

## *Supporting Information*

# Bias Voltage Controlled Electrode-Molecule Interface in Single-Molecule Junctions

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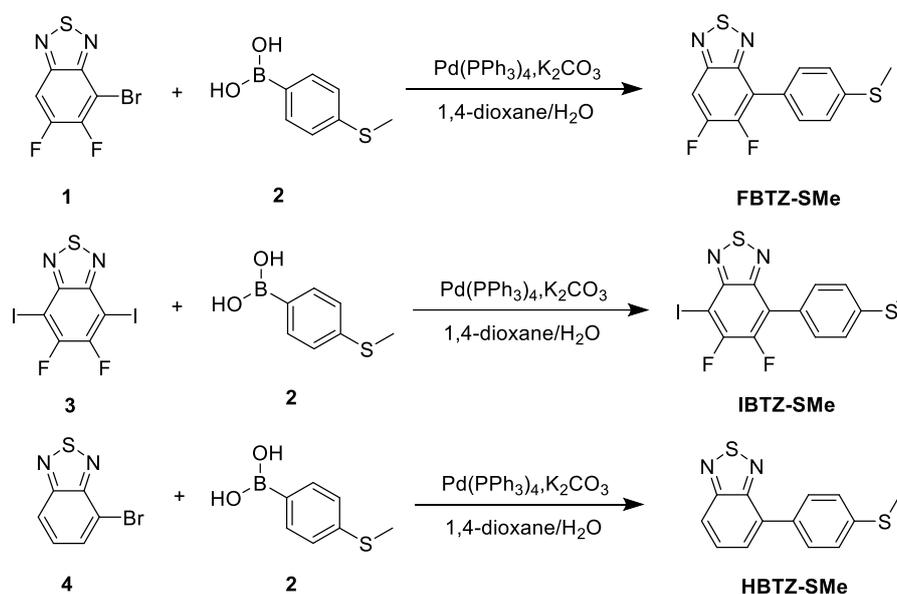
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## 1. General Information

All reactions were carried out under nitrogen atmosphere and anhydrous conditions unless otherwise indicated. The commercial reagents were purchased from Bidepharm, 9dingchem, Adamas-beta China and were used as received. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.20 mm silica gel plates using UV light as the visualizing agent. NMR spectra were recorded using a Bruker AVANCE III 400 MHz and 600 NMR MHz spectrometers. High-resolution mass spectra (HRMS) were recorded on a Waters GCT Premier TOF MS (EI).

## Molecular synthesis and characterization



**Scheme S1.** Synthetic routes for main intermediates and target products

**FBTZ-SMe:** 4-bromo-5,6-difluorobenzo[c][1,2,5]thiadiazole (**1**, 100mg, 0.40 mmol), 4-(methylthio)phenylboronic acid **2** (75.5 mg, 0.48 mmol), K<sub>2</sub>CO<sub>3</sub> (272.6 mg, 1.99 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (46 mg, 0.040 mmol) were added into 100 mL Schlenk tube under argon atmosphere. The degassed 1,4-dioxane (6 mL) and H<sub>2</sub>O (2 mL) were injected into the solution in sequence and stirred for 12 h at 100 °C. The crude product was extracted with DCM and washed with water. The solvent was concentrated by evaporation in a vacuum. The residue was further purified via chromatography on a silica gel column using DCM/PE=1:6 as eluent to give the product as yellow solid (83 mg, yield: 70.9%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.79 – 7.68 (m, 3H), 7.46 – 7.39 (m, 2H), 2.56 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 155.72 (d, J = 19.3 Hz), 153.15 (d, J = 19.3 Hz), 151.10 (d, J = 18.5 Hz), 150.90 – 150.56 (m), 148.54 (d, J = 18.6 Hz), 140.68, 130.87 (d, J = 2.9 Hz), 126.59 (dd, J = 2.7, 1.2 Hz), 126.09, 119.86 (d, J = 13.3 Hz), 104.69 (d, J = 21.2 Hz), 15.47. HRMS(EI): C<sub>13</sub>H<sub>8</sub>F<sub>2</sub>N<sub>2</sub>S<sub>2</sub> m/z [M]<sup>+</sup> calcd for 294.0097 found: 294.0099.

**IBTZ-SMe:** Yield: 60.5%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.71 (dd, J = 8.5, 1.3 Hz, 2H), 7.45 – 7.38 (m, 2H), 2.56 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 155.73 (d, J = 19.3 Hz), 153.16 (d, J = 19.4 Hz), 151.11 (d, J = 18.5 Hz), 150.88 – 150.57 (m), 148.55

(d,  $J = 18.6$  Hz), 140.69, 130.88 (d,  $J = 3.0$  Hz), 126.60 (dd,  $J = 2.7, 1.3$  Hz), 126.10, 119.86 (d,  $J = 14.9$  Hz), 104.69 (d,  $J = 21.3$  Hz), 15.48. HRMS(EI):  $C_{13}H_7F_2IN_2S_2$   $m/z$   $[M]^+$  calcd for 419.9063 found: 419.9067.

