

## Conjugated side-chains engineering of polymer donor enabling improved efficiency for polymer solar cells

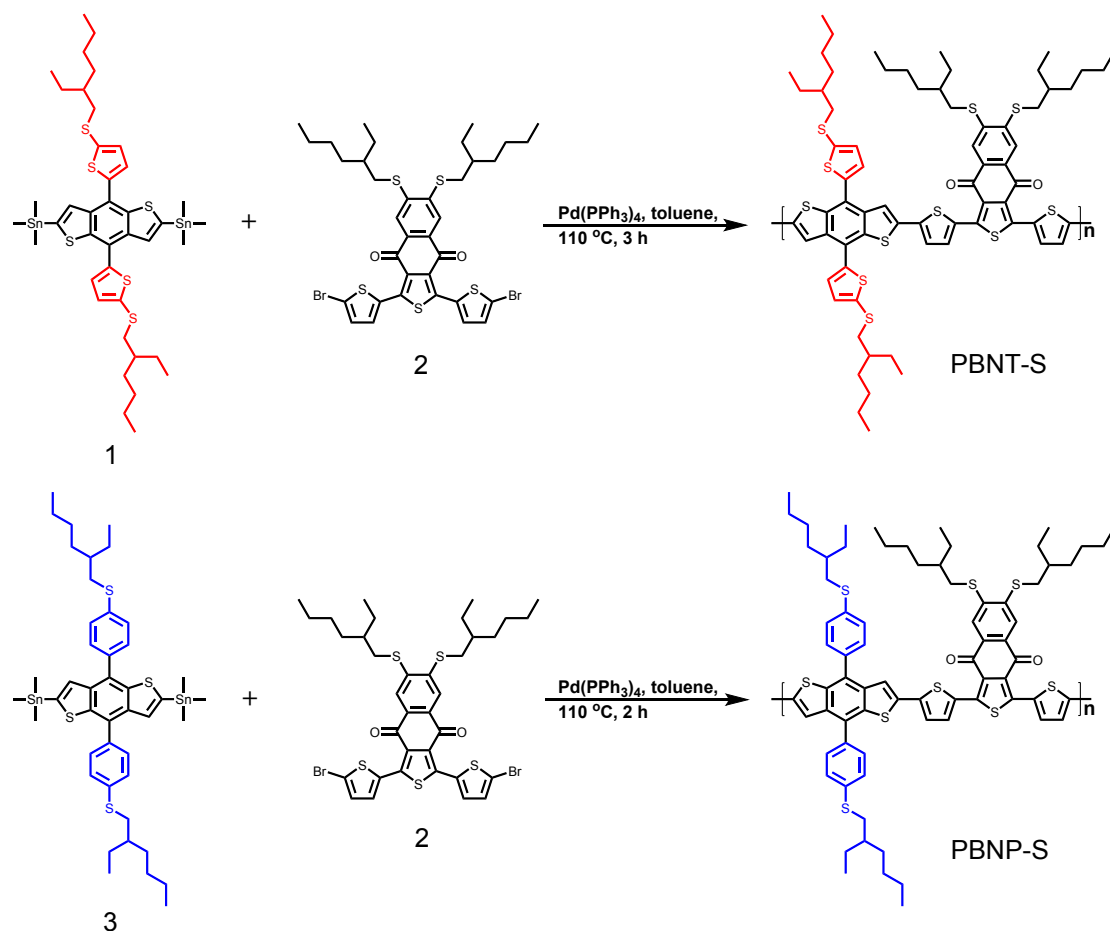
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### Materials synthesis:



Scheme S1 Synthetic routes of **PBNT-S** and **PBNP-S**.

### Synthesis of **PBNT-S**:

Monomer 1<sup>1</sup> (193.74 mg, 0.2 mmol) and Monomer 2<sup>2</sup> (164.97 mg, 0.2 mmol) were dissolved in 8 mL toluene in a 25 mL flask. After being purged with pure argon for 15 min, the solution was added Pd(PPh<sub>3</sub>)<sub>4</sub> (13 mg, 0.01 mmol) as catalyst, and then purged with argon for another 15 min. The polymerization was conducted by refluxing the solution at 110 °C for 3 h under argon atmosphere. The polymer was precipitated in 100 mL methanol after cooled to room temperature and was then subjected to column chromatography on silica gel using chloroform as the eluent to afford purified PBNT-S solution. The polymer was finally obtained as dark solid after precipitation and dried under vacuum overnight. (160 mg, yields: 60.6%,  $M_n = 17.6$  kDa,  $M_w = 45.1$  kDa, PDI = 2.56)

