

Supporting Information

Single molecular conductance investigation of BDT derivatives: an additional pattern found to induce through-space channels beyond π - π stacking

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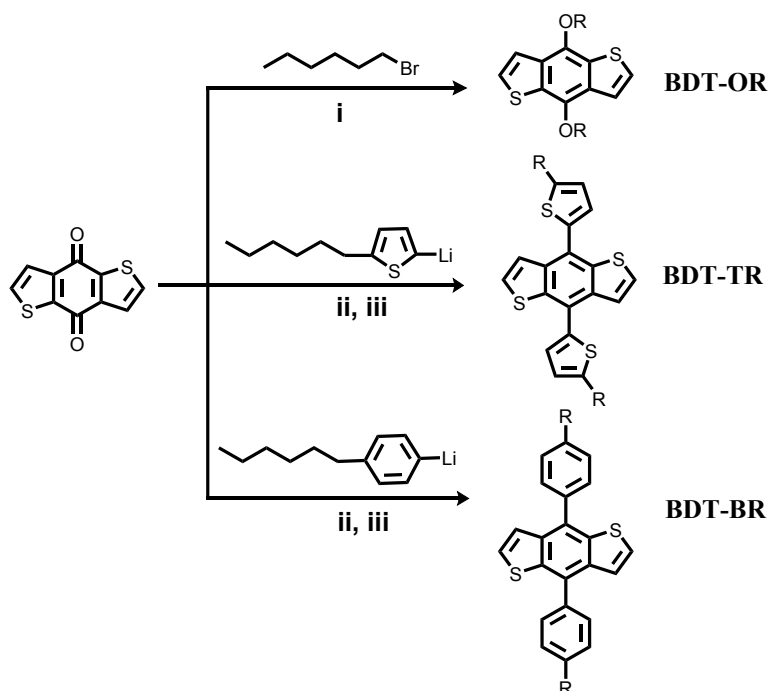
Pages:

- S2-5 Materials preparing and characterization methods**
- S5 Conductance measurement methods**
- S5 Calculation method**
- S6 Cyclic voltammetry (CV), and absorption spectrum**
- S6 Decay constant test**
- S7 2D of conductance vs Baseline Conductance histogram of BDT-OR, BDT-TR and BDT-BR**
- S7 Typical current signal of BDT-OR, BDT-TR, and BDT-BR**
- S8 Coordination models of molecular junctions**

Experimental section

General information

^1H NMR & ^{13}C NMR spectra were obtained on a Bruker NMR spectrometer operating at 600 and 150 MHz, respectively, in CDCl_3 using tetramethylsilane (TMS) as an internal standard. MALDI-TOF (matrix-assisted laser-desorption/ionization time-of-flight) mass spectra were performed on a Bruker BIFLEXIII TOF mass spectrometer. UV-vis absorption was done on a Shimadzu UV-2000. Cyclic voltammetry (CV) was performed on a CHI600D electrochemical workstation with a glassy carbon working electrode and a Pt wire counter electrode at a scanning rate of 0.05 V s^{-1} against a Ag/Ag^+ (0.1 M of AgNO_3 in acetonitrile) reference electrode in dichloromethane (DCM) of 0.1 mol L^{-1} and tetrabutylammoniumhexafluorophosphate as supporting electrolyte under Nitrogen bubbling. Materials: all solvents and materials were used as received from commercial suppliers. Synthetic routes of the BDT derived compounds are outlined in **Scheme S1**.

