

Isomeric Effects of Solution Processed Ladder-Type Non-Fullerene Electron Acceptors

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Materials

All starting materials and reagents were purchased from commercial sources and used without further purification unless otherwise specified. Solvents were dehydrated. Syringes, which were used to transfer reagents or solvents, were purged with nitrogen prior to use. 2,6-Bis(trimethyltin)- benzo[1,2-b:4,5-b'] dithiophene was used as received. Ethyl 2-bromothiophene-3-carboxylate was synthesized according to previously reported methods¹. The donor polymer J71 was used as received².

Characterization

UV-Vis spectra were measured using a Perkin-Elmer Lambda-9 spectrophotometer. The ¹H and ¹³C NMR spectra were collected on a Bruker AV400 and 600 spectrometer in deuterated chloroform solution with trimethylsilane (TMS) as reference. Matrix-Assisted Laser Desorption/ Ionization Time of Flight Mass Spectrometry MS-MALDI (TOF) were performed using a Bruker Autoflex II / Compass 1.0. Thermogravimetric analysis (TGA) was performed on a TA SDT 2960 from Mettler Toledo at a heating rate of 10 °C/min from room temperature to 800 °C in nitrogen. Cyclic voltammetry of the acceptor film was conducted in acetonitrile with 0.1 M of tetrabutylammonium hexafluorophosphate using a scan rate of 100 mV s⁻¹. ITO, Ag/AgCl and Pt mesh were used as a working electrode, reference electrode and counter electrode, respectively. Atomic force microscopy (AFM) images of the interfacial films were obtained using a Veeco Multimode V instrument. TEM images was recorded on a Tecnai G2 F20 S-TWIN instrument at 200 kV accelerating voltage.

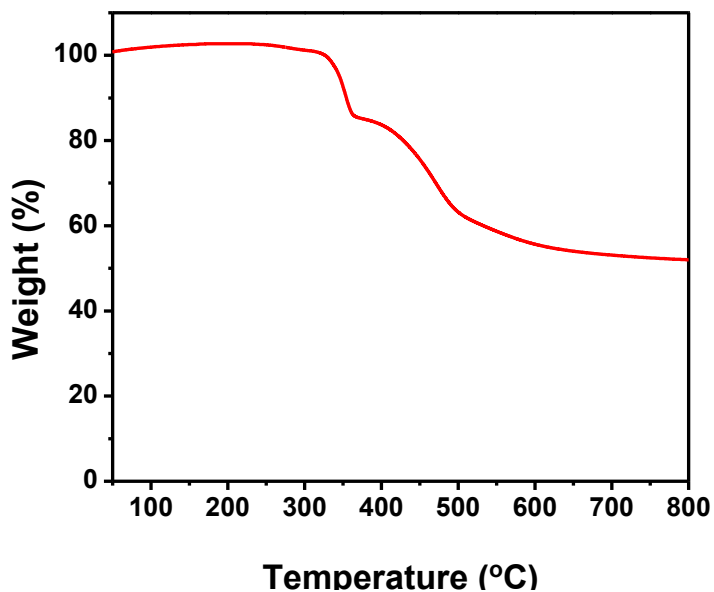


Figure S1. Thermogravimetric analysis (TGA) curve of BDT-IC with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under an inert atmosphere.

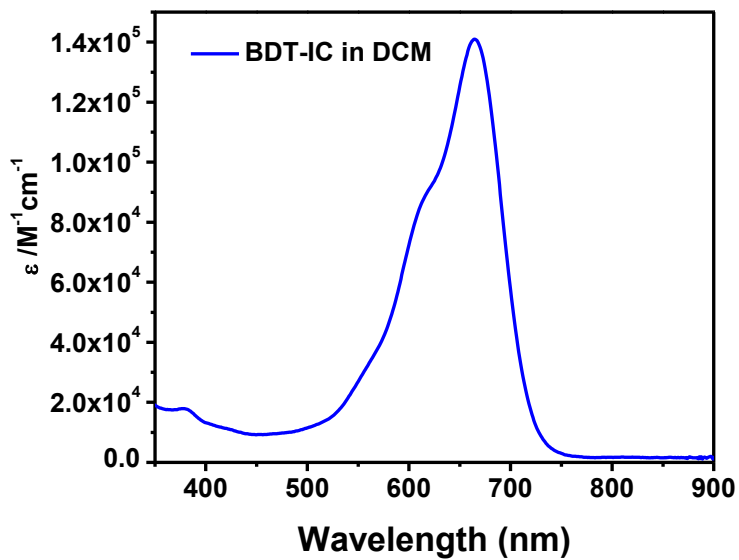


Figure S2. UV-vis absorption spectrum of BDT-IC in DCM.

