Supplementary information for

Single molecule identification via electric current noise

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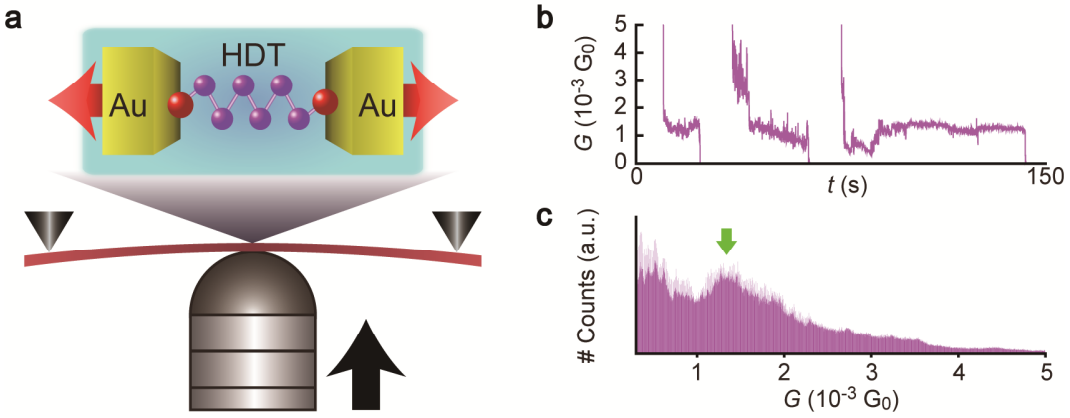
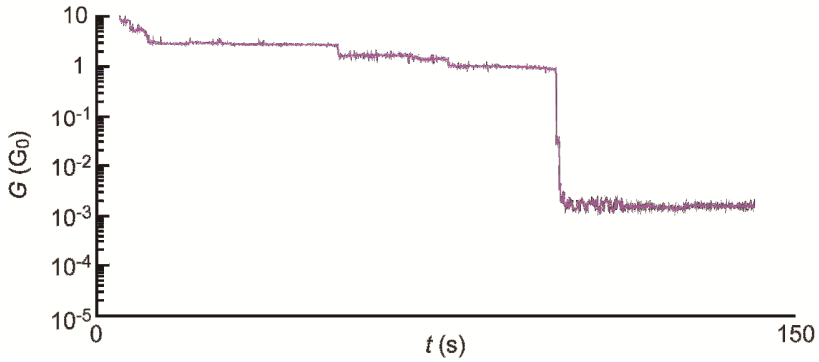
The Supplementary Information includes:

