Supporting Information

The binding details of 2-(methylthio)thiophene/furan anchor anchored to Au electrode in the formed molecular junction

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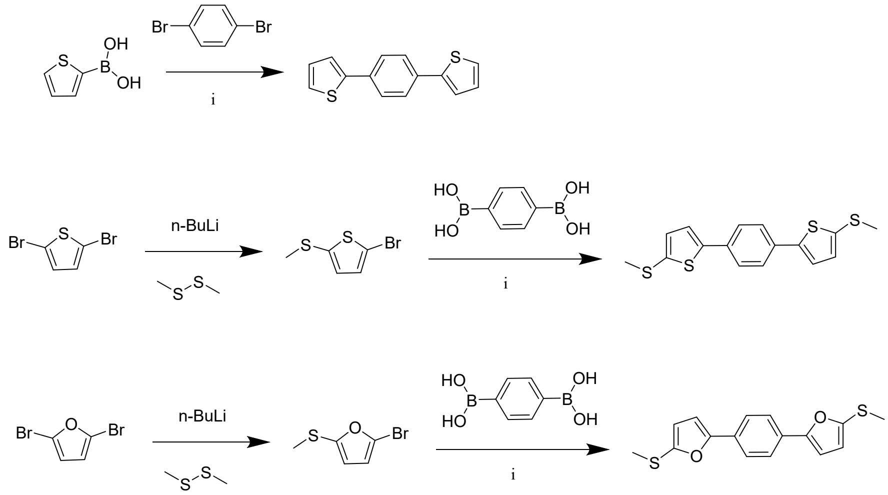
Pages:

S1. Synthetic routes

Materials: all solvents and reagents were used as received from commercial suppliers. ^{1}H NMR spectra were obtained on a Bruker NMR spectrometer operating at 600 MHz, in deuterated DMSO.

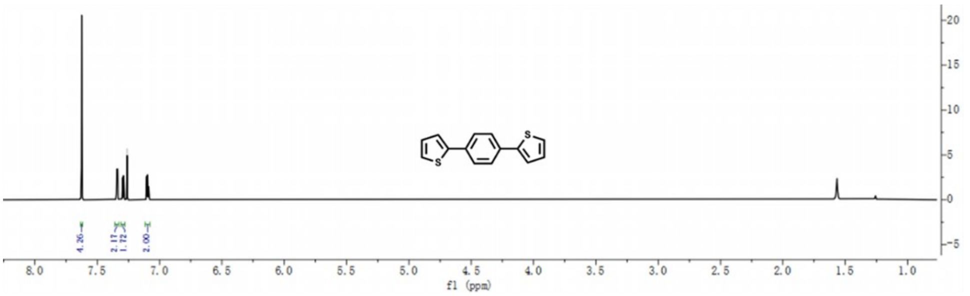


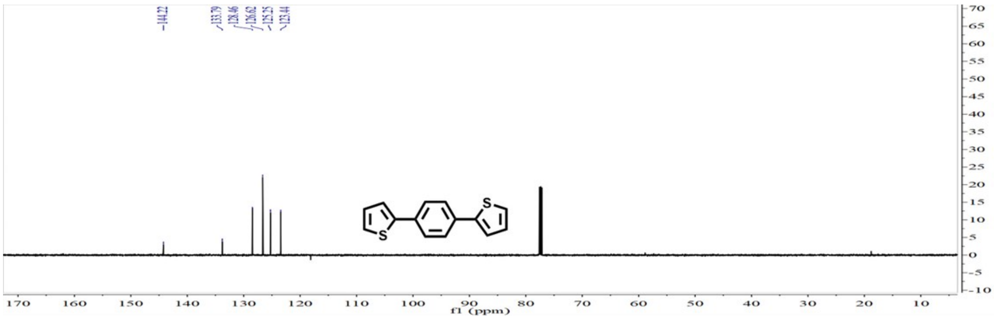
(i) K_2CO_3, $Pd(pph_3)_4$, toluene/ EtOH, 90°C, under N_2

