

Supporting information

Improved charge transport in fused-ring bridged hemi-isindigo-based small molecules by incorporating thiophene unit for solution-processed organic field-effect transistors

Guobing Zhang*, Ruikun Chen, Yue Sun, Boseok Kang, Mingxiang Sun, Hongbo Lu, Longzhen Qiu*, Kilwon Cho, Yunsheng Ding

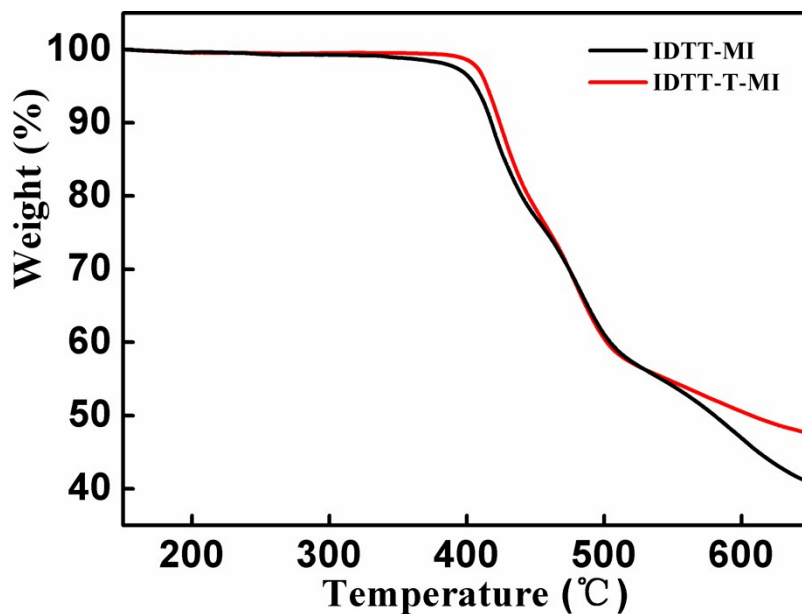


Fig. S1. The TGA curves of small molecules.

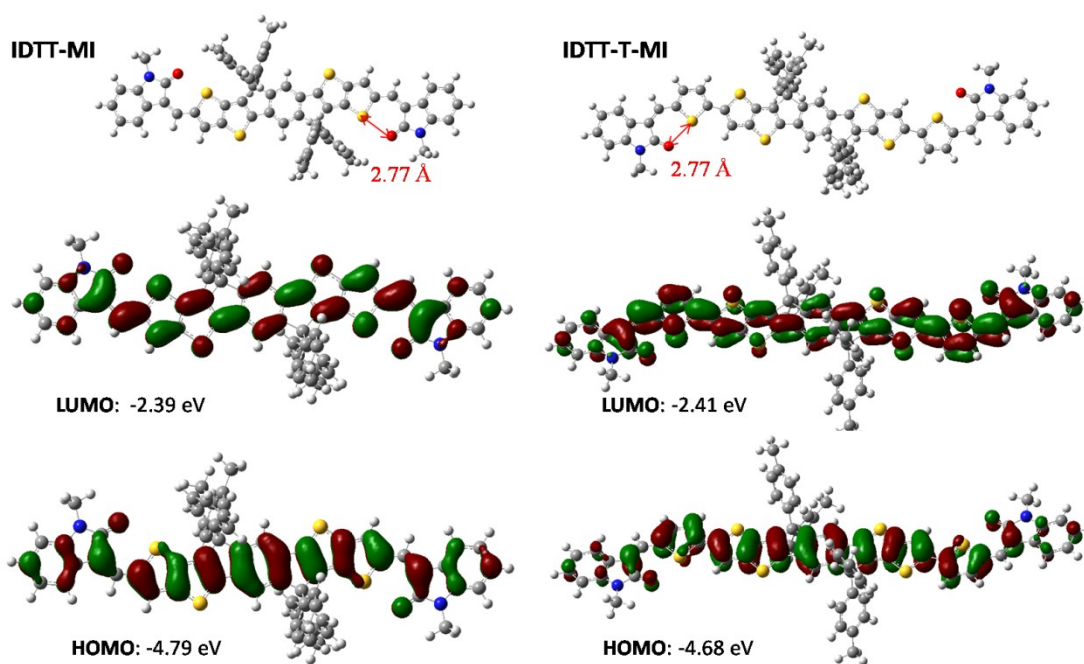


Fig. S2. The calculated LUMO/HOMO energy levels according to DFT calculations at the B3LYP/6-31G(d) level.