### Synthesis of **PBNP-S**:

Monomer 3<sup>3</sup> (143.5 mg, 0.15 mmol) and Monomer 2 (123.7 mg, 0.15 mmol) were dissolved in 8 mL toluene in a 25 mL flask. After being purged with pure argon for 15 min, the solution was added Pd(PPh<sub>3</sub>)<sub>4</sub> (9 mg, 0.008 mmol) as catalyst, and then purged with argon for another 15 min. The polymerization was conducted by refluxing the solution at 110 °C for 2 h under argon atmosphere. The polymer was precipitated in 100 mL methanol after cooled to room temperature and was then subjected to column chromatography on silica gel using chloroform as the eluent to afford purified PBNP-S solution. The polymer was finally obtained as dark solid after precipitation and dried under vacuum overnight. (150 mg, yields: 76.4%,  $M_n = 16.7$  kDa,  $M_w = 42.4$  kDa, PDI = 2.53)

### **Materials characterization**

Cyclic voltammetry was performed on a Zahner IM6e electrochemical workstation with a three-electrode system in a solution of 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> acetonitrile solution at a scan rate of 100 mV s<sup>-1</sup>. Glassy carbon disc coated with polymer film was used as the working electrode. A Pt wire was used the counter electrode and Ag/Ag<sup>+</sup> was used as

the reference electrode. Ferrocene/ferrocenium redox couple was used as the external standard and its redox potential is 0.06 V versus Ag/Ag<sup>+</sup>. The HOMO and LUMO energy levels were calculated from the onset of the oxidation and reduction potential of polymer using the following equations: HOMO = -e ( $\phi_{\text{ox}} + 4.74$ ) (eV); LUMO = -e ( $\phi_{\text{red}} + 4.74$ ) (eV), respectively.

### **Device Fabrication and Characterization**

The device was fabricated with a conventional architecture of glass/ITO/PDEOT:PSS/polymer:Y6/PDINO/Al. The ITO-coated glass was pre-cleaned and modified by a thin layer of PEDOT:PSS which was spin-cast from a PEDOT:PSS aqueous solution (Baytron P VP AI4083 from H. C. Stark) at 5000 rpm for 40 s, and then dried at 150 °C for 15 min in air. The thickness of the PEDOT:PSS layer is ~30 nm. Then the devices were transferred to a nitrogen-filled glove-box, where the active layer was spin-coated from chloroform solution containing PBNT-S (or PBNP-S):Y6 onto the PEDOT:PSS layer. For the optimized conditions, PBNT-S (or PBNP-S):Y6 (1:1.5, w/w) were dissolved in chloroform with a concentration of 7 mg/mL for donor and stirred under 45 °C for 6 h. After 1% (by volume) 1-phenylnaphthalene (PN) was added as additive, the solution was stirred at 45 °C for another 0.5 h. The blend film was spin-coated at 2500-3000 rpm for 30 s, followed by thermal annealing at 60 °C for 10 min. The PDINO buffer layer was deposited atop the active layer from the methanol solution with a concentration of 1.0 mg/mL at 3000 rpm for 40 s and functions as the cathode interfacial layer. Finally, top 100 nm Al electrode was deposited at a pressure of  $2.0 \times 10^{-5}$  Pa onto the PDINO layer with a shadow mask.

The current density-voltage ( $J-V$ ) measurement of the PSCs were measured under a illumination of AM 1.5G (100 mW cm<sup>-2</sup>) using a SS-F5-3A solar simulator (AAA grade, 50 × 50 mm<sup>2</sup> photobeam size) of Enli Technology CO., Ltd.. Masks were made using laser beamcutting technology and had well-defined areas of 0.056 cm<sup>2</sup> to define the effective areas for accurate measurement. The EQE was measured

