Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers. This journal is © the Partner Organisations 2018

Supporting Information

Construction of J-type Aggregates as Multi-functional Interlayers for Nonfullerene Polymer Solar Cells

Minming Wu, Jiadong Zhou, Yinqi Luo, Nan Zheng, Cong Wang, Linlin Liu, Zengqi Xie*, Yuguang Ma

Institute of Polymer Optoelectronic Materials and Devices, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, P. R. China. E-mail: <u>msxiez@scut.edu.com</u>

Table of contents:

1. General information	2
2. Synthesis and Characterization	2
3. Thermal analysis properties	6
4. Solubility tests	7
5. FT-IR experiments	8
6. Single-crystal structures	9
7. Optical and electrochemical properties	10
8. Theoretical calculations	12
9. Fabrication and characterization of solar cells	13
10. NMR spectra	16
11. TOF-MS spectra	

1. General information

Toluene was dried and distilled before use, other solvents and reagents were used as received. Stille coupling reactions were carried out under the protection of argon, other reactions were carried out in atmosphere. Bruker AVANCE Digital 600 MHz NMR workstation was employed to collect NMR spectra data at room temperature, using tetramethylsilane (TMS) or residual solvent as internal standard. Matrix-assisted laser desorption ionization time-of flight mass spectra (MALDI-TOF-MS) data were recorded on a Bruker BIFLEX III mass spectrometer. Thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC) data were measured on Netzsch TG 209 and DSC 209 under the protection of nitrogen. UV-Vis absorption spectra were recorded on a Shimadzu UV-3600 spectrometer. Jobin-Yvon Spex Fluorolog-3 was employed to record the fluorescence spectra. Cyclic voltammetry measurements were carried out on a CHI600D electrochemical workstation with a glassy carbon working electrode and a Pt wire counter electrode against a Ag/ AgNO₃ reference electrode in anhydrous DCM solution using 0.1 M Bu₄NPF₆ as the electrolyte. The potential of Ag/AgNO₃ reference electrode were calibrated by the ferrocene/ferrocenium redox couple (Fc/Fc+). Single crystal structure data were collected using Rigaku XtaLAB P2000 instrument. Xeuss 2.0 workstation were employed to record GIWAXS data.

2. Synthesis and Characterization



i: Ammonium acetate or 1-Propylamine, Acetic Acid, Reflux for 20 h ii:Pd(PPh_3)_4, Toluene, Reflux for 24 h

Scheme S1. Synthesis route of four molecules.

Synthesis of compound 2a. In a 250 mL one neck round bottle, 2.27 g (10 mmol) 4-bromophthalic anhydride and excessive 3.85g (50 mmol) ammonium acetate was added, after that, 50 mL acetic acid was added and stirred at room temperature. The reaction mixture was refluxed for 12 h. After cooling to room temperature, it was poured into water. The mixture was filtered and washed with water to obtain the product 2a as white powder (2.1 g, 93% yield.). ¹H NMR (600 MHz, DMSO-*d6*, δ): 11.47 (s, 1H), 8.01 (m, 2H), 7.75 (m, 1H).

Synthesis of compound 2b. The synthesis procedure of 2b is similar to that of compound 2a, with ammonium acetate replaced by 1-Propylamine. The crude product was purified by column chromatography with Dichloromethane: Petroleum Ether =2:1 as eluent to obtain the product 2b as white powder (89% yield). ¹H NMR (600 MHz, CDCl₃, δ): 7.96 (s, 1H), 7.84 (d, 1H), 7.71 (d, 1H), 3.69 (m, 2H), 1.74 (m, 2H), 1.03 (m, 3H).

Synthesis of compound 2a'. The synthesis procedure of 2a' is similar to that of compound 2a, with 4-bromophthalic anhydride replace by 4-bromo-1,8-naphthalic anhydride. The compound 2a' was obtained as white powder (90.5% yield). ¹H NMR (600 MHz, DMSO-*d6*, δ): 11.80 (s, 1H), 8.47 (m, 2H), 8.23 (m, 1H), 8.15 (m, 1H), 7.94 (m, 1H).

