

## Supporting Information

### **A perylenebisimide derivative with LUMO level of -4.56 eV for non-fullerene solar cells**

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## 1. Materials and measurement

All synthetic procedures were performed under argon atmosphere. Commercial chemicals were used as received. Dry solvents were distilled over 4 Å molecular sieves.

$^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra were recorded at 400 MHz and 100 MHz on a Bruker AVANCE spectrometer with  $\text{CDCl}_3$  as the solvent and tetramethylsilane (TMS) as the internal standard. Optical absorptions spectra were recorded on a JASCO v-570 spectrophotometer. Cyclic voltammetry was performed under an inert atmosphere with a scan rate of  $0.1 \text{ V s}^{-1}$  and 1 M tetrabutylammonium hexafluorophosphate in  $\text{CH}_2\text{Cl}_2$  as the electrolyte. The working, counter and reference electrodes were glassy carbon, Pt wire and Ag/AgCl, respectively. The concentration of the sample in the electrolyte was approximately 1 mM, based on monomers. All potentials were corrected against  $\text{Fc/Fc}^+$ . Steady state fluorescence spectra were recorded at room temperature using an Edinburgh Instruments FLS980 double-monochromator luminescence spectrometer equipped with a nitrogen-cooled near-IR sensitive photomultiplier (Hamamatsu). Atom force microscope (AFM) images of films were obtained by using a Digital Instruments Nanoscope IIIa Multimode atomic force microscope in tapping mode.

Photovoltaic devices with an inverted configuration were made by spin coating a ZnO sol-gel at 4000 rpm for 60 s onto pre-cleaned, patterned ITO substrates. The photoactive layer was deposited by spin coating a chloroform solution containing PDPP2TzT or PDPP2Tz2T and SdiCNPBI and the appropriate amount of processing additive such as DIO or *o*-DCB in air.  $\text{MoO}_3$  (10 nm) and Ag (100 nm) were deposited by vacuum evaporation at ca.  $4 \times 10^{-5}$  Pa as the back electrode.

The active area of the cells was  $0.04 \text{ cm}^2$ . The  $J-V$  characteristics were measured by a Keithley 2400 source meter unit under AM1.5G spectrum from a solar simulator (Enlitech model SS-F5-3A). Solar simulator illumination intensity was determined at  $100 \text{ mW cm}^{-2}$  using a monocrystal silicon reference cell with KG5 filter. Short circuit currents ( $J_{sc}$ ) under AM1.5G conditions were estimated from the spectral response and convolution with the solar spectrum. The external quantum efficiency was measured by a Solar Cell Spectral Response Measurement System QE-R3011 (Enli Technology Co., Ltd.). The thickness of the active layers in the photovoltaic devices was measured on a Veeco Dektak XT profilometer.

## 2. Synthesis of SdiCNPBI

SdiPBI was synthesized according to literature procedures.<sup>1</sup>

### **Br-SdiPBI**

SdiPBI (200 mg, 0.143 mmol) and 5 ml of Br<sub>2</sub> were combined in 30 ml acetic acid and stirred at 60 °C for 24 h. The reaction mixture was then poured into 100 ml of Na<sub>2</sub>SO<sub>3</sub> saturated aqueous solution, and the resulting precipitate was collected by filtration. The crude product was then washed with 200 mL of water and 100 ml of methanol followed by further purification by silica gel chromatography (dichloromethane: petrolether = 3:1) to give **Br-SdiPBI** as a red solid (207.9 mg, 0.134 mmol, 93%). <sup>1</sup>H NMR (300 MHz, 298K, CDCl<sub>3</sub>, ppm) δ 9.69 – 9.74 (m, 2H), 8.95 – 9.07 (m, 2H), 8.74 – 8.83 (m, 2H), 8.05 – 8.33 (m, 6H), 4.90 – 5.24 (m, 4H), 1.98 – 2.35 (m, 8H), 1.60 – 1.93 (m, 8H), 0.95 – 1.47 (m, 48H), 0.62 – 0.94 (m, 24H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, ppm) δ 164.2, 163.0, 141.2, 139.3, 138.6, 133.8, 133.6, 133.2, 132.4, 130.7, 129.9, 129.4, 128.9, 128.8, 128.2, 128.1, 127.7, 127.4, 127.2, 124.1, 123.4, 122.2, 121.4, 55.14, 55.10, 32.4, 31.8, 31.7, 26.7, 22.64, 22.60, 14.2, 14.1. MS (MALDI-TOF): m/z (M+H) = 1553.4 (calcd for C<sub>92</sub>H<sub>104</sub>Br<sub>2</sub>N<sub>4</sub>O<sub>8</sub>+H: 1553.63).