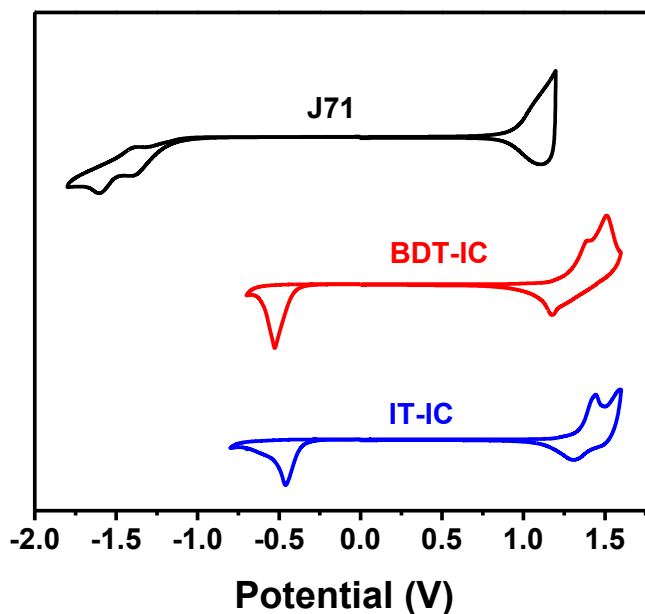


Figure S3. The cyclic voltammetry curves of J71, BDT-IC and IT-IC in CH₃CN /0.1 M [nBu₄N]⁺[PF₆]⁻ at 100 mV s⁻¹, the horizontal scale refers to the Ag/AgCl electrode. (the positive curves from 0 to 1.6 V is the process of oxidation and the negative curves from 0 to -2.0 V is the process of reduction)

Organic field-effect transistor (OFET) characterization:

All substrates were sequentially cleaned with acetone, detergent, deionized water (three times) and isopropyl alcohol using ultra-sonication and then dried under vacuum at 80 °C. The molecules were dissolved in chlorobenzene (CB) at 80 °C overnight and then the solution (5 mg/mL in CB) was purified by a filter with 0.45- μ m pores.

A top-gate/bottom-contact (TG/BC) OFET was used to evaluate the charge transport behavior. The patterned Au/SiO₂/Si substrates were immersed in a phenylethanethiol solution (5 mM in anhydrous toluene) for 4 h to construct the self-assembled monolayers, followed by washing with anhydrous toluene and isopropyl alcohol. The semiconducting layer was deposited by spin-coating onto the patterned

Au/SiO₂/Si substrate with self-assembled monolayer (SAM), followed by thermal annealing at 180°C for 5 min. A poly(perfluoroethylene-co-butenyl vinyl ether) (CYTOP)³ solution was spin-coated as the dielectric layer. After thermal annealing at 100 °C for 1 h, an aluminum layer (~50 nm) was thermally evaporated as the gate electrode.