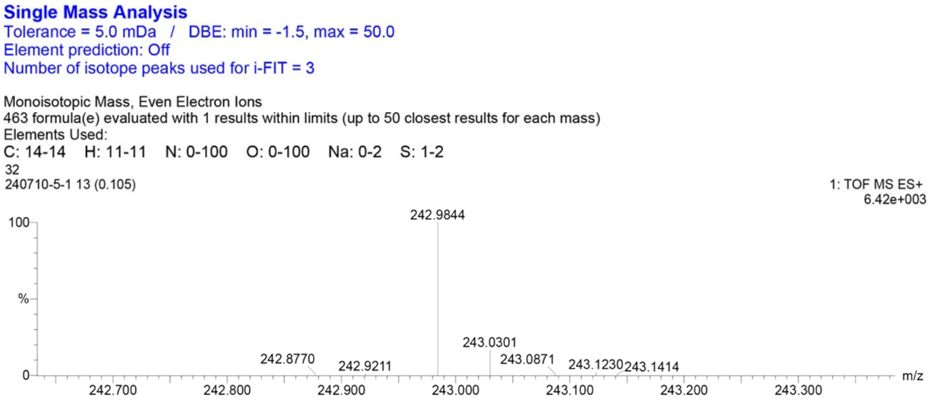
Scheme S1 Synthetic routes of TB, SMe-TB, and SMe-FB

1,4-di(thiophen-2-yl)benzene (TB)

Toluene (30 mL), ethanol (10 mL), 2 M aqueous Na_2CO_3 (7.5 mL), thiophen-2-ylboronic acid (0.282 g, 2.2 equiv), and 1,4-dibromobenzene (0.236 g, 1 mmol) were sequentially added to a 100 mL three-neck flask. The reaction mixture was bubbled for 15 min before adding $Pd(PPh_3)_4$ (52 mg, 3 mol %). Then, the reaction was bubbled for another 15 min and stirred at 90 °C overnight under a nitrogen atmosphere. The reaction was cooled to room temperature, extracted with CH_2Cl_2, and dried over Na_2SO_4. After the removal of the solvent, the residue was purified by column chromatography on a silica gel to afford TB (0.15 g, yield 62%) as a yellow gray solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.62 (s, 4H), 7.34 (dd, $J = 3.6$, 1.2 Hz, 2H), 7.29 (dd, $J = 5.1$, 1.1 Hz, 2H), 7.10 (dd, $J = 5.0$, 3.6 Hz, 2H). ^{13}C NMR (151 MHz, cdcl3) δ 144.22, 133.79, 128.46, 126.62, 125.25, 123.44. MS (TOF MS ES+): m/z $[M+H]^+$ calcd for $C_{14}H_{11}S_2$, 243.0302; found 243.0301.







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Single Mass Analysis
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Number of isotope peaks used for i-FIT = 3

