# **Supporting Information for**

## Pyran-annulated perylene diimides derivatives as non-fullerene

# acceptorsfor high performance organic solar cells

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- 1. Solid state UV-vis absorption spectra of TPA-PDI<sub>2</sub> and TPA-PDI<sub>3</sub>



**Figure S1.**Normalized UV-vis absorption spectra of **TPA-PDI**<sub>2</sub>and **TPA-PDI**<sub>3</sub> in the film state.

### 2. Electrochemical Characterization of the TPA-PDI<sub>2</sub> and TPA-PDI<sub>3</sub>

Electrochemical measurements of targeted two as-synthesized PDIs compounds thin films were performed under nitrogen in deoxygenated 0.1 M solutions oftetra-n-butylammonium hexafluorophosphate in dry acetonitile using a CHI 660C electrochemicalworkstation, a glassy carbon working electrode, a platinum wire auxiliary electrode, and an Ag/AgClreference electrode. Cyclic voltammograms were recorded at a scan rate of 50 mV s<sup>-1</sup>. The lowestunoccupied molecular orbital (LUMO) levels were estimated based on the onset reduction potential ( $E_{red}$ ), and the reduction potential was calibrated using ferrocene ( $E_{Fc/Fc+}$ ) as a reference ( $E_{red} = -[E_{measured} - E_{Fc/Fc+} + 4.8]$  eV). ferrocene as an internal standard. Under the same condition, the onset oxidation potential ( $E_{1/2}^{ox}$ ) of ferrocene was measured to be 0.432 V versus Ag/Ag<sup>+</sup>.

Table S1. The photophysical and electrochemical properties of TPA-PDI2TPA-PDI3.

Samples	$\lambda_{max}{}^a$	ε <sup>a</sup>	$\lambda_{onset}{}^a$	E <sub>HOMO</sub> <sup>b</sup>	E <sub>LUMO</sub> <sup>c</sup>	$E^{opt \ d}_{\ g}$	
	(nm)	$(\text{mol}^{-1} \text{ cm}^{-1})$	(nm)	(eV)	(eV)	(eV)	
TPA-PDI <sub>2</sub>	553	62168.3	733	-5.52	-3.83	1.69	
TPA-PDI <sub>3</sub>	553	90880.7	700	-5.55	-3.78	1.77	
<sup>a</sup> In dichloromethane solution; ${}^{b}E_{HOMO} = E_{LUMO} - E_{g}^{opt}$ ; <sup>c</sup> Using the CV method, $E_{red}$							
$= -[E_{\text{measured}} - E_{\text{Fc/Fc+}} + 4.8] \text{ eV}; ^{d}\text{Calculated from the empirical formula: } E^{\text{opt}}_{g} =$							
$1240/\lambda_{\text{onset}}$ .							

## 3. Computational Studies



Figure S2. Wave functions of compounds TPA-PDI<sub>2</sub> and TPA-PDI<sub>3</sub>.

Table S2. The calculated data of  $TPA-PDI_2$  and  $TPA-PDI_3$  (the HOMO, LUMO and band gap)

НОМО		LUMO	$\mathbf{E_{g}}^{cal}$			
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<b>TPA-PDI</b> <sub>2</sub>	-5.27	-3.33	1.93
<b>TPA-PDI</b> <sub>3</sub>	-5.34	-3.39	1.94

**Table S3.** Device data of OSCs based on the PBDB-T: TPA-PDI<sub>2</sub> and PBDB-T: TPA-PDI<sub>3</sub> blends measured under the illumination of AM 1.5 G, 100 mW cm<sup>-2</sup>.