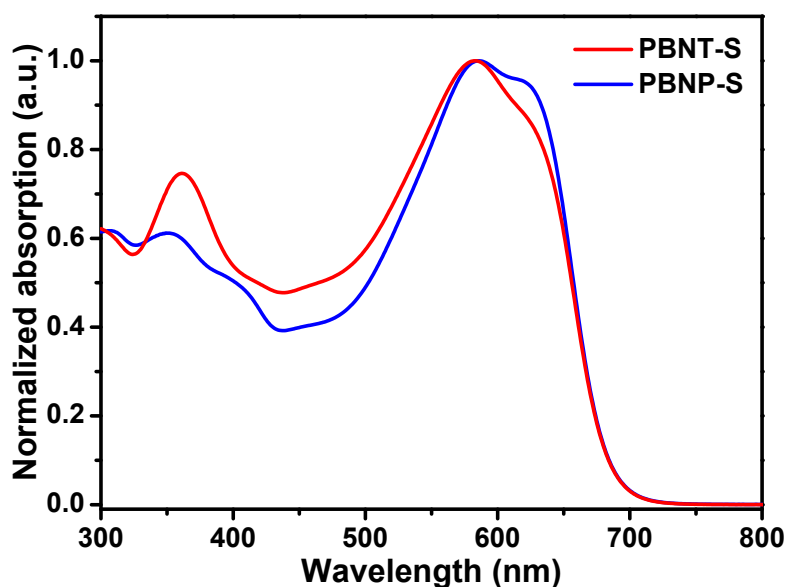
by using a Solar Cell Spectral Response Measurement System QE-R3011 (Enli Technology Co., Ltd.). The light intensity at each wavelength was calibrated by a standard singlecrystal Si solar cell.

*Mobility Measurement:* The devices with a structure of glass/ITO/PEDOT:PSS/active layer/MoO<sub>3</sub>/Al and a structure of glass/ITO/ZnO/active layer/PDINO/Al were fabricated to measure the hole and electron mobilities, respectively. The ZnO buffer layer (thickness 20 nm) was deposited atop the active layer from the mixed methanol:chloroform:*n*-butyl alcohol (1:1:14) solution of ZnO nanoparticles at a concentration of 10 mg/mL with 4000 rpm for 30 s. The fabrication of the devices is the same as that of photovoltaic devices as described above. The hole and electron mobilities were calculated by using the space-charge-limited current (SCLC) method.

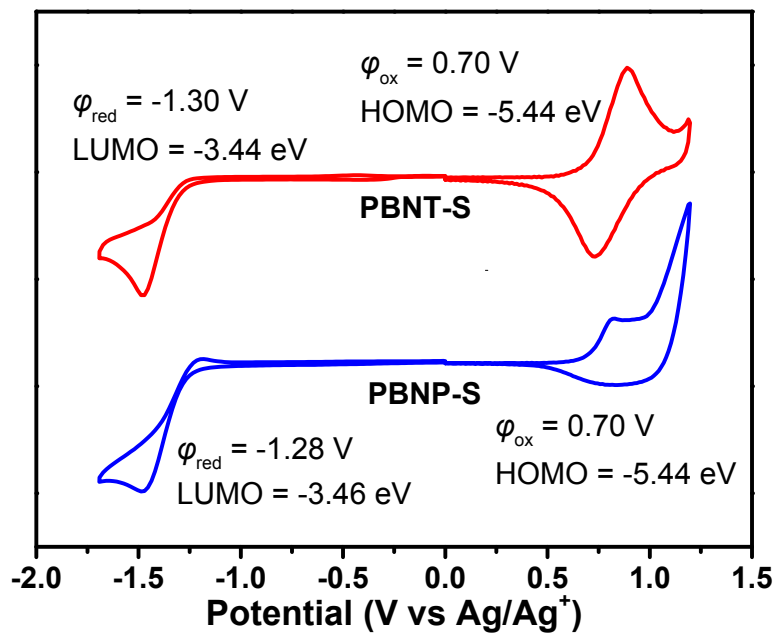
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$$J \cong (9/8)\epsilon\epsilon_0\mu_0V^2 \exp(0.89\sqrt{V/E_0L}) / L^3$$

