Supplementary information for

Single molecule identification via electric current noise

Makusu Tsutsui, Masateru Taniguchi & Tomoji Kawai

The Supplementary Information includes:

1. Supplementary Figures S1-S4

2. Supplementary References
Supplementary Figure S1. Repeated formation and breaking of Au-1,6-hexanediithiol (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 $G \sim 1.3 \times 10^{-3} G_0$ (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\textsuperscript{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 $G \sim 1.3$ m$G_0$. The conductance drop at 1 $G_0$ denotes breaking of a Au single-atom chain possessing a fully opened channel for electron transmission\textsuperscript{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\textsuperscript{44}. It is noticeable that $G \sim 1.3$ m$G_0$ is representative of conductance states of Au-HDT-Au single molecule bridges with hollow-hollow geometries at the metal-molecule linkages as reported previously\textsuperscript{45-47}. Therefore, we could attribute the conductance plateau at $G \sim 1.3$ m$G_0$ 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 $V_p = h\omega_p/e$, where $h\omega_p$ 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 $\nu$(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 $\delta_i$(CH$_2$), $\nu$(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 ($I_b-V_b$) curve obtained for a HDT single-molecule junction. Simmon’s model has been employed to fit the $I_b-V_b$ 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 $\Phi_B$ and width $L$\textsuperscript{45,51-53}. We fitted by using $\gamma$ and $\Phi_B$ as fitting parameters under an empirical criterion of $\beta = \gamma \Phi_B$ \textsuperscript{45,51-53} from literatures\textsuperscript{45,53} (green: $\gamma = 1.032$, $\Phi_B = 0.6$ eV; red: $\gamma = 0.843$, $\Phi_B = 0.9$ eV; $\gamma = 0.46$, $\Phi_B = 3.0$ eV). As we show above, we obtained a linear $I-V_b$ in case when $\Phi_B = 3$ 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 $\Phi_B$ 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