Synthesis of compound 2b'. The synthesis procedure of 2b' is similar to that of compound 2b, with ammonium acetate replaced by 1-Propylamine. The compound 2b' was obtained as white powder (88% yield). ¹H NMR (600 MHz, CDCl₃, δ): 8.66 (d, 1H), 8.57 (d, 1H), 8.42 (d, 1H), 8.05 (d, 1H), 7.85 (m, 1H), 4.12 (m, 2H), 1.77 (m, 2H), 1.01 (m, 3H).

Synthesis of IDT-BI-H. In a 50 mL two neck round bottle, 271 mg compound 2a (1.2 mmol), 616 mg IDT-di-Tin (0.5 mmol) and 20mL dry toluene were added, degassed and replaced with argon, after that 35 mg (0.03 mmol) Pd(PPh₃)₄ was added. The reaction mixture was refluxed for 24 h, after cooling to room temperature, 10 mL 1M aqueous KF solution was added, stirred at room temperature for 0.5 h. The mixture was extracted with chloroform, and purified by column chromatography using the mixture of chloroform and petroleum ether (v/v=2:1) as the eluent. The final product was orange solid (257 mg, 43% yield). ¹H NMR (600 MHz, CDCl₃, δ): 8.03 (s, 2H), 7.88 (m, 2H), 7.82 (m, 2H), 7.68 (s, 2H), 7.50 (s, 2H), 7.43 (m, 2H), 7.19 (m, 8H), 7.11 (m, 8H), 2.58 (m, 8H), 1.59 (m, 8H), 1.30 (m, 24H), 0.87 (m, 12H). ¹³C NMR (126 MHz, CDCl₃, δ) : 167.75, 167.54, 157.65, 153.92, 144.50, 143.29, 142.05, 141.44, 141.40, 135.55, 133.87, 130.32, 130.22, 128.69, 127.95, 124.49, 121.86, 119.94, 117.99, 63.34, 35.72, 31.86, 31.49, 29.28, 22.74, 14.24. MALDI-TOF-MS (m/z): calcd for C₈₀H₈₀N₂O₄S₂, 1197.7; found, 1197.5.

Synthesis of IDT-NI-H. The synthesis of IDT-NI-H was similar to IDT-BI-H, with compound 2a replaced by compound 2a'. The final product was red solid (292 mg, 45% yield). ¹H NMR (600 MHz, CDCl₃, δ): 8.73 (m, 2H), 8.63 (m, 2H), 8.57 (m,

2H), 8.54 (s, 2H) 7.86 (m, 2H), 7.76 (m, 2H), 7.55 (m, 2H), 7.33 (m, 2H), 7.25 (m, 8H), 7.11 (m, 8H), 2.58 (m, 8H), 1.60 (m, 8H), 1.29 (m, 24H), 0.86 (m, 12H). ¹³C NMR (126 MHz, CDCl₃, δ): 163.99, 163.66, 157.22, 153.65, 143.87, 142.27, 142.05, 141.60, 140.33, 135.51, 133.13, 131.42, 130.73, 130.42, 130.19, 128.69, 128.43, 127.99, 127.36, 125.51, 122.95, 121.57, 118.17, 63.46, 35.72, 31.86, 31.51, 29.27, 22.74, 14.24. MALDI-TOF-MS (m/z): calcd for C₈₈H₈₄N₂O₄S₂, 1297.8; found, 1297.5.

