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Effect of Modified Thiophene Anchor on Molecule-Electrode Bonding

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噻吩锚定基团的结构修饰对分子-电极结合的影响

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General information

S1 Synthetic routes and ^{1}H NMR spectra for BT-H, BT-Cl and BT-Hex

^{1}H NMR spectra were obtained on a Bruker NMR spectrometer operating at 600 in Chloroform-d using tetramethylsilane (TMS) as an internal standard.

Materials: all solvents and materials were used as received from commercial suppliers. And the preparing process of BT-H, BT-Cl and BT-Hex were as follows (Fig. S1):

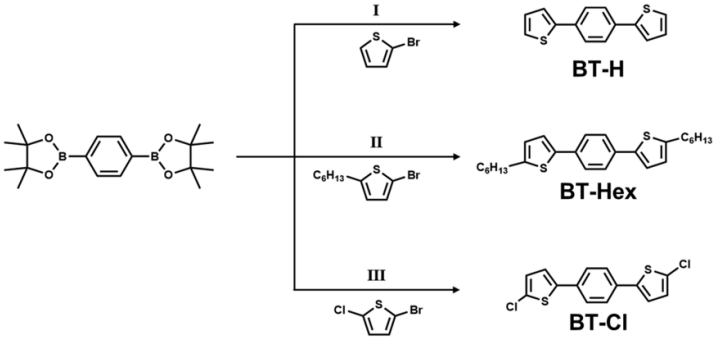

Fig. S1 Synthetic routes of BT-H, BT-Hex and BT-Cl. Reagents and conditions: (I), (II) and (III) K_2CO_3, H_2O, $Pd(PPh_3)_4$, toluene, ethanol, N_2, 78 °C for 24 h.

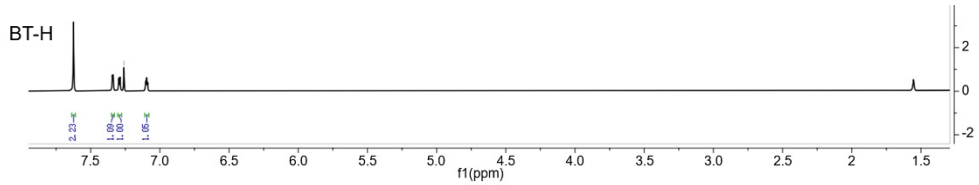

Fig. S2 ^{1}H NMR spectra of BT-H in $CDCl_3$.

Add 1,4-dibromobenzene (472 mg, 2 mmol) and 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (1.58 g, 4.8 mmol) into the three-necked flask. Add 3.2 g K_2CO_3 and 12 mL H_2O and stir for 10 min (under N_2 atmosphere). Then ethanol (40 mL) and toluene (60 mL) were added and stir for 10 min. Finally, $Pd(PPh_3)_4$ (55 mg) was added. After stirring for 30 min, it was heated to 78 °C, and then refluxed for 24 h. This mixture was poured into cold water and extracted with dichloromethane (DCM). The DCM layer was collected and dried over anhydrous $MgSO_4$. BT-H was obtained as a colorless crystalline solid (130 mg, 27%). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.62 (s, 2H), 7.34 (d, J = 3.6 Hz, 1H), 7.29 (d, J = 5.0 Hz, 1H), 7.10 (dd, J = 5.1, 3.6 Hz, 1H).

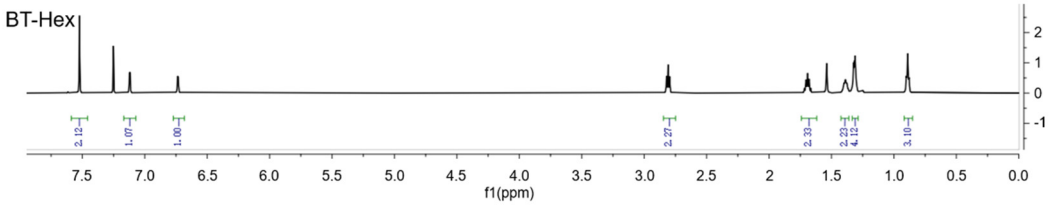

Fig. S3 ^{1}H NMR spectra of BT-Hex in $CDCl_3$.

1,4-bis(5-hexylthiophen-2-yl)benzene (363 mg, yield 59%) was synthesized as a green crystalline solid in a similar procedure of BT-H with 2-bromo-5-hexylthiophene instead of 2-bromothiophene. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.53 (s, 2H), 7.13 (d, J = 3.5 Hz, 1H), 6.74 (d, J = 3.5 Hz, 1H), 2.82 (t, J = 7.6 Hz, 2H), 1.70 (p, J = 7.6 Hz, 2H), 1.40 (t, J = 7.4 Hz, 2H), 1.32 (h, J = 3.2 Hz, 4H), 0.92–0.87 (m, 3H).

