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# **Supporting Information**

## Hyperbranched polymer as acceptor for polymer solar cells

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### S1.1 Experimental Part

Tris(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)amine **(a)** 5,12-dibromo-2,9-bis(2-ethylhexyl)anthra[2,1,9-def:6,5,10-d'e'f'] diisoquinoline-1,3,8,10(2H,9H)tetraone **(b)** and 5-bromo-2,9-bis(2-ethylhexyl)anthra[2,1,9def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone **(c)** were synthesized according to the literature procedures.



Scheme S1. The synthesis route of HP-PDI.

## Synthesis of HP-PDI.

A mixture of compound **a** (187 mg, 0.30 mmol), compound **b** (301 mg, 0.39 mmol), compound **c** (90.1 mg, 0.13 mmol), NaHCO<sub>3</sub> (1.25 g, 9.0 mmol), THF (40 mL), toluene (14 mL), and H<sub>2</sub>O (3 mL) was degassed before and after the addition of Pd(PPh<sub>3</sub>)<sub>4</sub> (5.7

mg, 5.0 µmol). The mixture was heated to reflux and stirred for 24 h under nitrogen atmosphere. Then compound c (208 mg, 0.30 mmol) and phenylboronic acid (20 mg) were added successively at a time interval of 10 h to end-cap the boronic acid ester and bromo end groups, respectively. The mixture was cooled down to room temperature and poured into acetone (200 mL). After stirred for 2 h, the resulted precipitates were collected by filtration and washed with acetone (15 mL) for three times. The collected precipitates were subsequently dissolved in CHCl<sub>3</sub> and filtrated. After removing most solvent, the concentrated solution was precipitated into acetone (200 mL). The precipitates were collected by filtration; extracted on Soxhlet apparatus with methanol, hexane and dichloromethane (DCM). Then the portion extracted by DCM was evaporated to dryness and purified by column chromatography on silica gel using hot CHCl<sub>3</sub> as eluent to yield HP-PDI as a dark red solid (125 mg, 20%). <sup>1</sup>H NMR (400 MHz, 1,2-dichlorobenzene-d<sub>4</sub>):  $\delta$  (ppm) 8.94 (m, 2H), 8.78 (m, 2H), 8.36 (m, 2H), 8.00 (m, 2H), 4.31 (m, 4H), 0.85-2.24 (m, 70H). <sup>13</sup>C NMR (400 MHz, solid): δ (ppm) 163.25, 148.57, 141.15, 133.32, 129.82, 122.98, 43.87, 37.75, 30.09, 23.46, 13.84, 11.80, 1.38. GPC (PS standards): M<sub>w</sub> = 13.0 kg mol<sup>-1</sup>,  $M_{\rm n}$  = 5.3 kg mol<sup>-1</sup>, and PDI = 2.45.

#### S1.2 Measurements and characterization

<sup>1</sup>H and spectra was recorded on a Bruker AV 400 spectrometer, <sup>13</sup>C spectra was measured by BRUKER AVANCE III 400 solid spectrometer. UV-visible absorption spectra were measured on a PerkinElmer UV-vis spectrometer model Lambda 750. PL spectra were tested by PerkinElmer-LS55 (LS-55). The thickness of blend films was measured by a Dektak 6 M surface profilometer. The electrochemical behavior of polymers was studied using cyclic voltammetry (CHI 630A Electrochemical Analyzer) with a three-electrode electrochemical cell in a 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> CH<sub>3</sub>CN solution under an atmosphere of nitrogen with a scanning rate of 0.1 V/S. A glassy carbon working electrode, a Pt wire counter electrode, and an Ag/AgNO<sub>3</sub> (0.01 M in CH<sub>3</sub>CN) reference electrode were used. The ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple was used as the internal reference standard. HOMO level were determined

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according to the equation  $E_{HOMO} = -e [E_{ox} + 4.80 - E_{(Fc/Fc+)}]$ . Similarly, LUMO level was also determined by  $E_{LUMO} = -e [E_{ox} + 4.80 - E_{(Fc/Fc+)}]$ .  $E_{(Fc/Fc+)}$  was measured to be 0.09 V.

