Charge Transport of Fluorinated Tetracyanoquinodimethane with Different Electronic States in Single-Molecule Junction

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Materials and instruments

Unless otherwise stated, all the chemicals were obtained from a commercial supplier (Adamas) and used without further purification. The UV-Vis spectra were obtained using SHIMADZU UV-3600Plus instruments in acetonitrile solution. Single molecule conductance measurements were carried out using Xtech STM-BJ instrument, and the data was analyzed using XMe open-source code. Bu_4NF_4TCNQ and $(Bu_4N)_2F_4TCNQ$ were synthesized according to reported literature (*Nat. Mater.* **2019**, *18*, 149-155).

Conductance measurement of single-molecule junctions

The single-molecule conductance was measured in 1,2,4-trichlorobenzene (TCB) solvent. The concentration of F4TCNQ was 0.1 mM. The Au substrates were prepared by slow evaporation of ~50/150 nm Cr/Au at 1 Å s^{-1} onto a silicon wafer. In STM-BJ measurement, the Au tip was controlled firstly by a stepper motor to obtain the approximate position to contact the substrate (less than 1 μm); thereafter the tip is controlled by a piezo stack under the voltage of 0.1 V, with the approach/retract speed of 16 nm/s. During breaking and forming junctions process, the bias is kept at 100 mV, the real-time conductance is recorded using a custom-built I-V converter with a sampling rate of 20 kHz. During the test process, the contact between Au tip and Au substrate was repeatedly formed and broken.

Calculation details

The calculations were conducted using the ATK software package with non-equilibrium Green's functions (NEGF). The junctions were divided into three regions: the left electrode (L), the central region (C), and the right electrode (R). The central region is often named as scattering region due to the charge carriers between the left and right electrodes scattering in this region. In our calculations, the three-layer Au (111) electrodes were selected as left and right electrodes. The central region includes the investigated molecule sandwiched between two five-layer Au (111) -(4 × 4) surfaces, where the molecule is connected to the Au atoms by CN-Au bonds. The generalized gradient approximation (GGA) of the exchange and correlation functional is the Perdew-Burke-Ernzerhof parameterization (PBE), the single-zeta polarized (SZP) basis set was employed for Au atoms and the double-zeta polarized (DZP) basis sets were used for other atoms. The k-point sampling was set to 2 × 2 × 150.

Figure. S1a-c shows the optimized structures of junctions containing F4TCNQ, where the terminal CN anchors bind to Au pyramid electrodes. The optimized junction structures are further used in energy dependent transmission function calculations. The energy-relative transmission spectra were calculated at zero bias with the k-point sampling of 7 × 7. The molecular orbital energy was obtained relative to the Fermi level of Au (111) electrode.