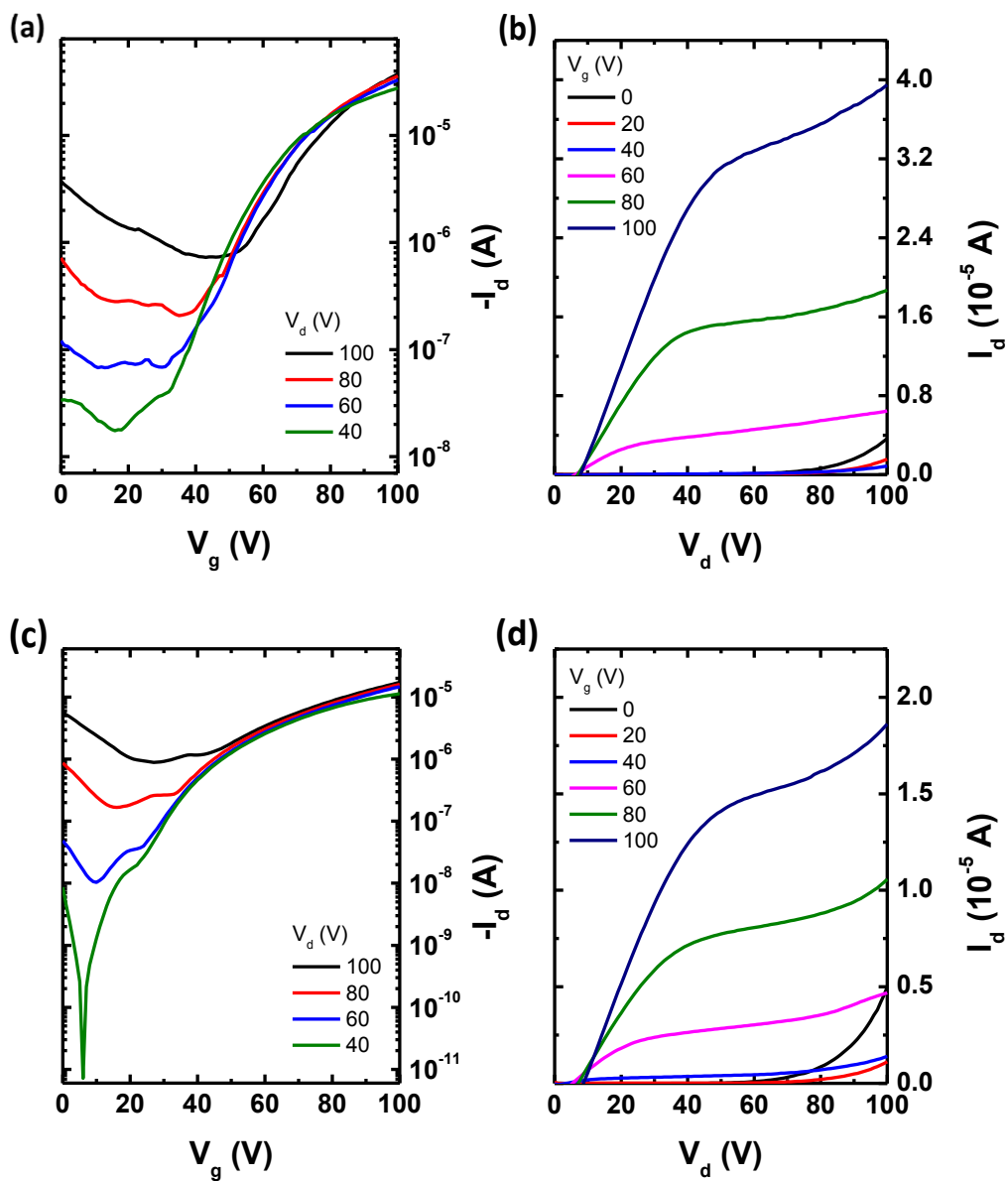


Figure S4. Transfer and output characteristics of BDT-IC (a and b) and IT-IC (c and d).

Device Fabrication and Characterization

The organic photovoltaic cells were fabricated in the configuration of ITO/PEDOT:PSS/J71:BDT-IC/PDINO/Al. ITO-coated glass substrates were sequentially cleaned with deionized water, acetone, ethanol, and isopropanol under sonication for 10 min each, and then treated by oxygen plasma for 15 min to generate the hydrophilic surface. The filtered PEDOT:PSS solution (Baytron P VP AI 4083 from H. C. Starck) was spin-coated onto the cleaned ITO-coated glass substrates at 4000 rpm, followed by baking at 150°C for 15 min in air. Subsequently, the substrates were transferred into a N₂-filled glove box for spin-coating of the photoactive layer. The active layer (ca. 130 nm) was then spin-coated from the blend solutions (16 mg mL⁻¹), which were prepared at 25 °C in chloroform. The mixed solutions were spin-coated on the top of the PEDOT:PSS layer at 1500 rpm for 90 s. Methanol solution of perylenediimide functionalized with amino *N*-oxide (PDINO) with a concentration of 1.5 mg/mL was then spin-coated on the photoactive layer at 3000 rpm for 30 s to obtain a thickness of ca. 10 nm. Finally, the Al cathode was deposited onto the PDINO buffer layer by thermal evaporation at a pressure of 5.0×10⁻⁵ Pa. The deposition rate and film thickness were monitored with a quartz crystal sensor. Shadow masks were used to define the active area (4.7 mm²) of the devices.