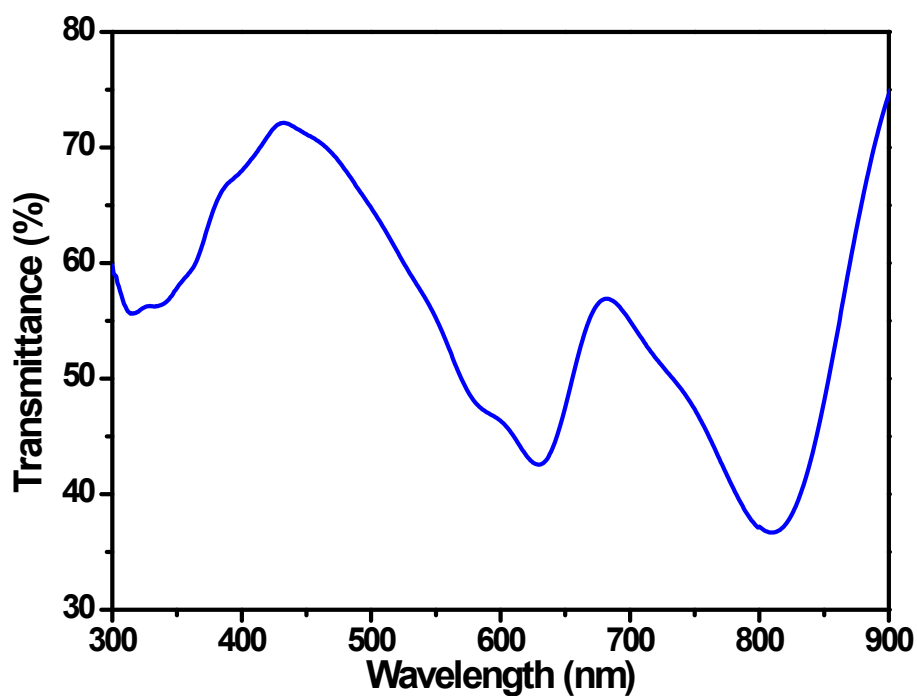
where  $\epsilon$  is the dielectric constant of the polymers,  $\epsilon_0$  is the permittivity of the vacuum,  $\mu_0$  is the zero-field mobility,  $E_0$  is the characteristic field,  $J$  is the current density, and  $L$  is the thickness of the film.



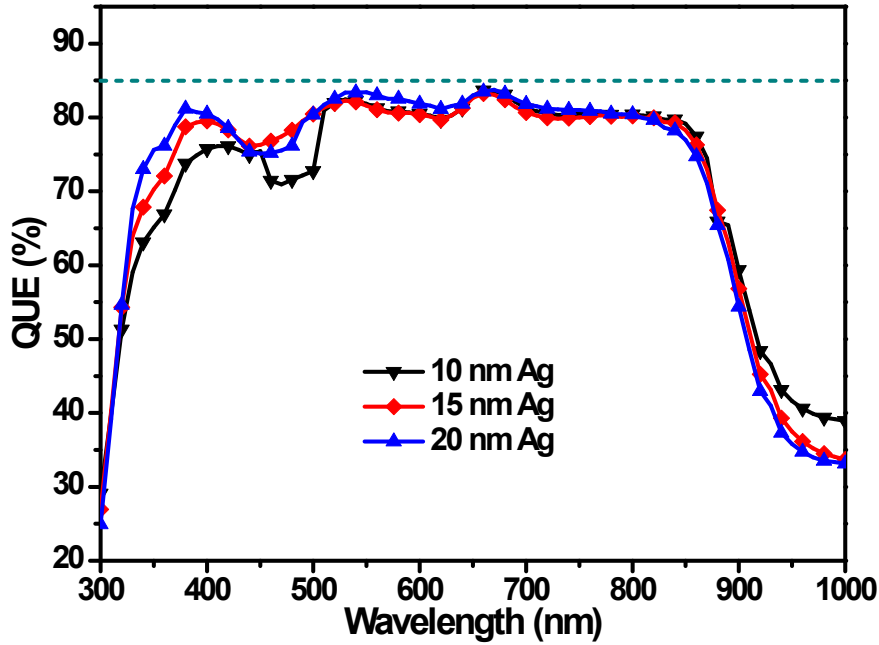
**Fig. S1** Normalized absorption spectra of PBNT-S and PBNP-S in dilute chloroform solution.



**Fig. S2** Cyclic voltammograms of PBNT-S and PBNP-S films on a glassy carbon electrode in 0.1 mol L<sup>-1</sup> Bu<sub>4</sub>NPF<sub>6</sub> acetonitrile solution at a scan rate of 100 mV s<sup>-1</sup>.