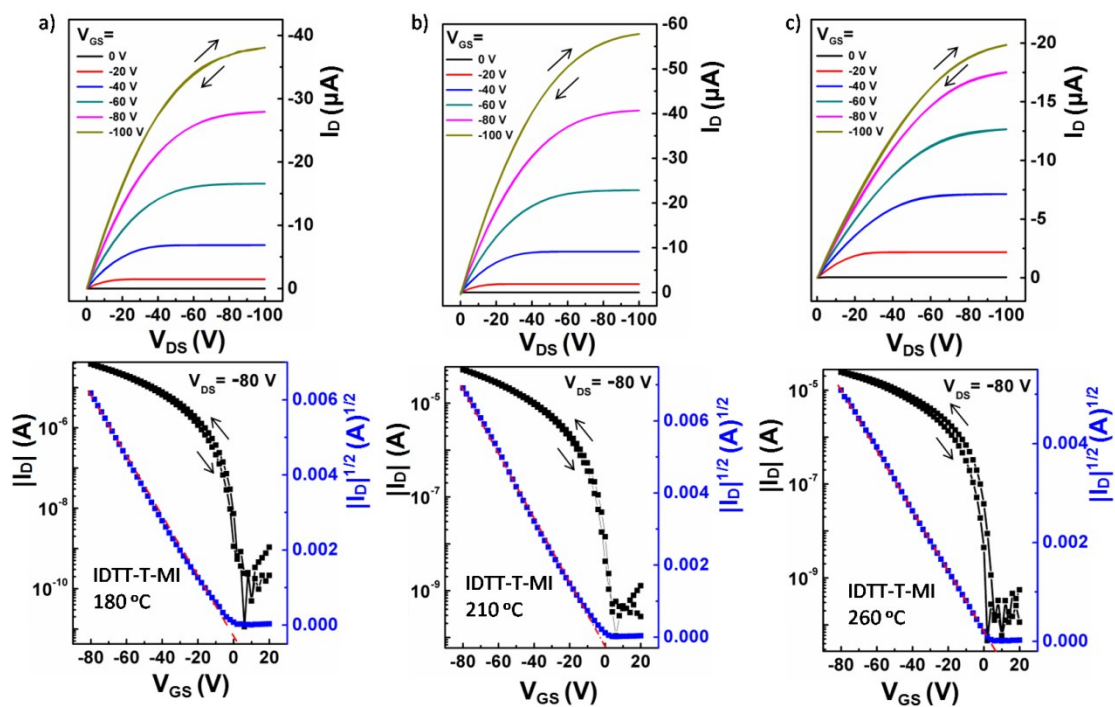


Fig. S3. The transfer and output characteristics of OFETs for the two small molecules. The films were spin-coated from chloroform solution.

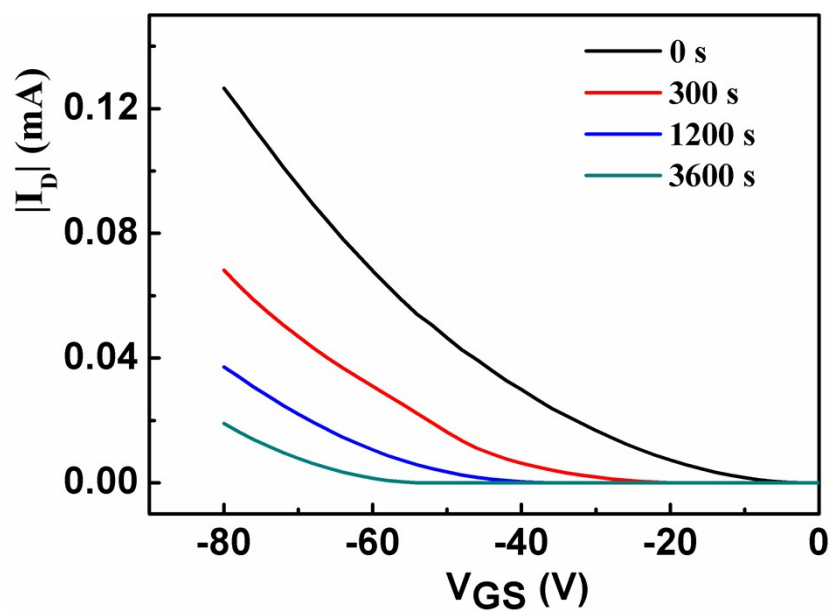


Fig. S4. The stability of continuous bias stress of IDTT-T-MI ($V_{DS} = -80$ V, $V_{GS} = -80$ V).