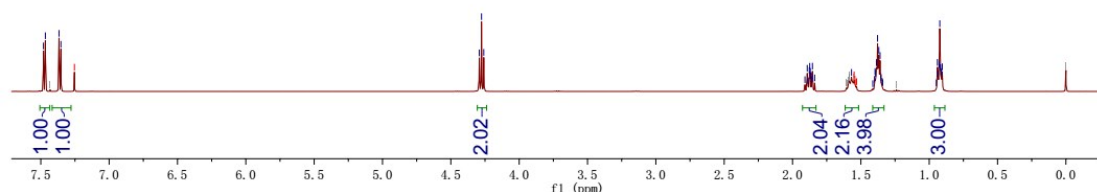
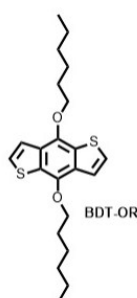


^a (i) AcOH, HCl, 80°C, under N_2 ; (ii) n-BuLi (3 equiv), THF, -78 °C; (iii) SnCl_2 , EtOH, HCl (10wt% solution), rt.

Scheme S1 Synthetic routes of BDT-OR, BDT-TR, and BDT-BR.

4, 8-bis(hexyloxy)benzo[1,2-b:4,5-b']dithiophene (BDT-OR)

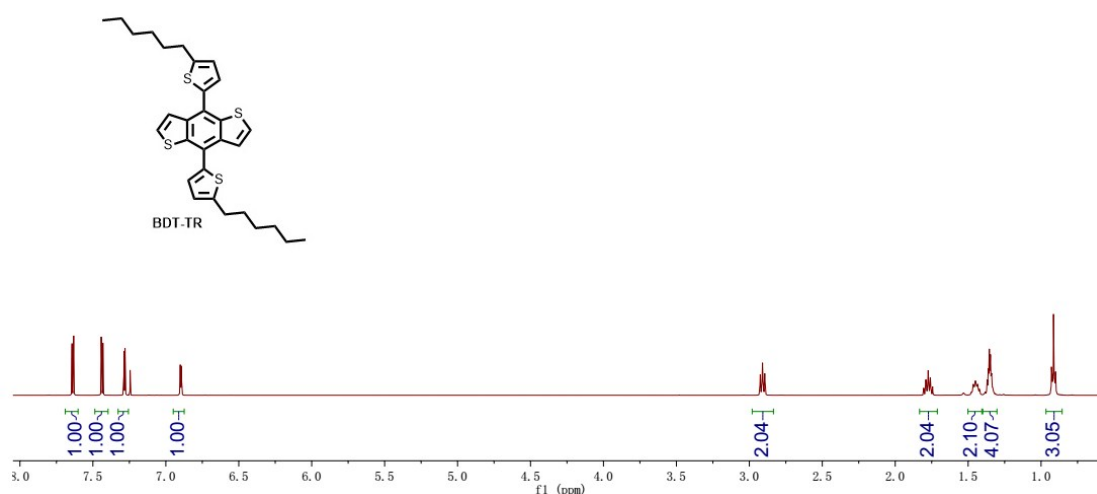
A portion of benzo[1,2-b:4,5-b']dithiophene-4,8-dione (0.50 g, 2.27 mmol), 50 mL of water, and 0.44 g of Zn powder (6.81 mmol) were added into a three neck flask. NaOH (0.44 g \times 4) was added and refluxed until it was dissolved. After 2 h, 1.12 g (6.82 mmol) of hexyl bromide and a catalytic amount of tetrabutylammoniumbromide were added to this mixture and refluxed for another 12 h. This mixture was poured into cold water and extracted with dichloromethane (DCM). The DCM layer was collected and dried over anhydrous MgSO_4 . The organic solvent was distilled and the residue was purified by column chromatography using ethyl DCM: petroleum ether (1: 30) as the eluent. BDT-OR was obtained as a white crystalline solid (0.66 g). Yield: 75%. ^1H NMR (500 MHz, Chloroform-d) δ 7.47 (d, J = 5.5 Hz, 1H), 7.36 (d, J = 5.5 Hz, 1H), 4.28 (t, J = 6.6 Hz, 2H), 2.01 – 1.74 (m, 2H), 1.57 (s, 2H), 1.43 – 1.30 (m, 4H), 1.06 – 0.75 (m, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 125.98, 120.31, 73.96, 31.65, 30.49, 25.74, 22.65, 14.09. MS (MALDI-TOF): m/z calcd for $\text{C}_{22}\text{H}_{30}\text{O}_2\text{S}_2$ 390.17; found 390.188.



