

Supporting Information

A Propeller-Shaped Perylene Diimides Hexamer as Nonfullerene Acceptor for Organic Solar Cells

Juncheng Liu, Sufei Xie, Shiyu Feng, Miao Li, Liangliang Wu, Xinjun Xu*, Xuebo Chen, Cuihong Li* and Zhishan Bo*^a

^aBeijing Key Laboratory of Energy Conversion and Storage Materials, College of Chemistry, Beijing Normal University, Beijing 100875, China.

*E-mail: licuihong@bnu.edu.cn, xuxj@bnu.edu.cn, zsbo@bnu.edu.cn

Experimental section

The structure of **HPB-PDI**₆ was characterized by MALDI-TOF mass spectroscopy and elemental analysis. Compounds **1**^{s1} (5-bromo-2,9-bis(1-hexylheptyl)anthra[2,1,9-def:6,5,10-d'e'f']diiso-quinoline-1,3,8,10(2H,9H)-tetrone) and **2**^{s2} (1,2-Bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)phenyl)acetylene) were prepared according to the literature procedures.

Procedures for the synthesis of compound **3**

A mixture of compound **1** (485 mg, 0.58 mmol), compound **2** (100 mg, 0.23 mmol), THF (40 mL) and H₂O (4 mL) was carefully degassed before and after Pd(PPh₃)₄ (0.012 mmol, 13.4 mg) was added. The mixture was stirred at reflux under N₂ for 72 h. After evaporation of the solvent under vacuum, the crude product was extracted twice with dichloromethane. The combined organic phase was dried over anhydrous MgSO₄. After removal of the solvent, the residue was purified by column chromatography on silica gel using petroleum ether/dichloromethane (v/v = 1:2) as an eluent to afford compound

3 (302 mg, 77%) as a red solid. ^1H NMR (500 MHz, CDCl_3 , δ): 8.70-8.59 (m, 10H), 8.22-8.19 (m, 2H), 7.93-7.91 (d, $J = 8.0$ Hz, 2H), 7.77-7.75 (d, $J = 8.0$ Hz, 4H), 7.57-7.55 (d, $J = 8.1$ Hz, 4H), 5.22-5.15 (m, 4H), 2.28-2.23 (m, 8H), 1.87-1.84 (m, 8H), 1.33-1.22 (m, 66H), 0.85-0.81 (m, 22H); ^{13}C NMR (125 MHz, CDCl_3 , δ): 164.79, 163.73, 142.68, 140.83, 136.17, 135.47, 134.86, 134.37, 133.61, 132.65, 131.62, 130.86, 130.18, 129.85, 129.20, 128.85, 128.65, 128.12, 127.55, 123.98, 123.62, 123.48, 123.01, 122.38, 90.52, 32.39, 31.78, 29.71, 29.23, 26.92, 22.60, 14.06. Anal. calcd for $\text{C}_{114}\text{H}_{130}\text{N}_4\text{O}_8$ (%): C, 81.29; H, 7.78; N, 3.33. Found (%): C, 81.03; H, 7.80; N, 3.32.

Procedures for the synthesis of **HPB-PDI₆**

A toluene (5 mL) solution of compound **3** (200 mg, 119 μmol) and $\text{Co}_2(\text{CO})_8$ (5 mg, 0.015 mmol) was stirred under nitrogen atmosphere at 110 °C for 24 h. After removal of the solvent, the residue was chromatographically separated on silica gel (eluent; hexane/ CH_2Cl_2 1:4) to give **HPB-PDI₆** as a red solid (96 mg, 48%). ^1H NMR (400 MHz, CDCl_3 , δ): 8.49-8.41 (m, 6H), 8.12-8.10 (m, 2H), 7.92-7.45 (m, 3H), 5.04-4.75 (m, 2H), 2.12-1.89 (m, 4H), 1.73-1.60 (m, 4H), 1.18-0.79 (m, 44H); ^{13}C NMR (100 MHz, CDCl_3 , δ): 164.5, 163.7, 163.5, 163.4, 140.7, 140.6, 140.4, 135.0, 134.9, 134.7, 129.2, 128.9, 128.5, 128.3, 128.2, 127.7, 127.6, 123.4, 123.3, 122.9, 122.5, 54.6, 54.0, 32.3, 32.2, 32.0, 31.7, 29.2, 29.1, 26.8, 26.6, 22.6, 22.4, 14.1, 13.7. Anal. calcd for $\text{C}_{342}\text{H}_{390}\text{N}_{12}\text{O}_{24}$ (%): C, 81.29; H, 7.78; N, 3.33. Found (%): C, 81.15; H, 7.82; N, 3.30. MALDI-TOF (m/z): Calcd. for $\text{C}_{342}\text{H}_{390}\text{N}_{12}\text{O}_{24}$: 5071.955 $[\text{M}+\text{Na}]^+$, Found 5071.952 $[\text{M}+\text{Na}]^+$.

