

Supporting Information

S···N conformational lock acceptor based on indacenodithiophene (IDT)
structure and high electronegative terminal end group

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Experimental Section

S1.1. Materials and Methods

5,5'-(((4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-2,7-diyl)bis(thiazole-2,5-diyl))bis(methaneylylidene))bis(1,3-diethyl-2-thioxodihydropyrimidine-4,6(1H,5H)-dione) (IDTz-BARS), and 5,5'-(((4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-2,7-diyl)bis(thiazole-2,5-diyl))bis(methaneylylidene))bis(1,3-dimethylpyrimidine-

2,4,6(1H,3H,5H)-trione) (IDTz-BARO) were synthesized in this work. (4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-2,7-diyl)bis(tributylstannane) ($\text{SnBu}_3\text{-IDT-SnBu}_3$) and 2-bromothiazole-5-carbaldehyde were purchased from SunaTech Inc.. All other reagents were purchased from www.tansoole.com and were used as received without further purification. ^1H nuclear magnetic resonance (NMR) spectra were measured using a 300 MHz spectrometer (Varian Mercury Plus). Elemental analysis was characterized by (ELEMNTAR vario El cube) Thermal analyses (TGA) was performed using METTLER TOLEDO TGA2 (TA Instruments) and thermal analyses (DSC) were performed using NETZSCH DSC214Polyma (TA Instruments) under an inert N_2 atmosphere, with heating/cooling rates of $10\text{ }^\circ\text{C min}^{-1}$. The ultraviolet–visible spectra were recorded using a UV-Visible spectrophotometer (UV-1780). Cyclic voltammetry experiments were performed with an electrochemical analyzer (CH Instruments) in acetonitrile solutions containing 0.1 M tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) as the supporting electrolyte, with Ag/AgNO_3 as the reference electrode, a platinum wire as the counter electrode, and a platinum working electrode. All the calculations are carried out with G09 ver. D software package. Geometry optimizations were carried out with DFT methods B3LYP for geometry. Basis set 6-31G(d) was adopted for the C, H, O, N, S and F atoms. Atomic force microscopy (AFM) measurements are performed by using a Dimension Icon Scanning Probe Microscope (Asylum Research, MFP-3D-Stand Alone) in tapping mode. The performance of the organic photovoltaic cell (OPV) was confirmed using a solar simulator (ss-x50, Enlitech). The current density-voltage (J–V) graphs of the devices were measured under AM 1.5G light conditions. Besides, the incident photon to converted current efficiency (IPCE) spectrum was measured using Newport IPCE system.

S1.2. Device fabrication

Bulk heterojunction OPV devices were fabricated with an inverted structure, consisting of indium tin oxide (ITO)/ZnO/active layer/ MoO_3 /Ag. Typically, the ZnO layer (~30 nm) acting as an electron transporting layer was coated onto ITO (pre-

cleaned with UV-ozone plasma), as previously reported. The active layer, which was prepared as follows: in chlorobenzene (total concentration = 23 mg·mL⁻¹), was fabricated by spin-coating at 3000 r/min for 30 s in a glove box filled with nitrogen. After drying the active layer, MoO₃ (~10 nm) and Ag (~100 nm) layers were formed by thermal evaporation under a base pressure of 2 × 10⁻⁴ Pa. The effective area of the device was 0.04 cm².

S1.3. Synthesis of Compound

S1.3.1. Synthesis of 5,5'-(((4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-2,7-diyl)bis(thiazole-2,5-diyl))bis(methaneylylidene))bis(1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione) (IDTz-BARO)

A mixture of compounds 1 (90.37 mg, 0.08 mmol), 1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (74.95 mg, 0.48 mmol), pyridine (0.5 ml) was stirred overnight in CHCl₃ at 65 °C. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. The residue was purified by silica gel column chromatography and eluent (dichloromethane / petroleum ether = 1 / 1, v / v) to obtain a dark red solid product (50.56 mg, 45.0%). ¹HNMR results are as follows: (CDCl₃ 300MHz): ¹HNMR results are as follows: (CDCl₃ 300MHz): δ8.62 (s, 2H), 8.36 (s, 2H), 7.15 (d, 8H), 7.06 (d, 8H), 3.14 (d, 12H), 2.56 (t, 8H), 1.57 (d, 8H), 1.28 (m, 64H), 0.86 (m, 24H). Element analysis for C₈₄H₈₈N₆O₆S₄, Calc.: C, 71.76; H, 6.31; N, 5.98. Found: C, 72.08; H, 5.96; N, 5.79%.