### **SdiCNPBI**

**Br-SdiPBI** (200 mg, 0.129 mmol), zinc cyanide (151.5 g, 1.29 mmol), 1,1'-bis(diphenylphosphino)ferrocene (dppf) (23.3 mg, 0.042 mmol), and tris(dibenzylideneacetone)dipalladium(0) (Pd<sub>2</sub>(dba)<sub>3</sub>) (11.8 mg, 0.013 mmol) were combined and dissolved in 15 mL 1,4-dioxane and refluxed for 12 h under a N<sub>2</sub> atmosphere. The reaction mixture was then poured into 100 ml of water and the resulting precipitate was collected by filtration. The crude product was then washed with 50 mL of water and 50 ml of methanol followed by further purification by silica gel chromatography (dichloromethane) to give **SdiCNPBI** as a dark red solid (161.4 mg, 87%). <sup>1</sup>H NMR (400 MHz, 298K, CDCl<sub>3</sub>, ppm) δ 9.72 – 9.81 (m, 2H), 8.96 – 9.07 (m, 2H), 8.83 – 8.96 (m, 2H), 8.03 – 8.50 (m, 6H), 4.90 – 5.21 (m, 4H), 1.98 – 2.35 (m, 8H), 1.60 – 1.93 (m, 8H), 1.05 – 1.35 (m, 48H), 0.71 – 0.86 (m, 24H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, ppm) δ 163.8, 163.0, 142.4, 137.4, 136.9, 136.3, 134.3, 132.3, 132.0, 131.7, 130.4, 129.7, 129.3, 129.1, 128.80, 128.75, 128.4, 128.2, 128.1, 124.2, 119.6, 108.7, 107.8, 55.4, 33.2, 31.8, 31.71, 31.67, 26.6, 22.61, 22.57, 14.13, 14.08. MS (MALDI-TOF): m/z (M+Na) = 1468.7 (calcd for C<sub>94</sub>H<sub>104</sub>N<sub>6</sub>O<sub>8</sub>+Na: 1468.8).