**Fig. S3** The transmittance spectra of the PBNP-S:Y6 (1:1.5, w/w) blend film with thickness of 95 nm.



**Fig. S4** QUE curves of the semitransparent devices with different Ag thickness.

**Table S1** Photovoltaic performance of the PSCs based on PBNT-S:Y6 and PBNP-S:Y6 with different D/A ratio under the illumination of AM 1.5 G at  $100 \text{ mW cm}^{-2}$ .

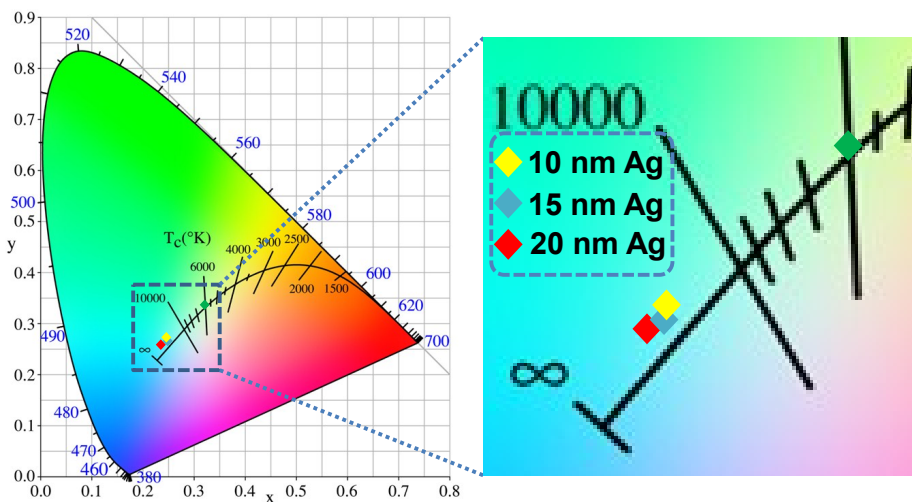
Active layer	D/A ratio	$V_{oc}$ [V]	$J_{sc}$ [ $\text{mA cm}^{-2}$ ]	FF [%]	PCE [%]
PBNT-S:Y6	1:0.5	0.899	12.14	37.0	4.04 [3.87]
	1:1	0.880	18.82	49.5	8.20 [8.04]
	1:1.5	0.875	19.37	51.4	8.71 [8.67]
	1:2	0.878	18.41	47.6	7.70 [7.65]
PBNP-S:Y6	1:0.5	0.895	13.46	41.6	5.01 [4.81]
	1:1	0.883	19.67	52.4	9.10 [8.88]
	1:1.5	0.882	20.46	57.5	10.38 [10.16]
	1:2	0.870	19.34	56.5	9.49 [9.37]

The values in square brackets are the average PCE obtained from 6 devices.

**Table S2** Photovoltaic performance of the PSCs based on PBNT-S:Y6 (1:1.5, w/w) and PBNP-S:Y6 (1:1.5, w/w) blend film with different processing conditions under the illumination of AM 1.5 G at  $100 \text{ mW cm}^{-2}$ .

Active layer	Treatment	$V_{oc}$ [V]	$J_{sc}$ [mA cm <sup>-2</sup> ]	FF [%]	PCE [%]
PBNT-S:Y6	1% DIO + TA 60 °C	0.817	23.01	53.2	10.00 [9.85]
	1% DPE + TA 60 °C	0.821	24.30	51.8	10.34 [10.26]
	1% NMP + TA 60 °C	0.811	19.26	50.3	7.88 [7.77]
	1% PN + TA 60 °C	0.798	23.00	60.5	11.10 [11.04]
PBNP-S:Y6	0.5% PN + TA 60 °C	0.821	24.81	65.9	13.42 [13.30]
	1% PN + TA 60 °C	0.810	25.50	69.4	14.31 [14.25]
	1% PN + TA 80 °C	0.810	24.08	69.8	13.62 [13.51]
	1% PN + TA 100 °C	0.810	25.45	66.7	13.74 [13.62]
	2% PN + TA 60 °C	0.805	22.76	68.4	12.53 [12.27]

The values in square brackets are the average PCE obtained from 6 devices.