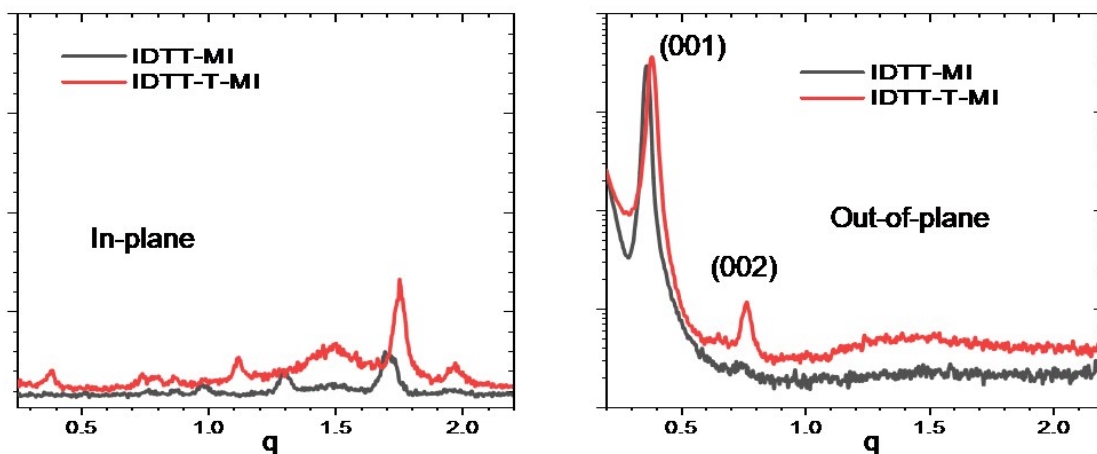


Fig. S5. Out-of-plane and in-plane line cuts of GIXD.

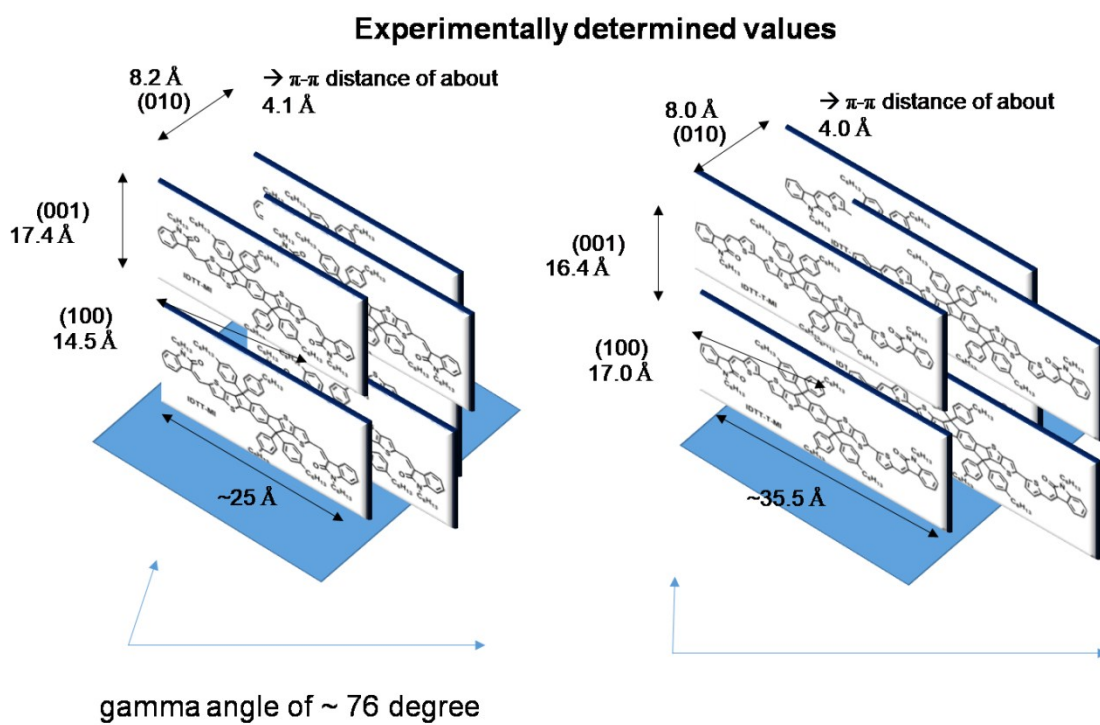


Fig. S6. Proposed molecular packing in the thin film of IDTT-MI and IDTT-T-MI.

