Supporting Information

for

Rational molecular engineering towards efficient non-fullerene small molecule acceptors for inverted bulk heterojunction organic solar cells

Yu-Qing Zheng, Ya-Zhong Dai, Yan Zhou, Jie-Yu Wang* and Jian Pei*

Beijing National Laboratory for Molecular Sciences, the Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China. E-mail: jianpei@pku.edu.cn, jieyuwang@pku.edu.cn

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1. General procedures and experimental details

¹H and ¹³C NMR spectra were recorded on a Bruker 400 MHz using CDCl₃ as solvent. ¹H NMR chemical shifts were referenced to TMS (0 ppm), and ¹³C NMR chemical shifts were referenced to CDCl₃ (77.00 ppm). Mass spectra were performed on a Bruker BIFLEX III mass spectrometer. Elemental analyses were carried out using a German Vario EL III elemental analyzer. Absorption spectra were recorded on PerkinElmer Lambda 750 UV-Vis Spectrometer. AFM experiments were carried out with a Nanoscope IIIa microscope (Multimode, Digital Instruments) under ambient conditions. Cyclic voltammetry was performed on BASI Epsilon workstation. Dichloromethane (for the solution) containing 0.1 M *n*-Bu4NPF₆ was used as a supporting electrolyte. Glassy carbon electrode was used as a working electrode and a platinum sheet as a counter electrode. All potentials were recorded versus Ag/AgCl as a reference electrode (scan rate: 50 mV s⁻¹).

Device Fabrication and Characterization

Preparation of the ZnO Precursor: 1 g of Zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O) and 0.28 g of ethanolamine (NH₂CH₂CH₂OH) were dissolved in 10 mL of 2-methoxyethanol (CH₃OCH₂CH₂OH) under stirring for 12 h.

Device fabrication: Before dried in a vacuum oven at 80 °C and 15 min oxygen plasma treatment, ITO-coated glass substrates were cleaned with acetone, detergent, distilled water and isopropanol. ZnO precursor was spin-coated onto the ITO-coated glass substrates at the speed of 4000 rpm for 30 s. Then, the substrates were annealed at 140 °C for 1 h and then were cooled to room temperature under vacuum. All the active layers were prepared by spin-coating at the speed of 1000 rpm for 15 s in the glove box. Before the electrode deposition, all the films were annealed at 100 °C for 15 min. MoO₃ (15 nm) and Ag (65 nm) were deposited onto the films by thermal evaporation (device active area: 15 mm²). All the devices were encapsulated in the glove box and tested under ambient condition. The PCE was tested under AM 1.5G irradiation with the intensity of 100 mW cm⁻² (Newport Solar Simulator 94021A)

calibrated by a NREL certified standard silicon cell (4 cm²). *J-V* curves were recorded with a Keithley 2636A semiconductor analyzer. IPCE test were carried out under monochromic illumination (Newport 74125 monochromator equipped with 66984 ARC lamp) and the calibration of the incident light intensity was performed with a calibrated silicon photodiode.

Compounds Characterization

Th-PhCHO: ¹H NMR (400 MHz, CDCl₃, ppm): δ 10.12 (s, 1H), 8.02 (d, J = 8.2 Hz, 2H), 7.92 (d, J = 8.3 Hz, 1H), 7.70 (d, J = 8.2 Hz, 2H), 7.68 – 7.66 (m, 2H), 7.49 (d, J = 8.3 Hz, 1H), 7.49 (dd, J = 8.3, 7.2 Hz, 1H), 7.36 – 7.28 (m, 4H), 7.11 (t, J = 7.7 Hz, 2H), 3.63 – 3.51 (m, 2H). Elemental Anal. Calcd. for C₄₁H₃₃NO₃S₂: C, 75.55; H, 5.10; N, 2.15; Found: C, 75.52; H, 5.14; N, 2.14.

Th-COOMe: ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.85 (d, J = 8.5 Hz, 1H), 8.23 (d, J = 7.6 Hz, 1H), 7.67 (d, J = 5.1 Hz, 2H), 7.53 (dd, J = 7.4, 7.3 Hz, 1H), 7.33 (dd, J = 4.9, 3.6 Hz, 2H), 7.27 (s, 2H), 7.03 (dd, J = 7.3, 1.6 Hz, 2H), 4.00 (s, 3H), 3.62 – 3.50 (m, 2H). HRMS (ESI) m/z: [M + H]⁺ calcd for C₃₆H₃₁NO₄S₂: 606.1761; Found: 606.1767.



2. Figures S1-S4

Fig. S1 Calculated orbitals of two molecules: a) HOMO of **Th-PhCHO**, b) LUMO of **Th-PhCHO**, c) HOMO of **Th-COOMe**, d) LUMO of **Th-COOMe** (B3LYP/6-31G(d)).

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Fig. S2 Absorption spectra of Th-PhCHO and Th-COOMe in thin films.



Fig. S3 PL spectra of a) pure Th-PhCHO; b) Th-PhCHO: P3HT; c) pure Th-COOMe; d) Th-COOMe: P3HT in films.



Fig. S4 SCLC curves of devices based on Th-PhCHO: P3HT and Th-COOMe: P3HT.