Measurements and characterization

Unless otherwise mentioned, all reactions were monitored by thin layer chromatography (TLC). ^1H and ^{13}C spectra were recorded on a Bruker AV 500 and JEOL 400M spectrometer. MS (MALDI-TOF) results were performed with an Autoflex III instrument. UV-visible absorption spectra were obtained on a PerkinElmer UV-vis spectrometer model Lambda 750. The electrochemical properties were investigated by cyclic voltammetry (CHI 630A Electrochemical Analyzer) with a three-electrode electrochemical cell in a 0.1 M Bu_4NPF_6 CH_3CN solution under nitrogen atmosphere with a scanning rate of 0.1 V/s. A Pt plate working electrode, a Pt wire counter electrode, and an Ag/AgNO_3 (0.01 M in CH_3CN) reference electrode were used. The ferrocene/ferrocenium (Fc/Fc^+) redox couple was regarded as the internal reference standard. Transmission electron microscopy (TEM) was performed on FEI Technai TF20 (Philip) transmission electron microscopy. Atomic force microscopy (AFM) measurements were performed under ambient conditions using a Digital Instrument Multimode Nanoscope IIIA in the tapping mode. The thickness of the blend films was obtained by a Dektak 6 M surface profilometer. The powder X-ray diffraction (XRD) patterns were collected using a PANalytical X'Pert PRO MPD diffractometer with Cu KR radiation.

Polymer Solar Cell Fabrication and Characterization

OSCs were fabricated with the device configuration of $\text{ITO}/\text{ZnO}/\text{PTB7-Th:Acceptor}/\text{MoO}_3(85 \text{ \AA})/\text{Ag}(100 \text{ nm})$. The conductivity of ITO was $15 \text{ } \Omega$. The ITO-coated glass were washed by deionized water, acetone, isopropanol and deionized water

successively. The glass were dried at 150°C for 15 minutes, the sol-gel ZnO (30 nm) were spin-coated on them and annealed at 200°C for 30 minutes. The blends of **PTB7-Th** and acceptor in 1,2-dichlorobenzene (DCB) with the polymer concentration of 10mg ml⁻¹ was stirred at 90°C for 3 hours to ensure a sufficient dissolution, and the solution was spin-coated onto the ZnO layer. Followed 8.5 nm thick MoO₃ film and 100 nm thick Ag layer were deposited sequentially to complete the device. Six cells with an 0.04 cm² each effective area were fabricated on one substrate. Current-voltage (I-V) and external quantum efficiency (EQE) measurements were performed in air without encapsulation.

The current-voltage characteristics were recorded at approximately 25°C 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 mWcm⁻² as the white light source, and the white light intensity was calibrated with a standard photovoltaic cell equipped with a KG5 filter (certificated by the National Institute of Metrology) and a Keithley 2400 source-measure unit. The EQE data were obtained using a solar cell spectral response measurement system (QER3011, Enli Technology Co. Ltd). A calibrated silicon detector was used to determine the absolute photo sensitivity at different wavelengths.

Space-Charge Limited Current Measurement

Devices with hole-only device structure of ITO/PEDOT:PSS (30 nm)/**PTB7-Th:Acceptor**/Au (100 nm) and electron-only configuration of FTO/**PTB7-Th:Acceptor**/Al (100 nm) were fabricated.

Dark J - V curves of the hole-only devices and electron-only devices were taken by the space-charge limited current (SCLC) method. The dark J - V curves of the devices were based on the Mott–Gurney equation: $J = 9\varepsilon_0\varepsilon_r\mu V^2/8L^3$. Here J is the space-charge limited current, ε_0 is the vacuum permittivity, ε_r is the permittivity of the active layer, μ is the hole mobility or the electron mobility, and L is the thickness of the active layer.

