Supporting Information

Small Bandgap Porphyrin-based Polymer Acceptors for Non-Fullerene Organic Solar Cells

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1. Materials and measurements

The synthetic procedures were performed under argon atmosphere. Commercial chemicals (from sigma-Aldrich, JK Chemical and TCI) were used as received. Compound 5,15-Diethynyl-10,20-bis(5-(2-ethylhexyl)- thienyl)-porphyrin zinc (II) (**M1**),¹ 4,9-dibromo-2,7-bis(2-decyltetradecyl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-

tetraone $(M2)^2$ and 5,12-dibromo-2,9-di(undecan-6-yl)anthra[2,1,9-*def*:6,5,10*d'e'f'*]diisoquinoline-1,3,8,10(2*H*,9*H*)-tetraone (M3)³ were prepared according to literature procedures.

¹H-NMR spectra were recorded at 400 MHz on a Bruker AVANCE spectrometer with tetramethylsilane (TMS) as the internal standard. The Molecular weight was determined with GPC at 140 °C on a PL-GPC 220 system using a PL-GEL 13µm Olexis column and *o*-DCB as the eluent against polystyrene standards. Optical absorption spectra were recorded on a JASCO V-570 spectrometer with a slit width of 2.0 nm and a scan speed of

1000 nm min⁻¹. Cyclic voltammetry was performed under an inert atmosphere at a scan rate of 0.1 V s⁻¹ and 1 M tetrabutylammonium hexafluorophosphate in acetonitrile as the electrolyte, a glassy-carbon working electrode coated with samples, a platinum-wire auxiliary electrode, and an Ag/AgCl as a reference electrode. The polymer thin films were fabricated from the polymer solutions in CB with 1% pyridine.

GIWAXS measurements were conducted on a Xenocs-SAXS/WAXS system with Xray wavelength of 1.5418 Å. The film samples were irradiated at a fixed angle of 0.2°. All film samples were prepared by spin-coating solutions on Si substrates with thermal annealing at 150 °C for 10 min.

Photovoltaic devices with inverted configuration were made by spin-coating a ZnO sol-gel⁴ at 4000 rpm for 60 s onto pre-cleaned, patterned ITO substrates. The photoactive layer was deposited by spin coating CB solution containing the polymer and the appropriate amount of pyridine as processing additive. The thin films were then transferred into the N₂-filled glove box and thermal annealed at hotplate before metal deposition. MoO₃ (10 nm) and Ag (100 nm) were deposited by vacuum evaporation at ca. 4×10^{-5} Pa as the back electrode.

The active area of the cells was 0.04 cm². 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 mW cm⁻² using a monocrystal silicon reference cell with KG5 filter. Short circuit currents 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.

Atomic force microscopy (AFM) images were recorded using a Digital Instruments Nano scope IIIa multimode atomic force microscope in tapping mode under ambient conditions.

2. Synthesis of the polymers PPorNDI

To a 50 mL two necked round-bottom flask were added **M1** (34.01 mg, 0.042 mmol), **M2** (49.96 mg, 0.046 mmol), anhydrous THF (2 mL) and triethylamine (0.3 mL), and the mixture was deoxygenated with argon for 30 min before Pd(PPh₃)₄ (1.58 mg, 1.4 µmol) and CuI (0.26 mg, 1.4 µmol) were added. The mixture was stirred at 85 °C for 24 h, after which it was precipitated in methanol and filtered through a Soxhlet thimble. The polymer was extracted with acetone, hexane, dichloromethane and CB (add 1 vol% pyridine). The CB fraction was evaporated and the polymer was precipitated in acetone. The polymer was collected by filtering over a 0.45 µm PTFE membrane filter and dried in a vacuum oven to yield **PPorNDI** (20 mg, 27.3%) as a dark solid. GPC (*o*-DCB, 140 °C): $M_n = 43.9$ kDa, $M_w = 92.1$ kDa and PDI = 2.10.

PPorPBI

Same procedure as for **PPorNDI** was used, but now **M1** (43.92 mg, 0.054 mmol) and **M3** (50.36 mg, 0.059 µmol) were used as the monomers and Pd(PPh₂)Cl₂ (1.24 mg, 1.7 µmol) was used as catalyst. Yield: 45 mg (55.4%). GPC (*o*-DCB, 140 °C): $M_n = 19.5$ kDa, $M_w = 23.9$ kDa and PDI = 1.23.

3. DFT calculations

The molecular geometries were optimized by density functional theory (DFT) at the B3LYP/6-31G** level.