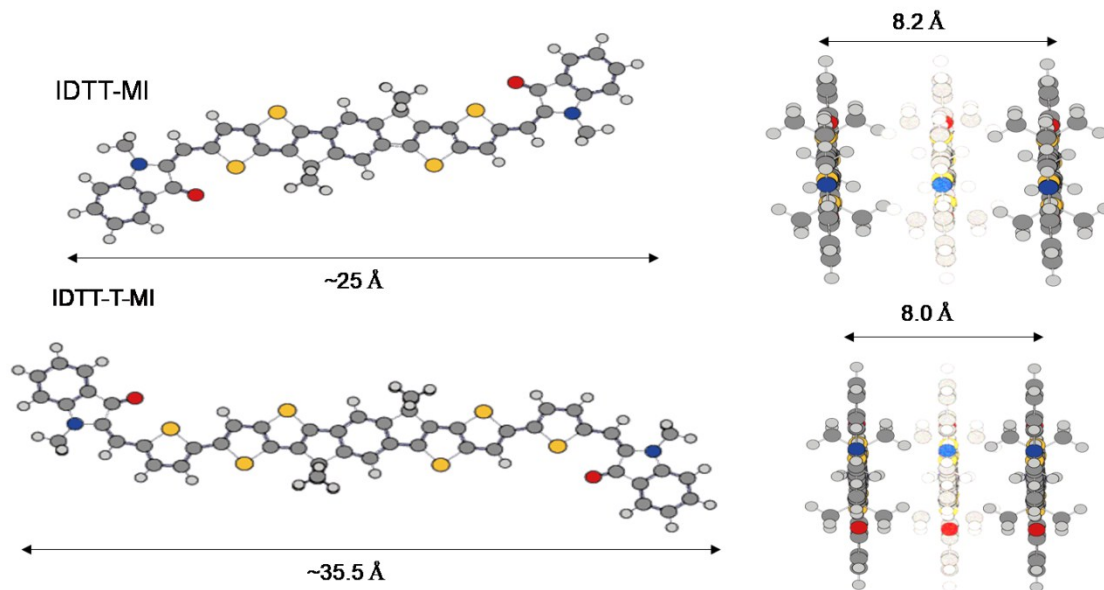


Fig. S7. Proposed structure of **IDTT-IDD-N**, theoretical distances were calculated from the DFT-simulated structure, the experimental values were estimated by using the GIXD data.

Table S1. The field-effect performances of small molecule-based devices.

molecule	Annealing Temperature (°C)	$\mu_{h,max}$ (cm ² V ⁻¹ s ⁻¹)	$\mu_{h,avg}$ (cm ² V ⁻¹ s ⁻¹) ^c	V _{th} (V)	I _{on} /I _{off}
	N/A	/	/	/	/
IDTT-MI ^a (Chloroform)	180	0.036	0.023	-8.8	3.1×10 ⁵
	210	0.012	0.009	-0.36	1.4×10 ⁵
	240	0.016	0.012	-10.2	1.3×10 ⁵
	N/A	/	/	/	/
IDTT-T-MI ^a (Chloroform)	180	0.26	0.24	-9.1	3.9×10 ⁵
	210	0.37	0.34	-10.2	1.8×10 ⁵
	240	0.80	0.73	-4.8	2.4×10 ⁵
	260	0.30	0.23	-9.8	6.1×10 ⁵
	N/A	/	/	/	/
IDTT-T-MI ^b (THF)	180	0.22	0.20	-1.1	9.8×10 ⁴
	210	0.32	0.27	-3.4	1.1×10 ⁵
	240	0.24	0.23	-5.4	8.7×10 ⁵
	260	0.18	0.16	-2.9	3.4×10 ⁵

^a Small molecules were spin-coated from chloroform solution.

^b IDTT-T-MI was spin-coated from tetrahydrofuran (THF) solution.

^c The performance data were calculated based on about 10-12 OFET devices.

Experimental section

All the commercially available reagents were used as received without further purification. Tetrakis(4-hexylphenyl)-indacenodithieno[3,2-*b*]thiophene-bis-(trimethylstannane) and tetrakis(4-hexylphenyl)-indacenodithieno[3,2-*b*]thiophene-bis-dehyde was purchased from Derthon Optoelectronics Materials Science Technology Co. LTD. Other chemicals used in this work were purchased from Shanghai Titan Scientific Co. LTD., China.

Measurements and characterization

Nuclear magnetic resonance (NMR) spectra were recorded using an Agilent VNMR600 machine (400 MHz). Mass spectra were measured using GCT-MS EI and Bruker Daltonics Biflex MALDI-TOF Analyzer in the MALDI mode. Thermogravimetric analysis (TGA) was conducted with a STA449F5 at a heating rate of 10°C/min under nitrogen flow. Absorption spectra were measured using solution in chloroform (1×10^{-6} M) and films cast onto quartz glass using Agilent Cary 5000 model spectrophotometer. Electrochemical cyclic voltammetry (CV) was conducted under nitrogen using a CHI 660D electrochemical analyzer in anhydrous acetonitrile solution containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate with a scan rate of 0.1 V/s. A platinum (Pt) electrode was used as both the working and auxiliary electrode. The Ag/Ag⁺ electrode was used as the reference electrode. The AgNO₃ solution (0.1 M) was used in the characterization. Grazing-incidence-X-ray diffraction (GIXD) measurements were performed using 3C beamlines at the Pohang Accelerator Laboratory (PAL) in Korea. The fabrication of GIXD samples was same as the devices (In the Section of Device Fabrication). The atomic force microscopy (AFM) images were obtained using a SPA300HV instrument.

Fabrication and characterization of OFET device

Bottom-gate/top-contact (BG/TC) OFETs devices were fabricated on a gate of n-doped Si with a 300-nm-thick SiO₂ dielectric layer (capacitance: 10.8 nF cm⁻²). The substrates were washed with a piranha solution (70 vol% H₂SO₄ and 30 vol% H₂O) and then treated with ultraviolet ozone. A modified layer of octadecyltrimethoxysilane (OTS) was spin coated onto the treated Si/SiO₂ substrate.