1. Supplementary Figures S1-S4

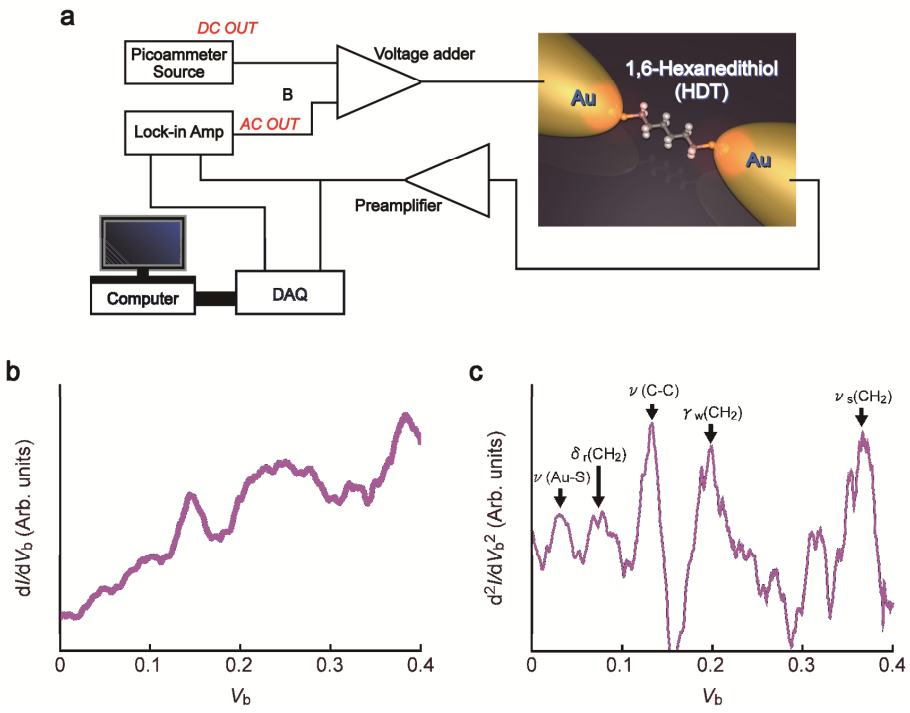
2. Supplementary References



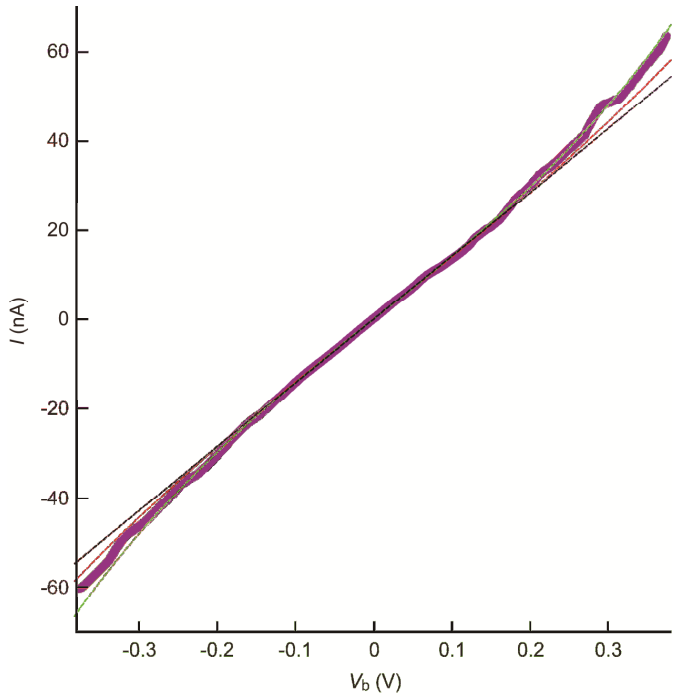
Supplementary Figure S1. Repeated formation and breaking of Au-1,6-hexanedithiol (HDT)-Au structures using a break junction method at room temperatures implemented prior to the sample cooling to 4 K. **(a)** A schematic illustration of MCBJ set up. In experiments, Au junction was opened/closed cyclically through controlling the substrate bending at the junction stretching speed v_d = 6 pm/s at room temperatures in a vacuum. **(b)** Conductance traces during stretching of junctions at v_d = 6 pm/s at room temperatures. Plateaus were often observed at $G \sim 10^{-3}\ G_0$ signifying formation of Au-HDT-Au single molecule bridges. **(c)** The corresponding histogram constructed with 150 *G*-*t* traces without any data selection reveals a peak at $G \sim 1.3\times10^{-3}\ G_0$ (green arrow).



Supplementary Figure S2. *G-t* curve during formation of a HDT single molecule bridge at 4 K. When a temperature was stabilized at 4 K, we created a HDT single molecule bridge using a self-breaking method[41,42]. In this method, a fused Au contact is stretched at a programmed speed until the junction conductance declines to below 5 G_0. Thereafter, the junction is stretched at v_d = 6 pm/s so as to gently rupture Au contact and form a stable molecular junction. The *G-t* curve exhibited a flat plateau at 1 G_0 and a subsequent conductance drop to G ~ 1.3 mG_0. The conductance drop at 1 G_0 denotes breaking of a Au single-atom chain possessing a fully opened channel for electron transmission[43], whereas the conductance plateau at G < 1 G_0 can be considered as signifying formation of a molecular bridge between the nano-MCBJ electrodes[44]. It is noticeable that G ~ 1.3 mG_0 is representative of conductance states of Au-HDT-Au single molecule bridges with hollow-hollow geometries at the metal-molecule linkages as reported previously[45-47]. Therefore, we could attribute the conductance plateau at G ~ 1.3 mG_0 to trapping of a single HDT molecule between two Au probes.



Supplementary Figure S3. Inelastic electron tunnelling spectroscopy (IETS) performed on a single HDT molecule at 4 K. **(a)** A measurement scheme based on a lock-in method used to acquire a single molecule IET spectrum. **(b)** Plots of differential conductance of a HDT single-molecule junction formed at 4 K as a function of bias voltage V_b. We observed a stepwise increase in dI/dV_b that signify contributions of inelastic channels to electron transmission through a HDT molecule at a characteristic bias voltage $V_p = \hbar\omega_p/e$, where $\hbar\omega_p$ and e are the molecular vibration energy of the IETS-active modes and the electron charge, respectively. **(c)** An IET spectrum obtained numerically from the dI/dV_b-V_b curve in **(b)**. Pronounced peaks are observed corresponding to the dI/dV_b steps in **(b)**. The peaks marked by arrows can all be assigned to the IETS-active molecular vibrational modes: The peak at $V_p = 32$ mV can be assigned to ν(Au-S) of a metal-molecule link, while the others at $V_p = 70$ mV, 133 mV, 198 mV, and 368 mV are attributable to $\delta_r(CH_2)$, ν(C-C), $\gamma_w(CH_2)$, and $\nu_s(CH_2)$ of an alkyl chain, in accordance to previous works[47-50]. This spectrum may thus be interpreted as a vibrational fingerprint for HDT molecules.



Supplementary Figure S4. Fitting of the average current versus bias voltage (<*I*>—V_b) curve obtained for a HDT single-molecule junction. Simmon's model has been employed to fit the <*I*>-V_b plots shown in Fig. 2a of the main text, which describes exponential dependence of current flowing through a double-barrier tunnelling system on the tunnelling barrier height Φ_B and width L[45, 51-53]. We fitted by using γ and Φ_B as fitting parameters under an empirical criterion of $\beta = \gamma\Phi_B$ □ 0.8 Å^{-1} from literatures[45,53] (green: γ = 1.032, Φ_B = 0.6 eV; red: γ = 0.843, Φ_B = 0.9 eV; γ = 0.46, Φ_B = 3.0 eV). As we show above, we obtained a linear *I*-V_b in case when Φ_B = 3 eV. This situation corresponds to an alignment of the Au Fermi level to the middle of the HOMO-LUMO gap of a hexanedithiol (HDT) molecule. To fit the plots with the Simmon's model, we find that Φ_B has to be lowered to 0.6 eV, the value of which seems to be too low considering the relatively wide HOMO-LUMO gap of HDT molecules (6 eV). These results serve to support the validity of the linear elastic tunnelling contributions assumed in the present study.

Supplementary References

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