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Supplementary information

Modulating electron transport through single-molecule junctions by heteroatom substitution

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1. Single-molecular conductance of M_S

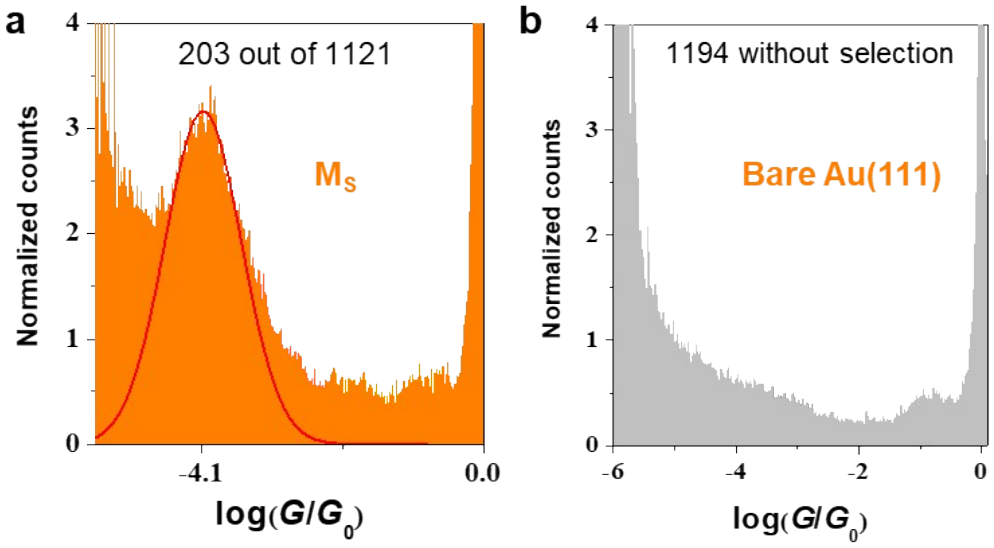

Fig. S1 one-dimensional conductance histograms of (a) M_S with data selection (203 out of 1121) and (b) bare Au (111) without any data selection, the counts are normalized by the number of conductance curves.

In order to confirm the conductance value of 4,4'-diaminodiphenyl sulfide (M_S), we objectively select the conductance traces with step features, and 203 out of 1121 curves (~18 %) are used to construct the conductance histogram shown in Fig. S1a, an obvious peak at $10^{-4.1}$ G_0 is consistent with the conductance value of M_S in Fig. 2c without any data selection. And this low probability of forming the single-molecule junctions might arise from the thioether in the backbone that could bind to Au.[1] Besides, the formation of amine-thioether junctions could still be seen in conductance histogram at ~ 10^{-2} G_0 (Fig. S1a). Furthermore, the controlled experiment without molecules on Au (111) exhibits no peaks and background at $10^{-4.1}$ G_0 in Fig. S1b. Thus it's reasonable to assign the broad conductance peak to M_S in Fig. 2c.

2. The two-dimensional conductane histgoram

It's reported that the most probable absolute distance z* for the stretching of molecular junctions [2, 3] could be described as:

$$z^* = \Delta z^* + 0.5 \text{ nm},$$

where the Δz^* is stretched distance determined from the plateau distribution in every conductance curve, and 0.5 nm is the snap back distance for Au electrode upon breaking Au contacts. We have analyzed the Δz^* of those molecular junctions obtained from $10^{-5.0}$ G_0 to $10^{-0.3}$ G_0 (0.5 G_0) in every conductance curve and the two-dimensional conductance histograms are shown in Fig. S2, around 0.3 nm was found for all molecules, indicating that molecular junctions break at a similar length. Thus the absolute distance is ~ 0.8 nm, which is comparable with the ~ 0.97 nm distance between two $-NH_2$ groups of M_C, M_O and M_S obtained from the optimized molecule structures in Fig 1b.

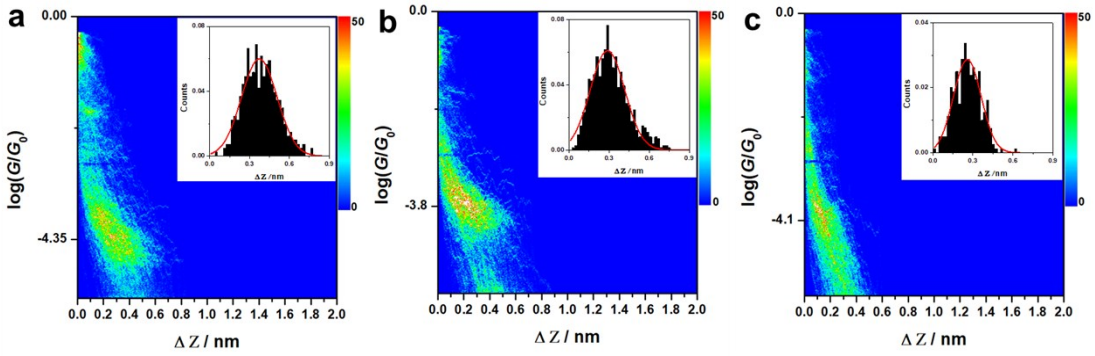

Fig. S2 The two-dimensional conductance histograms of (a) M_C, (b) M_O and (c) M_S , and insert panels are stretching distance distributions obtained from $10^{-5.0}$ G_0 to $10^{-0.3}$ G_0 (0.5 G_0) in every conductance curve and the counts were normalized by the numbers of conductance curves.

