Electronic Supplementary Information

Kinetic investigation of chemical process in single-molecule junction

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CONTENTS

Adaptive threshold analysis (ATA)

In order to detect the characteristic plateaus appeared in the current–time (*I–t*) measurements, ATA[1] was employed. Since the signal-to-noise ratio of the tunneling current is low, conventional constant thresholds are not effective for the plateau detection. Thus, the thresholds were defined in a recursive manner using local average $\mu(k)$ and standard deviation $\sigma(k)$ calculated as follows,

$$\mu(k) = a\mu(k-1) + (1-a)i(k),$$

$$\sigma^2(k) = a\sigma^2(k-1) + (1-a)(i(k) - \mu(k))^2.$$

The parameter a is close to 1 and is used for a first-order low-pass filter in calculating $\mu(k)$ and $\sigma(k)$ from each measured current at data point k, $i(k)$, in a given *I–t* trace.

The first threshold was defined as,

$$\eta_S(k) = \mu(k) + S\sigma(k),$$

where S is a positive parameter to determine the sensitivity of the plateau detection. The onset of the plateau region was determined when the current exceeds $\eta_S(k)$. Then, the second threshold was prepared using the average and the standard deviation at the onset of the plateau, k_0, according to the following definition,

$$\eta_E = \mu(k_0) + E\sigma(k_0),$$

where E is again a positive parameter and $0 \leq E < S$. The end of the plateau was located at the data point where the current decreased below η_E.

Verification of ATA

We generated simulated *I*–*t* data having a variety of slopes in the background current and magnitudes of the plateaus (Fig. S1a) to verify the plateau detection by ATA. The slopes correspond to the deviation of the background arising from the unwanted drift of the STM system. The onset of the plateau was included at the 1000th data point, and the magnitudes of the plateaus were represented as signal-to-noise ratios (SNRs) in the simulated data. For each combination of the slope and the SNR, 1000 traces were prepared and analyzed by ATA. Typical results were shown in Fig. S1a, where the arrowheads indicate the detected plateau onset. Figure S1b summarizes the accuracy of the plateau detection by ATA for all the investigated combinations of the slope and SNR. It can be seen that the ATA successfully detects the plateaus, except for

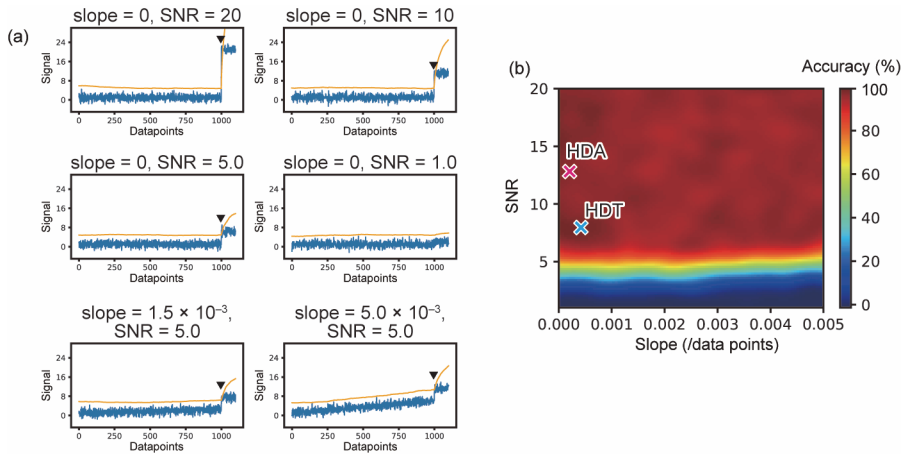

Fig. S1. (a) Simulated *I*–*t* traces and the ATA thresholds $\eta_s(k)$. The parameters *S* and *a* for the threshold calculations were 4 and 0.995, respectively. Arrowheads indicate the detected plateau onsets. (b) Simulated map for the ATA accuracy of the plateau detection. Crosses indicate the SNRs and slopes of the measured traces for HDT (cyan) and HDA (magenta).

the small SNR. In addition, the accuracy was less affected by the slopes, reflecting the advantage of the recursively defined threshold values.