Samples	V <sub>oc</sub> (V)	I <sub>sc</sub> (mA/cm <sup>2</sup> )	FF	PCE (%)	PCE <sub>max</sub> (%)
TPA-PDI <sub>2</sub>	$0.865 \pm 0.005$	3.837 ±0.201	0.368±0.004	1.221 ±0.132	1.314
TPA-PDI <sub>3</sub>	0.910±0.005	10.276 ±0.213	0.624 <u>±</u> 0.005	5.598±0.184	5.840

#### 4. Space charge-limited current (SCLC) device fabrication

The structure of electron-only devices is ITO/ZnO/active layers /ZrAcAc/Aland the structure of hole-only devices isITO/ $V_2O_5$ / active layers / $V_2O_5$ /Al.The fabrication conditions of the active layer films are same with those for the solar cells. The charge mobilities are generally described by the Mott-Gurney equation:<sup>1</sup>

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

where *J* is the current density,  $\varepsilon_0$  is the permittivity of free space (8.85×10<sup>-14</sup> F/cm),  $\varepsilon_r$  is the dielectric constantof used materials,  $\mu$  is the charge mobility, *V* is the applied voltageand L is the active layer thickness. The  $\varepsilon_r$  parameter is assumed to be 3, which is a typical value for organic materials. In organic materials, charge mobility is usually field dependent and canbe described by the disorder formalism, typically varying withelectric field, E=V/L, according to the equation:

$$\mu = \mu_0 \exp[0.89\gamma \sqrt{\frac{V}{L}}]$$

where  $\mu_0$  is the charge mobility at zero electric field and  $\gamma$  is aconstant. Then, the Mott-Gurney equation can be described by:

$$J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu_0 \frac{V^2}{L^3} \exp[0.89\gamma \sqrt{\frac{V}{L}}]$$

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Figure S3. Dark current density-voltage characteristics for (a) hole-only and (b) electron-only devices with optimized **PBDB-T:TPA-PDI**<sub>2</sub> and PBDB-T:TPA-PDI<sub>3</sub>BHJ films.

Table S4. Hole and electron mobility of TPA-PDI<sub>2</sub>, TPA-PDI<sub>3</sub>, PBDB-T:TPA-PDI<sub>2</sub> and PBDB-T:TPA-PDI<sub>3</sub> BHJ films.

	Hole mobility	electron mobility	
Samples	$cm^2 V^{-1} s^{-1}$	$cm^2 V^{-1} s^{-1}$	
PBDB-T:TPA-PDI <sub>2</sub>	0.000565	0.000223	
PBDB-T:TPA-PDI <sub>3</sub>	0.000784	0.000385	
TPA-PDI <sub>2</sub>	_	0.000598	
TPA-PDI <sub>3</sub>	_	0.000634	
PBDB-T	0.001275	_	

### 5. Film and Device Characterization

The ultraviolet-visible (UV-Vis) absorption spectra of neat and blend films were obtained using a Shimadzu UV-3101 PC spectrometer. The current-voltage (I-V) curves of all OSCs were measured in a high-purity nitrogen-filled glove box using a 5/17

Keithley 2400 source meter. AM 1.5G irradiation at 100 mW/cm<sup>2</sup> provided by An XES-40S2 (SAN-EI Electric Co., Ltd.) solar simulator (AAA grade, 70×70 mm<sup>2</sup> photobeam size), which was calibrated by standard silicon solar cells (purchased from Zolix INSTRUMENTS CO. LTD). The external quantum efficiency (EQE) spectra of solar cells were measured in air conditions by a Zolix Solar Cell Scan 100. The morphology of the active layers was investigated by atomic force microscopy (AFM) using a Dimension Icon AFM (Bruker) in a tapping mode.



Figure S4. J<sub>ph</sub> versus V<sub>eff</sub> curves of PBDB-T:TPA-PDI<sub>2</sub> and PBDB-T:TPA-PDI<sub>3</sub>.

Table	<b>S5.</b>	Key	photovoltaic	parameters	calculated	from	the	$J_{ m ph}$ - $V_{ m eff}$	curves	of
PBDB	-T:T	PA-P	DI <sub>2</sub> and PBDE	B-T:TPA-PD	I <sub>3</sub> based dev	vices a	fter a	annealing	<b>5</b> .	