Synthesis of IDTT-BI-H. The synthesis of IDTT-BI-H was similar to IDTT-BI-H, with IDT-di-Tin compound replaced by IDTT-di-Tin. The final product was orange solid (288 mg, 44% yield). ¹H NMR (600 MHz, CDCl₃, δ): 8.04 (s, 2H), 7.90 (m, 2H), 7.83 (m, 2H), 7.71 (s, 2H), 7.56 (m, 2H), 7.19 (m, 8H), 7.13 (m, 8H), 2.57 (m, 8H), 1.57 (m, 8H), 1.28 (m, 24H), 0.86 (m, 12H). ¹³C NMR (126 MHz, CDCl₃, δ) : 167.59, 167.43, 153.99, 146.60, 145.04, 142.92, 142.59, 142.24, 141.27, 139.95, 136.32, 134.90, 133.94, 130.48, 130.42, 128.78, 128.11, 124.51, 120.08, 118.99, 117.43, 63.13, 35.74, 31.84, 31.40, 29.32, 22.73, 14.23. MALDI-TOF-MS (m/z): calcd for C₈₄H₈₀N₂O₄S₂, 1309.8; found, 1309.4.

Synthesis of IDTT-BI-C3. The synthesis of IDTT-BI-C3 was similar to IDT-BI-H, with compound 2a replaced by compound 2b and IDT-di-Tin replaced by IDTT-di-Tin. The final product was orange solid (335 mg, 45% yield). ¹H NMR (600 MHz, CDCl₃, δ): 8.02 (s, 2H), 7.86 (d, 2H), 7.80 (d, 2H), 7.70 (s, 2H), 7.55 (s, 2H), 7.19 (d, 8H), 7.13 (d, 8H), 3.66 (m, 4H), 2.57 (m, 8H), 1.72 (m, 4H), 1.59 (m, 8H), 1.24~1.37 (m, 28H), 0.96 (m, 6H), 0.86 (m, 12H). ¹³C NMR (126 MHz, CDCl₃, δ) : 168.32, 168.23, 153.95, 146.60, 144.85, 142.88, 142.20, 140.75, 140.00, 136.30, 134.72, 133.48, 130.09, 130.04, 128.76, 128.12, 124.03, 119.75, 118.69, 117.38, 63.13, 39.90, 35.75, 31.84, 31.40, 29.85, 29.32, 22.73, 22.08, 14.23, 11.49. MALDI-TOF-MS (m/z): calcd for C₉₀H₉₂N₂O₄S₄, 1392.6; found, 1393.5.

Synthesis of IDTT-NI-H. The synthesis of IDTT-NI-H was similar to IDT-BI-H, with compound 2a replaced by compound 2a' and IDT-di-Tin compound replaced by IDTT-di-Tin. The final product was red solid (288 mg, 41% yield). ¹H NMR (600 MHz, CDCl₃, δ): 8.77 (m, 2H), 8.65 (m, 2H), 8.57 (m, 2H), 7.85 (m, 2H), 7.80 (m, 2H), 7.61 (m, 2H), 7.58 (m, 2H), 7.24 (m, 8H), 7.15 (m, 8H), 2.58 (m, 8H), 1.58 (m, 8H), 1.28 (m, 24H), 0.86 (m, 12H). ¹³C NMR (126 MHz, CDCl₃, δ): 163.96, 163.67, 153.93, 146.50, 144.37, 142.55, 142.22, 140.47, 140.12, 136.33, 135.35, 133.24, 131.48, 130.62, 130.42, 130.21, 128.78, 128.68, 128.18, 127.44, 122.96, 122.62, 121.64, 117.46, 63.24, 35.75, 31.84, 31.41, 29.31, 22.73, 14.23. MALDI-TOF-MS (m/z): calcd for C₉₂H₈₄N₂O₄S₂, 1409.9; found, 1409.3.

Synthesis of IDTT-NI-C3. The synthesis of IDTT-NI-C3 was similar to IDT-BI-H, with compound 2a replaced by compound 2b' and IDT-di-Tin replaced by IDTT-di-Tin. The final product was orange solid (321 mg, 43% yield). ¹H NMR