S1.3.2. Synthesis of 5,5'-(((4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-2,7-diyl)bis(thiazole-2,5-diyl))bis(methaneylylidene))bis(1,3-diethyl-2-thioxodihydropyrimidine-4,6(1H,5H)-dione) (IDTz-BARS)

A mixture of compounds 1 (90.37 g, 0.08 mmol), 1,3-diethyl-2-thioxodihydropyrimidine-4,6(1H,5H)-dione (96.29 g, 0.48 mmol), pyridine (80.5 ml) was stirred overnight in CHCl₃ at 65 °C. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. The residue was purified by

silica gel column chromatography and eluent (dichloromethane / petroleum ether = 1 / 1, v / v) to obtain a dark blue solid product (47.76 g, 40.0%). ¹HNMR results are as follows: (CDCl₃ 300MHz): δ8.61 (s, 2H), 8.38 (s, 2H), 7.72 (s, 2H), 7.54 (s, 2H), 7.16 (d, 8H), 7.10 (d, 8H), 4.56 (dd, 8H), 2.57 (t, 8H), 1.57 (d, 16H), 1.26 (m, 64H), 0.86 (m, 24H). Element analysis for C₈₈H₉₆N₆O₄S₆, Calc.: C, 70.74; H, 6.48; N, 5.62. Found: C, 70.51; H, 6.56; N, 5.51%.

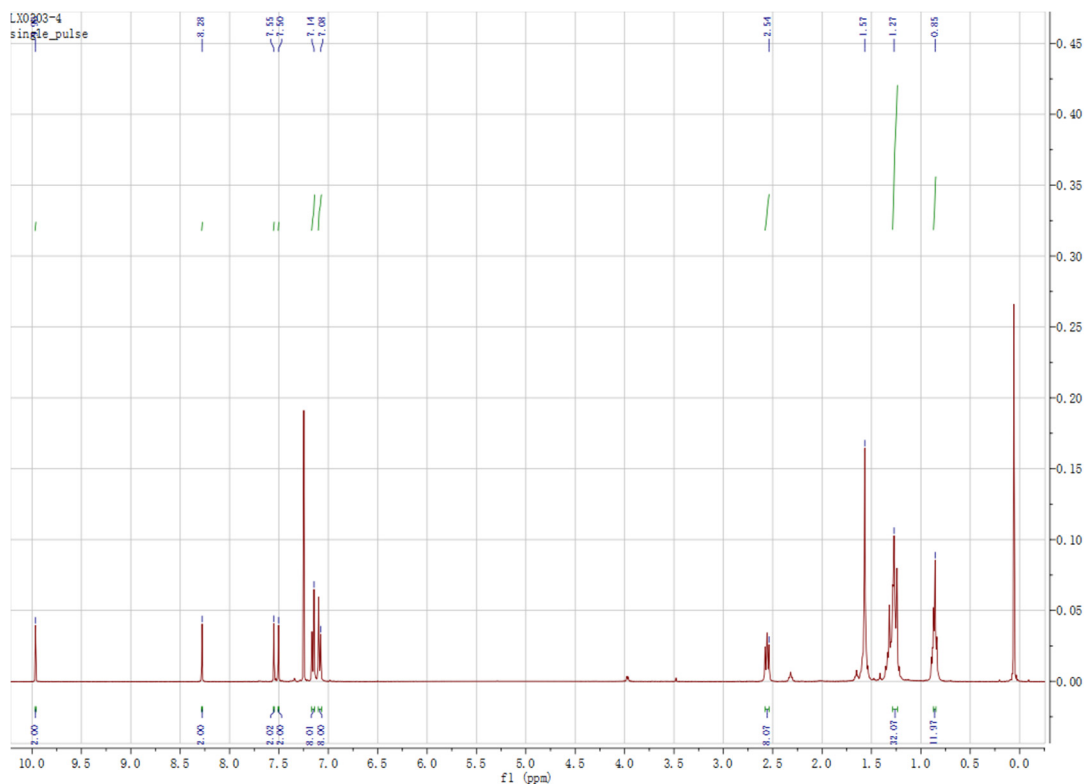


Figure S1. ^1H of compound 1. (r.t., in CDCl_3).