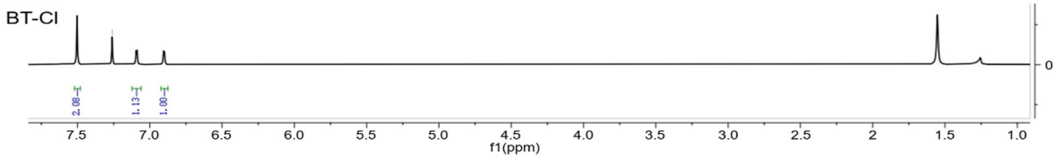

Fig. S4 ^{1}H NMR spectra of BT-Cl in $CDCl_3$.

1,4-bis(5-chlorothiophen-2-yl)benzene (138 mg, yield 22%) was synthesized as a green crystalline solid in a similar procedure of BT-H with 2-bromo-5-chlorothiophene instead of 2-bromothiophene. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.50 (s, 2H), 7.09 (d, J = 3.9 Hz, 1H), 6.90 (d, J = 3.9 Hz, 1H).

S2 Typical G-D traces for BT-H and its corresponding conductance histogram

The conductivity of single molecule of BT-H was measured under the condition of current amplifier multiple of 10^6 V·A^{-1}, with gold quantum conductance (G_0) indicated in Fig. S5. In the resulting one-dimensional conductance histogram (Fig. S5b), there are also two conductance peaks, which are consistent with the results measured under the condition of current amplifier multiple of 10^7 V·A^{-1}.

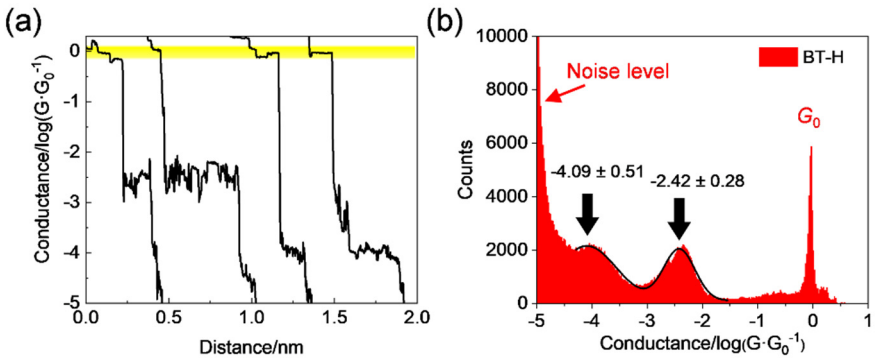

Fig. S5 (a) Typical Conductance-Distance curves of BT-H; (b) Conductance histogram of BT-H.

S3 Uv-Vis absorption spectra, CV, and the energy level diagram for BT-H, BT-Cl and BT-Hex

In order to obtain the energy level of BT-H, BT-Cl and BT-Hex, the electrochemical properties of the molecules were measured by cyclic voltammetry (Fig. S6). The initial redox potential of BT-H, BT-Cl and BT-Hex were estimated to be 1.33, 1.24 and 1.45 eV, respectively. According to $E_{HOMO} = -e(E_{ox} + 4.8 - E_{Fc})$ (eV) (where e is the electron charge, $E_{Fc} = 0.53$ eV was measured in the same condition). HOMO levels of BT-H, BT-Cl and BT-Hex should be −5.60, −5.72 and −5.51 eV, respectively. We also used UV-visible absorption to characterize the optical properties of these molecules, as shown in Fig. S6. The optical bandgaps (E_g^{opt}) of BT-H, BT-Cl and BT-Hex can be estimated from the absorption threshold (Fig. S6), which are 3.43, 3.24 and 3.31 eV, respectively. Their LUMO levels can be calculated as $E_{LUMO} = E_{HOMO} + E_g^{opt}$. Therefore, the HOMO level of the molecule is closer to the Fermi level instead of their LUMO, which means HOMO functioning as their dominant charge transport channels, and their conductivity trend of G_L state is consistent with their positions relative to the E_F level (Fig. S6).

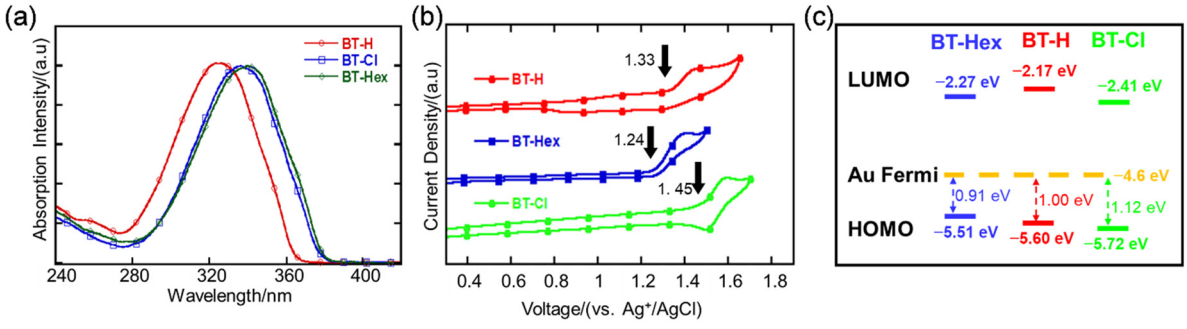

Fig. S6 (a) The absorption spectra; (b) The cyclic voltammetry curve; (c) The energy level diagram of BT-H, BT-Hex and BT-Cl with respect to Au Fermi level.