The semiconductor material was dissolved in chloroform, and then the solution (~6 mg/mL) was spin-coated on OTS-treated Si/SiO₂ substrate at a rotation speed of 5000 rpm in a glove box. The small molecule films were annealed at different temperatures (180–260 °C) in a glove box. The Au source-drain electrodes were prepared by thermal evaporation (~30 nm). The OFETs devices had a channel length (*L*) of 130 μm and a channel width (*W*) of 760 μm. The devices were characterized under air condition using a Keithley 4200 semiconductor parametric analyzer. The saturation-regime mobility (μ_{sat}) was obtained using the following equation: $I_d = (W/2L)C_i\mu_{sat}(V_g - V_{th})^2$. Where I_d is the drain current, C_i is the capacitance of the gate dielectric, V_g is the gate-source voltage, and V_{th} is the threshold voltage.

Synthesis

1-hexyl-indoline-2,3-dione (1). Anhydrous potassium carbonate (3.67 g, 26.5 mmol), 1-hydro-indoline-2,3-dione (3 g, 20.4 mmol), and 1-iodohexane (5.62 g, 26.5 mmol) was dissolved in anhydrous *N,N*-dimethylformamide (DMF, 40 mL) under nitrogen atmosphere. The reaction mixture was heated to 60 °C and stirred for overnight. Then quenched with water. The organic layer was extracted with dichloromethane and dried with anhydrous sodium sulfate. The residue was purified by flash chromatography on silica gel with hexane/ethyl acetate (10:1) as eluent to give the titled compound **1** as red solid (4.1 g, 87%). ¹H NMR (400 MHz, CDCl₃) δ = 7.27 (d, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 6.6 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 1.71–1.61 (m, 2H), 1.39–1.28 (m, 6H), 0.88 (dd, *J* = 9.3, 4.7 Hz, 3H).

1-hexyl-indoline-2-one (2). Compound **1** (4 g, 17.3 mmol) was dissolved in a mixed solution of ethanol (5 mL) and hydrazine hydrate (30 mL) under a nitrogen atmosphere. The reaction mixture was heated to 110 °C and stirred under reflux overnight. After cooling to room temperature, the solution was poured into water and extracted with dichloromethane, dried over anhydrous magnesium sulfate. The residue was purified by flash chromatography on silica gel with hexane/ethyl acetate (5:1) as eluent to give the titled compound **2** as yellow liquid (2.8 g, 75%). ¹H NMR (400 MHz, CDCl₃) δ = 7.28–7.22 (m, 2H), 7.02 (t, *J* = 7.3 Hz, 1H), 6.83 (d, *J* = 7.8 Hz,

1H), 3.72–3.67 (m, 2H), 3.51 (s, 2H), 1.66 (dd, $J = 15.1, 7.6$ Hz, 2H), 1.38–1.28 (m, 6H), 0.88 (dd, $J = 9.3, 4.7$ Hz, 3H).

(Z)-3-((5-bromothiophen-2-yl)methylene)-1-hexylindolin-2-one(3). Compound **2** (1 g, 4.6 mmol) and 5-bromothiophene-2-carbaldehyde (1.32 g, 6.9 mmol) were dissolved in anhydrous chloroform under a nitrogen atmosphere. Then piperidine (10 mL) was added dropwise to the reaction solution. The reaction mixture was heated to 80 °C and stirred overnight. After cooling to room temperature, the solution was poured into water and extracted with dichloromethane, dried over anhydrous magnesium sulfate. The residue was recrystallized from n-hexane to give the titled compound **3** as a yellow solid (1.2 g, 67%). ¹H NMR (400 MHz, CDCl₃) δ 7.58 (d, $J = 0.5$ Hz, 1H), 7.51 (dd, $J = 7.6, 0.5$ Hz, 1H), 7.37 (dd, $J = 4.0, 0.5$ Hz, 1H), 7.30–7.26 (m, 1H), 7.12 (d, $J = 4.0$ Hz, 1H), 7.05 (td, $J = 7.6, 0.9$ Hz, 1H), 6.86 (d, $J = 7.8$ Hz, 1H), 3.82–3.76 (m, 2H), 1.71 (dt, $J = 15.2, 7.4$ Hz, 2H), 1.34 (ddd, $J = 11.1, 9.7, 6.3$ Hz, 6H), 0.88 (t, $J = 7.0$ Hz, 3H).

IDTT-MI. The dried two-necked flask was charged with Compound **2** (0.3 g, 1.4 mmol), tetrakis(4-hexylphenyl)-indacenodithieno[3,2-*b*]thiophene-bis-dehyde (0.15 g, 0.14 mmol), and anhydrous chloroform (20mL). The solution was degassed by nitrogen flow for 30 min. Then piperidine (5 drops) was added to the reaction solution. The reaction mixture was heated to 80 °C and stirred 24h. After cooling to room temperature, the mixture was poured into a solution and extracted with dichloromethane. The combined organic layer was dried over anhydrous magnesium sulfate. After removing the solvent, the residue was purified by silica gel column chromatography with petroleum ether/chloroform (2:1) as eluent to afford a red solid (105 mg, 51%). ¹H NMR (400 MHz, CDCl₃) δ 8.42 (s, 2H), 7.59 (s, 2H), 7.55 (s, 2H), 7.49 (d, $J = 7.5$ Hz, 2H), 7.26 (s, 2H), 7.24 (d, $J = 8.3$ Hz, 8H), 7.12 (d, $J = 8.3$ Hz, 8H), 7.04 (d, $J = 7.7$ Hz, 2H), 6.86 (d, $J = 7.7$ Hz, 2H), 3.82 (t, $J = 7.5$ Hz, 4H), 2.63–2.52 (m, 8H), 1.66 (dd, $J = 51.1, 7.3$ Hz, 12H), 1.36–1.26 (m, 36H), 0.89 (m, 18H). MS(MALDI-TOF): m/z 1473.64 ([M+H]⁺).