The current density-voltage (*J*-*V*) characteristics were measured using a Keithley 2450 Source-Measure Unit. An Oriel Sol3A Class AAA Solar Simulator (model, Newport 94023A) with a 450 W xenon lamp and an air mass (AM) 1.5 filter was used as the light source. The light intensity was calibrated to 100 mW

cm^{-2} by a Newport Oriel 91150V reference cell. The *EQE* was measured with a solar cell spectral response measurement system (Enli Technology Co., Ltd., QE-R3011). The light intensity was calibrated using a single-crystal Si photovoltaic cell as a standard.

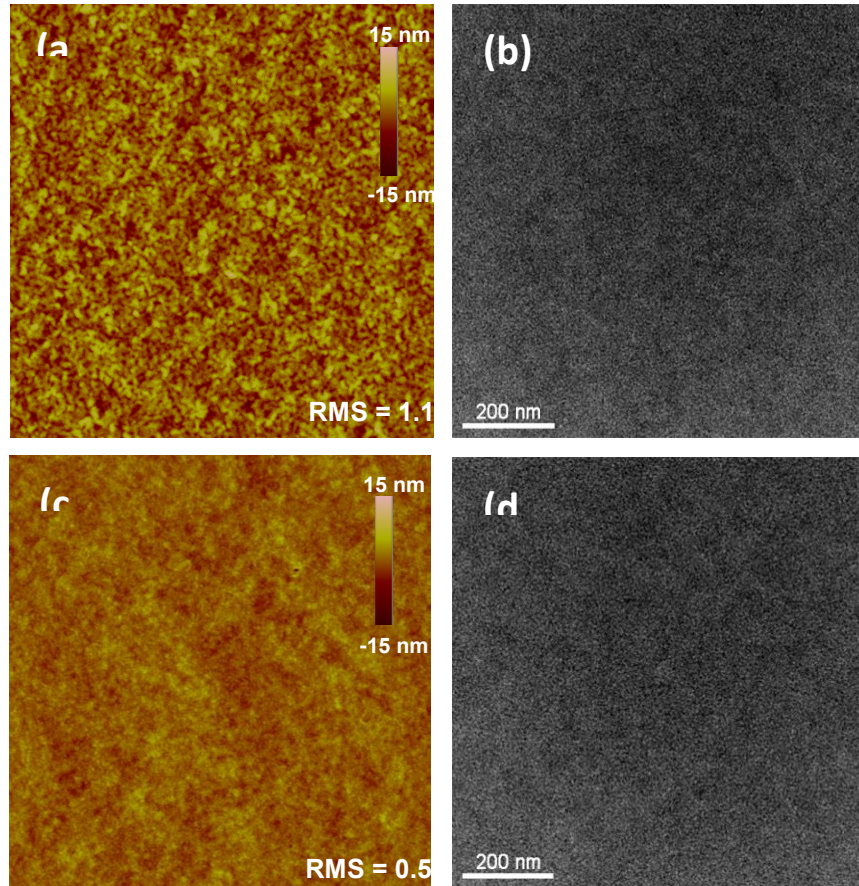


Figure S5. (a) AFM topographic image ($5 \times 5 \mu\text{m}$) and (b) TEM image of J71:BDT-IC (1:1.2, w/w) and J71:IT-IC (1:1, w/w) blend films cast from chloroform solution.