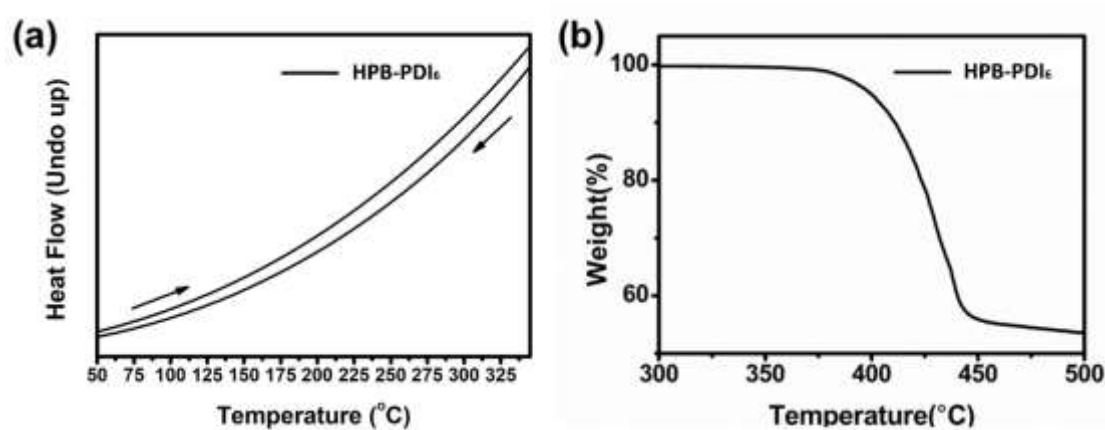


Figure S1. (a) DSC plot of **HPB-PDI₆** with a heating rate of 10°C/min under N₂ atmosphere, (b) TGA curves of **HPB-PDI₆** with a heating rate of 10°C /min under N₂ atmosphere

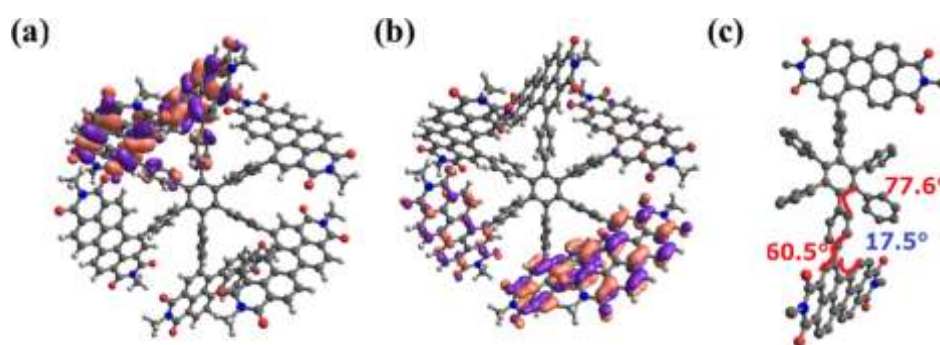


Figure S2. HOMO (a, -5.85 eV) and LUMO (b, -3.49 eV) orbitals of **HPB-PDI₆**; The schematic diagram of torsion angles in the optimized geometry of **HPB-PDI₆** (c).