IDTT-T-MI. Compound **3** (0.064 g, 0.16 mmol), tetrakis(4-hexylphenyl)-

indacenodithieno[3,2-*b*]thiophene-bis-(trimethylstannane) (0.1 g, 0.07 mmol), and chlorobenzene (8 mL) were charged in a dry Schlenk tube, Pd₂(dba)₃ (3 mg) and P(*o*-tol)₃ (4 mg) were quickly added after 30 minutes of nitrogen purge. The tube was capped and heated to 130 °C for 12 h. After cooling to room temperature, the mixture was poured into a solution and extracted with dichloromethane. The combined organic layer was dried over anhydrous sodium sulfate. After removing the solvent, the residue was purified by silica gel column chromatography using a mixture of petroleum ether/ chloroform (2:1) to afford a red solid (60 mg, 49%). ¹H NMR (400 MHz, C₂D₂Cl₄, 90 °C) δ= 7.77 (d, J = 4.0 Hz, 2H), 7.69–7.61 (m, 6H), 7.57 (d, J = 7.5 Hz, 2H), 7.34 (d, J = 7.7 Hz, 2H), 7.32–7.27 (m, 10H), 7.20 (d, J = 8.1 Hz, 8H), 7.11 (t, J = 7.5 Hz, 2H), 6.92 (d, J = 7.8 Hz, 2H), 3.87 (t, J = 7.4 Hz, 4H), 2.71–2.64 (m, 8H), 1.86–1.69 (m, 12H), 1.49–1.38 (m, 36H), 0.96 (t, J = 6.8 Hz, 18H). MS(MALDI-TOF): m/z 1637.66 ([M+H]⁺).

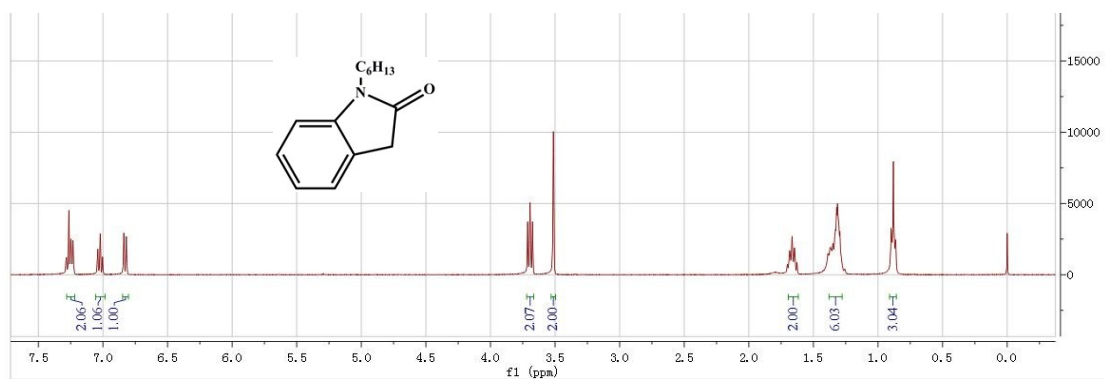


Fig. S8. 1H NMR spectrum of compound **2** in $CDCl_3$.