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32
240710-5-1 13 (0.105)                                                    1: TOF MS ES+
                                                                              6.42e+003
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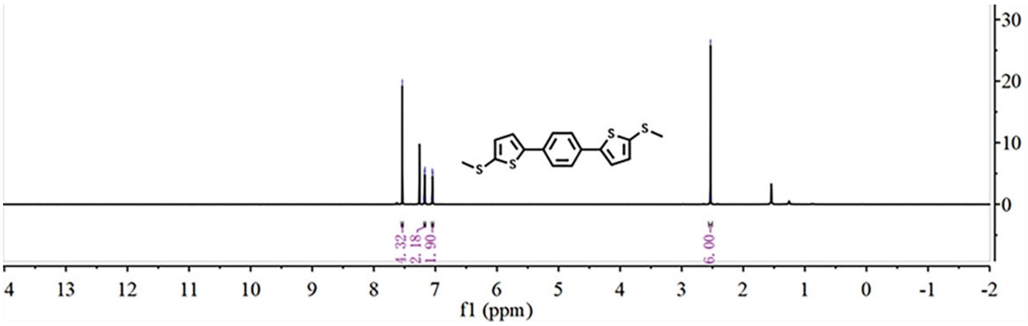
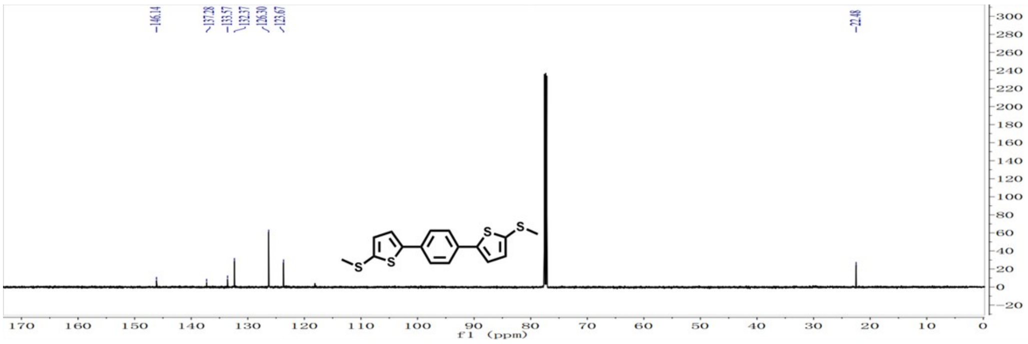
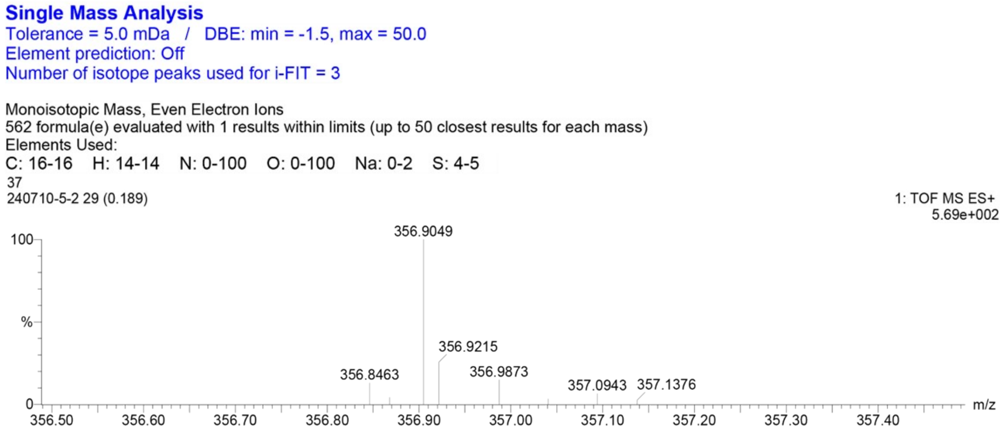
1,4-bis(5-(methylthio)thiophen-2-yl)benzene (SMe-TB)

2,5-dibromothiophene 0.8 g (3.3 mmol, 1.0 equiv) was added into dry tetrahydrofuran (THF) (30 mL) and stirred under argon. The mixture was cooled to -78℃ and kept for 5 min. n-Butyllithium (1.52 mL, 2.5 mol/L) was added in 10 min under vigorous stirring, and then the reaction solution was stirred for 0.5 h at the same temperature. 1,2-dimethyldisulfane (3.3 mmol, 0.31 g) was added to the reaction bottle in one portion. The reaction was increased to the room temperature and stirred overnight. THF was distilled under reduced pressure and further purified by column chromatography to afford 2-bromo-5-(methylthio)thiophene (0.33 g, yield 48%) as a light yellow oily substance.

1,4-bis(5-(methylthio)thiophen-2-yl)benzene (57 mg, yield 31%) was synthesized as a yellow solid in a procedure similar to that of TB except 2-bromo-5-(methylthio)thiophene and 1,4-phenylenediboronic acid were used instead of thiophen-2-ylboronic acid and 1,4-dibromobenzene. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.54 (s, 4H), 7.17 (d, *J* = 3.8 Hz, 2H), 7.05 (d, *J* = 3.7 Hz, 2H), 2.53 (s, 6H). ^{13}C NMR (151 MHz, cdcl3) δ 146.14, 137.28, 133.57, 132.37, 126.30, 123.67, 22.48. MS (TOF MS ES+): m/z [M+ Na] $^+$ calcd for $C_{16}H_{14}NaS_4$, 356.9876; found 356.9873.