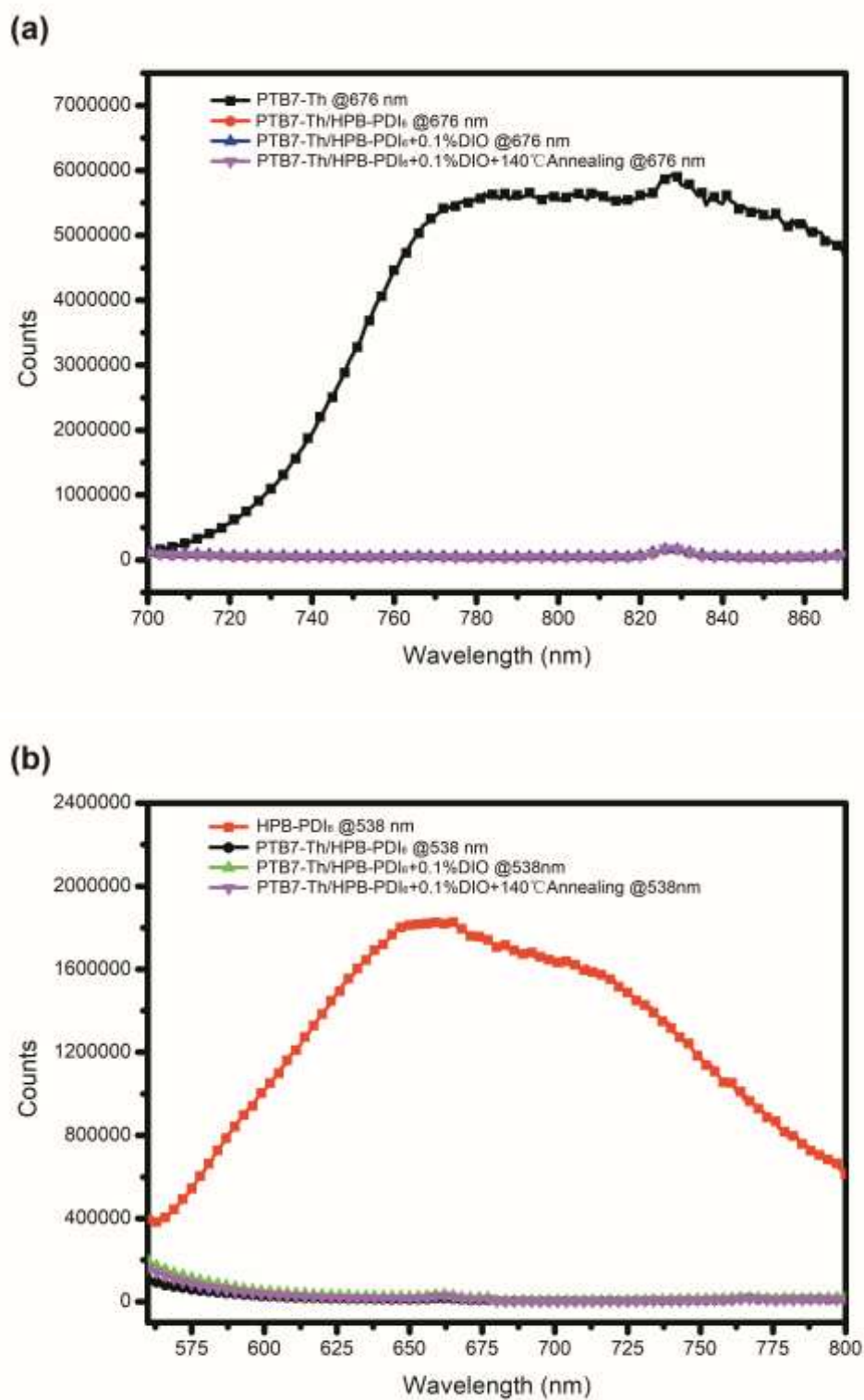


Figure S3. Photoluminescence quenching experiment of (a) the pristine PTB7-Th film, the PTB7-Th/HPB-PDI₆ blend film, the PTB7-Th/HPB-PDI₆ with 0.1%DIO film and

the PTB7-Th/**HPB-PDI**₆ with 0.1% DIO film and annealing at 140 °C for 5 minutes; (b) the pristine **HPB-PDI**₆ film and PTB7-Th/**HPB-PDI**₆ blend film at different conditions.

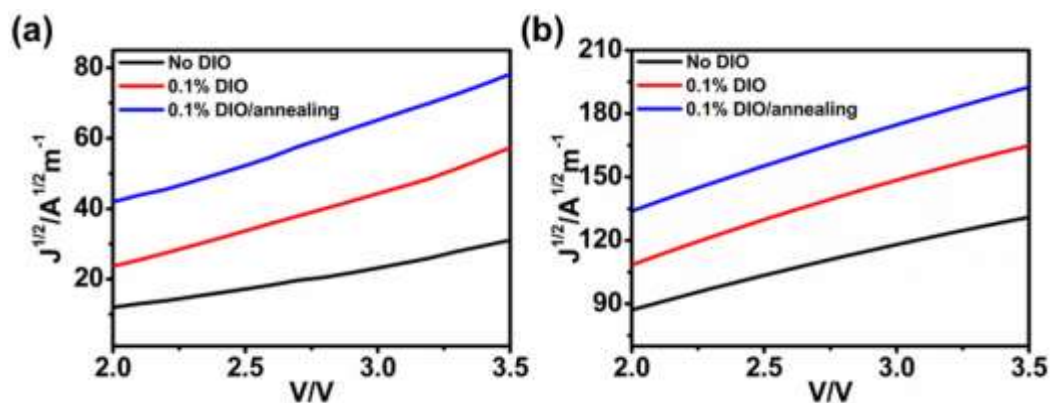


Figure S4. $J^{1/2}$ - V curves of PTB7-Th: **HPB-PDI**₆ based devices for μ_e (a) and μ_h (b) by SCLC.