4, 8-Bis(5-((2-ethylhexyl)thio)thiophen-2-yl)benzo[1,2-b:4,5-b']-dithiophene (BDT-TR)

2-hexyl-5-bromothiophene (2.1 g, 9.1 mmol) were dissolved in anhydrous tetrahydrofuran (THF) in a three necks flask under nitrogen protection. After the mixture being cooled down to $-78\text{ }^\circ\text{C}$, n-BuLi (4.0 mL, 2.5 M) was added dropwise, the

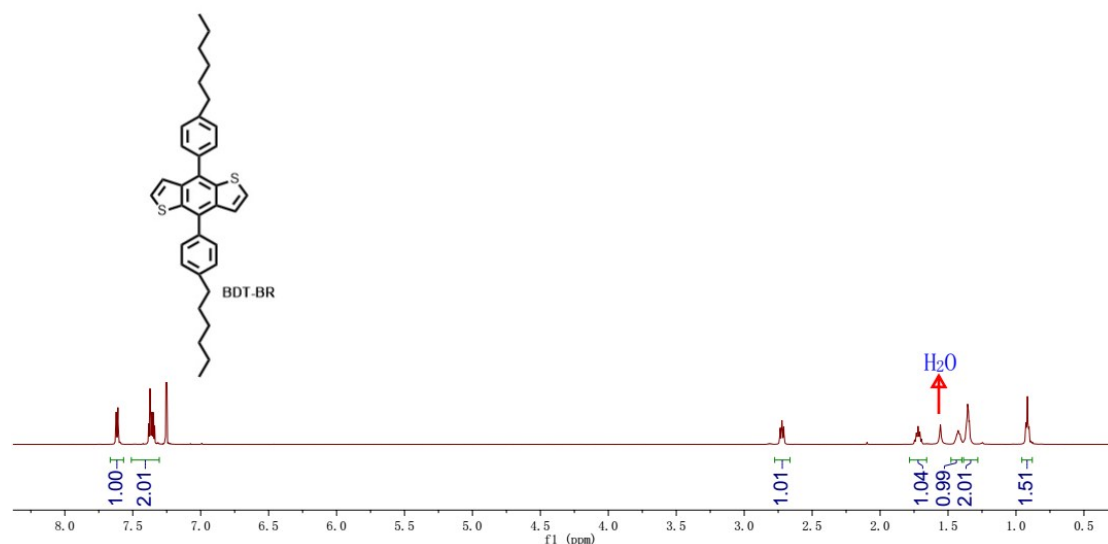
mixture was stirred under $-50\text{ }^{\circ}\text{C}$ for one more hour. Then benzo[1,2-b:4,5-b']dithiophene-4,8-dione (0.67 g, 3.0 mmol) was added into the reaction solution. The mixture was stirred under room temperature for another 3 h. $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (16.4 g, 72.8 mmol) in 10 vol% HCl (30 mL) was added and the mixture was stirred at $50\text{ }^{\circ}\text{C}$ overnight. The reaction mixture was poured into water and extracted with DCM. The organic layer was collected and dried over anhydrous MgSO_4 . Further purification was carried out by column chromatography using petroleum ether as eluent to obtain pure compound as a light yellow oil liquids (0.99 g, yield = 61%). ^1H NMR (500 MHz, Chloroform-d) δ 7.64 (d, $J = 5.7\text{ Hz}$, 1H), 7.44 (d, $J = 5.7\text{ Hz}$, 1H), 7.28 (d, $J = 3.5\text{ Hz}$, 1H), 6.90 (dt, $J = 3.5, 1.0\text{ Hz}$, 1H), 3.03 – 2.82 (m, 2H), 1.87 – 1.69 (m, 2H), 1.51 – 1.40 (m, 2H), 1.36 (ddd, $J = 7.3, 4.5, 2.9\text{ Hz}$, 4H), 1.04 – 0.86 (m, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 147.13, 138.95, 136.94, 136.48, 127.76, 127.74, 127.44, 124.25, 123.42, 76.94, 31.59, 30.26, 28.92, 22.61, 14.12. MS (MALDI-TOF): m/z calcd for $\text{C}_{30}\text{H}_{34}\text{S}_4$ 522.15; found 522.175.