Space Charge Limited Current (SCLC) Measurement

Hole and electron mobilities were measured using the following device structures: ITO/PEDOT:PSS/ J71:BDT-IC/Au for hole-only measurements and ITO/ZnO/ J71:BDT-

IC /PDINO/Al for electron-only measurements. The space charge limited current mobilities were calculated by Mott-Gurney equation:

$$J = \frac{9\varepsilon_r\varepsilon_0\mu V^2}{8L^3}$$

where J is the current density, $\varepsilon_r = 4$ is the relative dielectric constant of active layer material, ε_0 is the permittivity of free space, μ is the mobility of hole or electron, L is the thickness of the active layer, and V is the applied voltage. As shown in Figure 7&8, the hole and electron mobilities of J71 : BDT-IC (1:1.2,w/w) are estimated as 1.13×10^{-4} and $1.90 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ respectively, corresponding to nearly balanced charge transport ($\mu_e/\mu_h = 1.7$).

GIXD diffraction Characterization

Grazing incidence x-ray diffraction (GIXD) characterization of the thin films was performed at beamline 7.3.3, at the Advanced Light Source (ALS), Lawrence Berkeley National Lab (LBNL). The x-ray energy was 10 keV and operated in the top off mode. The scattering intensity was recorded on a 2D image plate (Pilatus 1M) with a pixel size of $172 \mu\text{m}$ (981×1043 pixels). The samples were ~ 10 mm long in the direction of the beam path, and the detector was located at a distance of 300 mm from the sample center (distance calibrated by a AgB reference). The incidence angle was chosen to be 0.16° (above critical angle) for GIXD measurement. OPV samples were prepared on PEDOT:PSS covered Si wafers in a similar manner to the devices. RSoXS was performed at beamline 11.0.1.2 Lawrence Berkeley National Lab. Thin films were transferred onto Si_3N_4 substrate and the experiment was done in transition mode.