Single Mass Analysis
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Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
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240710-5-2 29 (0.189)

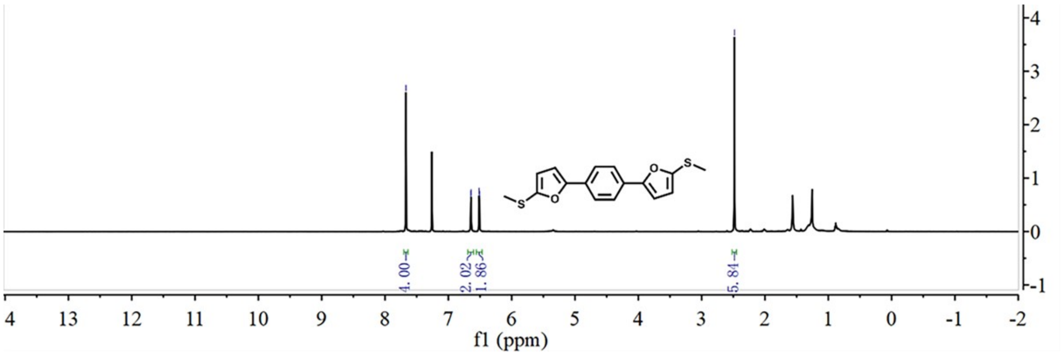
1: TOF MS ES+
5.69e+002

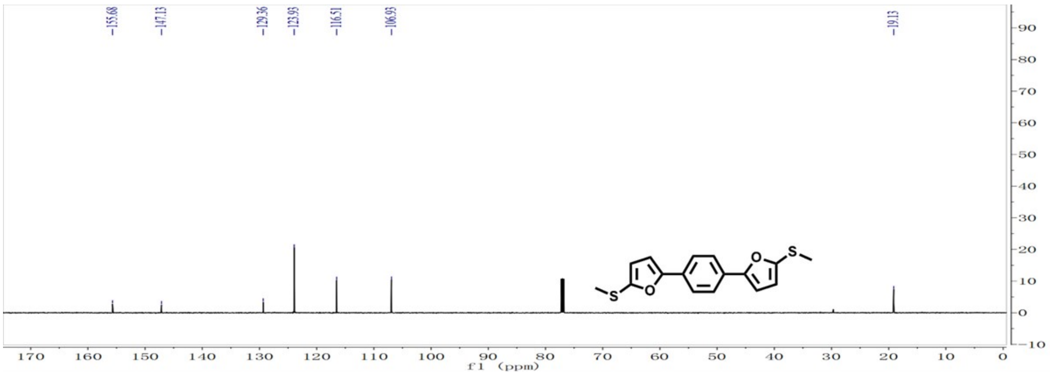
1,4-bis(5-(methylthio)furan-2-yl)benzene (SMe-FB)

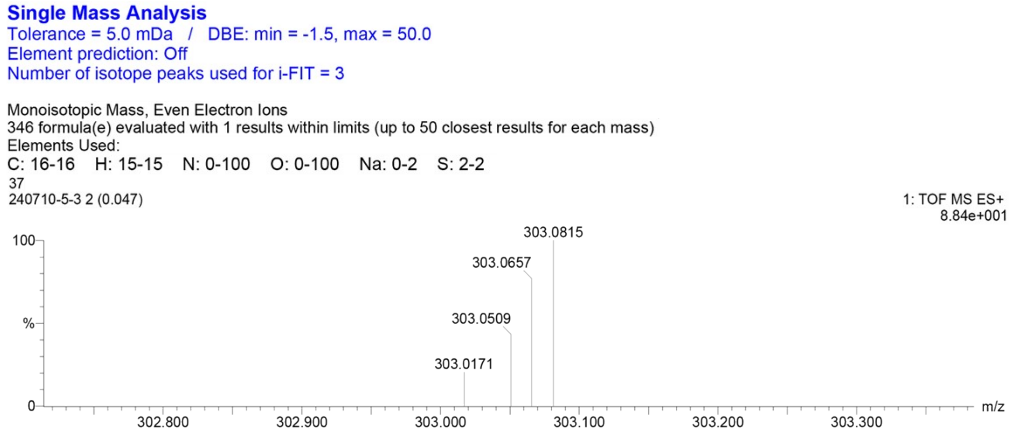
2-bromo-5-(methylthio)furan (0.13 g, yield 15%) was synthesized as colorless oily substance in a procedure similar to that of 2-bromo-5-(methylthio)thiophene except

2,5-dibromofuran was used instead of 2,5-dibromothiophene.