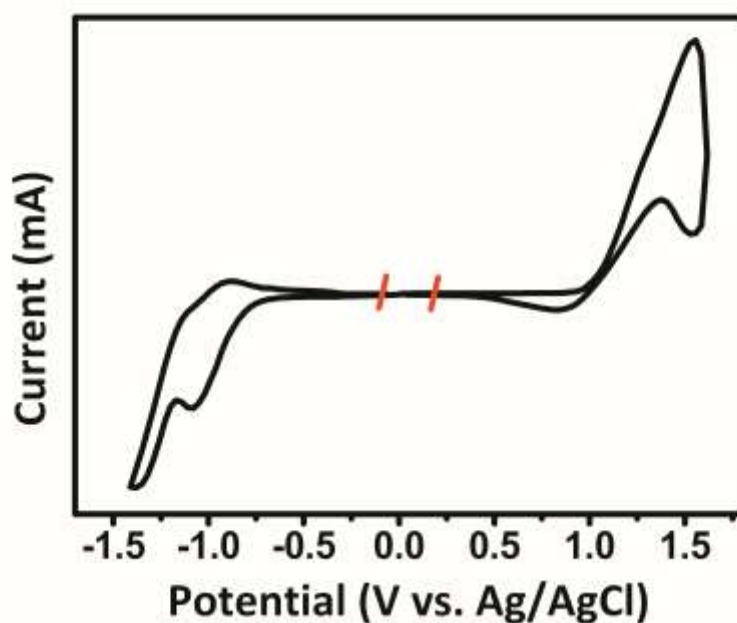


Figure S5. Cyclic voltammograms of **HPB-PDI**₆ in acetonitrile solution containing 0.1M Bu_4NPF_6 using Ag/AgCl as the reference electrode

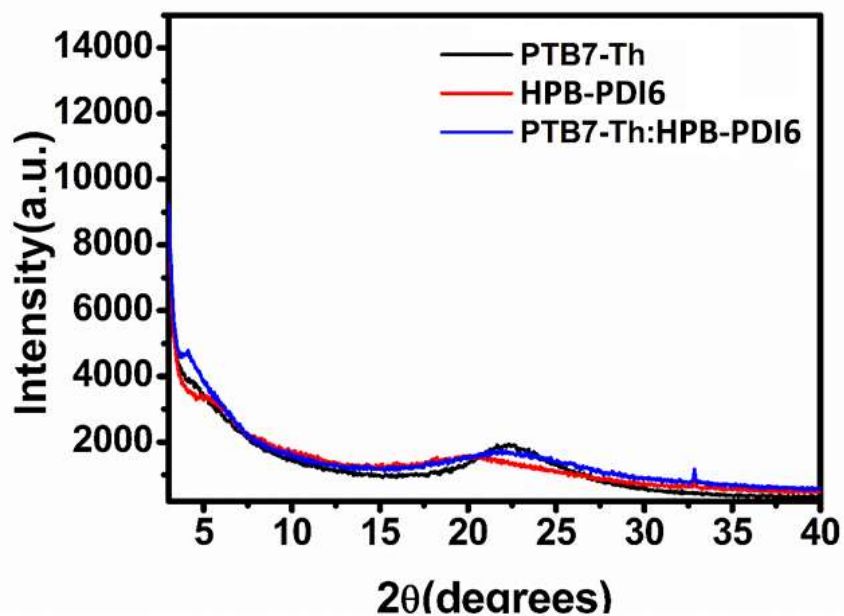


Figure S6. XRD images of PTB7-Th, HPB-PDI₆ and PTB7-Th: HPB-PDI₆ films.