Fig. S1 DFT frontier molecular orbitals and molecular geometry for the segments of PPorNDI and PPorPBI. PPorNDI shows a coplanar structure while PPorPBI has a twisted backbone with a dihedral angle of ca. 20 degree due to the larger steric hindrance between the porphyrin and PBI units.

4. GIWAXS



Fig. S2 Characteristics of PTB7-Th thin film spin-coated from CB/1% pyridine. (a) GIWAXS patters and (b) the out-of-plane and in-plane cuts of the corresponding GIWAXS patterns.

	In-plane (100)		Out-of-plane (010)	
	<i>q</i> (Å)	d (Å)	<i>q</i> (Å)	<i>d</i> (Å)
PPorNDI	0.26	24.2	1.83	3.43
PPorPBI	0.29	21.7	1.78	3.53
PTB7-Th	0.29	21.7	1.72	3.65
PTB7-Th:PPorNDI	0.25	25.1	1.61	3.90
PTB7-Th:PPorPBI	0.25	25.1	1.63	3.85

Table S1. Crystallographic Parameters of the Pure Polymers and blends in Thin Films. *q* values for all the thin films are exacted from diffraction peaks in the GIWAXS patterns.

5. Solar cells performance

Table S2. Characteristics of PTB7-Th:PPorNDI based solar cells spin coated from different solution and ratio.

Solvent	Ratio	Thickness	$J_{ m sc}$	$V_{\rm oc}$	FF	PCE
		[nm]	[mA cm ⁻²]	[V]		[%]
CB/pyridine (1%)	1:1	55	6.0	0.66	0.43	1.69
CB/pyridine (5%)	1:1	45	5.21	0.64	0.44	1.46
CB/pyridine (10%)	1:1	60	5.37	0.64	0.41	1.42
CB/pyridine (1%)	1:2	60	4.16	0.66	0.41	1.14
CB/pyridine (1%)	2:1	70	6.56	0.66	0.40	1.76

Solvent	Ratio	Thickness	$J_{ m sc}$	$V_{\rm oc}$	FF	PCE
		[nm]	[mA cm ⁻²]	[V]		[%]
CB/pyridine (1%)	1:1	50	10.98	0.64	0.46	3.21
CB/pyridine (5%)	1:1	50	11.16	0.64	0.46	3.3
CB/pyridine (10%)	1:1	50	11.22	0.65	0.44	3.46
CB/pyridine (10%)	1:2	50	8.68	0.64	0.41	2.31
CB/pyridine (10%)	2:1	60	11.79	0.65	0.40	3.02

Table S3. Characteristics of PTB7-Th:PPorPBI based solar cells spin coated from different solution and ratio.

6. AFM images



Fig. S3 (a,b) AFM height images $(3 \times 3 \ \mu m^2)$ and (c,d) phase images of optimized PTB7-Th:acceptor thin films. (a,c) PTB7-Th:PPorNDI. (b,c) PTB7-Th:PPorPBI. The RMS roughness is included in the AFM images.

7. SCLC measurement

Both the hole and electron mobilities were calculated with the Mott-Gurney equation in the SCLC region (slope = 2 in log*J* vs log*V* plots):

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

Where ε_0 is the permittivity of the vacuum, ε_r is the dielectric constant of the polymer (assumed to 3), and *L* is the thickness of the polymer layer.



Fig. S4 *J-V* curves in the space charge limited region for (a) ITO/PEDOT:PSS/polymer/Au for holes and (b) ITO/ZnO/polymer/Al for electrons.

Table S4. Hole and electron mobilities in o by SCLC measurement.

Active layer	$\mu_{\rm h} ({\rm cm}^2{ m V}^{-1}{ m s}^{-1})$	$\mu_{\rm e} ({\rm cm}^2{\rm V}^{-1}{\rm s}^{-1})$	$\mu_{\rm h}/\mu_{\rm e}$
PTB7-Th:PPorNDI	2.4×10 ⁻⁸	2.4×10 ⁻⁷	0.1
PTB7-Th:PPorPBI	9.0×10 ⁻⁸	1.6×10 ⁻⁷	0.56

8. NMR spectra



Fig. S5 ¹H-NMR of the polymer PPorNDI recorded at 100 °C with 1,2-dichlorobenzene- d_4 as the solvent. 1 vol% pyridine was added to improve the solubility of the polymers.



Fig. S6 ¹H-NMR of the polymer PPorPBI recorded at 100 °C with 1,2-dichlorobenzene- d_4 as the solvent. 1 vol% pyridine was added to improve the solubility of the polymers.

9. References

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