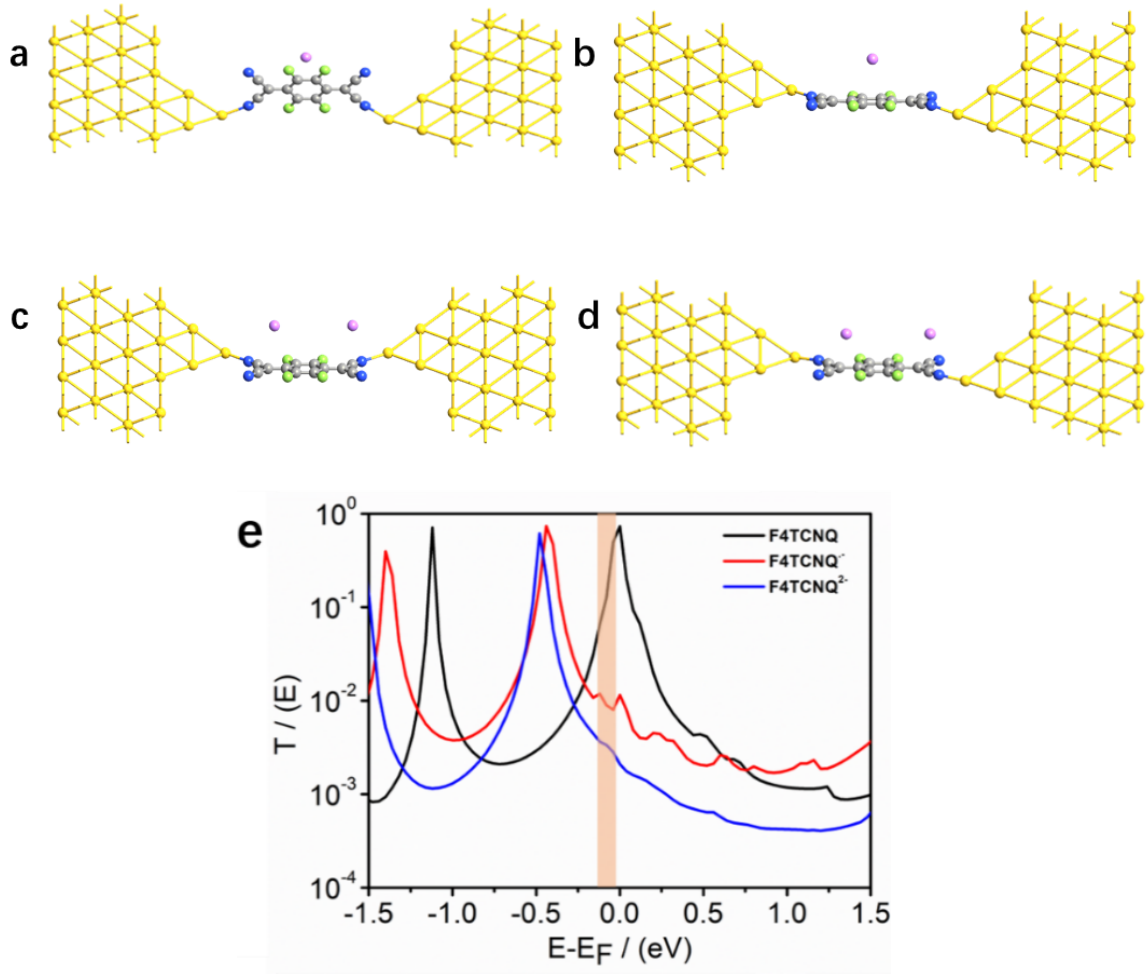

Fig. S1. Schematic of $F4TCNQ^{\cdot-}$(a-b) and $F4TCNQ^{2-}$(c-d) bound to Au electrodes by the same side anchoring and opposite side anchoring. Brown, blue, green, purple and gold spheres represent C, N, F, Li and Au atoms, respectively. (e) Transmission curves of F4TCNQ, $F4TCNQ^{\cdot-}$ and $F4TCNQ^{2-}$ with the opposite side anchoring.

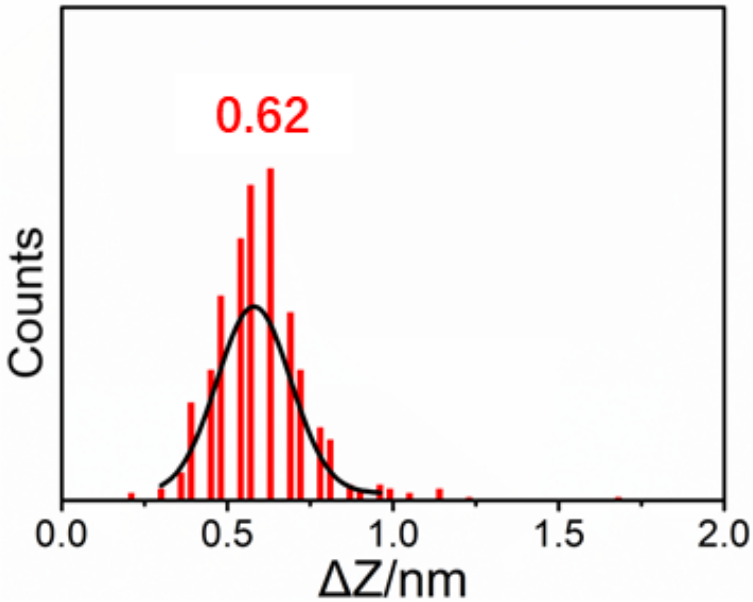

Fig. S2. The relative-displacement distribution for LG state of neutral F4TCNQ junction.