**FBTZ-SMe:** Yield: 70.7%.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.01 – 7.96 (m, 1H), 7.90 – 7.85 (m, 2H), 7.67 (dd,  $J = 4.9, 0.9$  Hz, 2H), 7.44 – 7.38 (m, 2H), 2.56 (s, 3H).  $^{13}C$  NMR (150 MHz,  $CDCl_3$ )  $\delta$  155.75, 153.56, 139.34, 134.09, 134.05, 129.78, 129.69, 127.37, 126.56, 120.52, 15.79. HRMS (EI):  $C_{13}H_{10}N_2S_2$   $m/z$   $[M]^+$  calcd for 258.0285 found: 258.0287.

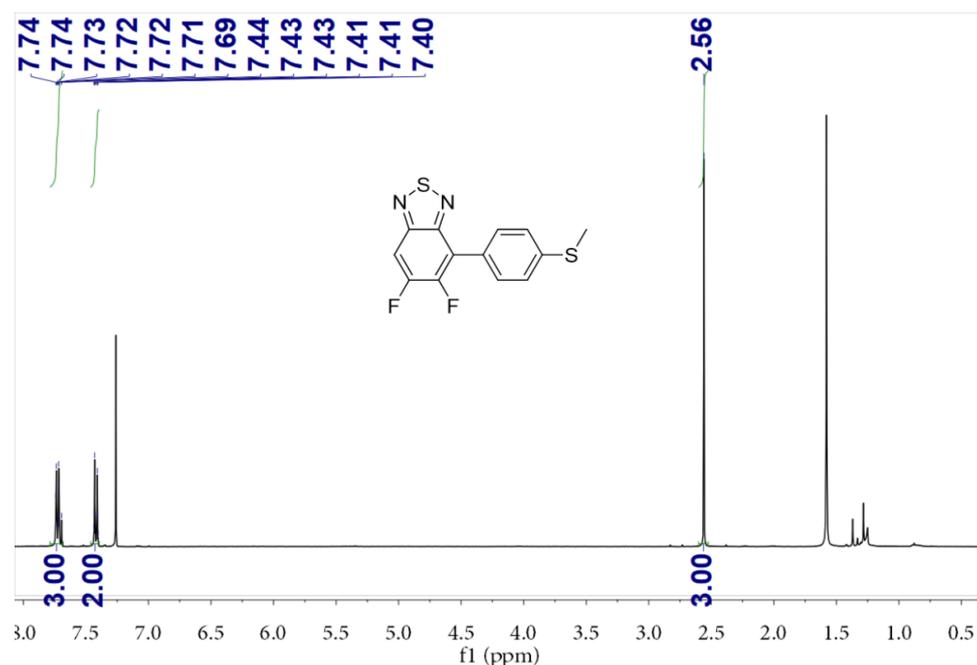


Figure S1.  $^1H$  NMR-spectrum (400 MHz,  $CDCl_3$ ) of FBTZ-SMe

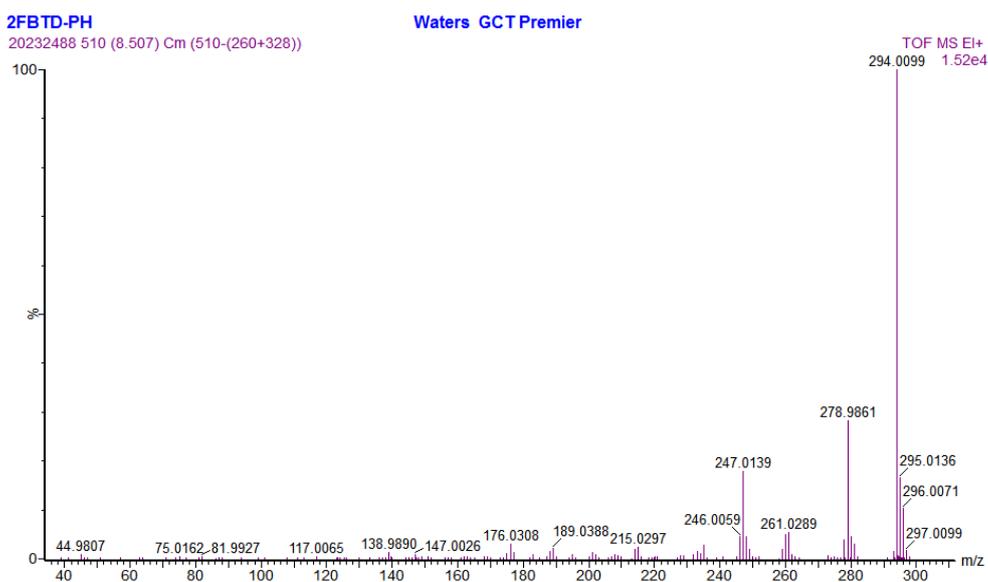


Figure S2. HRMS spectrum of FBTZ-SMe

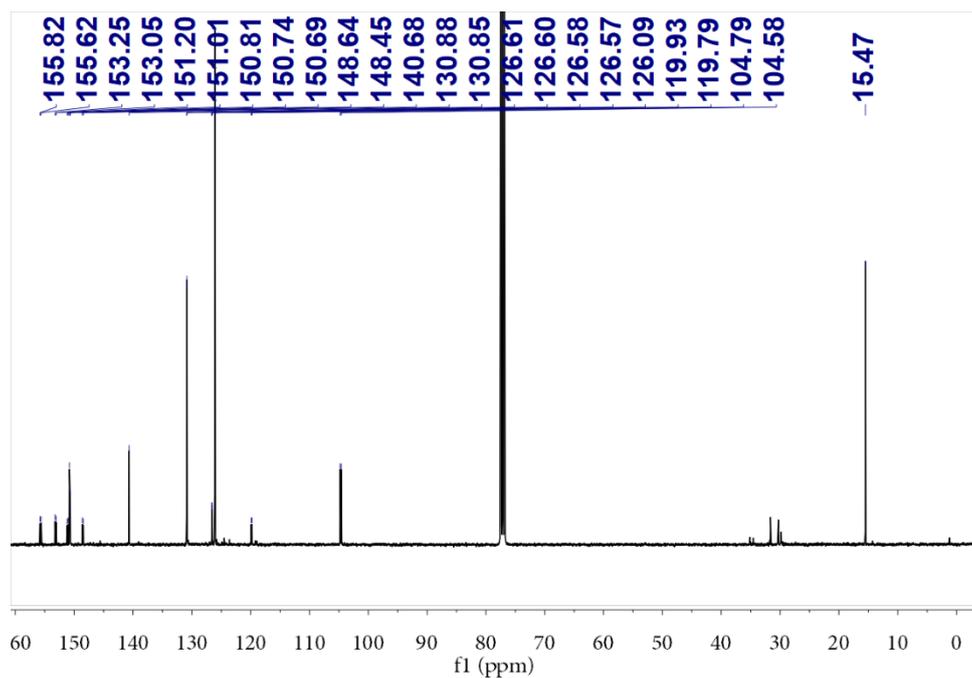


Figure S3.  $^{13}\text{C}$  NMR-spectrum (100 MHz,  $\text{CDCl}_3$ ) of FBTZ-SMe