### **3. <sup>1</sup>H-NMR of Br-SdiPBI and SdiCNPBI**

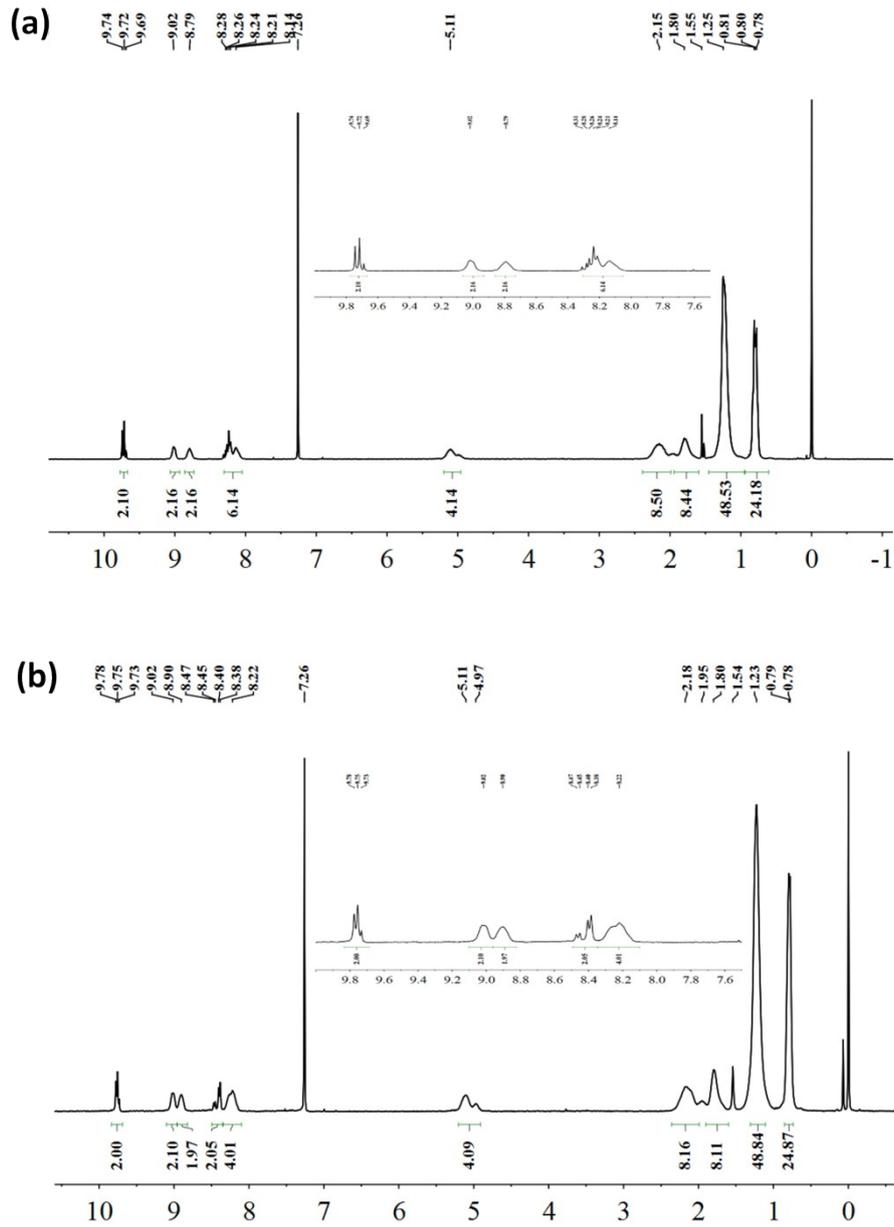
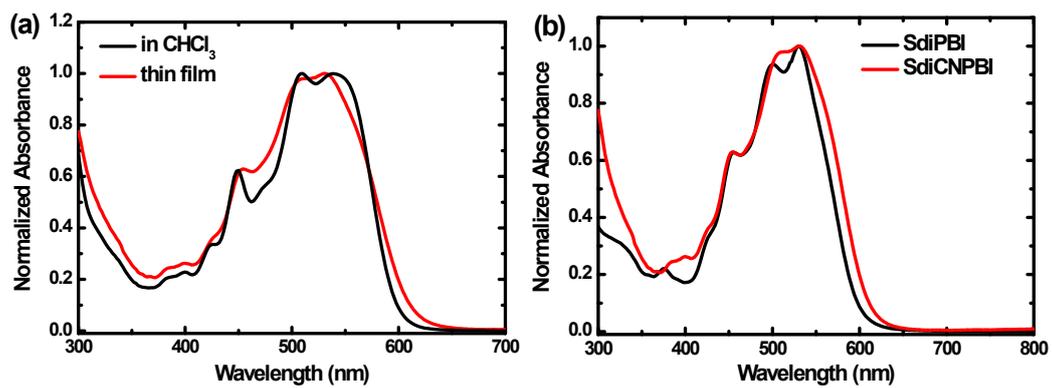