(600 MHz, CDCl₃, δ): 8.73 (d, 2H), 8.65 (d, 2H), 8.58 (d, 2H), 7.85 (d, 2H), 7.78 (m, 2H), 7.59 (s, 2H), 7.57 (s, 2H), 7.24 (d, 8H), 7.15 (d, 8H), 4.17 (m, 4H), 2.58 (m, 8H), 1.79 (m, 4H), 1.60 (m, 8H), 1.23~1.39 (m, 28H), 1.03 (m, 6H), 0.86 (m, 12H). ¹³C NMR (126 MHz, CDCl₃, δ): 164.36, 164.10, 153.88, 146.50, 144.21, 142.51, 142.19, 140.75, 140.16, 139.27, 136.32, 135.20, 131.59, 130.77, 129.75, 129.14, 128.76, 128.64, 128.19, 127.44, 123.20, 121.95, 117.42, 63.23, 42.17, 35.75, 31.84, 31.41, 29.32, 22.73, 21.55, 14.23, 11.68. MALDI-TOF-MS (m/z): calcd for C₉₈H₉₆N₂O₄S₄, 1493.6; found, 1493.5.



Figure S1. TGA curves (Left) and DSC curves (Right) of (a) IDTT-BI-H, (b) IDTT-NI-H, (c) IDT-BI-H and (d) IDTT-NI-H



Figure S2. UV-Vis absorption spectra of the as-spun film from THF solution and after rinsing film from chlorobenzene of (a) IDT-BI-H, (b)IDT-NI-H, (c)IDTT-BI-H and (d)IDTT-NI-H.



Figure S3. FT-IR spectra of four molecule aggregates and related reference materials.

IDTT-BI-C3 and IDTT-NI-C3 were used as reference materials. Compared with IDTT-BI-C3 and IDTT-NI-C3 reference materials, four molecules showed new H-bonded C=O vibration (C=O···H-C and C=O···H-N) and H-bonded N-H vibration peaks indicating the formation of intermolecular hydrogen bonds.

6. Single-crystal structures

_

Molecule	IDT-BI-H	IDT-NI-H	IDTT-BI-H	IDTT-NI-H	
Chemical formula	$C_{40}H_{40}NO_2S$	C ₄₄ H ₄₂ NO ₂ S	$C_{84}H_{80}N_2O_4S_4$	$C_{92}H_{81}N_2O_4S_4$	
<i>M</i> _r	598.79	648.84	1309.74	1406.82	
Crystal system, space group	Triclinic, PT	Triclinic, PT	Monoclinic, $P2_1/c$	Triclinic, PT	
Temperature (K)	100	102	100	100	
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.8009 (8), 12.3786 (18), 16.3465 (19)	7.1299 (11), 14.6780 (13), 17.037 (2)	13.5245 (6), 24.687 (3), 20.6534 (9)	14.3142 (10), 16.7266 (12), 18.5616 (11)	
α, β, γ (°)	102.889 (12), 95.068 (9), 108.260 (11)	74.911 (9), 81.895 (13), 89.178 (10)	90, 102.064 (4), 90	105.723 (6), 109.469 (6), 90.336 (6)	
V (Å ³)	1624.3 (4)	1703.9 (4)	6743.4 (9)	4010.6 (5)	
Ζ	2	2	4	2	
Radiation type	Cu Ka	Cu Ka	Cu Kα	Cu Kα	
μ (mm ⁻¹)	1.15	1.14	1.72	1.48	
Crystal size (mm)	$0.2\times0.1\times0.06$	$0.12 \times 0.1 \times 0.04$	$0.2 \times 0.1 \times 0.06$	$0.2\times0.1\times0.06$	
T_{\min}, T_{\max}	0.831, 1.000	0.852, 1.000	0.770, 1.000	0.749, 1.000	
No.ofmeasured,independentandobserved[I > 2σ(I)]reflections	13263, 5646, 2934	16317, 6524, 2472	36523, 12960, 7049	37804, 13982, 5355	
R _{int}	0.09	0.126	0.103	0.091	
$(\sin \theta / \lambda)_{max} (\text{\AA}^{-1})$	0.597	0.624	0.624	0.597	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.105, 0.336, 1.04	0.095, 0.288, 0.95	0.145, 0.419, 1.06	0.108, 0.385, 1.05	
No. of reflections	5646	6524	12960	13982	
No. of parameters	399	435	836	918	
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	
$\Delta ho_{max}, \Delta ho_{min}$ (e Å ⁻³)	1.36, -0.62	0.61, -0.37	1.49, -0.91	1.14, -0.53	

 Table S1. Crystal Data and Structure Refinements parameters.