S4 Statistical junction length of BT-H, BT-Cl and BT-Hex

The length information of the conductance platform of the three molecules was statistically obtained from the conductance distance typical curve, as shown in Fig. S7.

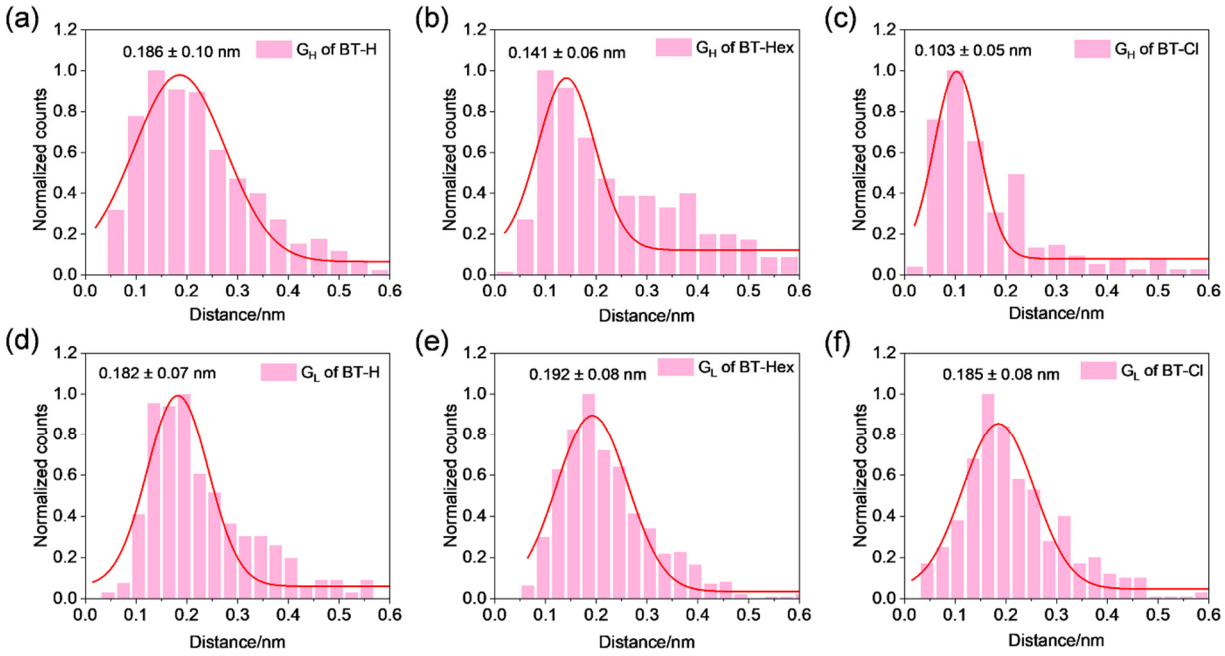

Fig. S7 (a–f) Relative displacement distribution of high and low conductivity of BT-H, BT-Hex and BT-Cl.

S5 2D covariance histogram of BT-Hex and BT-Cl

We analyzed the correlation between the two structural states of high and low conductivity of the three molecules by means of two-dimensional covariance plots, as shown in Fig. S8. Two-dimensional covariance histograms are used to determine the correlation between the high and low conductance of a molecule occurring in a typical trace, with positive, negative and no correlations indicated in blue, black and white respectively. The two-dimensional covariance histograms show that the two binding modes of the molecules BT-H, BT-Hex and BT-Cl are independent of each other.

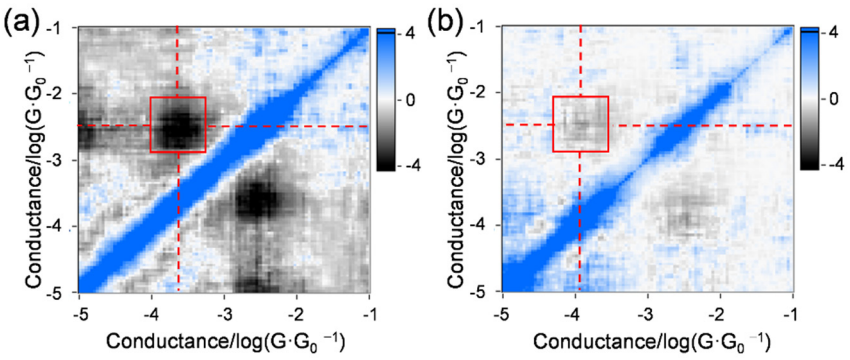

Fig. S8 (a, b) 2D covariance histogram of BT-Hex and BT-Cl.

S6 Calculated NICS value of BT-H, BT-Cl and BT-Hex

We placed the virtual atoms 1 Å above the ring plane and calculated the NICS values for BT-H, BT-Cl and BT-Hex. If the calculated NICS(1)zz is negative, the ring is considered to be aromatic, and it is generally assumed that the greater the negative value, the greater the aromaticity; otherwise, it is anti-aromaticity.