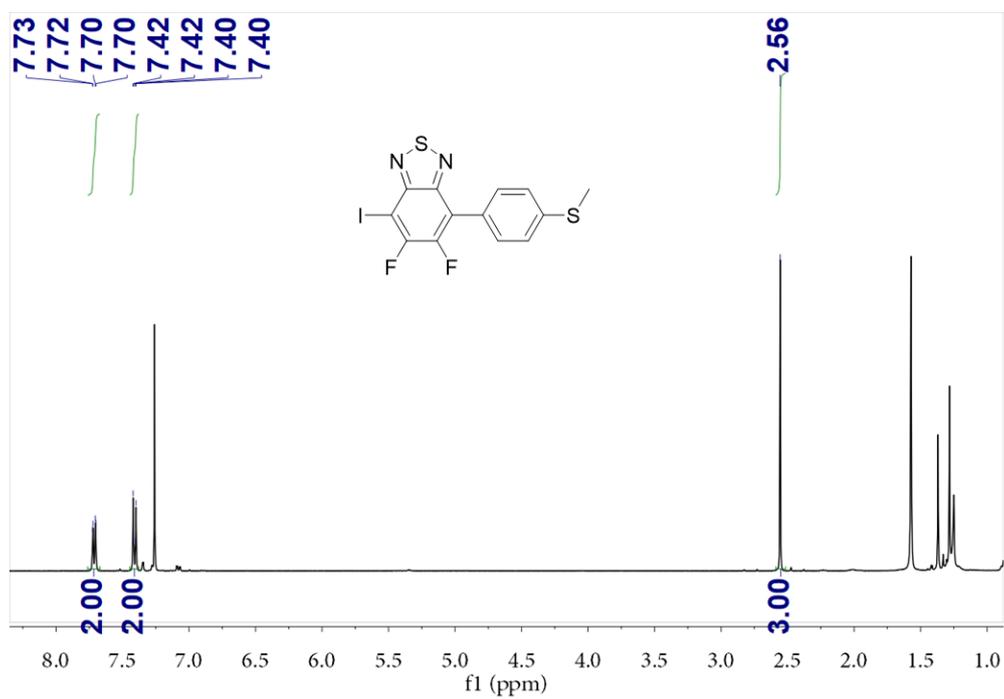
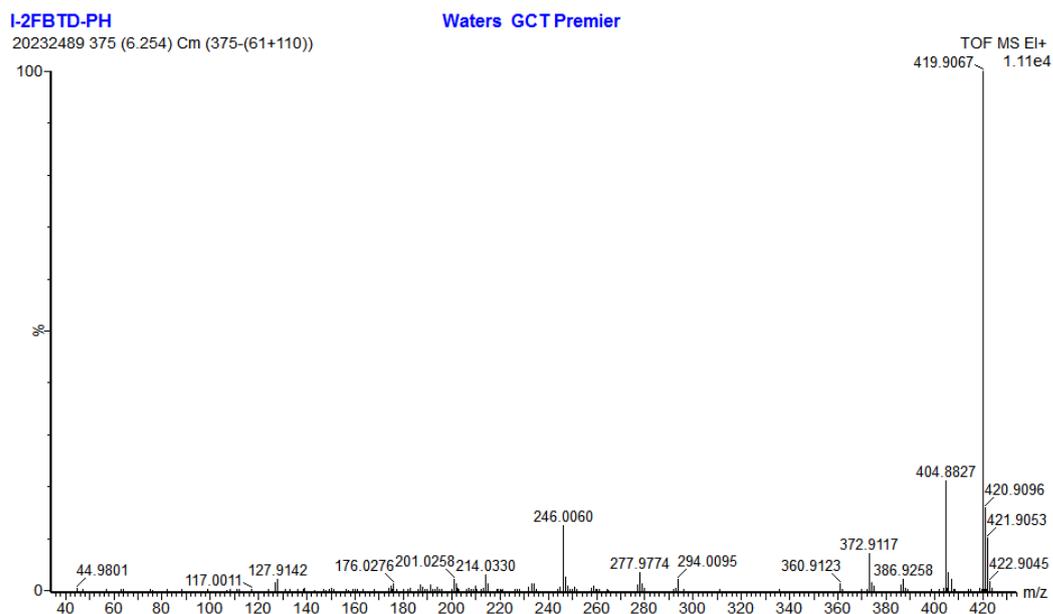
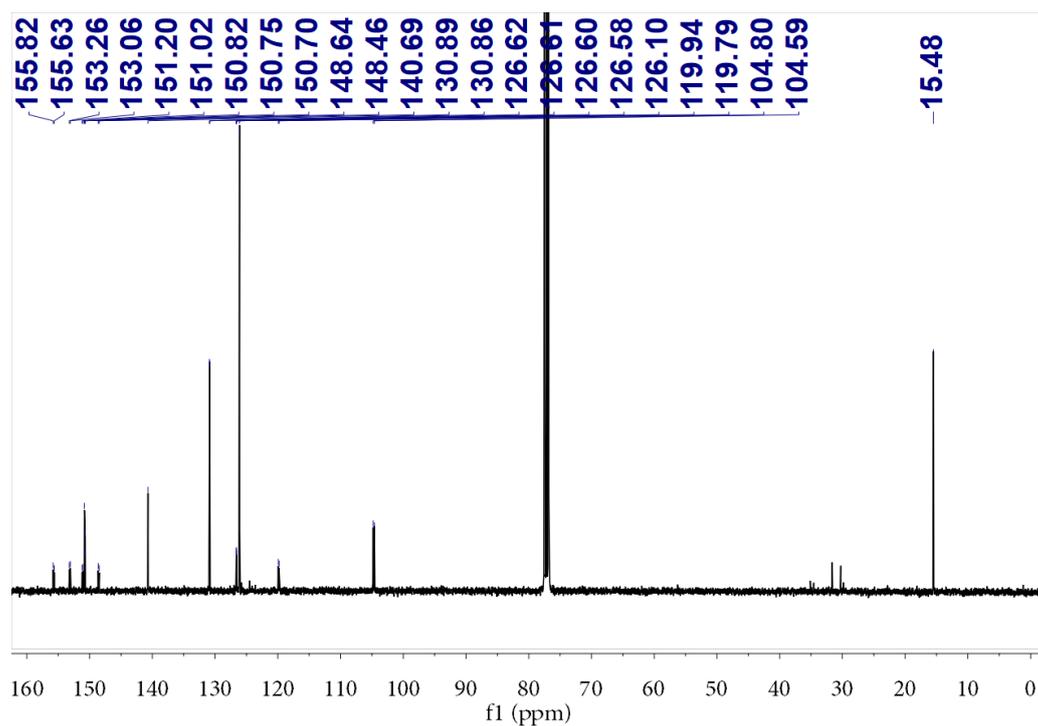