4, 8-Bis(5-((2-ethylhexyl)thio)thiophen-2-yl)benzo[1,2-b:4,5-b']-dithiophene (BDT-BR)

BDT-BR (0.79 g, yield 52%) was synthesized as a white solid in a similar manner of BDT-TR with 1-bromo-4-hexylbenzene instead of 2-bromo-5-hexylthiophene. ^1H NMR (600 MHz, Chloroform-d) δ 7.62 (d, $J = 7.9\text{ Hz}$, 1H), 7.42 – 7.31 (m, 2H), 2.72 (t, $J = 7.9\text{ Hz}$,

1H), 1.72 (td, J = 9.4, 8.7, 6.6 Hz, 1H), 1.42 (q, J = 7.1, 6.3 Hz, 1H), 1.35 (dq, J = 6.8, 3.5 Hz, 2H), 0.92 (dq, J = 7.1, 3.1, 2.6 Hz, 1.5H). ¹³C NMR (151 MHz, Chloroform-d) δ 142.91, 136.52, 130.33, 129.18, 128.78, 127.02, 123.07, 35.91, 31.77, 31.39, 29.16, 22.65, 14.15. MS (MALDI-TOF): m/z calcd for C₃₄H₃₈S₂ 510.24; found 510.226.



Single molecular conductance measurement

The conductance measurements were performed on an electrochemical scanning probe microscope (Agilent 6500) by adopting the Scanning tunneling microscope (STM) based recognition tunneling method. By maintaining a fixed distance between the tip and the substrate, a target molecule can be trapped in such nano gap accidentally to form a conducting loop. The target molecules were diluted to a concentration of 1mM in 1, 2, 4-trichlorobenzene (TCB) and the conductance measurements were also performed in the same solvent condition.

Electronic structure and Transport calculations

Density functional theory (DFT) calculations were performed on the Gaussian 09_B01 package. The geometry of the ground state of the three molecules in the gas phase was optimized using B3LYP/6-31G (d, p) basic set.

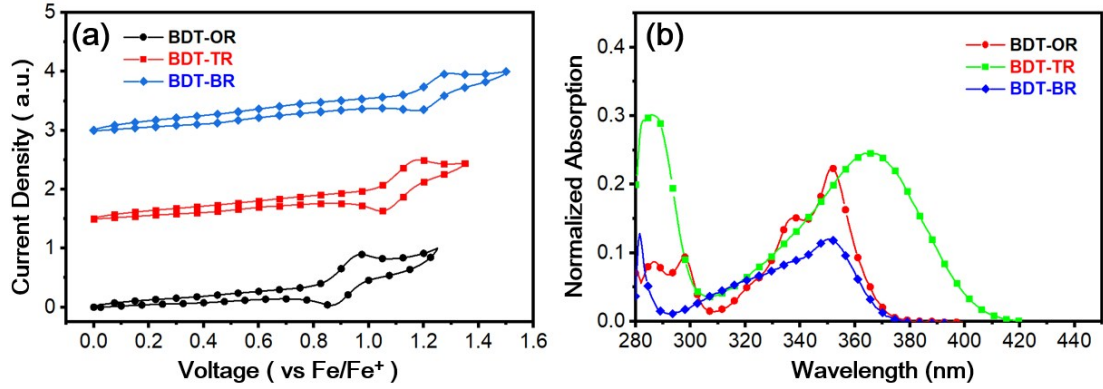


Figure S1. The cyclic voltammety (a), and absorption spectrum (b) of BDT-OR, BDT-TR, and BDT-BR.