3. The impact of torsion angles of biphenyl rings on conductance

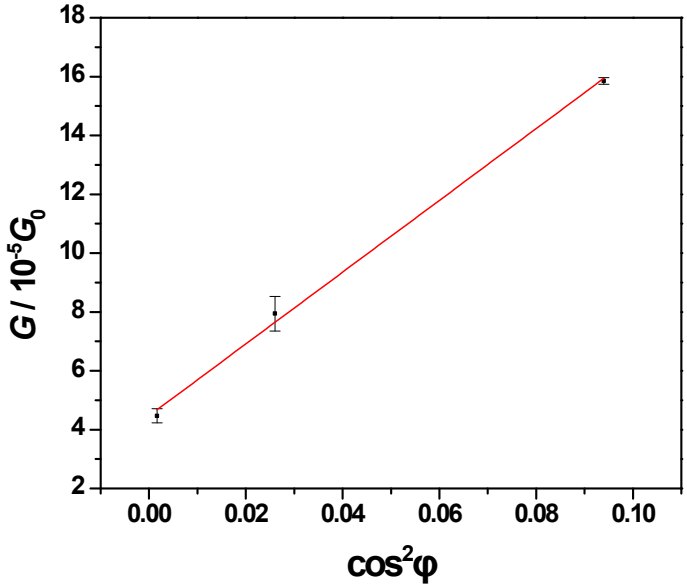

Fig. S3 The conductance of M_C, M_O and M_S vs. $\cos^2\varphi$, where φ is the torsion angle of biphenyl rings.

It's reported that the molecular conductance of biphenyl derivatives depends on the torsion angle φ between two phenyl rings. [4, 5] As φ increases from 0° (flat) to 90° (perpendicular), the conductance value goes down because of weakening π-π coupling, and DFT calculations also reveal that the junction conductance *G* is proportional to $\cos^2\varphi$ for non-resonance electron tunneling. We plot the conductance of M_C, M_O and M_S vs. $\cos^2\varphi$, a good linear fit is observed in Fig. S3.

4. The proceduces for conductance measurement

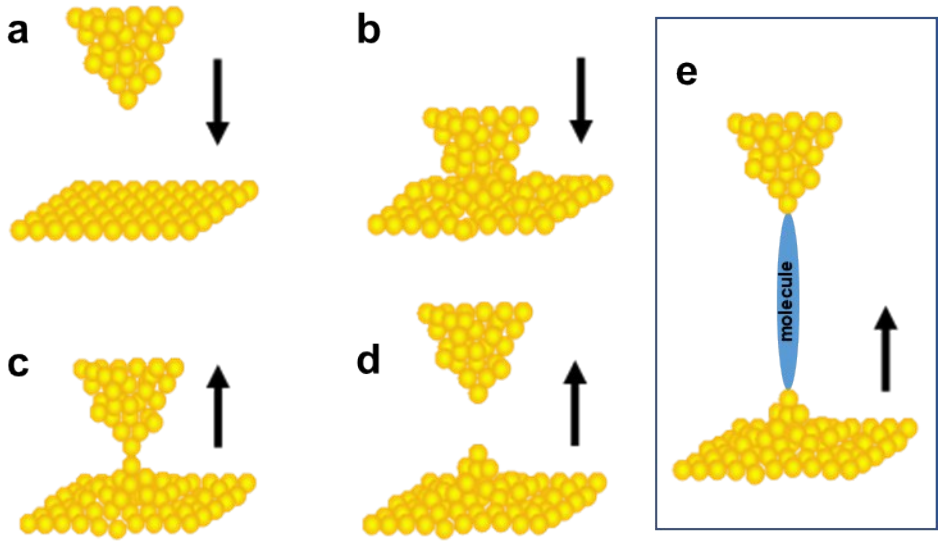

Fig. S4 (a) STM tip approaches to the substrate, (b) Tip contacts the substrate with the tip current reach the pre-setpoint, (c) Tip withdraws from the substrate with a given speed and nanowire between the tip and substrate is formed. (d) The nanowire is broken. (e) The metal-molecule-metal junction is formed after the broken of the nanowire.

References

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