Figure S4.  $^1\text{H}$  NMR-spectrum (400 MHz,  $\text{CDCl}_3$ ) of IBTZ-SMe



**Figure S5.** HRMS spectrum of **IBTZ-SMe**



**Figure S6.**  $^{13}\text{C}$  NMR-spectrum (100 MHz,  $\text{CDCl}_3$ ) of **IBTZ-SMe**

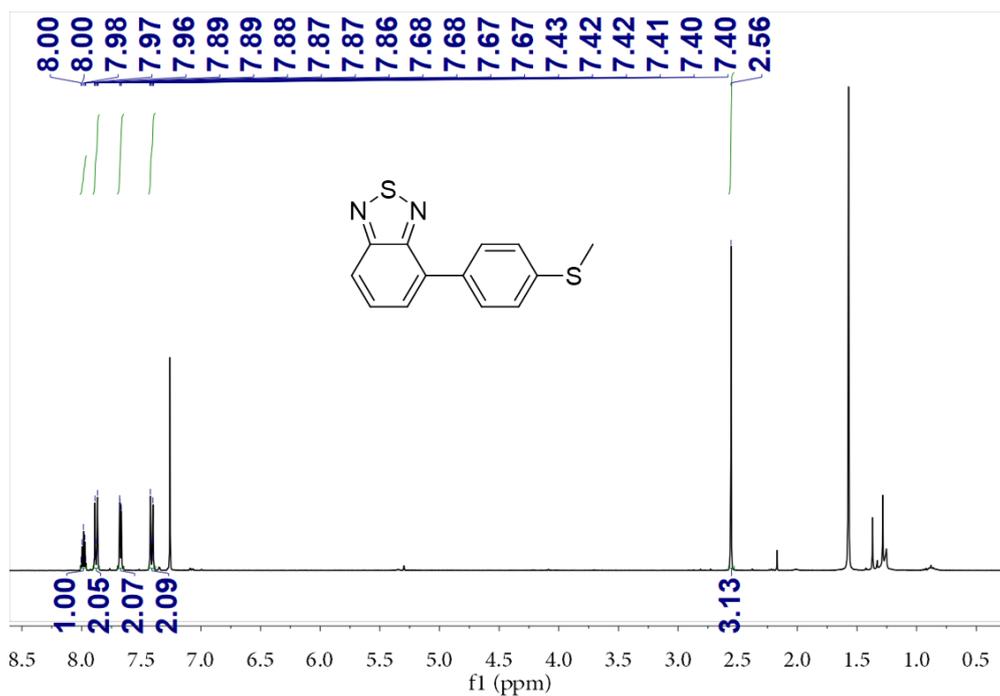


Figure S7.  $^1\text{H}$  NMR-spectrum (400 MHz,  $\text{CDCl}_3$ ) of HBTZ-SMe

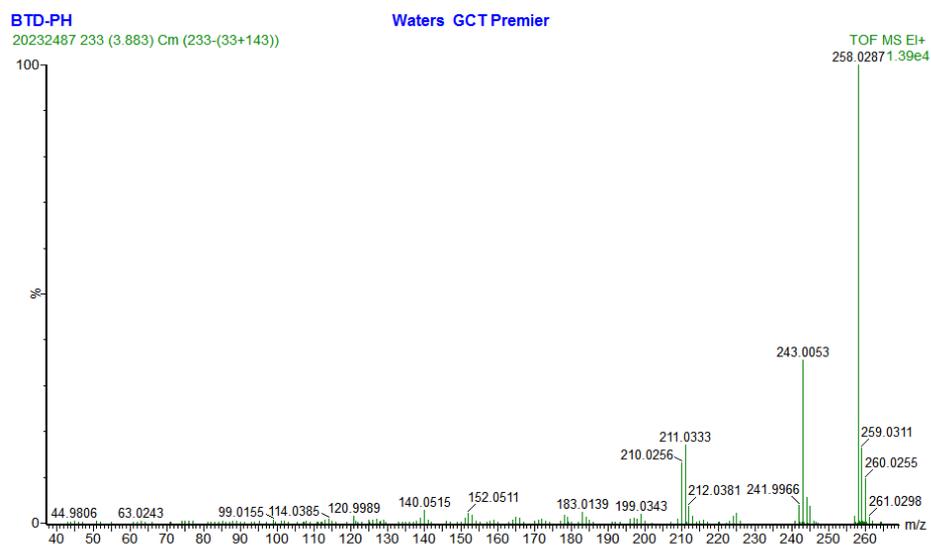
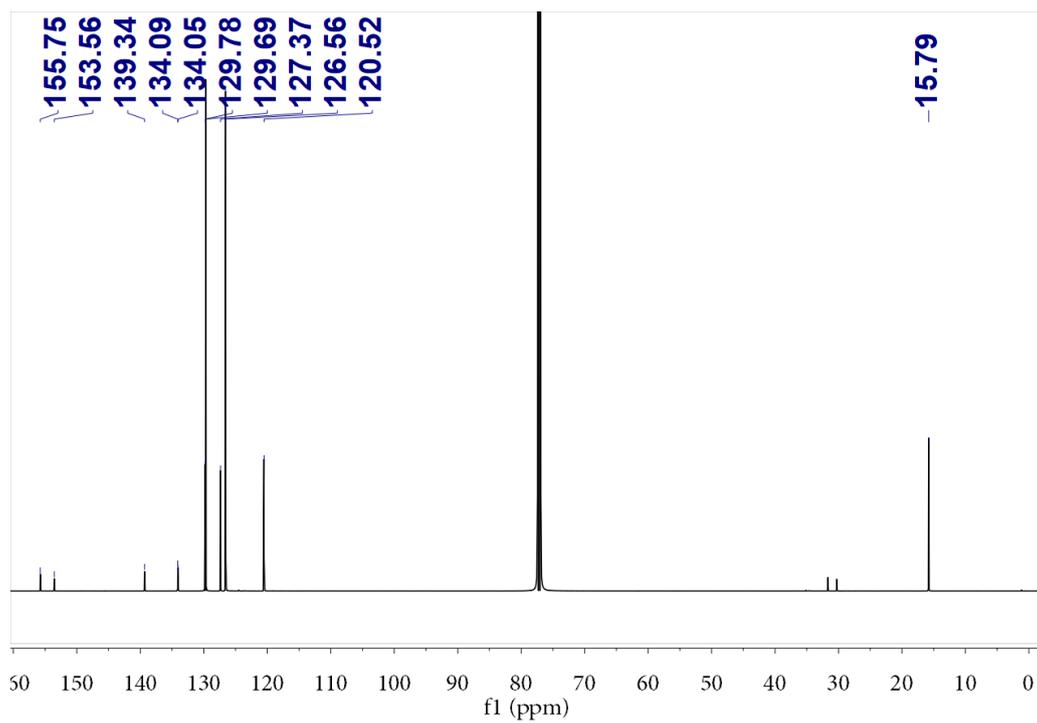