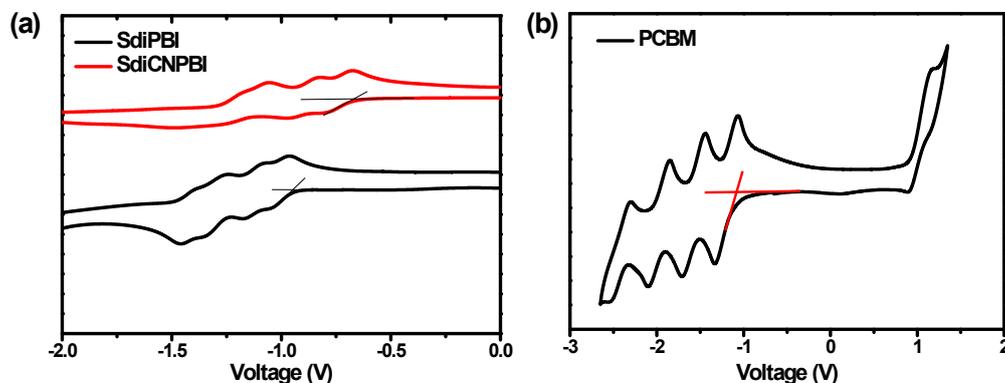
Fig. S1  $^1\text{H}$ -NMR spectra of Br-SdiPBI and SdiCNPBI.

#### 4. Absorption spectra of SdiPBI and SdiCNPBI



**Fig. S2 (a)** Absorption spectra of SdiCNPBI in CHCl<sub>3</sub> solution and in solid state films. (b) Absorption spectra of SdiPBI and SdiCNPBI in the solid-state.

## 5. CV

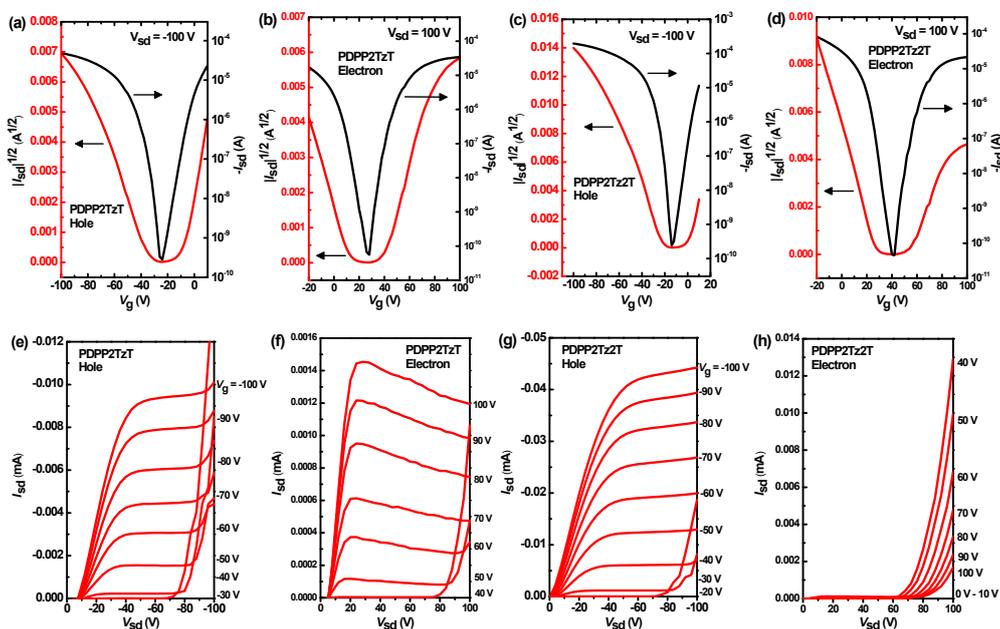


**Fig. S3** Cyclic voltammogram of (a) the SdiPBI and SdiCNPBI in CH<sub>2</sub>Cl<sub>2</sub> and (b) PCBM in *o*-DCB. Potential vs. Fc/Fc<sup>+</sup>. The LUMO level of PCBM was calculated as -4.16 eV.

