using an Oriel Newport 150W solar simulator (AM 1.5G), and the light intensity was calibrated with a Newport reference detector (Oriel PN 91150 V). The EQE measurements of the devices were performed in air with an Oriel Newport system (Model 66902). The thickness of the active layer was measured on a Kla-TencorAlpha-StepD-120 Stylus Profiler. The thickness of the

J52-FS: Y6 and PE2: Y6 based films are estimated to be 100 and 110 nm, respectively. AFM images were obtained on a Multimode Digital Instrument (D3100) in ScanAsyst mode. Two-dimensional grazing incidence X-ray diffraction (2D-GIXD) analyses were measured at the XEUSS SAXS/WAXS equipment. The data were obtained with an area Pilatus 100k detector with a resolution of 195 × 487 pixels (0.172 mm × 0.172 mm). The X-ray wavelength was 1.54 Å, and the incidence angle was 0.2°. The samples were spin-coated onto the PEDOT:PSS/Si substrate.

Photovoltaic device fabrication

The PSC devices were fabricated with a configuration of ITO/ PEDOT: PSS/ active layer/ Ca/ Al. A thin layer of PEDOT: PSS (40 nm, Baytron PH1000) was spin-cast on pre-cleaned ITO-coated glass at 3000 rpm, 30s. After baking at 150℃ for 15 min, the substrates were transferred into glovebox. Optimized devices were prepared under the following conditions. The Donor: Acceptor (D: A) ratio of 1:1.2 (w/w) was dissolved in chloroform (CF) with a total concentration of 18 mg/mL for J52-FS: Y6 and PE2: Y6 with the solvent additive of 1-chloronaphthalene (CN) (0.5%, v/v). Then they were stirred for 1 hour at 40℃. Afterwards, the active layers were spin-coated from the above solution with a speed of 3000 rpm for 30s onto the PEDOT: PSS layer. The thickness of the photoactive layer is in the range of 100-110 nm. Subsequently, J52-FS: Y6 devices were annealed at 110℃ for 10min. For PE2: Y6, SVA was first carried out in glovebox that the blend films were loaded in the middle of Petri dish containing 200 uL chloroform for 60 s, and then were annealed at 110℃ for 10min. Finally, a Ca (20 nm)/Al (80nm) metal top electrode was thermal evaporated onto the active layer under about 3×10^{-4} Pa. The active area of the device was 0.04 cm^2 defined by shadow mask.

Carrier Mobilities

The carrier mobilities of the polymer was investigated by the space charge limited current (SCLC) method. The hole mobility of the blend films was measured with the device structure of ITO/ PEDOT:PSS/ active layer/Au (80 nm) while the electron mobility of the blends was measured with the device structure of ITO/ TiOx/ active layer/ Al (80 nm).

The SCLC model is described by modified Mott-Gurney law:

$$J = \frac{9}{8}\varepsilon_0 \varepsilon_r \mu \frac{V^2}{L^3}$$

where J stands for current density, ε0 is the permittivity of free space (8.85×10^{-12} C V^{-1} m^{-1}), εr is the relative dielectric constant of the transport medium (assuming that of 3.0), μ is the carrier mobility, and L is the thickness of the active layer. V is the internal potential in the device, and $V=V_{app}-V_{bi}$, where V_{app} is the voltage applied to the device, and V_{bi} is the built-in voltage resulting from the relative work function difference between the two electrodes (the V_{bi} values of hole-only and electron-only devices were all selected as 0 V).