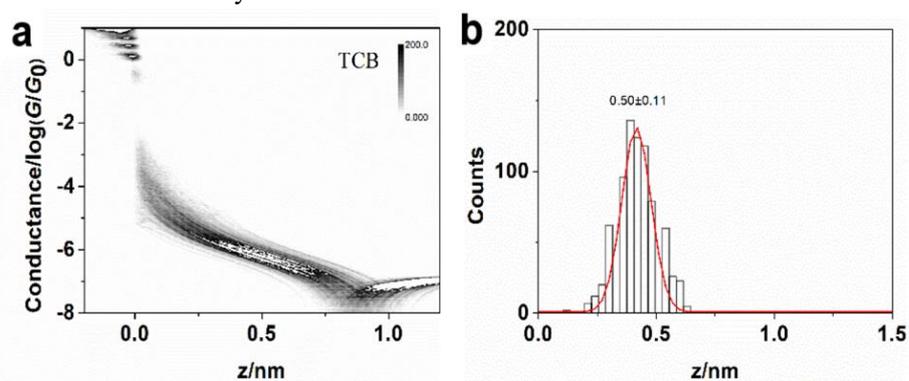
Figure S8. HRMS spectrum of HBTZ-SMe



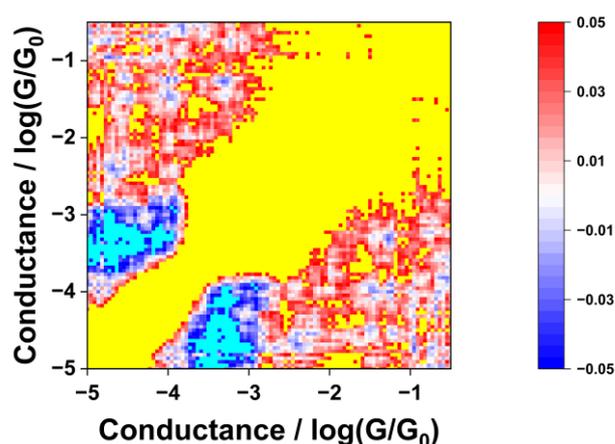
**Figure S9.**  $^{13}\text{C}$  NMR-spectrum (150 MHz,  $\text{CDCl}_3$ ) of **HBTZ-SMe**

## 2. Conductance measurements

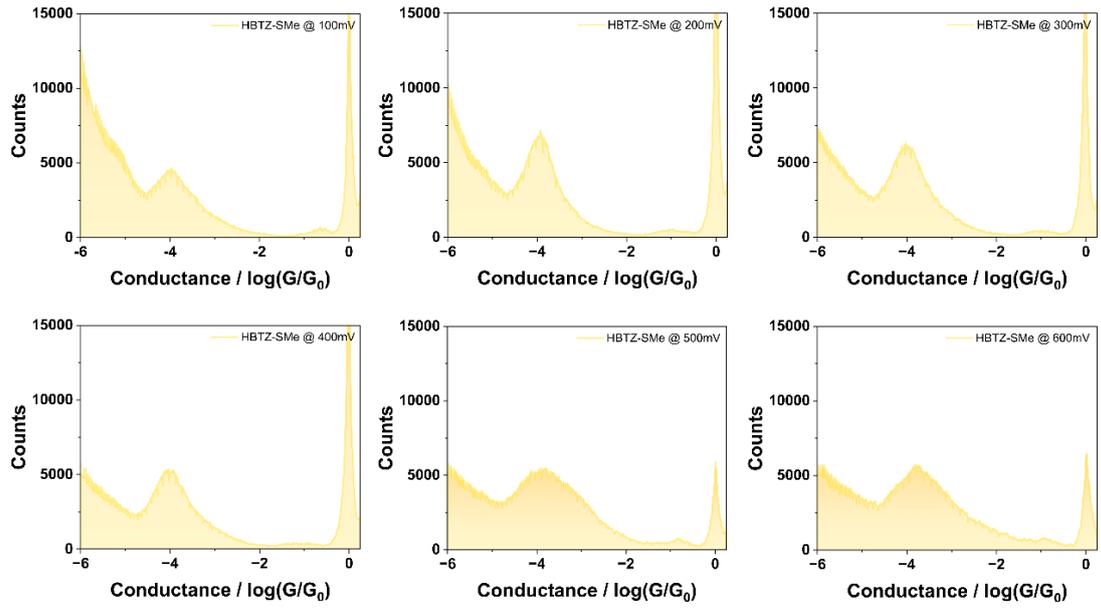
All the STM-BJ experiments were performed in TCB solution ( $\sim 0.2$  mM concentration) under ambient conditions at room temperature. During the conductance measurements, the Au tip (99.999% purity) and the substrate coated with a gold layer were used as the two electrodes. Under an applied tip bias voltage, the Au tip was driven to move in and out of contact with the substrate to form and break molecule junctions. During this process, the current was recorded continuously and the conductance was calculated by the formula  $G = I/V$ . One-dimensional conductance histograms and two-dimensional conductance histograms were constructed by compiling  $>3000$  collected conductance traces without any data selection.