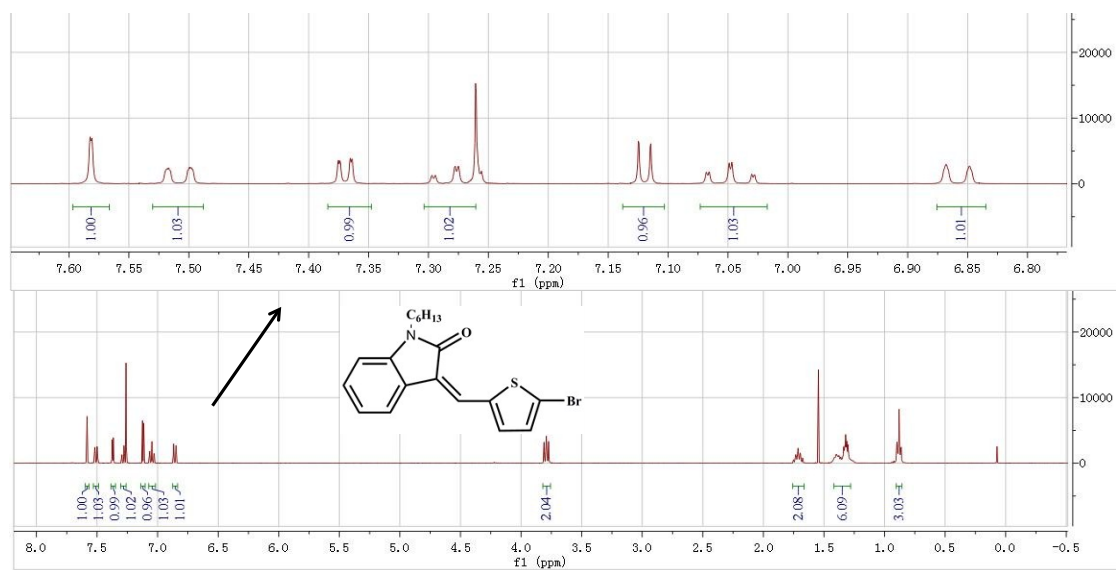


Fig. S9. 1H NMR spectrum of compound **3** in $CDCl_3$.

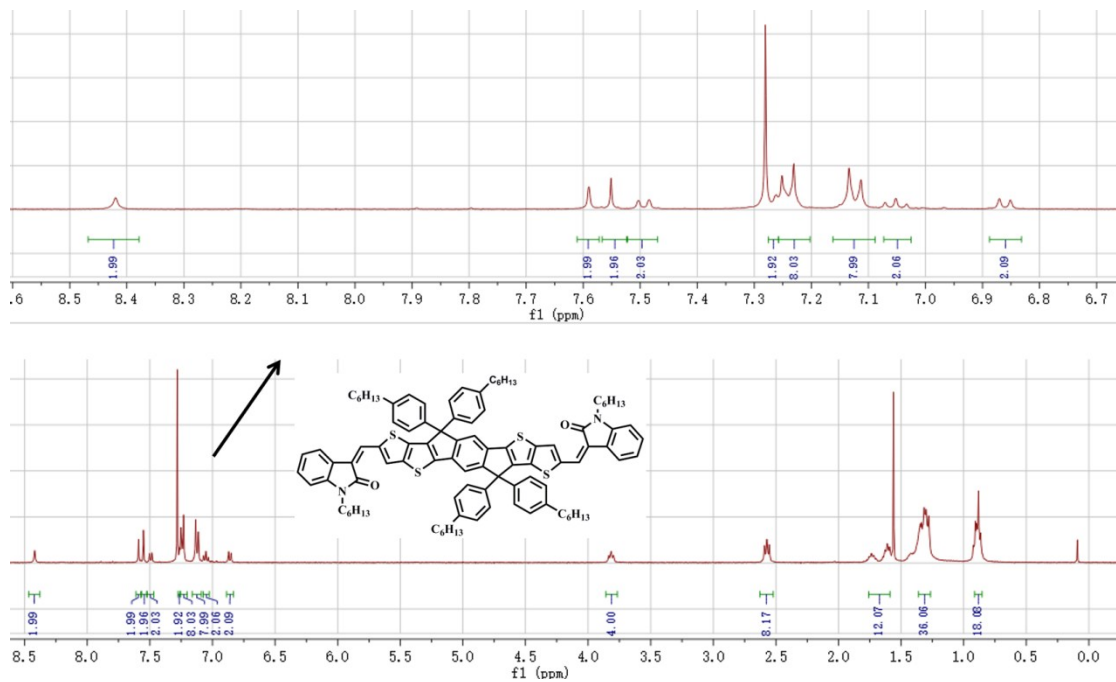


Fig. S10. ^1H NMR spectrum of IDTT-MI in CDCl_3 .

