Electronic Supplementary Information for:

Enhancing performance of electron acceptor ITIC-Th via tailoring end groups

Zeyuan Li,^{‡a} Shuixing Dai,^{‡a} Jingming Xin,^b Lin Zhang,^b Yang Wu,^b Jeromy Rech,^c Fuwen Zhao,^d Tengfei Li,^a Kuan Liu,^a Qiao Liu,^a Wei Ma,^b You Wei,^c Chunru Wang^d and Xiaowei Zhan^a*

^aDepartment of Materials Science and Engineering, College of Engineering, Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, Peking University, Beijing 100871, China. *E-mail address*: xwzhan@pku.edu.cn

^bState Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, China.

^cDepartment of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290, United States.

^dInstitute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. [‡]Zeyuan Li and Shuixing Dai contributed equally.

Materials

Unless stated otherwise, solvents and chemicals were obtained commercially and were used without further purification. Compounds 1^1 and 2^2 were synthesized according to our previous works. Compound **3** was purchased from Solmer Material Inc.

Synthesis

ITIC-Th2: Compound 2 (165 mg, 0.15 mmol) and compound 1 (138 mg, 0.60 mmol)

were added to a three-necked flask. After being flushed by a gentle stream of argon for 15 min, the solid materials were fully dissolved by chloroform (25 mL). Then pyridine (0.6 mL) was added. The reaction was stirred at 65 °C for 14 h. After cooling to room temperature, the mixture was washed with methanol to remove remnant terminal groups. The crude product was purified by column chromatography with dichloroform: petroleum ether (1:3, v/v) as the eluent to obtain ITIC-Th2 as a dark green solid (100 mg, 61% yield). ¹H-NMR (400 MHz, CDCl₃): δ 8.89 (s, 2H), 8.54 (t, *J* = 8.8 Hz, 2H), 8.27 (s, 2H), 7.83 (s, 2H), 7.70 (t, *J* = 6.8 Hz, 2H), 6.88 (m, 4H), 6.60 (m, 4H), 2.72 (t, *J* = 7.6 Hz, 8H), 1.60 (m, 8H), 1.30 (m, 24H), 0.83 (m, 12H). ¹³C-NMR (100 MHz, CDCl₃): δ 184.69, 157.20, 154.90, 154.76, 154.65, 152.27, 146.16, 146.10, 145.35, 142.90, 140.03, 138.83, 137.45, 136.15, 135.69, 134.93, 133.55, 125.35, 122.59, 121.11, 117.46, 114.12, 113.90, 113.15, 113.05, 111.79, 111.60, 69.14, 56.02, 30.47, 30.31, 29.24, 28.68, 27.84, 21.48, 13.00. MS (MALDI-TOF): m/z 1524 (M⁺). Anal. Calc. for C₈₈H₇₀F₄N₄O₂S₈: C, 67.78; H, 4.63; N, 3.68. Found: C, 67.72; H. 4.55; N, 3.65.

ITIC-Th3: Compound **2** (111 mg, 0.10 mmol) and compound **3** (104 mg, 0.46 mmol) were added to a three-necked flask. After being flushed by a gentle stream of argon for 15 min, the solid materials were fully dissolved by chloroform (25 mL). Then pyridine (0.6 mL) was added. The reaction was stirred at 65 °C for 15 h. After cooling to room temperature, the mixture was washed by methanol to remove remanent terminal groups. The crude product was purified by column chromatography with dichloroform: petroleum ether (1:1, v/v) as the eluent to obtain ITIC-Th3 as the dark blue solid (56 mg, 50% yield). ¹H-NMR (300 MHz, CDCl₃): δ 8.83 (s, 2H), 8.18 (d, *J* = 7.8 Hz, 4H), 7.85 (d, *J* = 6.3 Hz, 2H), 7.80 (s, 2H), 6.89 (m, 4H), 6.60 (m, 4H), 3.97 (s, 6H), 2.72 (t, *J* = 7.4 Hz, 8H), 1.62 (m, 8H), 1.31 (m, 24H),