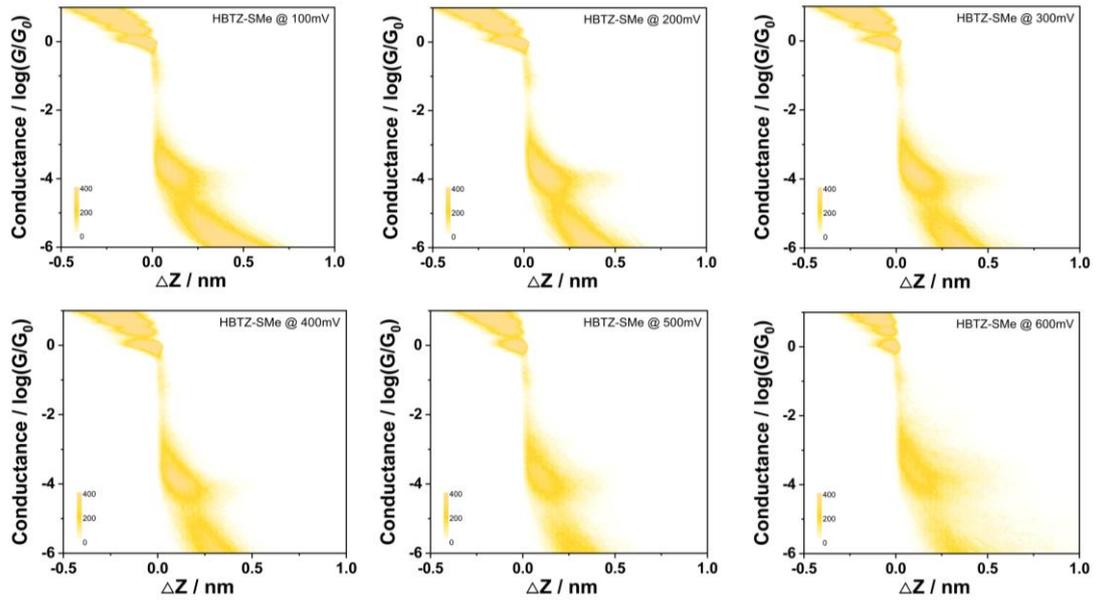
**Figure S10.** (a) Two-dimensional conductance histogram of blank solvent. (b) Relative displacement distribution. The conductance ranges to determine the relative displacement distribution are from  $10^{-0.3}$  to  $10^{-6.0} G_0$ . No obvious conductance peak signal was found in the blank solvent measurement. The stretching distance is  $\Delta Z = 0.50 \pm 0.11$  nm (the error is the standard deviation), corresponding to the gold snap-back distance.



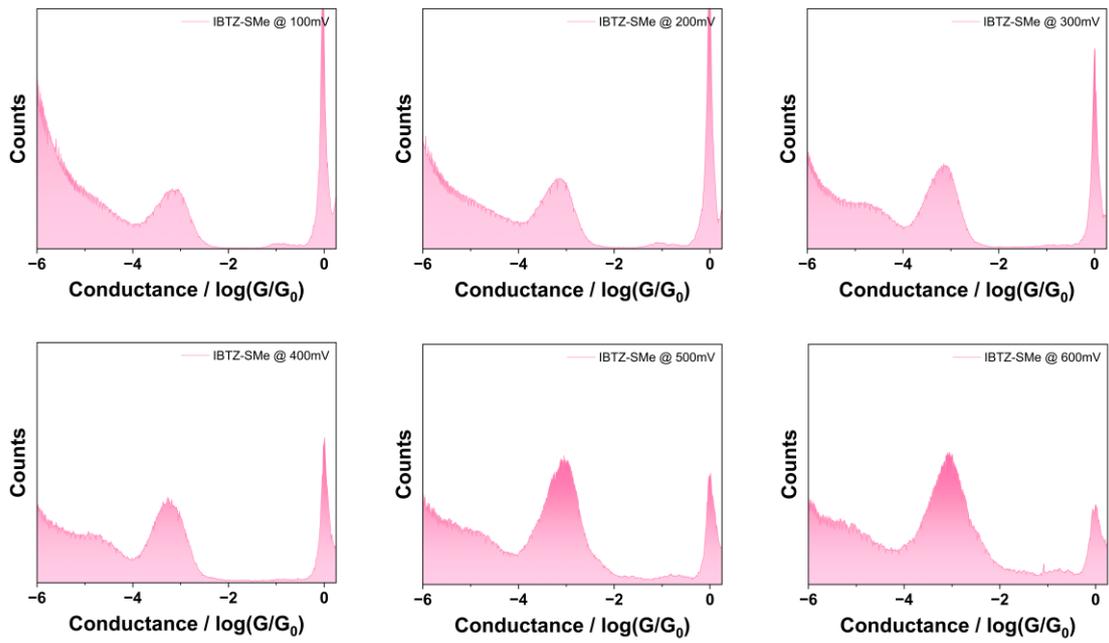
**Figure S11.** 2D covariance histogram of FBTZ-SMe under 400 mV constructed from 4100 conductance–displacement traces