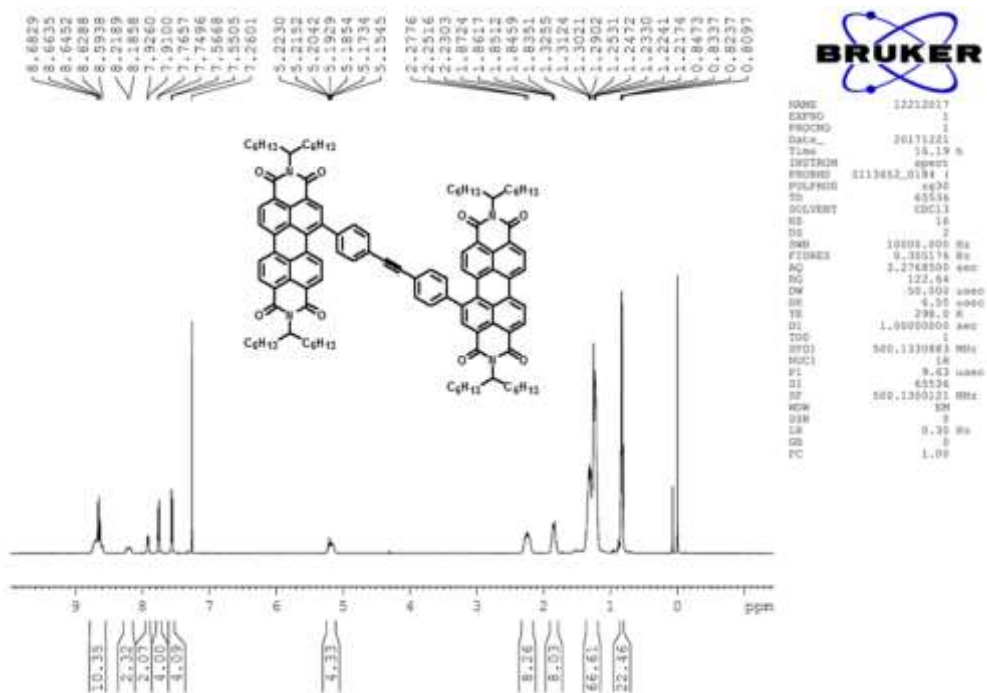


Figure S7. ¹H NMR spectrum of Compound 3.

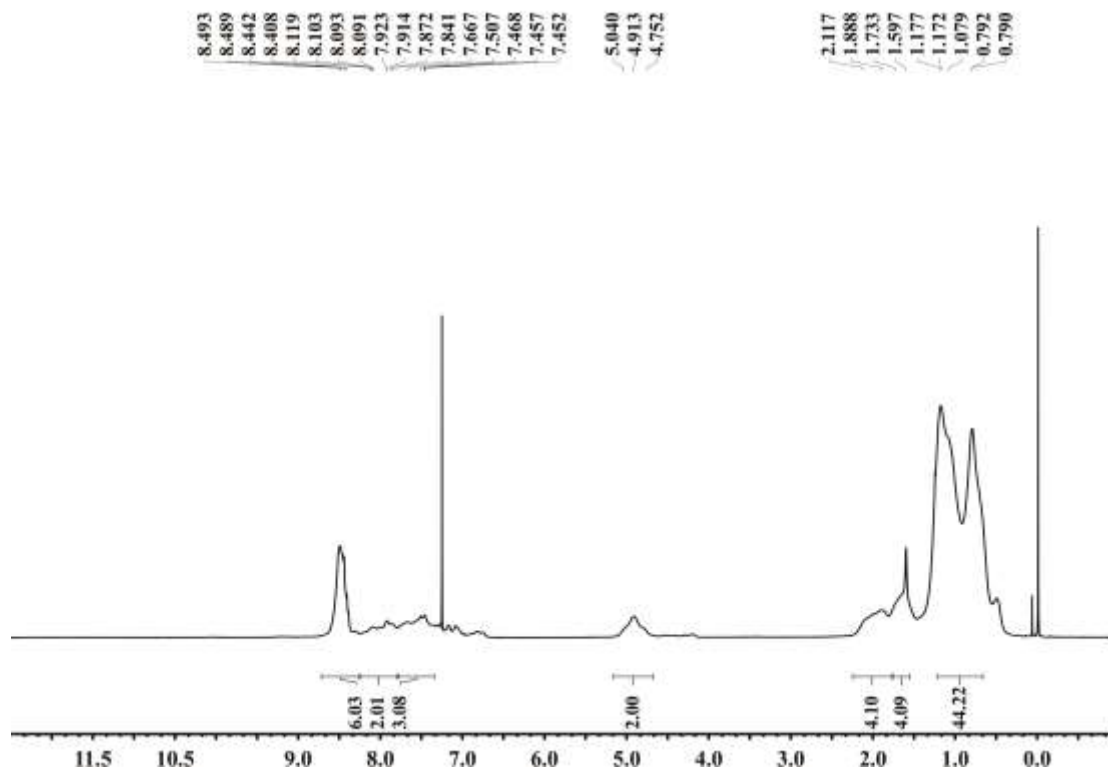


Figure S8. ^1H NMR spectrum of HPB-PDI₆.