In the case of single transmitting channel, the conductance is given by (S1):

$$G = G_0 \Gamma(E_F) = \frac{\Gamma^2}{\varepsilon^2 + \Gamma^2} G_0 \quad (\text{S1})$$

Γ is the coupling strength, ε is the difference in energy between the Fermi energy of the electrodes. Stronger coupling intensity and narrower energy difference can produce larger conductance.

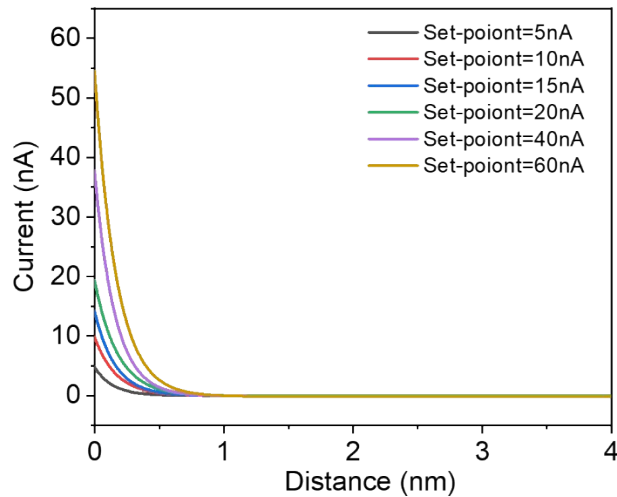


Figure S2 Tunneling experiment in pure solvent TCB. (According to the set-point setup, a bare probe stayed above gold substrate in 1, 2, 4-trichlorobenzene solvent with absence of target molecules, then retracted from the substrate at a speed of 40 nm/s, during which the tunneling current decay curve were monitored. Data are shown for set-point currents of 5, 10, 15, 20, 40 and 60 nA, as the same parameter in tunneling recognition method. All curves are well-fitted by an exponential function $I = I_0 \exp(-\beta x)$ where I_0 is the set-point current, β is the inverse decay length and x is the probe displacement. Then the average values for β was determined by fitting decay curves

for each set-point.)

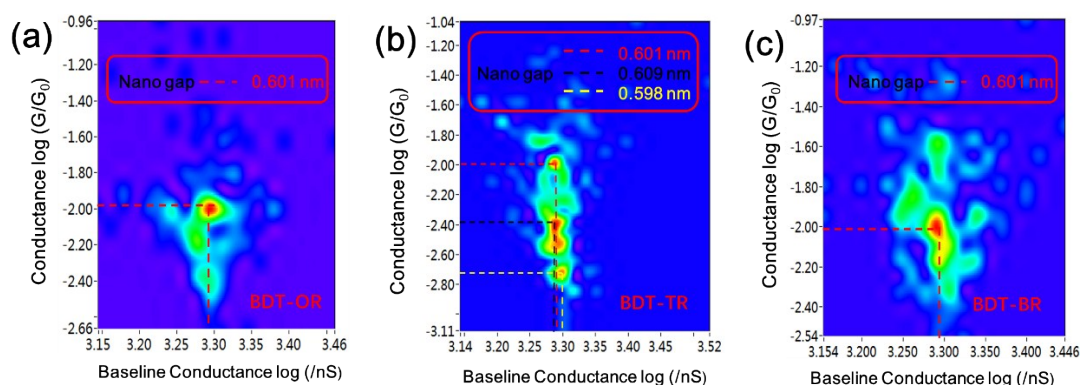


Figure S3 Two-dimensional conductance vs Baseline Conductance histogram of BDT-OR, BDT-TR and BDT-BR.

2D conductance vs baseline conductance histogram were constructed with $I(t)$ curves of target molecules. Each 2D histogram presents the relative probability occurrence of differentiated conductance values at corresponding baseline conductance (converted from the set-point current), which is marked by the color scale bar with low occurrence in blue region and high occurrence in red region. Heatmap of BDT-OR, BDT-TR, BDT-BR show that maximum of conductance among three target molecules (red line) extend to a similar nano gap. According to tunneling function $G=G_0\exp(-\beta L)$, the corresponding nano gap is 0.601nm.