## 6. FETs

The organic field-effect transistors were fabricated on a commercial Si/SiO<sub>2</sub>/Au substrate purchased from First MEMS Co. Ltd. A heavily N-doped Si wafer with a SiO<sub>2</sub> layer of 300 nm served as the gate electrode and dielectric layer, respectively. The Ti (2 nm)/Au (28 nm) source–drain electrodes were sputtered and patterned by a lift-off technique. Before deposition of the organic semiconductor, the gate dielectrics were treated with octadecyltrichlorosilane (OTS) in a vacuum oven at a temperature of 120 °C, forming an OTS self-assembled monolayer. The treated substrates were rinsed successively with hexane, chloroform, and isopropyl alcohol. Polymer thin films were spin coated on the substrate from CHCl<sub>3</sub> solution with a thickness of around 30 – 50 nm. The devices were thermally annealed at 120 °C for 10 min in a glovebox filled with N<sub>2</sub> before the measurement. The devices were measured on an Keithley 4200 SCS semiconductor parameter analyzer at room temperature. The mobilities were calculated from the saturation region with the following equation:  $I_{SD} = (W/2L)C_i\mu(V_G - V_T)^2$ , where  $I_{SD}$  is the drain–source current,  $W$  is the channel width (1400 μm),  $L$  is the channel length (50 μm),  $\mu$  is the field-effect mobility,  $C_i$  is the capacitance per unit area of the gate dielectric layer, and  $V_G$  and  $V_T$  are the gate voltage and threshold voltage, respectively. This equation defines the important characteristics of electron mobility

( $\mu$ ), on/off ratio ( $I_{\text{on}}/I_{\text{off}}$ ), and threshold voltage ( $V_T$ ), which could be deduced by the equation from the current–voltage plot.



**Fig. S4.** (a), (c), (e) and (g) p-type and (b), (d), (f) and (h) n-type transfer and output curves for the FETs based on PDPP2TzT and PDPP2Tz2T with BGBC configuration. (a) – (d) Transfer curves. (e) – (h) Output curves. (a), (b), (e) and (f) for PDPP2TzT. (c), (d), (g) and (h) for PDPP2Tz2T.

**Table S1.** Field-effect hole (h) and electron (e) mobility of the DPP polymer thin films. The thin films were thermally annealed at 120 °C for 10 min before measurement.

Polymer		Mobility [ $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ ]	$V_T$ [V]	On/off ratio
PDPP2TzT	h	0.14	-35	$2 \times 10^5$
	e	0.16	41	$6 \times 10^5$
PDPP2Tz2T	h	0.54	-23	$8 \times 10^5$
	e	0.16	55	$5 \times 10^5$

## 7. Solar cells of PDPP2TzT:SdiCNPBI

**Table S2.** Characteristics of PDPP2TzT:SdiCNPBI (1:1) solar cells fabricated from different conditions.

Solvent	Thickness (nm)	$J_{\text{sc}}$ ( $\text{mA}/\text{cm}^2$ )	$V_{\text{oc}}$ (V)	FF	PCE (%)
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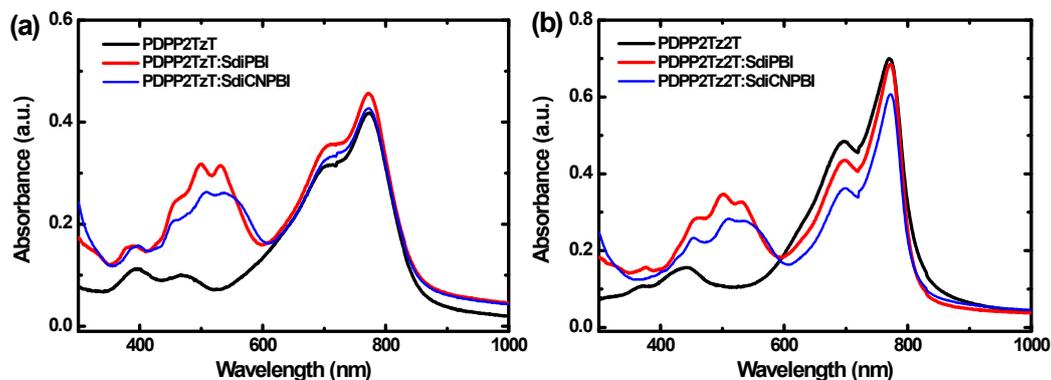
CHCl <sub>3</sub>	80	2.6	0.80	0.33	0.69
CHCl <sub>3</sub> /DIO (1%)	75	2.9	0.78	0.34	0.75
CHCl <sub>3</sub> /DIO (2%)	70	2.5	0.79	0.32	0.63
CHCl <sub>3</sub> / <i>o</i> -DCB (10%)	60	2.2	0.77	0.32	0.53
CHCl <sub>3</sub> / <i>o</i> -DCB (5%)	60	2.7	0.81	0.33	0.71
CHCl <sub>3</sub> / <i>o</i> -DCB (5%)	70	1.6	0.76	0.33	0.39
CHCl <sub>3</sub> / <i>o</i> -DCB (5%)	90	1.9	0.78	0.34	0.52