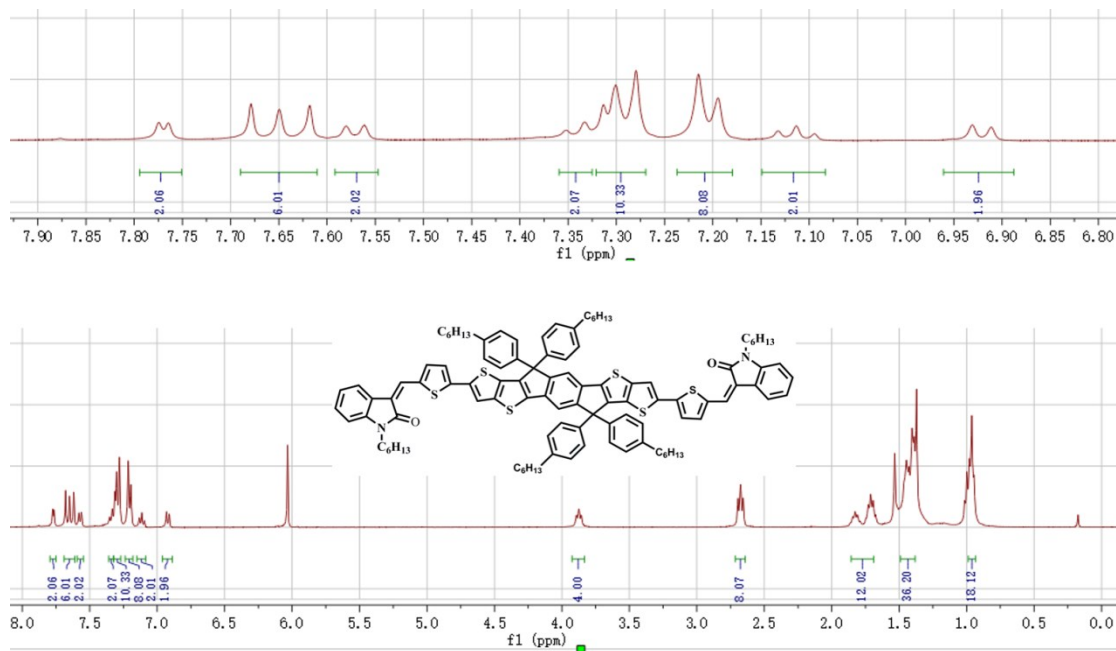


Fig. S11. ^1H NMR spectrum of IDTT-T-MI in $\text{C}_2\text{D}_2\text{Cl}_4$ (90°C).

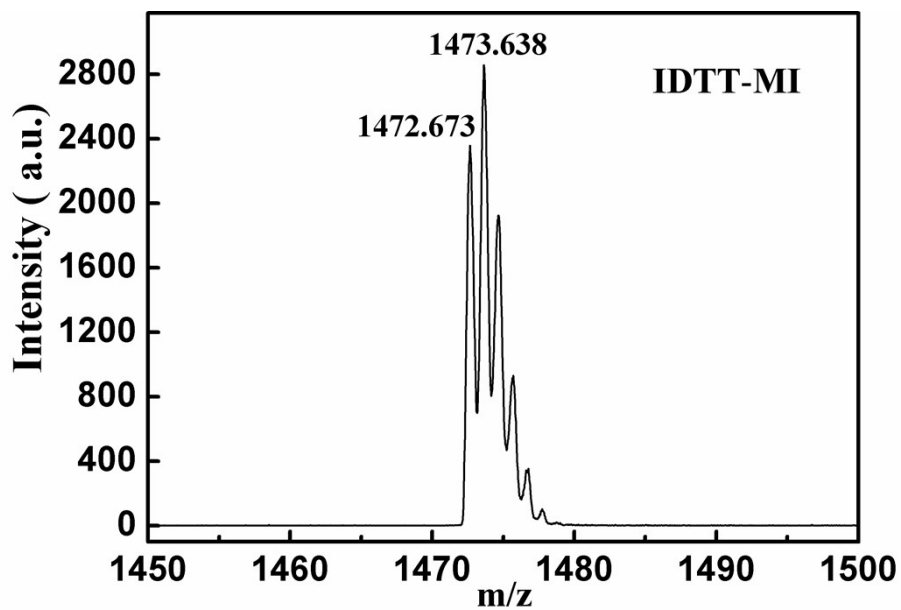


Fig. S12. MALDI-TOF-MS of IDTT-MI.

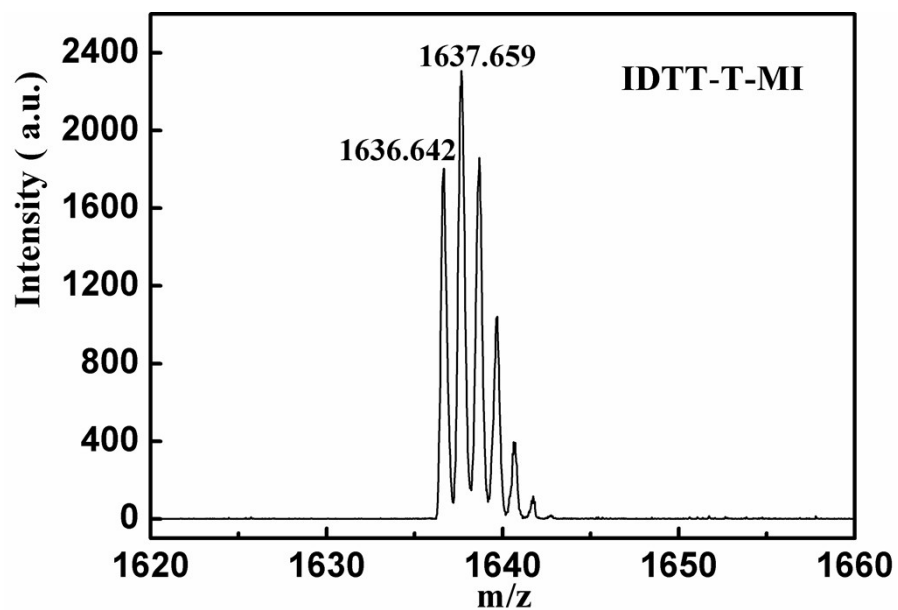


Fig. S13. MALDI-TOF-MS of IDTT-T-MI.