1,4-bis(5-(methylthio)furan-2-yl)benzene (38 mg, yield 22%) was synthesized as a yellow solid in a procedure similar to that of TB except 2-bromo-5-(methylthio)furan and 1,4-phenylenediboronic acid were used instead of thiophen-2-ylboronic acid and 1,4-dibromobenzene. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.67 (s, 4H), 7.64 (d, *J* = 3.3 Hz, 2H), 6.51 (d, *J* = 3.3 Hz, 2H), 2.48 (s, 6H). ^{13}C NMR (151 MHz, cdcl3) δ 155.68, 147.13, 129.36, 123.93, 116.51, 106.93, 19.13.MS (TOF MS ES+): m/z [M+H] $^+$ calcd for $C_{16}H_{15}O_2S_2$, 303.0513; found 303.0509.






Single Mass Analysis
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Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
346 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
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37
240710-5-3 2 (0.047)

1: TOF MS ES+
8.84e+001

S2. The table of the key differences between our study and previous work

Table S1 The table of the key differences between our study and previous work, focusing on aspects such as research purpose, research methods, and conclusions

	Our study	**b**[1]	**c**[2]	**d**[3]	**e**[4]	**f**[5]
Research purpose	To reveal the binding details of methylthiothiophene/furan anchors with gold electrodes.	To enhance on the single-molecule conductivity through bidentate connections.	To reveal how bidentate anchor affects the electrical conductance	To study the application of hemilabile ligands in molecular electronics.	To study the nature of self-assembled monolayers (SAMs) of molecules with bidentate anchoring groups	Investigating the binding nature of a "tripodal" anchor.
Research methods	STM-BJ	STM-BJ	STM-BJ	STM-BJ	XPS+ X-ray absorption	XPS, STM, et. al
Conclusions	methylthiothiophene/furan anchoring groups (with simple preparing procedure) are actually bidentate anchors	dithiocarbonate linking group can enhance conductance of conjugated organic oligomers as compared to the thiol linking group	this bidentate anchor enhances the electrical conductance of the molecular junctions by one order of magnitude as compared to monodentate anchor.	semi-reversible ligands can enable the single-molecule junction to reversibly switch between monodentate and bidentate contacts during compression and stretching processes	Molecules with more anchoring groups form SAM layer of better quality, especially for the series with pyridine-2,6-diyldimethanethiol anchor	OAE derivative can give homogeneous, densely packed, monolayer Langmuir–Blodgett (LB) film at Au surface with 'tripodal' anchor

S3. Typical G-D traces for TB, SMe-TB, and SMe-FB

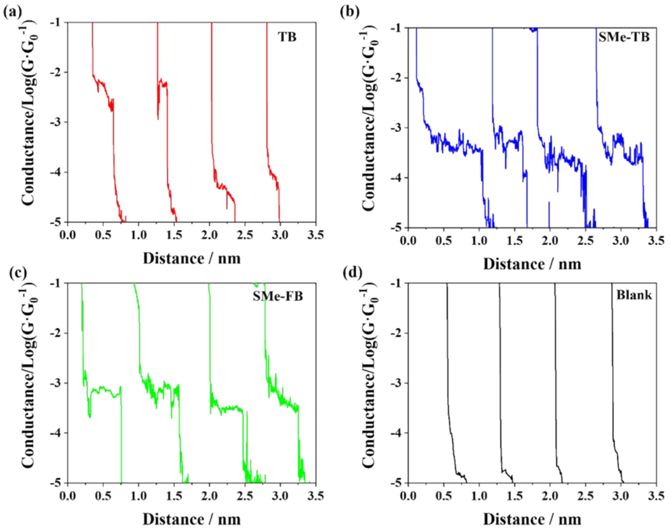

Figure S1 Typical conductance-displacement traces for (a) TB, (b) SMe-TB, (c)SMe-FB, and (d) blank

S4. 2D conductance−distance histogram and relative displacement distribution of TB

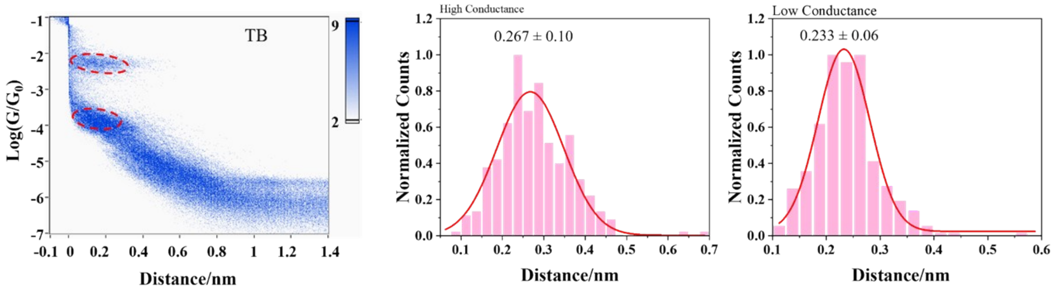

Figure S2 (a) The 2D conductance–distance histogram of TB (b) relative displacement distribution of TB

To gather more comprehensive information on the conductance signals, we generated a two-dimensional (2D) histogram of the combined G-D traces for TB. The plateau lengths were determined to be 0.233 nm for the G_l of TB, which is shorter than the plateau length observed for SMe-TB.