0.83 (m, 12H). ¹³C-NMR (100 MHz, CDCl₃): δ 185.95, 164.48, 159.31, 154.37, 151.01, 145.93, 145.26, 145.15, 142.40, 141.47, 140.26, 138.85, 136.22, 135.11, 134.74, 129.24, 125.33, 124.42, 122.90, 122.55, 120.96, 177.20, 113.68, 113.42, 107.77, 68.41, 55.95, 55.13, 30.47, 30.31, 29.23, 28.68, 27.86, 21.67, 21.49, 13.01. MS (MALDI-TOF): m/z 1512 (M⁺). Anal. Calc. for C₈₈H₇₈N₄O₄S₈: C, 69.90; H, 5.20; N, 3.71. Found: C, 69.88; H, 5.24; N, 3.64

Measurements and characterization

The ¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker AVANCE 300 and 400 MHz spectrometer in CDCl₃. The elemental analysis was measured by a Flash EA1112 elemental analyzer. The UV-vis absorption spectra were taken on a JASCO V-570 UV-vis spectrophotometer in solution (chloroform) and thin film (on a quartz substrate). Electrochemical measurements were carried out under nitrogen on a deoxygenated solution of tetra-n-butylammonium hexafluorophosphate (0.1 M) in acetonitrile at a potential scan rate of 100 mV s⁻¹ employing a computer-controlled Zahner IM6e electrochemical workstation, a glassy-carbon working electrode coated with films, a platinum-wire auxiliary electrode, and an Ag wire anodized with AgCl as a reference electrode. The potentials were referenced to a ferrocenium/ferrocene (FeCp2^{+/0}) couple using ferrocene as an external standard. Thermogravimetric analysis (TGA) measurements were carried out using a Shimadzu thermogravimetric analyzer (Model DTG-60) under flowing nitrogen gas at a heating rate of 10 °C min⁻¹. Differential scanning calorimetry (DSC) measurements were performed using a TA Instruments differential scanning calorimeter (Q2000) under nitrogen at a heating rate of 10 °C min⁻¹. The nanoscale morphology of the blends was observed employing a Multimode 8 scanning probe microscopy (Bruker) in the tapping mode.

GIWAXS measurements were performed at beamline 7.3.3 at the Advanced Light Source. Samples were prepared on Si substrates using identical blend solutions as those used in devices. The 10 keV X-ray beam was incident at a grazing angle of 0.09°-0.15°, selected to maximize the scattering intensity from the samples. The scattered X-rays were detected using a Dectris Pilatus 2M photon counting detector.

R-SoXS transmission measurements were performed at beamline 11.0.1.2 at the Advanced Light Source (ALS).³ Samples for R-SoXS measurements were prepared on a PSS modified Si substrate under the same conditions as those used for device fabrication, and then transferred by floating in water to a 1.5 mm \times 1.5 mm, 100 nm thick Si₃N₄ membrane supported by a 5 mm \times 5 mm, 200 µm thick Si frame (Norcada Inc.). 2D scattering patterns were collected on an in-vacuum CCD camera (Princeton Instrument PI-MTE). The sample detector distance was calibrated from diffraction peaks of a triblock copolymer poly (isoprene-b-styrene-b-2-vinyl pyridine), which has a known spacing of 391 Å. The beam size at the sample is approximately 100 µm \times 200 µm.