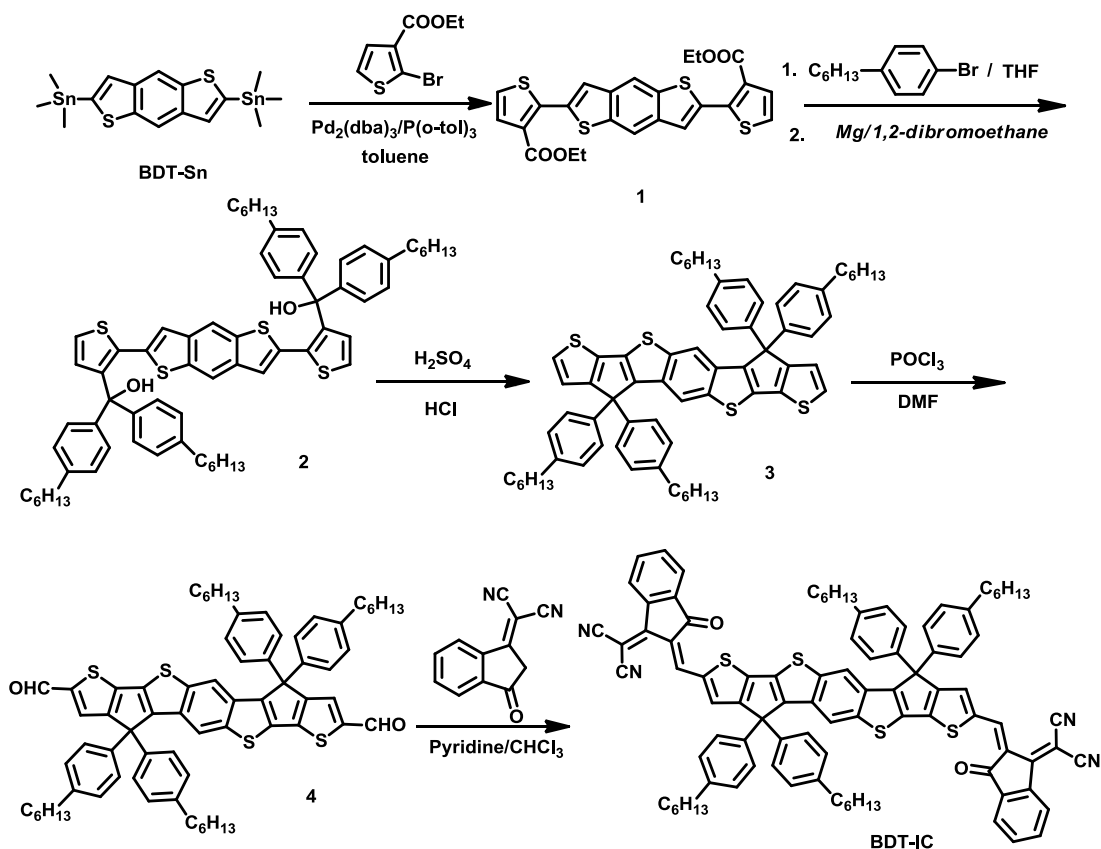
Computational Methods

All the calculations of electron densities of the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) for IT-IC and BDT-IC were performed by Amsterdam Density Functional (ADF) program^{3,4}. Both the HOMO-LUMO gap, and reorganization energy of IT-IC and BDT-IC, were calculated by GGA:PW91, with the basis set of TZP.

Synthesis

The synthetic route for BDT-IC is shown in **Scheme S1**. Whereas IT-IC is obtained via the nucleophilic addition reaction with p-hexylphenyllithium and an acid-promoted intramolecular annulation, we synthesized the 7-fused number ring of BDT-IC via a Grignard reagent with reflux, followed by acid-promoted intramolecular Friedel-Crafts cyclization. BDCPDT was isolated with 58% yield. It was further reacted with phosphorus oxychloride to afford compound 4 as a red solid with 83% yield. Subsequent Knoevenagel condensation between compound 4 and 3-(dicyanomethylidene)indan-1-one resulted in BDT-IC with 82% yield. The chemical structure of each compound was characterized by ¹H NMR, ¹³C NMR, and Matrix-Assisted Laser Desorption/ Ionization Time of Flight Mass Spectrometry (MALDI-TOF MS).

Scheme S1. The synthetic route for BDT-IC.



Synthesis of Compound 1

The BDT-Sn (1.54 g, 2.0 mmol) was dissolved in toluene (10 mL), DMF (1 mL) and the ethyl 2-bromothiophene-3-carboxylate (1.18 g, 5.0 mmol) was added. The mixture was deoxygenated by bubbling nitrogen gas for 30 min and then $\text{Pd}_2(\text{dba})_3$ (15 mg, 0.8 mol%) and $\text{P}(\text{o-tol})_3$ (29 mg, 4.8 mol %) were added. The resulting mixture was heated in a microwave reactor at 120 °C for 5 min, 150 °C for 3 h. After cooling to room temperature, the mixture was extracted with dichloromethane (DCM). The organic phase was collected and dried over anhydrous Na_2SO_4 . Then the solvent was evaporated and the crude product was purified using silica gel chromatography with 1:1, DCM: hexane as the eluent. Evaporation of the solvent yielded the product as a yellow solid (890 mg,

92%). ¹H NMR (600 MHz, CDCl₃, δ): 8.21 (s, 2H), 7.75 (s, 2H), 7.55 (d, *J* = 6.0 Hz, 2H), 7.30 (d, *J* = 6.0 Hz, 2H), 4.34 (q, *J* = 6.0 Hz, 4H), 1.32 (t, *J* = 6.0 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃, δ): 163.0, 142.6, 138.1, 137.9, 134.9, 130.7, 129.2, 125.0, 124.9, 116.7, 60.9, 14.2.