S5. binding energy (E_b) for SMe-TB and SMe-FB

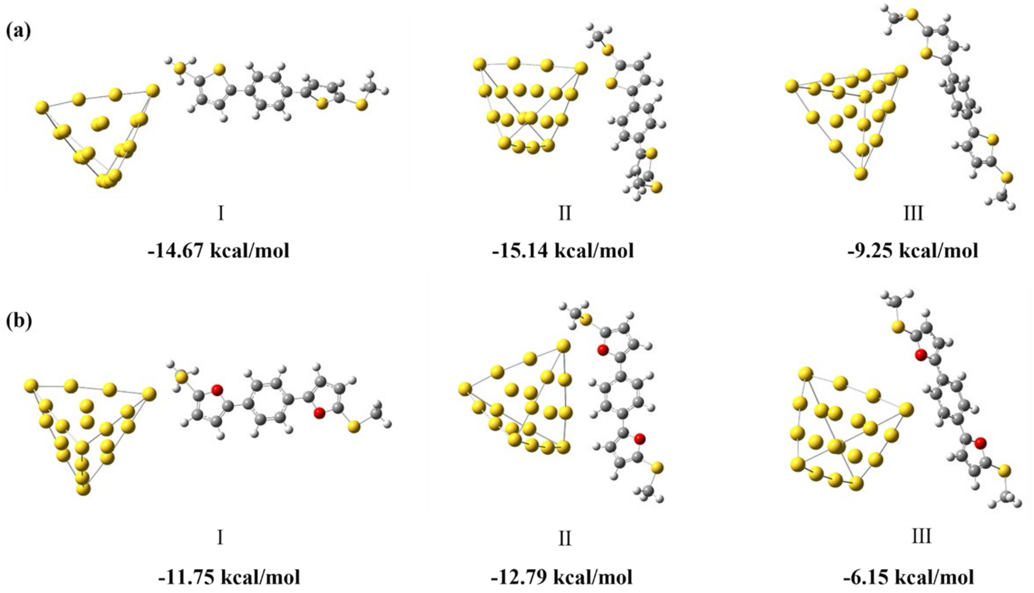

Figure S3. Binding energy (E_b) of several kinds of possible contact modes (I, II, and III) for (a) SMe-TB and (b) SMe-FB. I: only -SMe S interacting with Au, II: both two S or S/O atoms interacting with Au, III: only thiophene S or furan O interacting with Au

Through comparing the binding energy (E_b) of the studied configurations, we find that molecules using furan O or thiophene S to bind electrode (mode III) is much weaker than those using other two binding styles (mode I and II) that are likely responsible for the experimentally observed conductance signals. Especially for mode III of SMe-FB, the furan O lacks considerable binding ability to stabilize the gold electrode, consequently the gold atom is moved, poised to the center of the benzene ring in the optimized structure, with an interaction energy of -6.15 kcal/mol.

S6. X-ray photoelectron spectroscopy (XPS) tests of gold plate samples modified with TB, SMe-TB, or SMe-FB

We conducted X-ray photoelectron spectroscopy (XPS) tests of gold plate samples modified with TB, SMe-TB, or SMe-FB, respectively. Solution containing TB, SMe-TB, or SMe-FB with a concentration of 1 mM was dropped onto the Au plate (6*6 mm). After 12 hours, these samples were washed with anhydrous ethanol, dried by nitrogen flow before XPS test. It shows two $2p_{3/2}$ peaks at 161.56 eV, 162.23 eV for TB, resulting from thiophene S absorbed onto the gold surface as shown in Figure S4(a). More peaks are produced by SMe-TB, locating at 161.61 eV, 162.30 eV, and 164.04 eV in Figure S4(b). This is consistent with others' report which shows the gold surface modified with two kinds of S atoms simultaneously [6]. For SMe-FB, we can see the Au-S interacting peaks at 161.66 eV and 162.45 eV as depicted in Figure S4(c), corresponding to Au-S bonding. In addition to this, the peak at 531.83 eV in Figure S4(d) can be assigned to Au-O bond, as suggest by our previous report where O was used to bind to Au [7]. Thus, XPS result also shows that SMe-FB uses O and S to form molecular junction, consistent with our result obtained from conductance study.