Fabrication and characterization of photovoltaic cells

Organic solar cells were fabricated with the structure: ITO/ZnO/FTAZ:acceptor/MoOx/Ag. Patterned indium tin oxide (ITO) glass (sheet resistance = $15 \Omega \square^{-1}$) was precleaned in an ultrasonic bath with acetone and isopropanol, and treated in an ultraviolet–ozone chamber (Jelight Company, USA) for 20 min. ZnO layer (ca. 30 nm) was spin-coated at 3000 rpm onto the ITO glass from ZnO precursor solution (a mixture of zinc acetate dehydrate (100 mg), 2-methoxyethanol (973 µL) and ethanolamine (28.29 µL) stirred overnight), and then baked at 200 °C for 30 min. A FTAZ: acceptor mixture (12.5 mg mL⁻¹ in total) in chloroform solvent was spin-coated at 3000 rpm on the ZnO layer to form a photosensitive layer (ca. 100 nm). Then the MoO₃ layer (ca. 5 nm) and Ag (ca. 80 nm) were evaporated onto the surface of the photosensitive layer under vacuum (ca. 10^{-5} Pa). The active area of the device was ca. 4 mm². The *J*–*V* curve was measured using a computer-controlled B2912A Precision Source/Measure Unit (Agilent Technologies), under an XES-70S1 (SAN-EI Electric Co., Ltd.) solar simulator (AAA grade, 70×70 mm² photobeam size) coupled with AM 1.5 G solar spectrum filters used as the light source, and the optical power at the sample was 100 mW cm⁻². The external quantum efficiency (EQE) spectrum was measured using a Solar Cell Spectral Response Measurement System QE-R3011 (Enlitech Co., Ltd.). The light intensity at each wavelength was calibrated using a standard single crystal Si photovoltaic cell.

Mobility measurement

Hole-only or electron-only devices were fabricated using the architectures ITO/PEDOT: PSS/FTAZ:acceptor/Au for holes and Al/FTAZ:acceptor/Al for electrons. For hole-only devices, the pre-cleaned ITO glass was spin-coated with PEDOT:PSS (ca. 35 nm), then FTAZ:acceptor blend was spin-coated as photovoltaic devices, then Au (ca. 80 nm) was evaporated under vacuum (ca. 10⁻⁵ Pa). For electron-only devices, Al (ca. 80 nm) was evaporated onto pre-cleaned glass under vacuum, FTAZ: acceptor blend was spin-coated, then Al (ca. 80 nm) was evaporated under vacuum. The mobility was extracted by fitting the current density–voltage curves using space charge limited current (SCLC). The equation is as follows

$$J = (9/8)\mu\varepsilon_{r}\varepsilon_{0}V^{2}exp(0.89(V/E_{0}L)^{0.5})/L^{3}$$

where *J* is current density, μ is hole or electron mobility, ε_r is relative dielectric constant, ε_0 is permittivity of free space, $V = V_{appl} - V_{bi}$, E_0 is characteristic field, *L* is the thickness of organic layer. The thickness of organic layer was measured on DektakXT (Bruker).



Scheme S1 Synthetic routes of ITIC-Th2 and ITIC-Th3.



Fig. S1 TGA curves (a) and DSC curves (b) of ITIC-Th2 and ITIC-Th3.



Fig. S2 *J-V* characteristics in the dark for electron-only devices based on ITIC-Th series.



Fig. S3 J-V characteristics in the dark for hole-only (a) and electron-only devices (b) based on

FTAZ: ITIC-Th series blends.



Fig. S4 AFM height (top) and phase (bottom) images of (a) FTAZ:ITIC-Th, (b) FTAZ:ITIC-Th1, (c) FTAZ:ITIC-Th2, (d) FTAZ:ITIC-Th3 blends under optimized device conditions (1:1.5, w/w; 0.25% DIO, v/v). 2.0 μ m × 2.0 μ m.



¹H NMR spectrum of ITIC-Th2.







¹³C NMR spectrum of ITIC-Th3.

Table S1 Electron mobility and hole mobility of FTAZ:ITIC-Th series blends

blend	$\mu_{\rm h}({\rm cm}^2{\rm V}^{-1}{\rm s}^{-1})$	$\mu_{\rm e} ({\rm cm}^2{\rm V}^{-1}{\rm s}^{-1})$	$\mu_{ m h}/\mu_{ m e}$
FTAZ:ITIC-Th	1.0×10^{-3}	1.6×10^{-4}	6.7
FTAZ:ITIC-Th1	6.2×10^{-4}	3.5×10^{-4}	1.8
FTAZ:ITIC-Th2	1.3×10^{-3}	5.1 × 10 ⁻⁴	2.6
FTAZ:ITIC-Th3	2.4×10^{-3}	7.2×10^{-4}	3.3

Reference

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