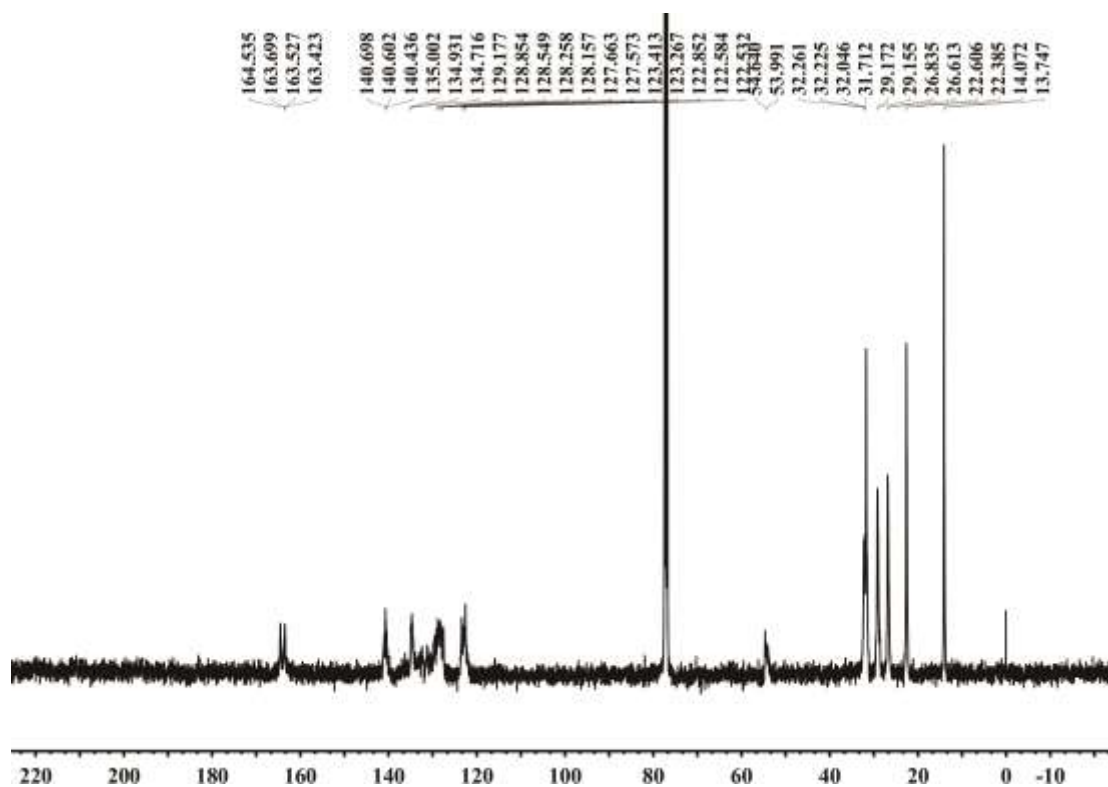


Figure S9. ^{13}C NMR spectrum of HPB-PDI₆.

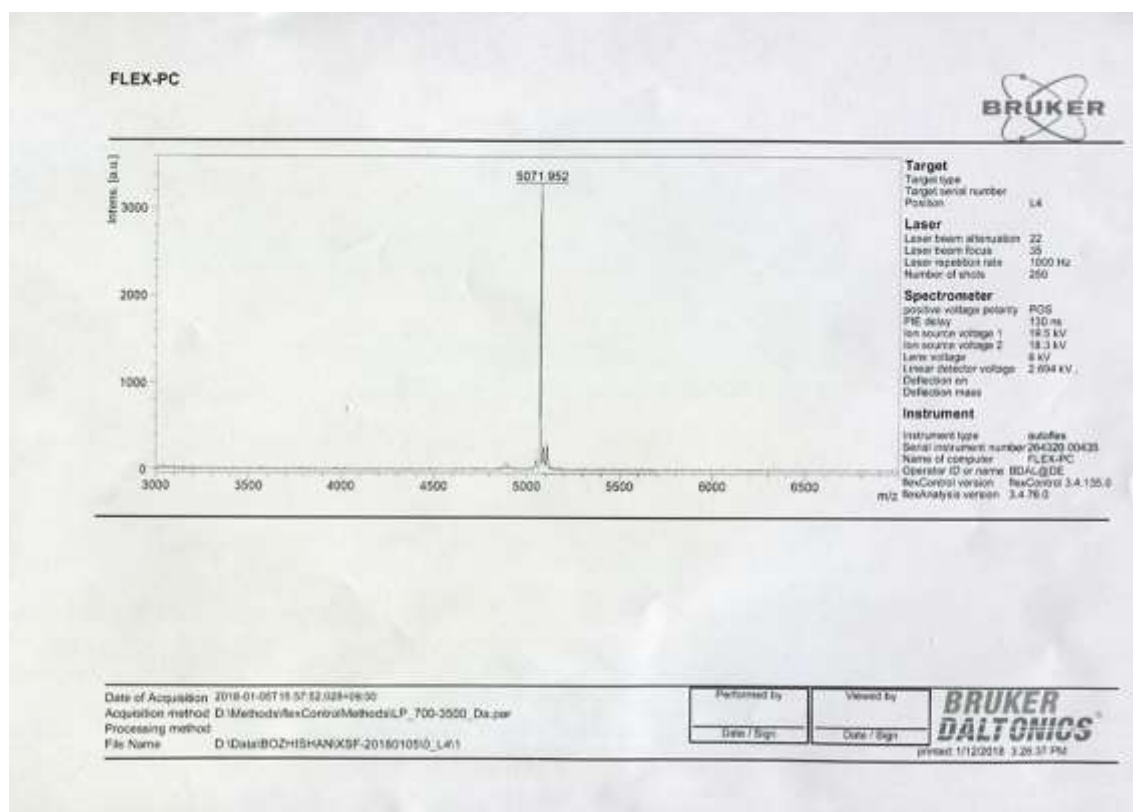


Figure S10. MALDI-TOF image of **HPB-PDI₆**.