Figure S4. Cyclic voltammetry curves of (a) IDT-BI-H, (b) IDT-NI-H, (c) IDTT-BI-H and (d) IDTT-NI-H.

Cyclic voltammetry (CV) was employed to calculate the frontier molecular orbital energy levels of IDT-BI-H, IDT-NI-H, IDTT-BI-H and IDTT-NI-H with ferrocene/ferrocenium (Fc/Fc+) as the reference. The CV was performed in DCM solution, and the CV curves were shown in Figure S4. The HOMO levels were determined using the formula:

$$HOMO = -e[E_{ox} - E_{DCM}(Fc/Fc^+) + 4.8](eV) \quad \text{(Equation S1)}$$

where E_{ox} refer to the onsets of oxidation, $E_{DCM}(Fc/Fc^+)$ were measured to be 0.37 V to an Ag/AgNO₃ reference electrode. The CV parameters were listed in Table S2, in which LUMOs were calculated from optical band gaps using following equation:

$$E_{LUMO} = E_{HOMO} + \frac{1240}{\lambda_{onset}} (eV)$$
 (Equation S2).

Table S2. Optical and electrochemical properties of four molecules.

Molecule	$\begin{array}{l} \lambda_{s,\;max} \\ [nm]^{a)} \end{array}$	$\lambda_{s, max}$ [L·mol ⁻¹ ·cm ⁻¹]	$\begin{array}{l} \lambda_{f,\ max} \\ [nm]^{b)} \end{array}$	E_{g}^{opt} [eV] ^{c)}	HOMO [eV] ^{d)}	LUMO [eV] ^{e)}
IDT-BI-H	471	6.5×10 ⁴	507	2.21	-5.54	-3.33
IDT-NI-H	479	5.7×10 ⁴	533	2.02	-5.42	-3.40
IDTT-BI-H	485	8.9×10 ⁴	520	2.14	-5.24	-3.10
IDTT-NI-H	488	7.3×10 ⁴	504	2.07	-5.26	-3.19

^{a)} Absorption maximum in THF solution; ^{b)} Absorption maximum in annealed thin film; c) Optical band gap calculated from the absorption edge of thin film; d) HOMO energy level estimated from the onset of oxidation potential; e) LUMO energy calculated from Equation S2.

Table S3. The photoluminescence quantum yields of four molecules in thin film state.

Molecule	IDT-BI-H	IDT-NI-H	IDTT-BI-H	IDTT-NI-H
PLQY [%]	24	16	13	20

8. Theoretical calculations



Figure S5. Frontier molecular orbitals and geometry of the optimized structure of (a) IDT-BI-H, (b)IDT-NI-H, (c)IDTT-BI-H and (d)IDTT-NI-H as simulated by DFT calculations at the B3LYP/6-31G(d,p) level.

Theoretical calculations were processed to investigate the geometrics and electronic properties of IDT-BI-H, IDT-NI-H, IDTT-BI-H and IDTT-NI-H. The optical ground state geometries were calculated by density functional theory (DFT) at B3LYP/6-31G(d,p) level, as shown in Figure. S4. The HOMOs were delocalized over the electron rich core for all the molecules; while the LUMOs of IDT-NI-H and IDTT-NI-H were mainly localized in the NI-H electron deficient end group, which is different from that of IDT-BI-H and IDTT-BI-H whose LUMOs were delocalized over the electron rich core and electron deficient BI-H end group. The difference in the LUMOs localization were due to difference torsion angles of four molecules, that is IDT-BI-H and IDTT-BI-H possess much smaller torsion angles (21.2° and 23.3°, respectively) than IDT-NI-H and IDTT-NI-H (43.3° and 46.0°).