	J <sub>sat</sub> (mA.cm <sup>-2</sup> )	$J_{ph}^{b}$ (mA.cm <sup>-2</sup> )	J <sub>ph</sub> <sup>c</sup> (mA.cm <sup>-2</sup> )	J <sup>b</sup> <sub>ph</sub> /J <sub>sat</sub> (%)	J <sub>ph</sub> <sup>c</sup> /J <sub>sat</sub> (%)
PDBT-T: TPA-PDI <sub>2</sub>	4.732	4.059	2.527	85.8	53.4
PDBT-T: TPA-PDI <sub>3</sub>	10.875	10.270	8.702	94.4	80.0

<sup>a</sup>The Jph under condition of  $V_{eff} = 3.0 \text{ V}$ ;<sup>b</sup>The J<sub>ph</sub> under short circuit condition;<sup>c</sup>The J<sub>ph</sub> under maximum power output condition.

### 6. Synthesis and Characterization

#### **Bis(4-bromophenyl)phenylamine (S1)**

Under the condition of the dark, asolution of N-bromosuccinimide (7.26 g, 40.8 mmol) in dry DMF (80 mL) cooled to 0 °C, then a solution of triphenylamine (5.00 g, 20.35 mmol) in dry DMF (60 mL) was added dropwise and stirred at 0°C for 4h. the mixture was poured into water (200 mL) and extracted with  $CH_2Cl_2$ . The extracted phase was dried with  $Na_2SO_4$  and evaporated under reduced pressure, which was purified through silica gel column chromatography with hexane-dichloromethane (60:1) as eluent to give dibromotriphenylamine **S1** as a white solid (6.75 g, 82.7%).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  7.33 (d, 4H), 7.26 (dd, 2H), 7.06 (m, 3H), 6.23 (d, 4H).

#### N, N'-bis-[4-(trimethylsilylethynyl)phenyl]phenylamine (S2)

To a flask were added **S1**(20.1 g, 50 mmol), trimethylsilylacetylene (17.64 mL, 125 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (5.7 g, 5 mmol), CuI (952 mg, 5 mmol), diisopropylamine (50 mL) and dry toluene (100 mL), and the mixture was stirred under nitrogen at 80 °C for overnight, then cooled to room temperature. After the completion of the reaction, the reaction mixture was diluted with DCM (150 mL), filtered over Celite, and concentrated under reduced pressure, which was purified silica gel column chromatography with gradient elution of hexane : ethyl acetate (95:5) to give compound **S2** as a yellow oil (16.4 g, 75% yield).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  0.23 (s, 18H), 6.95 (d, 4H), 7.06 (d, 2H); 7.26 (d, 2H), 7.32 (d, 6H).

### N, N'-Bis-(4-ethynylphenyl)phenylamine (TPA-2EY)

Potassium carbonate (3.2 g, 23.2 mmol) was added into a DCM/MeOH (30 mL/30 mL) solution of **S2** (1.0 g, 2.32 mmol), and then the mixture was stirred at room temperature for 6 h. The mixture solution was poured into water (50 mL) and then extracted by CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated under vacuum. The crude product was purified by flash column chromatography on silica gel with n-hexane/dichloromethane as eluent to give **TPA-2EY** as a pale yellow solid (0.67 g, 90% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  3.04 (s, 2H), 6.99 (d, 4H), 7.09 (d, 2H), 7.29 (t, 1H), 7.35 (d, 6H).

#### Tris(4-bromophenyl)amine (S3)

Under the condition of the dark, to a solution of triphenylamine (4.01 g, 16.4 mmol) in DMF (80 mL) in an ice-bath was added dropwise a solution of N-bromosuccinimide (9.06 g, 50.9 mmol) in DMF (30 mL). After complete addition, the solution mixture was warmed up to room temperature. After stirring overnight, the reaction was quenched with ice-water, extracted with ethyl acetate, and then separated. The combined organic layers was washed with brine, dried over anhydrous sodium sulfate and evaporated in vacuum, followed by recrystallization from ethanol to afford a white solid of compound **S3** (7.13 g, 90% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  7.35 (d, 2H), 6.92 (d, 2H).