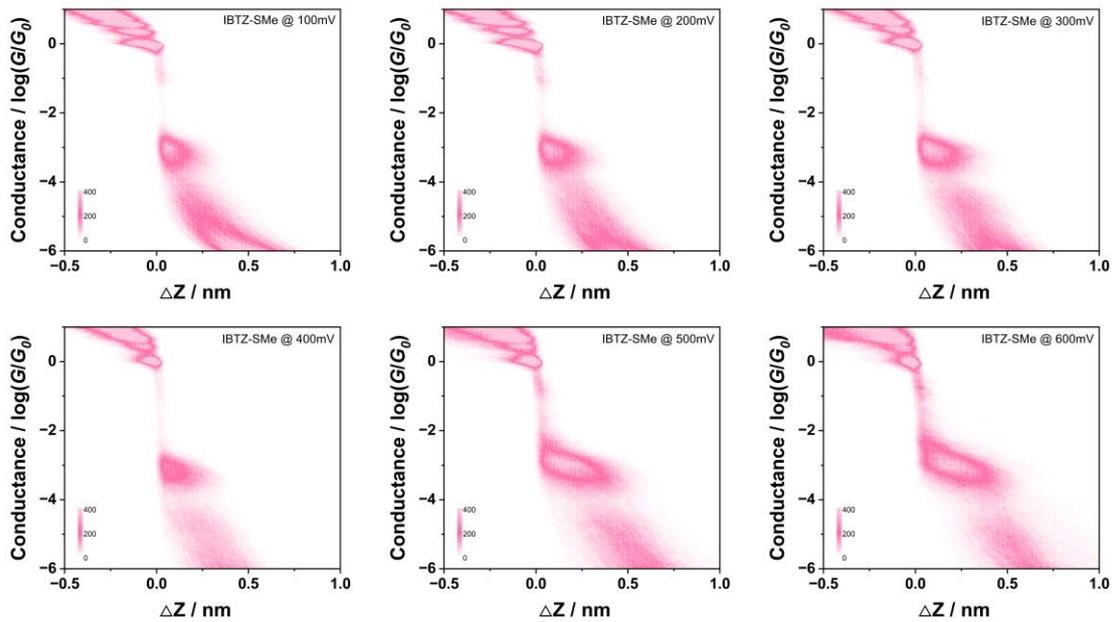
**Figure S12.** 1D conductance histograms of **HBTZ-SMe** under the bias voltage ranging from 100 to 600 mV.



**Figure S13.** 2D conductance histograms of **HBTZ-SMe** under the bias voltage ranging from 100 to 600 mV.



**Figure S14.** 1D conductance histograms of IBTZ-SMe under the bias voltage ranging from 100 to 600 mV.



**Figure S15.** 2D conductance histograms of IBTZ-SMe under the bias voltage ranging from 100 to 600 mV.

### 3. DFT calculation

The molecular devices used in the electron transport simulations are calculated with a combination of DFT and nonequilibrium Green's function (NEGF), using the Quantum ATKQ-2022.03 package. The surface of the gold electrode was cut into a pyramid structure. In the initial configuration of the device, the S atom and the C atom of fluorine substituted arenes acting as the anchoring group was attached to the gold atom at the top of the pyramid. The distance between the S atom and the gold atom of the electrode was controlled at about 2.6 Å, the N atom and gold atom was set about 2.2 Å, and the C atom and the gold atom was set at about 2.1 Å. Then the devices were sent to Quantum ATK for geometry optimization. The FHI pseudopotential with a double- $\zeta$  basis set was used for Au atoms, and the PseudoDojo pseudopotential with a medium basis set was used for other atoms. A real-space grid with an equivalent energy cutoff of 80 Hartree and the k-points of 3, 3, 134 was used for geometry optimization, and the force threshold is 0.05 eV/Å. The transmission spectrums with the bias voltage ranging from -1 to 1 V were calculated, transverse k points are set to 7, 7.

The binding energies were conducted using the Gaussian 09 suite of the program<sup>1</sup>. The molecules investigated were fully optimized and calculated by the hybrid meta exchange-correlation M06-2X functional including empirical dispersion corrections DFT-D3 method<sup>2, 3</sup>, and were performed using the tight convergence criterion, which was always followed by the calculation of harmonic vibrational modes. The M06-2X functional has been demonstrated to be dependable for formation of Au-C bond via numerous benchmark calculations<sup>4</sup>. We adopted the LANL2TZ basis sets<sup>5</sup> for Au atoms and the 6-311G (d,p) basis sets<sup>6</sup> for hydrogen, carbon, oxygen, fluorine and sulfur atoms. To simulate the action of the electric field, we applied a field strength of  $E_F = +0.002$  a.u. (about 1.03 V/nm) along the initial direction of C-Au and N-Au bond. All basis sets are obtained from the Basis Set Exchange library.