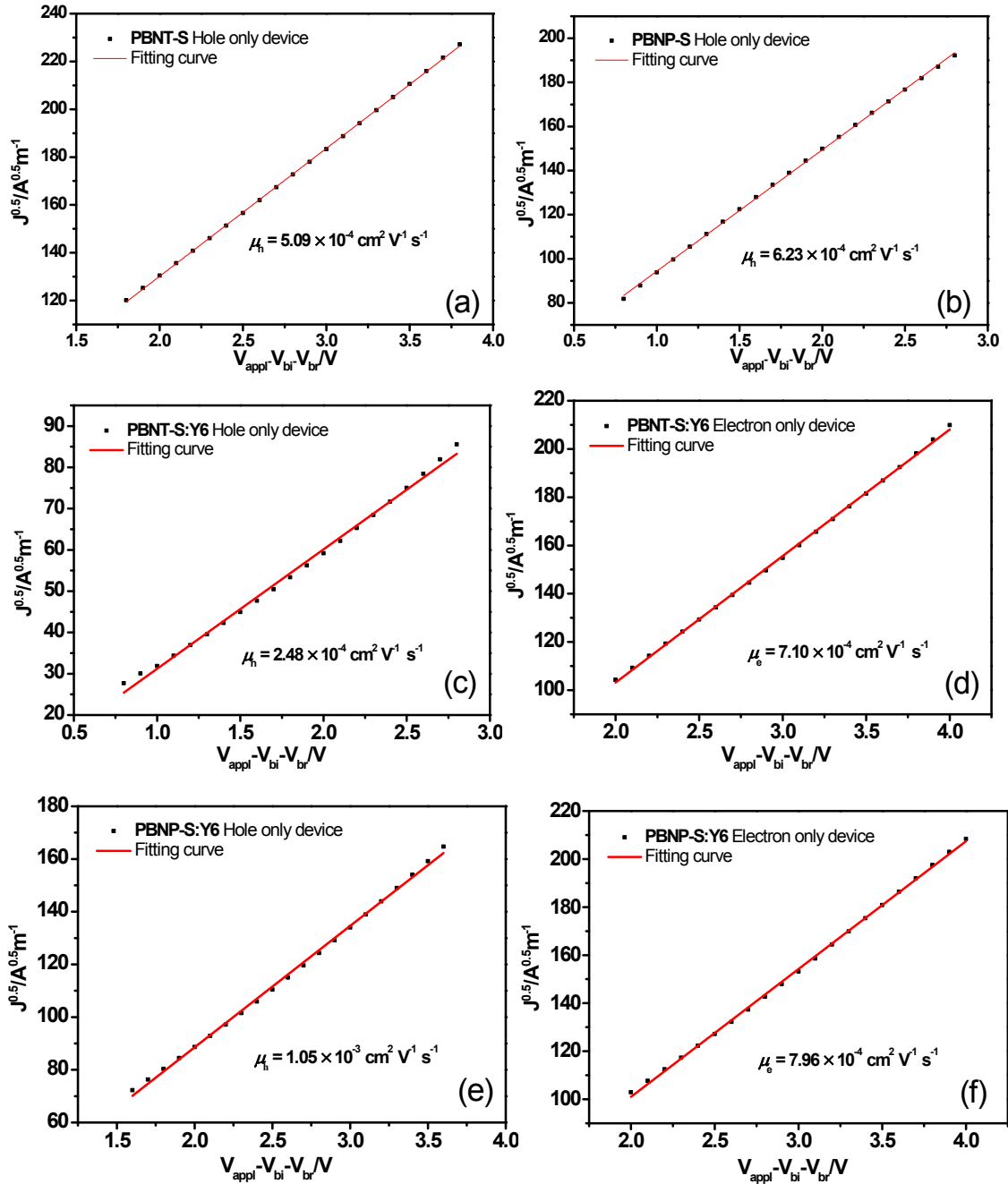


**Fig. S5** The representation of color coordinates of semitransparent devices with different Ag thicknesses under AM 1.5 G illumination on the CIE chromaticity diagram.

**Table S3** The color coordinates, correlated color temperature (CCT) and color rendering index (CRI) of the transmitted light of the semitransparent devices with different thick Ag cathode.

Ag [nm]	CIE [x, y]	CCT [K]	CRI
10	(0.2526, 0.2690)	17531	97

15	(0.2514, 0.2660)	18805	96
20	(0.2468, 0.2648)	21049	95



**Fig. S6**  $J^{0.5}$  vs  $(V_{\text{app}} - V_{\text{bi}} - V_{\text{br}})$  plots of hole-only and electron only devices of pristine and blend films.

## References

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