Electronic Supplementary Information

Tuning the binding configurations of single-molecule junctions by molecular co-assembly

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Experiments and methods

Raman measurements

55 nm Au nanoparticles were prepared according to Frens' method,[1] namely, 1.5 mL of 1 wt% sodium citrate solution was quickly added into 200 mL of 0.01 wt% boiling $HAuCl_4$ solution. Then the mixture was refluxed for 20 min to obtain the spherical nanoparticles. The 55 nm Au@ ca. 2 nm SiO_2 nanoparticles were prepared according to the previous report[2]: 0.4 mL of 1 mM (3-Aminopropyl) trimethoxysilane (APTMS) solution was dropwise added into 30 mL of the as-prepared Au solution, and the mixture was stirred for 15 min at room temperature. Next, 3.2 mL of 0.54 wt% sodium silicate solution was quickly added to the solution. Finally, the solution was transferred to 99°C bath and stirred for 30 min for the coating of a silica shell with a thickness of about 2 nm. The 1.5 mL of hot solution was cooled in an ice bath to stop the reaction immediately, then were centrifuged at 4500 rpm twice and washed with Milli-Q water for the Raman measurements. The Raman experiments were carried out on a confocal microscope Raman system (Renishaw InVia). The excitation wavelength was 633 nm, and a 50× microscope objective with a numerical aperture of 0.55 was used.

STM breaking junction measurements

Conductance measurement was carried out on a modified Nanoscope IIIa STM (Veeco, US). Au wire (0.25 mm diameter,99.999%) was used to make STM tip, and Au (111) was used as the substrate. The tip was insulated by thermosetting polyethylene to reduce Faraday current at several pA level. Before each experiment, the substrate was polished by electrochemical method and annealed with butane gun. We carried out the conductance measurements in different concentrations of 1-ethylimidazole (EIM) containing 0.1 mM sample molecule at room temperature. The procedure of STM-BJ method is briefly described as follows. Firstly, the tip is driven toward the substrate to reach conductance value more than several G_0, then the tip is pulled away from the substrate at a constant speed of 20 nm/s. During the process, molecular junctions can be formed. Meanwhile, the current of the tip is recorded at a sampling rate of 20 kHz.

Thousands of tip current curves are collected to construct the conductance histogram without data selection. The conductance measurement is carried out at a bias voltage of 100 mV.

Computational models and methodology

The density functional theory (DFT) calculations were performed by the Vienna *ab initio* simulation package[3] (VASP). The electron exchange and correlation was described by the generalized gradient approximation (GGA) with the Perdew, Burke, Ernzerhof (PBE)[4] functional. The ionic cores were represented by projector augmented wave (PAW) potentials with a cutoff energy of 400 eV. According to our previous study[5], a lattice cell of three-layer p(4×4) Au(111) surface was built to optimize adsorption structure of molecule (4,4'-BPY or 1-ethylimidazole) in vacuum and Au(111) surface with four 1-ethylimidazole and thirty water molecules as solvent was built to optimize adsorption structure of 4,4'-BPY molecule in solution. DFT-D3 method[6] was employed to describe the van der Waals (vdW) interaction between adsorbate and solvent. The bottom two layers of Au surface were fixed, while the top one was relaxed. The Brillouin zone[7] was sampled by k-points mesh of 2×1×1 for structure optimization. The convergence criterion for the energy calculation was set to 1.0×10^{-5} eV; while the force tolerance was set to 0.01 eV $Å^{-1}$. The adsorption energy (E_{ad}) of the different adsorbates follows the equation:

$$E_{ad} = E_{total} - (E_{sub} + E_{gas})$$

Where the E_{total}, E_{sub}, E_{gas} represent the total energy of substrate after adsorption, bare substrate, and the adsorbate molecule (4,4'-BPY or 1-ethylimidazole) in the gas phase, respectively.

Supplementary Figures

Fig. S1 In-situ STM images

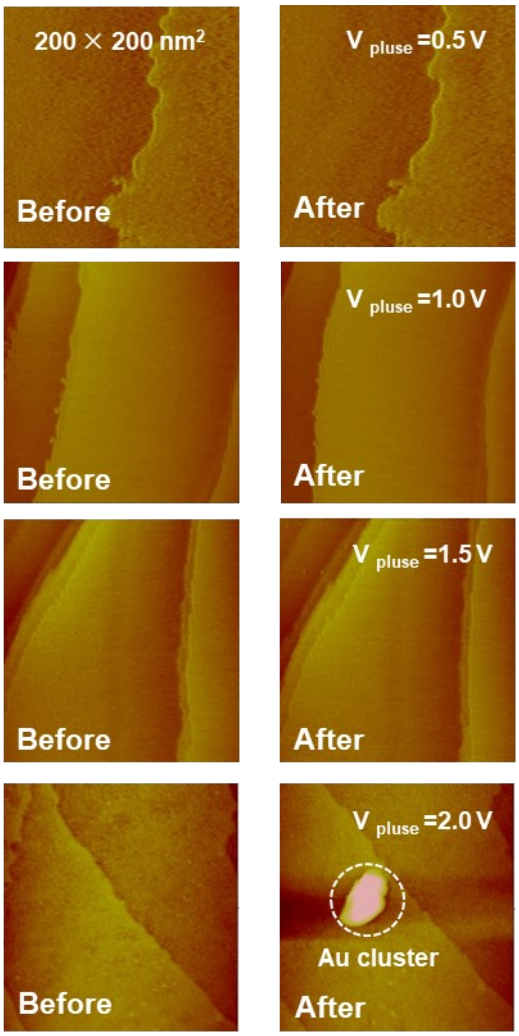

Fig. S1 200 × 200 nm^2 STM image obtained before and after conductance measurements with different pulse voltages (I_{set} = 0.3 nA, V_{bias} = 0.1 V).