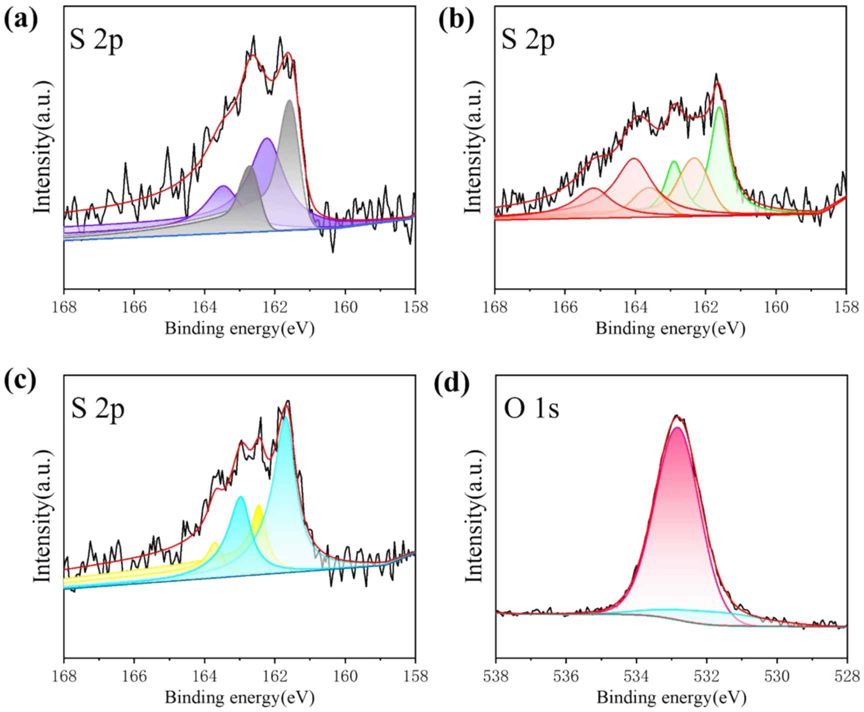

Figure S4. S 2p spectrum of (a) TB, (b) SMe-TB, and (c) SMe-FB adsorbed on Au, (d) O 1s spectrum of SMe-FB adsorbed on Au.

References

[1] Y. Xing, T.-H. Park, R. Venkatramani, S. Keinan, D. N. Beratan, M. J. Therien and E. Borguet, *Journal of the American Chemical Society*, 2010, **132**, 7946-7956.

[2] L. Herrer, A. Ismael, S. Martín, D. C. Milan, J. L. Serrano, R. J. Nichols, C. Lambert and P. Cea, *Nanoscale*, 2019, **11**, 15871-15880.

[3] N. Ferri, N. Algethami, A. Vezzoli, S. Sangtarash, M. McLaughlin, H. Sadeghi, C. J. Lambert, R. J. Nichols and S. J. Higgins, *Angewandte Chemie International Edition*, 2019, **58**, 16583-16589

[4] F. Sander, J. P. Hermes, M. Mayor, H. Hamoudi and M. Zharnikov, *Physical Chemistry Chemical Physics*, 2013, **15**, 2836-2846.

[5] E. Escorihuela, P. Cea, S. Bock, D. C. Milan, S. Naghibi, H. M. Osorio, R. J. Nichols, P. J. Low and S. Martin, *Journal of Materials Chemistry C*, 2020, **8**, 672-682.

[6] D. A. Beattie, I. M. Kempson, L.-J. Fan and W. M. Skinner, *International Journal of Mineral Processing*, 2009, **92**, 162-168.

[7] M. Huang, Q. Zhou, F. Liang, L. Yu, B. Xiao, Y. Li, M. Zhang, Y. Chen, J. He, S. Xiao and S. Chang, *Nano Letters*, 2021, **21**, 5409-5414.