## Tris[4-(trimethylsilylethynyl)phenyl]phenylamine (S4)

To a flask were added **S3** (2.41 g, 5 mmol), trimethylsilylacetylene (2.82 mL, 20 mmol),  $Pd(PPh_3)_4$  (0.85g, 0.75 mmol), CuI (0.14 g, 0.75 mmol), diisopropylamine (10 mL) and dry toluene (20 mL) under argon protection, and the mixture was stirred under nitrogen at 80 °C for overnight. then cooled to room temperature. After the

completion of the reaction, concentrated under reduced pressure, which was purified silica gel column chromatography with gradient elution of hexane-ethyl acetate (20:1) to give compound **S4** as a light yellow solid (2.51g, 94% yield).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  0.26 (s, 27H); 6.98 (d, 6H); 7.36 (d, 6H).

### Tris(4-ethynylphenyl)amine (TPA-3EY)

Potassium carbonate (1.38 g, 10.00 mmol) was added into a CH<sub>2</sub>Cl<sub>2</sub> / MeOH (30 mL / 30 mL) solution of S4 (1.24 g, 2.32 mmol), and then the mixture was stirred at room temperature for 6 h. The mixture solution was poured into water (50 mL) and then extracted by  $CH_2Cl_2$  (50 mL  $\times$  2). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated under vacuum. The crude product was purified by flash column chromatography silica on gel with n-hexane/dichloromethane (10:1) as eluent to give **TPA-3EY** as a yellow solid (0.66 g, yield 89 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ 7.36 (d, 6H), 6.99 (d, 6H), 3.0 (s, 3H).

### 7. Spectroscopic data



Figure S5.<sup>1</sup> H NMR spectrum of compound**Py-PDI-Br.** 



Figure S6.<sup>13</sup>C NMR spectrum of compound**Py-PDI-Br.** 11/17



Figure S7. HRMS profile of compound Py-PDI-Br.

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Figure S8.<sup>1</sup> H NMR spectrum of compound TPA-PDI<sub>2</sub>.



Figure S9.<sup>13</sup>C NMR spectrum of compound TPA-PDI<sub>2</sub>.



Figure S10.<sup>1</sup> H NMR spectrum of compound TPA-PDI<sub>3</sub>.



Figure S11.<sup>13</sup>C NMR spectrum of compound TPA-PDI<sub>3</sub>.



Figure S12. HRMS profile of compound TPA-PDI<sub>2</sub>.



Figure S13. HRMS profile of compound TPA-PDI<sub>3</sub>.



Figure S14. FT-IR profile of compound TPA-PDI<sub>2</sub>.



Figure S15. FT-IR profile of compound TPA-PDI<sub>3</sub>.



Figure S16. Thermogravimetric analysis (TGA) graphs for compounds  $TPA-PDI_2$ and  $TPA-PDI_3$  in nitrogen atmosphere. Heating rate: 10 °C /min.

Figure S17. The molecular structures of PBDB-T,  $TPA-PDI_2$  and  $TPA-PDI_3$ . Reference

1. (a) H. Cha, D. S. Chung, S. Y. Bae, M. J. Lee, T. K. An, J. Hwang, K. H. Kim,

Y. H. Kim, D. H. Choi, C. E. Park, Adv. Funct. Mater.2013, 23, 1556;(b) S. Y.

Chang, H. C. Liao, Y. T. Shao, Y. M. Sung, S. H. Hsu, C. C. Ho, W. F. Su, Y. F.

Chen, J. Mater. Chem. A. 2013, 1, 2447; (c) Y. Zhang, D. Deng, K. Lu, J. Zhang,
B. Xia, Y. Zhao, J. Fang, Z. Wei, Adv. Mater. 2015, 27, 1071.