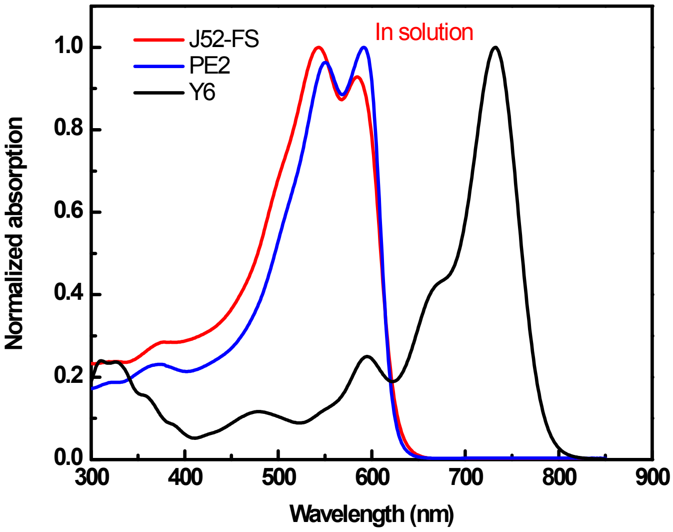

Figure S1. Normalized absorption spectra of polymers and Y6 in CF solution.

Table S1. Optical and electrochemical properties of the two polymers and **Y6.**

Compounds	$\lambda_{max}(nm)$	$\lambda_{onset}(nm)$	$E_g^{opt}(eV)$	$E_{HOMO}(eV)$	$E_{LUMO}(eV)$
J52-FS	542	642	1.93	-5.32	-3.39
PE2	545	637	1.95	-5.41	-3.53
Y6	821	931	1.33	-5.65	-4.10

Table S2. The photovoltaic performance of J52-FS: Y6 (1: 1.2, w/w) and PE2: Y6 (1: 1.2, w/w) under different total concentration and spin-coating speed. (Annealed at 110°C for 10 min.)

Devices	Total concentration (mg/mL)	rpm	V_{oc} (V)	J_{sc} (mA/cm2)	FF	PCE (%)
J52-FS : Y6	14	2000	0.80	20.28	0.59	9.57
		2500	**0.80**	**19.42**	**0.63**	**9.79**
		2800	0.80	17.07	0.64	8.74
	16	**2000**	**0.81**	**22.44**	**0.57**	**10.36**
		2500	0.81	19.92	0.60	9.68
	18	2500	0.81	22.86	0.56	10.37
		3000	**0.81**	**22.92**	**0.57**	**10.58**
		3500	0.80	20.15	0.58	9.35
PE2: Y6	16	1800	0.83	21.12	0.68	11.92
		2000	0.83	19.67	0.70	11.43
		2500	**0.83**	**22.29**	**0.70**	**12.95**
	18	2000	0.82	23.17	0.68	12.92
		2500	0.83	23.07	0.69	13.21
		3000	**0.83**	**23.21**	**0.69**	**13.29**

Table S3. The photovoltaic performance of J52-FS: Y6 (1: 1.2, w/w) under different solvent additives (0.5 vol%) at a total concentration of 18mg/mL. (Annealed at 110℃ for 10 min.)

additives	V_{oc} (V)	J_{sc} (mA/cm2)	FF	PCE (%)
CN	0.81	21.39	0.59	10.22
CP	0.81	22.05	0.57	10.18
DPE	0.80	19.40	0.58	9.00

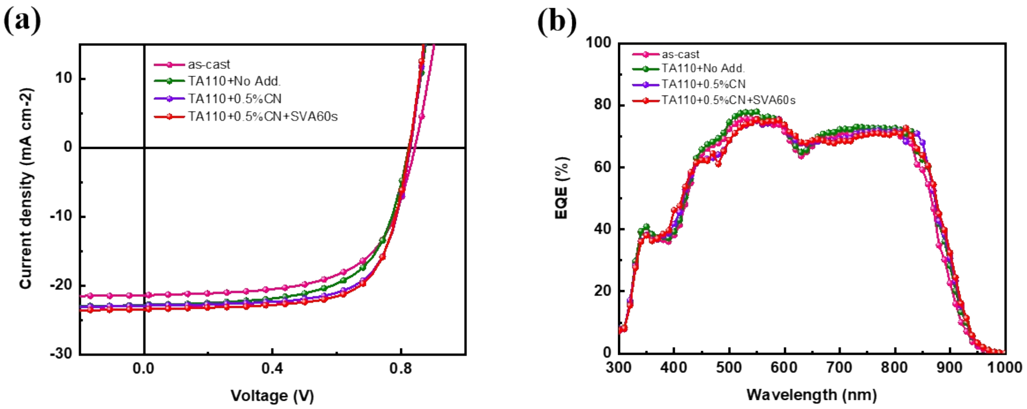

Figure S2. (a) *J–V* curves of the PE2: Y6 under different fabrication conditions. (b) EQE curves of the corresponding devices.