#### S1.3 Polymer Solar Cells Fabrication and Characterization

PSCs were fabricated with the device configuration of ITO/ZnO/PFN-OX/ PTB7-**Th:Acceptor**/MoO<sub>3</sub>/Ag. The conductivity of ITO is 15  $\Omega$ /square. A precleaned ITO substrate was treated by UV-ozone for 20 min. A thin layer of ZnO was spin-coated on top of cleaned ITO substrate at 3500 rpm for 60 s and annealing at 200 °C for 35 min on a hotplate before transferred into a glove box. A cross-linkable layer PFN-OX was spin coated with ~5 nm thickness on ZnO layer in glove box and annealing at 150 °C for 25 min. A mixture of PTB7-Th and SM-PDI or HP-PDI in 1,2-dichlorobenzene (DCB) was stirred at 90 °C for 3 h to ensure sufficient dissolution and then the blend solution was spin-coated onto ZnO layer, which was heated at 90 °C for 6 min, to form the active layer. The top electrode was thermally evaporated with an 8.5 nm  $MoO_3$  layer and followed by a 100 nm Ag film at a pressure below  $10^{-7}$  Torr through a shadow mask. On one substrate six cells with an effective area of 0.04 cm<sup>2</sup> for each were fabricated. Current-voltage (I-V) and external quantum efficiency (EQE) measurements were conducted in air without encapsulation. I-V characteristics were recorded at room temperature using an Agilent B2902A Source Meter under the illumination of an AM1.5G AAA class solar simulator (model XES-301S, SAN-EI) with an intensity of 100 mW cm<sup>-2</sup> and the white light intensity was calibrated with a standard single-crystal Si solar cell. The device stability of devices was tested by devices stored in the glove box without encapsulation.

#### S1.4 Space-Charge Limited Current Measurement

Hole-only devices with a structure of ITO/PEDOT:PSS (30 nm)/**PTB7-Th**:Acceptor/Au (100 nm) and electron-only devices with a configuration of FTO/**PTB7-Th**:Acceptor/Al (100 nm) were fabricated. FTO substrates were prepared by etching the commercial FTO substrates with HCl and Zn powders. The blend solution of **PTB7-Th** and **SM-PDI** or **HP-PDI** in 1,2-dichlorobenzene (DCB) was spin-coated onto PEDOT:PSS layer ,

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which was heated at 90 °C for 6 min, to form the active layer like PSC devices, and 100 nm of Au was thermally evaporated at a pressure of 10<sup>-4</sup> Pa through a shadow mask. For electron-only devices, the blend solution of **PTB7-Th** and **SM-PDI** or **HP-PDI** in 1,2-dichlorobenzene (DCB) was spin-coated on the clean FTO substrates to form active layer. Al electrodes (100 nm) were vacuum deposited on polymer thin films. Dark J–V curves of the hole-only devices and electron-only devices were measured by the space-charge limited current (SCLC) method. Dark *J–V* curves of devices were fitted by using the Mott–Gurney equation:  $J = 9\varepsilon_0\varepsilon_r\mu V^2/8L^3$ , where *J* is the space charge limited current,  $\varepsilon_0$  is the vacuum permittivity,  $\varepsilon_r$  is the permittivity of the active layer,  $\mu$  is the hole mobility or the electron mobility, and *L* is the thickness of the active layer.

#### S1.5 DFT calculation of SM-PDI and HP-PDI

To shed light on the twisty angle of adjacent PDI units for SM-PDI and HP-PDI, computational study was performed by density functional theory method (B3LYP/6-31G(d)) .<sup>S1, S2, S3</sup> To reduce the load, 2-ethylhexyl chains at **SM-PDI** were replaced by methyl groups for model compound PDI1. Because HP-PDI might not be fully branched, the twisty angles of HP-PDI were evaluated by branched model molecule PDI1 and liner model molecule PDI2 simultaneously. (Fig1, FigS2, ESI<sup>+</sup>). As shown in Fig. S2, the three dihedral angles of adjacent PDI groups in **PDI1** were calculated to be 107°, 116° and 128°, respectively. According to Jenekhe and Wang's works, the aggregation of PDI based small molecular acceptors could be gradually reduced along with the increase of dihedral angle between adjacent PDI units.<sup>S2</sup> Because the dihedral angle of PDI in SM-PDI was not large enough, big domain in devices was therefore predictable. The dihedral angle of **PDI2** was evaluated to be 123°, similar to that of PDI1, suggesting the twisty angles of PDI units in HP-PDI was all in the range from 107° to 128°. Although the adjacent PDI units in HP-PDI were not vertical enough, the quasi-spherical branched structure of HP-PDI could also suppress the aggregation of PDI units, both high electron mobility and good exciton separation could be anticipated.

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Fig. S1 XRD images of SM-PDI and HP-PDI films in a similar thickness.



Fig. S2. Chemical structures (a, b) and corresponding top view (a1, b1) and side view

(a2, a2) of optimized geometries of by DFT calculations (B3LYP/6-31G(d)).



**Fig. S3** Cyclic voltammetry curves of **SM-PDI** (a) and **HP-PDI** (b) as thin films on glassy carbon working electrodes.

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Fig. S4 Nitrogen adsorption/desorption isotherms of SM-PDI and HP-PDI.



Fig. S5 Pore size distributions of SM-PDI and HP-PDI powders.



**Fig. S6.** The efficiency plotted versus storage time for organic solar cells based on **SM-PDI** and **HP-PDI**. Measurements were tested on five devices.



**Fig. S7**  $J^{1/2}$ -V curves of **SM-PDI** and **HP-PDI** based devices for  $\mu_e$  (a) and  $\mu_h$  (b) calculations by the SCLC method.



Fig. S8 Solid state <sup>13</sup>C NMR spectra of HP-PDI.

## References

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