

Supplementary Information

Mechanism Study of Molecular Deformation of 2,2',5',2''-tetramethylated p-terphenyl-4,4''-dithiol Trapped in Gold Junctions

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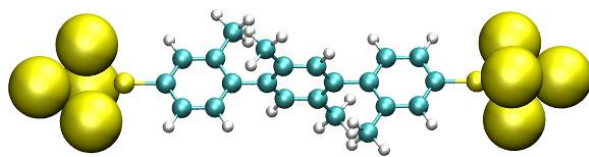


Figure S1. The Au₄-**1**-Au₄ junction model for Raman simulations.

To evaluate the possibility of the charge injection onto the trapped molecules, we optimized the Au₄-**1**-Au₄ junction as a whole system by varying the charge states from -6 to +6. We found that D_{IPT} hardly changes and the net charges are almost injected onto the electrodes. Furthermore, we found that the ionization potential and electron affinity for **1** molecule is 8.09 and 10.92 eV, which is also very hard to realize in experiment. The hard injection of charges can be attributed to the strong bonding between the molecule and the electrodes, which has also been proven by many researches (phys. stat. sol. (b) 245, No. 8, 1455–1470 (2008); Chem. Soc. Rev., 2015, 44, 902—919; J. Phys. Chem. B 2002, 106, 8306-8312; J. Phys. Chem. B 2000, 104, 5661-5665).

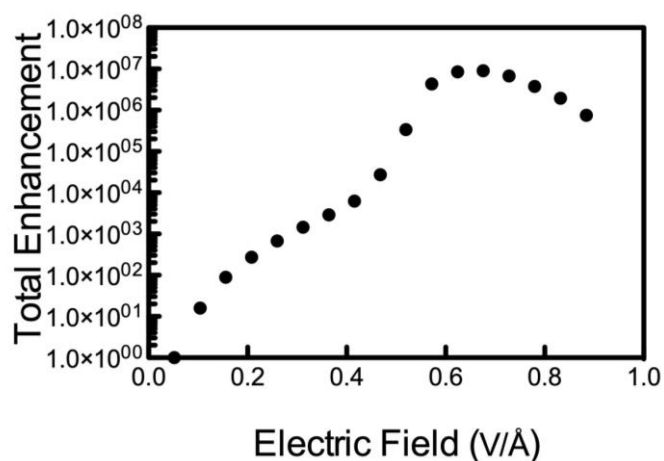


Figure S2. The total Raman enhancement factor for **1** molecule under different electric fields by multiplying chemical and physical (electromagnetic) enhancement factors.

The total enhancement was obtained by multiplying chemical and physical (electromagnetic) enhancement factors, as shown in [Figure S2](#). We can see that the Raman enhancement can reach to 10^7 , which agrees well with traditional SERS or TERS experimental observations.

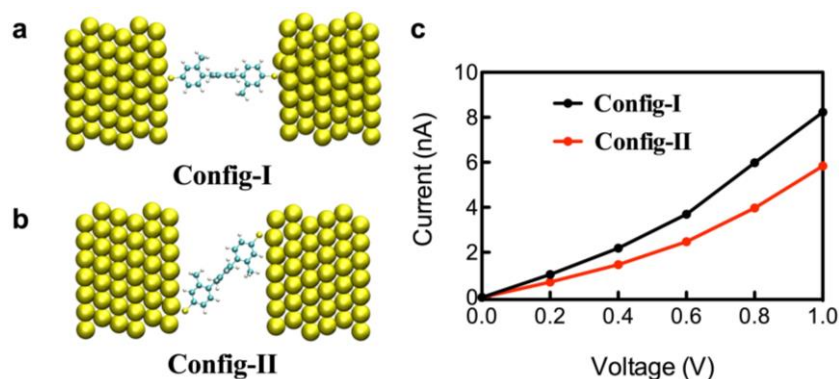


Figure S3. (a,b) The optimized geometries of Au-1-Au junctions with different electrode distance (named Config-I and Config-II hereafter). (c) The comparison of I-V properties for Config-I and Config-II.