## 8. Solar cells of PDPP2Tz2T:SdiCNPBI

**Table S3.** Characteristics of PDPP2Tz2T:SdiCNPBI(1:1) solar cells fabricated from different conditions.

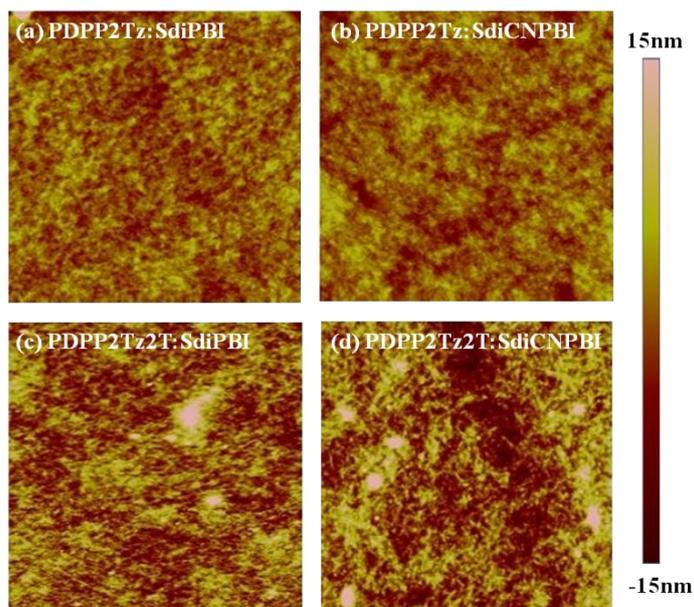
Solvent	Thickness (nm)	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (V)	FF	PCE (%)
CHCl <sub>3</sub>	100	4.4	0.75	0.33	1.1
CHCl <sub>3</sub> /DIO (0.2%)	100	5.5	0.77	0.34	1.4
CHCl <sub>3</sub> /DIO (0.5%)	110	5.1	0.76	0.29	1.1
CHCl <sub>3</sub> /DIO (1%)	80	4.1	0.76	0.38	1.20
CHCl <sub>3</sub> / <i>o</i> -DCB (5%)	60	3.7	0.75	0.42	1.2
CHCl <sub>3</sub> /DIO (0.2%)	60	3.3	0.74	0.41	1.0
CHCl <sub>3</sub> /DIO (0.2%)	70	3.9	0.75	0.44	1.3

## 9. Absorption spectra of the pure and blended thin films



**Fig. S5** Absorption spectra of the pure polymer and blended thin films. These films were further used to perform PL measurement as shown in Fig. 3.

## 10. AFM images of photo-active layers



**Fig. S6** AFM height image ( $3 \times 3 \mu\text{m}^2$ ) of the photo-active layers. The fabrication condition is referred to Table 2. The root mean square (RMS) roughness is 0.89 nm, 0.86 nm, 1.49 nm and 1.80 nm for (a) – (d).

## 11. Reference

- [1] W. Jiang, L. Ye, X. Li, C. Xiao, F. Tan, W. Zhao, J. Hou and Z. Wang, *Chem. Commun.*, 2014, **50**, 1024-1026.