Synthesis of Compound 3

Two drops of 1,2-dibromoethane were added to a suspension of Mg turnings (0.2 g, 8.0 mmol) in anhydrous THF (50 mL) and placed under a nitrogen atmosphere. 1-bromo-4-hexylbenzene (1.9 g, 8.0 mmol) was then slowly added to the mixture and stirred for 1h at room temperature. A Grignard reagent was added dropwise to the mixture of compound 1 (728 mg, 1.5 mmol) in THF (50 mL). The reaction was heated at reflux for 12h, and then water was added and extracted with diethyl ether (3 × 50 mL). The organic extracts were combined and dried over anhydrous Na₂SO₄. After removal of the solvent, the crude product was charged into three-neck flask. Acetic acid (50 mL) and concentrated HCl (0.5 mL) were added and the mixture was refluxed for 4 h. Then the mixture was poured into water and extracted with hexane. The resulting crude compound was purified by silica gel chromatography using a mixture of hexane/DCM (10:1) as the eluent to give a light yellow solid (886 mg, 58%). ¹H NMR (400 MHz, CDCl₃, δ): 7.88 (s, 2H), 7.24 (d, *J* = 4.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 8H), 7.08 (d, *J* = 4.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 8H), 2.55 (d, *J* = 8.0 Hz, 8H), 1.60-1.53 (m, 8H), 1.28-1.27 (m, 24H), 0.87 (t, *J* = 8.0 Hz, 12H). ¹³C NMR (100 MHz, CDCl₃, δ): 161.1, 148.6, 141.2, 141.0, 138.7, 136.9, 136.2, 130.6, 128.0, 127.6, 126.4, 122.5, 115.6, 62.0, 53.0, 35.1, 31.2, 30.8, 28.7, 22.1, 13.6. MS (MALDI) *m/z*: M⁺, 1018.7.

Synthesis of Compound 4

In a dry three neck round-bottomed flask, compound 3 (1.3 g, 1.0 mmol) was dissolved in dimethylformamide (DMF, 50 mL) and placed under a nitrogen atmosphere. The solution was cooled to 0 °C and stirred while phosphorus oxychloride in dichloroethane (1.0 mL, 10.5 mmol) was added dropwise. The mixture was stirred for 1 h at 25 °C, and then stirred for 5 h at 105°C. After reaction, the mixture was cooled to room temperature and poured into ice water. 1 M NaOH solution was added and extracted with DCM, The resulting crude compound was purified by silica gel column chromatography using a mixture of hexane/DCM (3:2) as the eluent to give an orange solid (892 mg, 83%). ¹H NMR (400 MHz, CDCl₃, δ): 9.80 (s, 2H), 7.98 (s, 2H), 7.69 (s, 2H), 7.16 (d, J = 8.0 Hz, 8H), 7.07 (d, J = 8.0 Hz, 8H), 2.55 (t, J = 8.0 Hz, 8H), 1.60-1.53 (m, 8H), 1.35-1.25 (m, 24H), 0.86 (t, J = 8.0 Hz, 12H). ¹³C NMR (100 MHz, CDCl₃, δ): 182.2, 161.4, 153.0, 146.1, 144.8, 142.4, 142.0, 137.2, 137.0, 130.9, 130.7, 128.3, 127.5, 116.9, 62.4, 35.1, 31.2, 30.8, 28.6, 22.1, 13.6. (MALDI) m/z: M⁺, 1074.5.

Synthesis of BDT-IC

1,1-dicyanamethylene-3-indanone (194mg, 1.0 mmol) was added into the mixture of compound 4 (400 mg, 0.3 mmol) in anhydrous chloroform with pyridine (1 mL), the reaction was deoxygenated with nitrogen for 30 min and then refluxed for 10 h. After cooling to room temperature, the product was poured into methanol and the precipitate was filtered off, and then extracted with DCM and washed in water. The crude product was purified by silica gel column chromatography using a mixture of hexane/DCM (3:2) as the eluent to give a purple solid (351 mg, 82%). ¹H NMR (600 MHz, CDCl₃, δ): 8.88 (s, 2H), 8.68 (d, J = 6.0 Hz, 2H), 8.01 (s, 2H), 7.92 (m, 2H), 7.74 (m, 4H), 7.70 (s, 2H), 7.17 (d, J = 12.0 Hz, 8H), 7.11 (d, J = 12.0 Hz, 8H), 2.57 (t, J = 6.0 Hz, 8H), 1.60-1.53

(m, 8H), 1.35-1.29 (m, 24H), 0.87 (t, J = 6.0 Hz, 12H). ¹³C NMR (100 MHz, CDCl₃, δ): 188.5, 162.8, 160.2, 156.0, 155.3, 143.9, 142.6, 140.5, 139.9, 138.7, 138.2, 138.1, 137.3, 136.8, 135.0, 134.3, 131.7, 128.9, 128.0, 125.2, 123.6, 121.6, 118.0, 114.7, 68.7, 62.7, 35.5, 31.7, 31.2, 29.1, 22.6, 14.1. (MALDI) m/z: M⁺, 1427.5.

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