It is well known that the orientation and position of the molecule relative to the electrode will largely affect the properties of the junction. As a result, we compared the properties of two junctions with different electrode distance: 19 v.s. 15 Å (named as Config-I and Config-II hereafter, shown in [Figure S3a](#) and [S3b](#)). Geometrical optimization shows that a tilting configuration is obtained in Config-II, compared to the perpendicular configuration in Config-I. Furthermore, we found that the current value of Config-II is a little smaller than that of Config-I at the same voltage ([Figure S3c](#)). This phenomenon can be attributed to the fact that sulfur adsorbs on bridge sites in Config-II while hollow sites in Config-I.

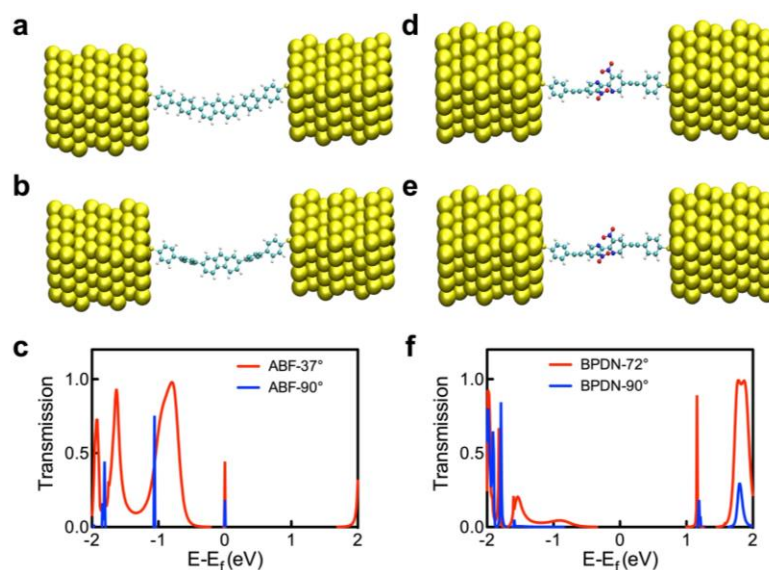


Figure S4. (a,d) The fully optimized geometries of 2,7-bis(4'-amino[1,1'-biphenyl]-4-yl)-9H-fluoren (ABF) and bipyridyl-dinitro oligophenylene-ethynylene dithiol (BPDN) single-molecule devices. (b) Optimized structures of ABF with the dihedral between the fluoren and the nearby phenyl groups set to 90 °. (e) Optimized structures of BPDN with the dihedral between the two central pyridyl-dinitro groups set to 90 °. (c,f) Transmission spectra for (a,b,d,e) structures.

We studied the charge transport properties of 2,7-bis(4'-amino[1,1'-biphenyl]-4-yl)-9H-fluoren (ABF) and bipyridyl-dinitro oligophenylene-ethynylene dithiol (BPDN) single-molecule devices. [Figure S4a](#) and [S4d](#) show the fully optimized geometries of ABF and BPDN molecular junctions. For ABF, the dihedral between the fluoren and the nearby phenyl groups was found to be 37 °. Then this dihedral was constrained as 90 ° and the optimized structure is shown in [Figure S4b](#). Similarly, the dihedral between the two central pyridyl-dinitro groups for BPDN was found to be 72 °. Then we optimized BPDN by fixing this dihedral at 90 ° (shown in [Figure S4e](#)). Charge transport calculations show that internal dihedral angle rotation largely affects the charge transport properties. Smaller dihedral angles make the transmission peak close to Fermi level and bring high transmission peaks, which will enlarge the corresponding conductance. This conclusion agrees well with our investigation on **1** and **2** molecules.