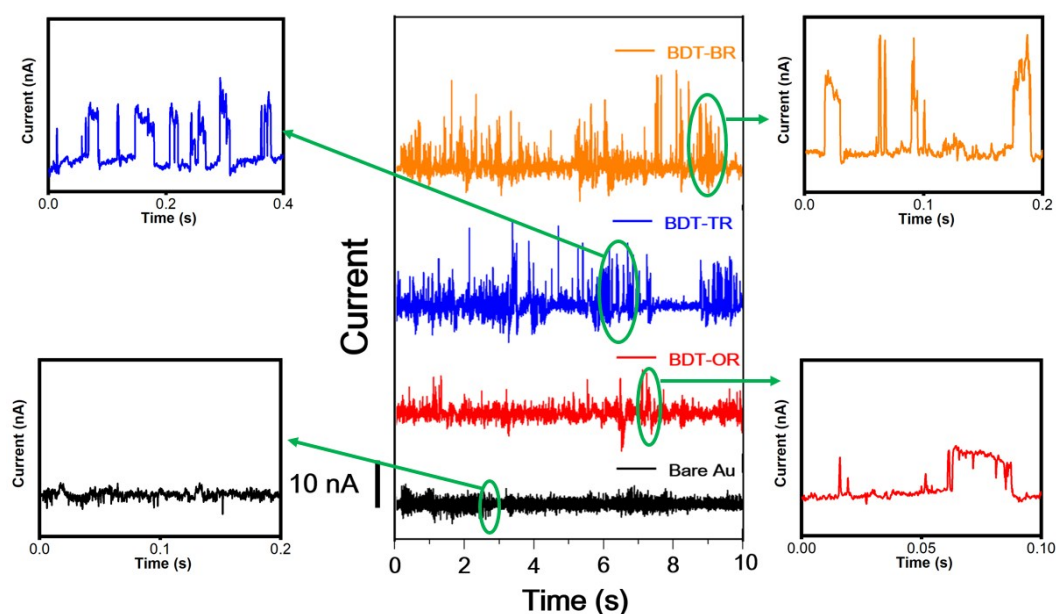
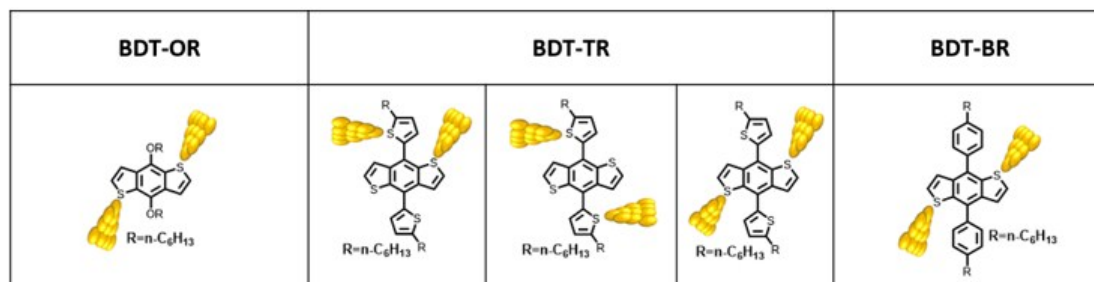


Figure S4 Typical current signal of BDT-OR, BDT-TR, and BDT-BR compared with bare Au. (Typical current-time traces of target molecules and control experiment. Typical $I(t)$ curves were obtained in the STM measurements with a background tunneling current of 20 nA at a bias of 0.01 V. The trace of target molecules presented lots of typical switching spikes (inset shows the details), while no identical signals were

observed in control experiment.)



Scheme S2 Coordination models of BDT-OR, BDT-TR, and BDT-BR. And their corresponding maximum possible conductance.