Fig. S1 shows in-situ STM images recorded before and after breaking junctions with different V_{pulse} on the z-piezo for constructing molecular junctions. Obviously, at low V_{pulse}, there are no Au clusters or holes on the Au (111) substrate after the conductance measurements. Only V_{pulse} is as large as 2.0 V, an Au cluster about 2 nm in height left on the Au(111) substrate could be observed after the breaking junction experiments.

Fig. S2 Conductance histogram of EIM

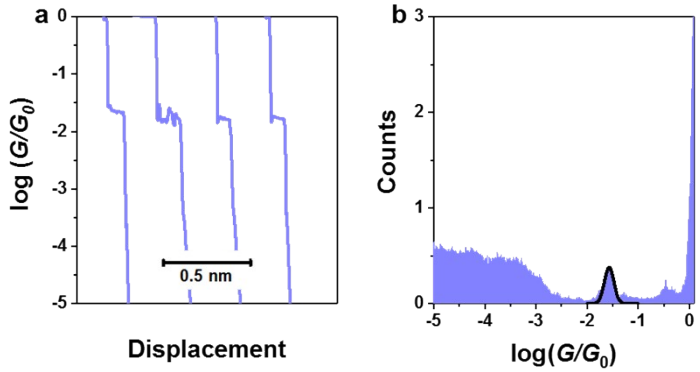

Fig. S2 (a) Typical original conductance–distance traces of pure EIM and (b) 1D conductance histogram of EIM.

Fig. S3 Conductance histograms obtained in air

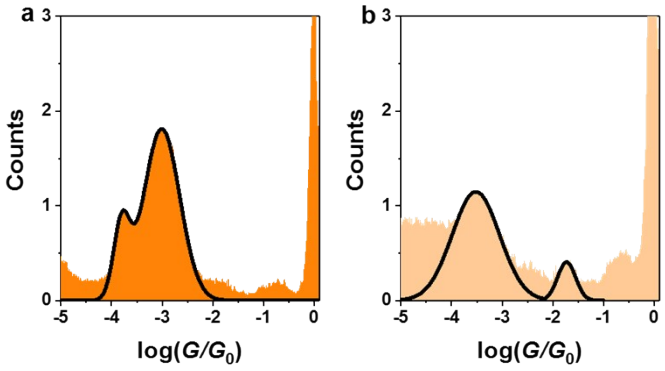

Fig. S3 (a) 1D conductance histograms obtained in air with the dry self-assembled monolayer formed in (a) 0.1 mM 4,4'-BPY and (b) 10 mM EIM + 0.1 mM 4,4'-BPY sloutions.

Fig. S4 SEM and TEM images

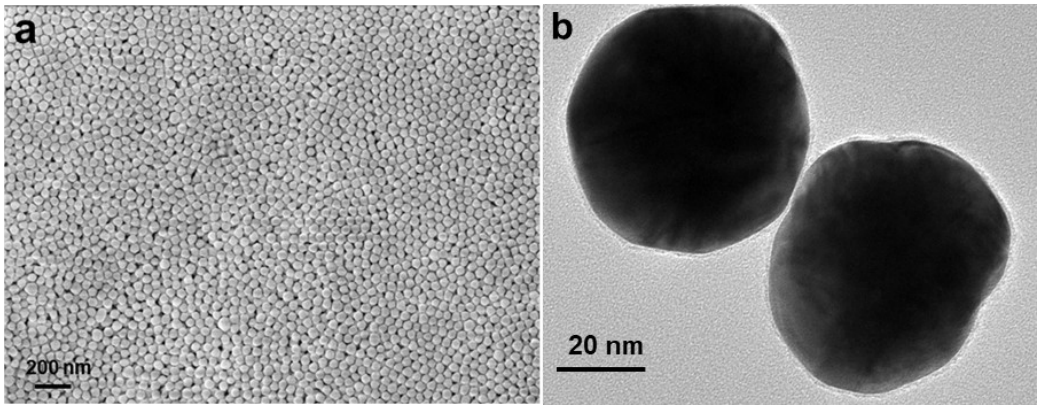

Fig. S4. The (a) SEM and (b) TEM image of as-prepared 55 nm Au @1~2 nm SiO_2.

Fig. S5 Optimized adsorption geometries

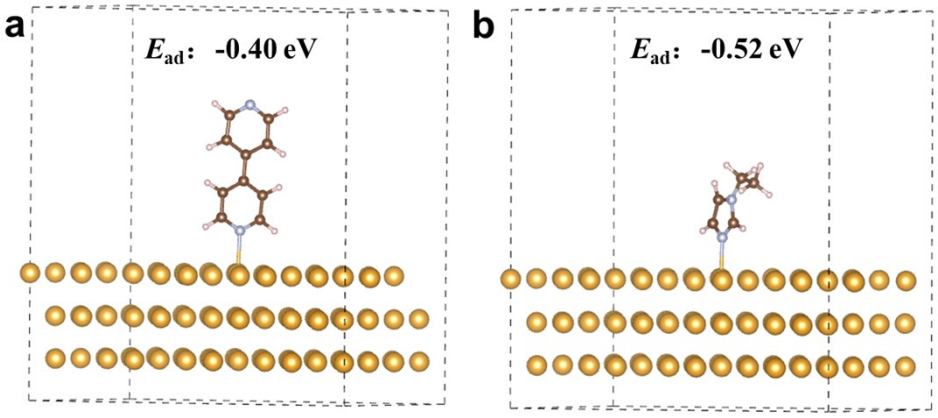

Fig. S5. The optimized adsorption geometries of (a) 4,4'-BPY and (b) 4 EIM molecules on the Au (111) surface.

References

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