Table S4. The photovoltaic performance of PE2: Y6 under different fabrication conditions.

Conditions	V_{oc} (V)	J_{sc} (mA/cm2)	FF	PCE (%)
As-cast	0.84	21.35	0.63	11.30
[a] TA110+No Add.	0.82	22.94	0.63	12.04
TA110+0.5%CN	0.83	23.21	0.69	13.29
[b] TA110+0.5%CN+SVA60s	**0.83**	**23.24**	**0.70**	**13.50**

[a] TA110 represented for thermal annealing at 110℃, No Add. namely no additives.

[b] SVA60s means the blend films were treated by solvent vapor annealing for 60s.

Table S5. The photovoltaic performance of PE2: Y6 (1: 1.2, w/w, 18mg/mL) under different vol% CN at 110℃, 10 min thermal annealing.

Additive (vol% CN)	V_{oc} (V)	J_{sc} (mA/cm2)	FF	PCE (%)
0	0.82	22.94	0.64	12.04
0.3%	0.84	22.30	0.68	12.74
0.5%	0.83	23.21	0.69	13.29
0.8%	0.82	23.26	0.68	12.97
1.0%	0.82	22.07	0.70	12.67

Table S6. The photovoltaic performance of PE2: Y6 (1: 1.2, w/w, 18mg/mL) under different thermal annealing temperature.

TA (℃)	V_{oc} (V)	J_{sc} (mA/cm2)	FF	PCE (%)

[a]--	0.84	21.35	0.63	11.30
100	0.84	21.24	0.69	12.31
110	0.83	23.21	0.69	13.29
130	0.81	20.48	0.70	11.61
150	0.79	21.30	0.68	11.44

[a] as-cast.

Table S7. The photovoltaic performance of PE2: Y6 (1: 1.2, w/w, 18mg/mL) under different SVA time followed by TA110℃, 10min.

SVA(s)	V_{oc} (V)	J_{sc} (mA/cm2)	FF	PCE (%)
0	0.83	23.21	0.69	13.29
30	0.83	21.42	0.69	12.27
60	0.83	23.24	0.70	13.50
90	0.82	20.51	0.70	11.70
120	0.82	22.78	0.69	12.89

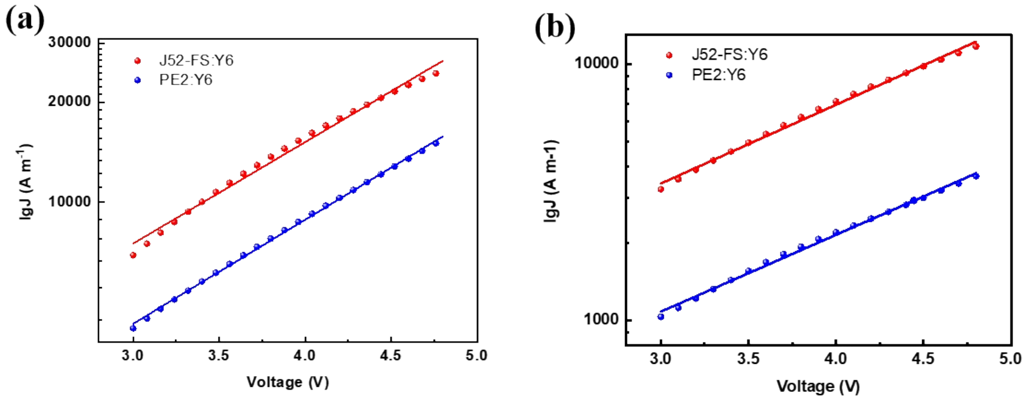

Figure S3. *J-V* semi-logarithm characteristics of the (a) hole-only and (b) electron-only devices.