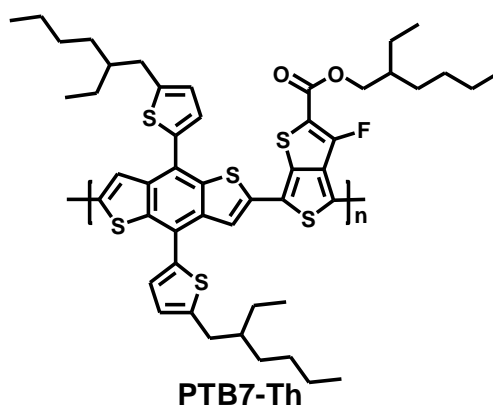


Figure S11. Chemical Structure of **PTB7-Th**

Table S1. Summary of the photovoltaic properties of **PTB7-Th: HPB-PDI₆** based devices (DCB as solvent)

Device(D:A)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	PCE (%)
1.5:1	0.91	12.39	43.0	4.85
1.5:1	0.91	13.43	41.7	5.08

1:1	0.89	13.18	43.5	5.12
1:1	0.92	14.01	45.0	5.80
1:1.5	0.88	13.27	41.0	4.78
1:1.5	0.88	13.27	41.0	4.78
1:2	0.87	11.31	38.8	3.79
1:2	0.91	11.10	39.3	3.98
1:2.5	0.91	9.90	37.4	3.38
1:2.5	0.91	10.73	39.1	3.84

Device(D:A)	Additives	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	PCE (%)
1:1	---	0.89	13.18	43.5	5.12
	---	0.90	12.64	38.1	4.38
	0.05%DIO	0.90	13.26	43.7	5.20
	0.05%DIO	0.90	14.76	42.6	5.65
	0.10%DIO	0.91	13.22	47.8	5.77
	0.10%DIO	0.92	14.32	46.5	6.14
	0.15%DIO	0.90	13.25	45.1	5.40
	0.15%DIO	0.91	13.88	46.2	5.81
	0.20%DIO	0.90	13.72	43.4	5.37
	0.20%DIO	0.91	13.81	45.2	5.69

Device(D:A)	Additives	Annealing		V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	PCE (%)
		Temperature(°C)					
1:1	0.10%DIO	100		0.91	13.89	46.0	5.81
		120		0.91	13.97	46.4	5.91
		140		0.91	14.74	47.7	6.39
		160		0.91	14.34	47.8	6.23
		180		0.87	13.67	44.9	5.32

Device(D:A)	Additives	Annealing		V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	PCE (%)
		time(min/140°C)					
1:1	0.10%DIO	0		0.92	13.89	46.0	5.81
		0		0.91	13.98	45.7	5.80
		2		0.93	13.28	47.0	5.84
		2		0.91	13.63	45.5	5.58
		5		0.92	15.11	48.0	6.63
		5		0.92	14.74	47.7	6.39
		10		0.93	13.54	47.3	6.00
		10		0.90	14.21	46.1	5.82
		30		0.92	13.90	46.3	5.95
		30		0.91	14.07	46.9	5.92
		60		0.93	13.65	48.9	6.23
60		0.91	14.14	47.6	6.08		

We have made 192 devices to get the optimized condition and the best 10 devices are listed in Table S2. The average PCE is $6.23 \pm 0.05(\%)$.

Table S2. The averaged 10 devices.

	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	PCE (%)
1	0.92	14.35	47.8	6.23
2	0.92	15.11	48.0	6.63
3	0.92	14.74	47.7	6.39
4	0.91	14.59	46.4	6.08
5	0.92	14.27	47.0	6.11
6	0.94	13.49	48.3	6.12
7	0.93	13.64	48.9	6.23
8	0.93	13.84	47.9	6.19
9	0.92	14.32	46.5	6.14
10	0.92	13.24	50.4	6.14

S1 Y. Zhao, X. Li, Z. Wang, W. Yang, K. Chen, J. Zhao and G. G. Gurzadyan, *J. Phys. Chem. C.*, 2018, **7**, 3756-3772.

S2 M. Takase, A. Nakajima and T. Takeuchi, *Tetrahedron Lett.*, 2005, **46**, 1739-1742.