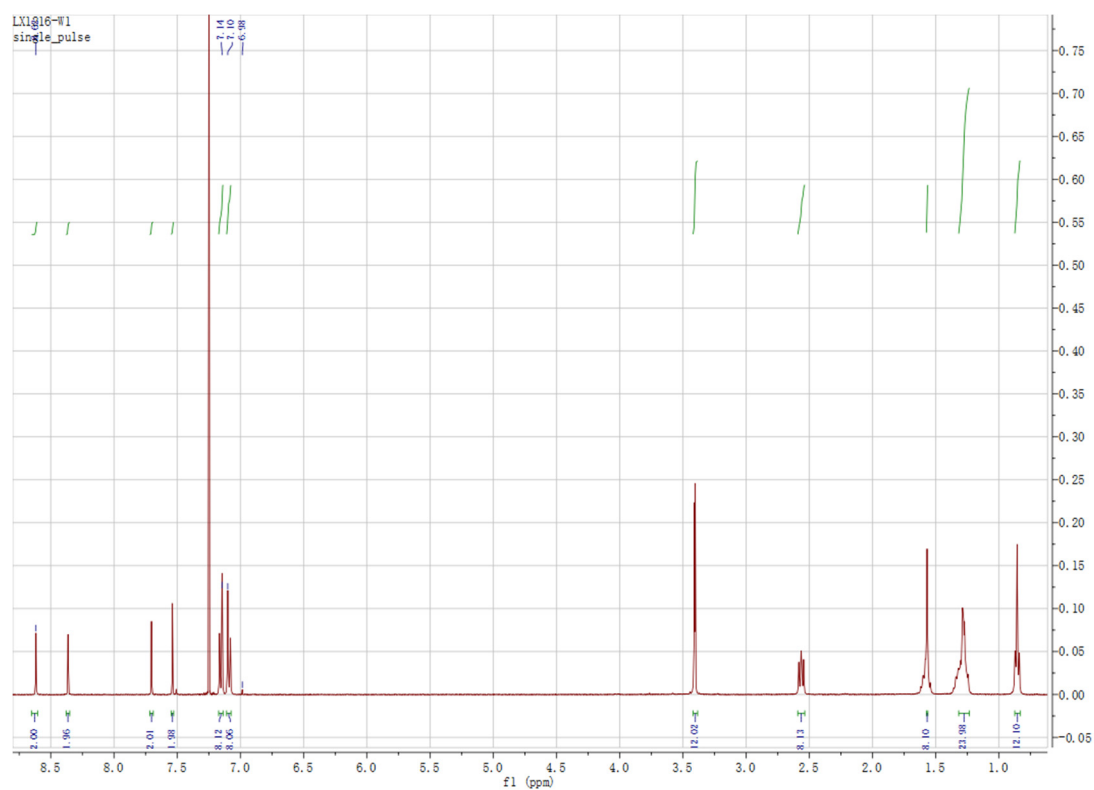


Figure S2. ^1H of compound IDTz-BARO. (r.t., in CDCl_3).

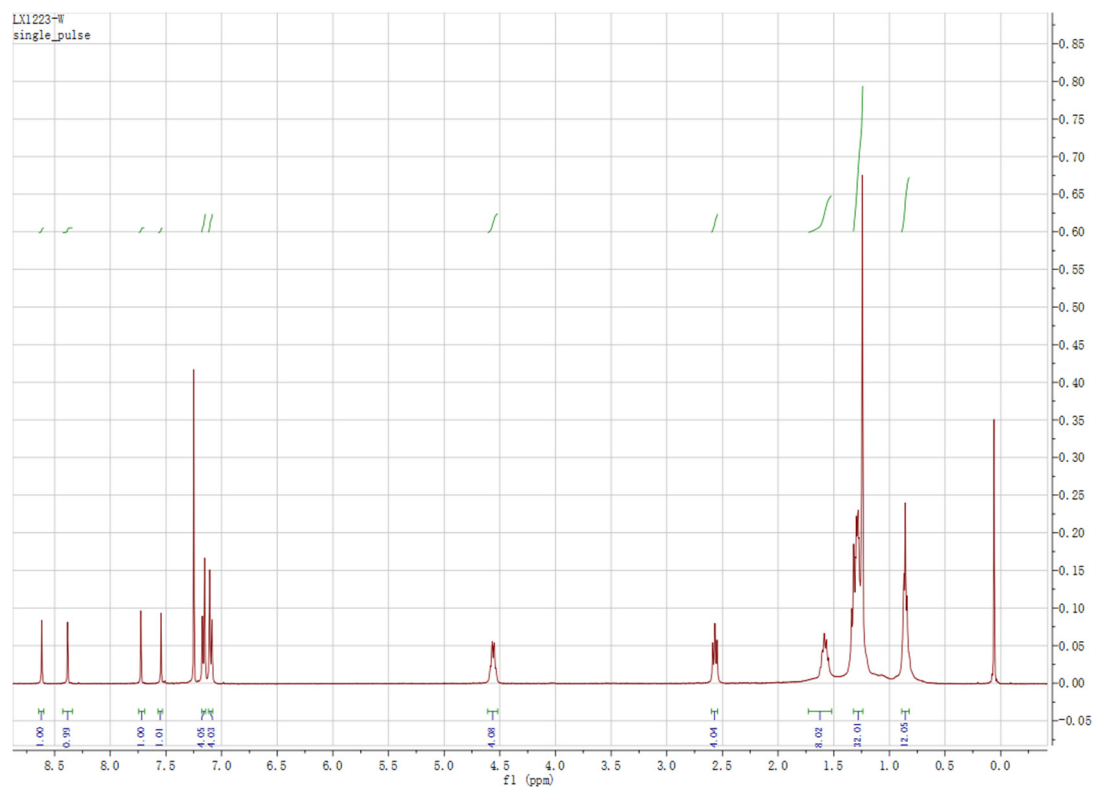


Figure S3. ^1H of compound IDTz-BARS. (r.t., in CDCl_3).