9. Fabrication and characterization of solar cells

All the solar cell devices were fabricated in conventional structure device configurations: ITO/ZnO/(w/o J-aggregates)/PBDB-T:ITIC/MoO₃/Al. The ITO glass substrates were cleaned by detergent, DCM, isopropyl and ultrapure water under sonication successfully, and dried in oven before use. Sol-gel-derived ZnO interlayer (30 nm) was prepared by spin-coating the solution of zinc acetate in 2-methoxyethanol: 2-aminoethanol onto ITO, followed by thermal treatment at 200°C for 1 h. Then the cathode interlayer films were spin-coated onto ZnO layer from 1 mg/mL related solution in anhydrous THF. Subsequently, PBDB-T:ITIC (1:1 weight ratio) in a 20 mg/mL chlorobenzene solution was spin-coated at 2500 rpm for 60 s to obtain a film thickness of ~100 nm. Then, 10 nm MoO₃ and 100 nm Al were deposited onto the active layer by thermo evaporation through a shadow mask in a vacuum chamber with base pressure of 1×10^{-6} mbar. All film thickness was determined by the surface profiler (Alpha Step-500, Tencor). The active layer area was 0.04 cm². The current density-voltage (*J-V*) tests were carried out on a computer controlled Keithley 2400 source meter under a light intensity of 100 mW cm⁻² illumination from an AM 1.5G solar simulator (Taiwan, Enlitech SS-F5). The EQE tests were performed on a commercial EQE measurement system (Taiwan, Enlitch, QE-R). Electron-only mobilities of the devices were measured by space-charge limited current (SCLC) methods using device configuration: ITO/Al/ZnO/(w/o J-aggregates)/PBDB-T:ITIC /CsF/Al. The mobilities were measured by fitting the dark *J-V* current to the model of a single carrier SCLC, and were calculated using Mott-Gurney equation:

$$J_{sc} = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{L^3}$$
 (Equation S3)

where Jsc is the short-cut current, ε_0 is the permittivity of free space, as 8.85×10^{-12} F/m, ε_r is the permittivity of the material, usually taking as 3. μ is the zero-field electron mobility, V is the effective voltage and L is the thickness of active layer. The electron mobilities were calculated from the slope of $J^{1/2}$ -V curves.



Figure S6. Energy level diagram of the components of the inverted devices.

Kelvin probe was used to measure the work function of cathode interlayers. The work function of ZnO was determined as -4.3 eV, while those of the J-aggregates covered ZnO with the thickness of organic layer ~10 nm were found as low as -3.4 eV as shown in Figure S6. The introduction of high energy level molecules lowered the work function of ZnO layer, thus promoted the formation of ohmic contact with the ITIC acceptor, which is beneficial for higher charge extraction efficiency and lower recombination losses.

Thickness [nm]	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]
None	0.91	16.05	68.54	10.01
~30	0.90	16.54	68.32	10.17
~20	0.89	16.55	68.96	10.31
~10	0.89	16.89	69.07	10.38

Table S4. Photovoltaic properties of IDT-BI-H based devices with various thickness.

Table S5. Photovoltaic properties of IDT-BI-H based devices with various thermal treatment temperatures.

Temperature [°C]	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]
None	0.90	17.09	67.07	10.20
80	0.89	17.27	69.00	10.60
140	0.89	17.00	69.30	10.48



Figure S7. Dark J-V curves of four cathode modifiers and bare ZnO interlayer based devices.



Figure S8. (a) J-V curves and (b) $J^{1/2}$ -V characteristics of electron-only devices based on four cathode modifiers and bare ZnO interlayer.



Figure S10. ¹³C NMR of IDT-BI-H.



Figure S11. ¹H NMR of IDT-NI-H.







Figure S13. ¹H NMR of IDTT-BI-H.



Figure S14. ¹³C NMR of IDTT-BI-H.



Figure S15. ¹H NMR of IDTT-BI-C3.







Figure S17. ¹H NMR of IDTT-NI-H.







Figure S19. ¹H NMR of IDTT-NI-C3.



Figure S20. ¹³C NMR of IDTT-NI-C3.







Figure. S22 TOF-MS spectrum of IDT-NI-H.