The accuracy of the plateau detection in the experiments of the HDT and HDA was evaluated based on the simulated accuracy map in Fig. S1b. The noise levels and the slopes of the background current were evaluated from the whole data sets of *I*–*t* measurements for HDT and HDA. The SNRs were calculated from the conductance of the single-molecule junctions and the noise levels. The resulting SNRs and slopes were plotted in Fig. S1b. Both plots were found to be in the high accuracy region, indicating the successful plateau detection by ATA.

One dimensional (1D) histograms of single-molecule conductance

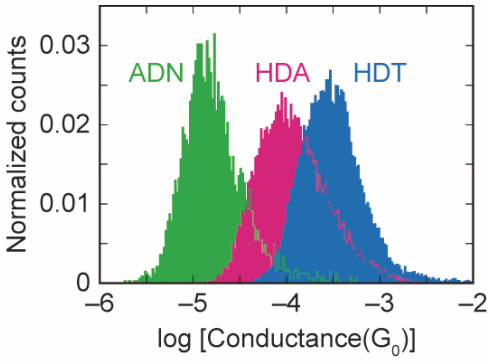

Fig. S2. 1D conductance histograms for single-molecule junctions of adiponitrile (ADN; green), hexanediamine (HDA; magenta), and hexanedithiol (HDT; cyan), measured from the current–time (*I*–*t*) experiments. Bias voltage, 0.4 V.

Cumulative histogram for single-molecule junction of adiponitrile (ADN)

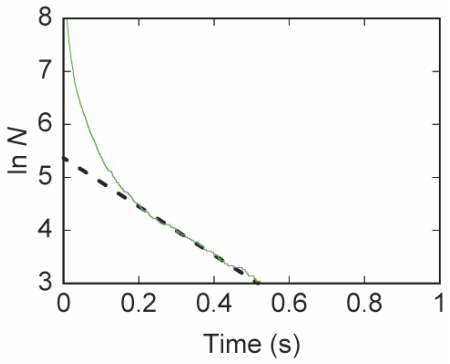

Fig. S3. Cumulative histograms for ADN constructed based on the lifetime of junctions observed in *I*–*t* experiments. The total number of the junctions, *N*, were plotted against their lifetimes.

Experimental Procedures

General. The reagents were of the highest grade available. Small pieces of a gold wire (0.25 mm diameter, 99.95%) were electrochemically etched in a 3 M NaCl in 1% perchloric acid at an AC voltage of 10 V.[2] They were then washed by sonication in pure water, dipping in "piranha solution" (7:3 concentrated H_2SO_4/H_2O_2. *Caution: piranha solution reacts violently with organic compounds and should not be stored in closed containers*), and finally, thoroughly washed with pure water. Ultraflat gold films initially grown epitaxially on mica were used as Au(111) substrates.[3] The gold substrate was immersed in the 50 μM solution of the target molecule (HDT, HDA or ADN). After washing with water, the substrate was placed on an STM sample plate.

Current measurements. The tunneling current measurements were performed on an SPM 5100 (Agilent Technologies, Santa Clara, CA). In the break-junction (BJ) measurements, a set-point current of 75 nA was employed. After a short delay time of 100 ms, the STM tip was pulled up at a velocity of approximately 60 nm/s with the feedback loop of STM disabled, and current–distance (*I–z*) traces were recorded. In *I–t* measurements, a set-point currents of 50, 20, and 2 nA for HDT, HDA and ADN, respectively, were used, and *I–t* traces were recorded with the tip held stationary by disabling the feedback loop for 2 s. Both the *I–z* and *I–t* traces were recorded at a 20 kHz sampling frequency. The current measurements were repeated using independently prepared tips and sample surfaces to ensure the reproducibility.

References

1. T. Harashima, Y. Hasegawa, S. Kaneko, M. Kiguchi, T. Ono and T. Nishino, *Angew. Chem. Int. Ed.*, 2019, **58**, 9109-9113.
2. D. Gingery and P. Bühlmann, *Rev. Sci. Instrum.*, 2007, **78**, 113703.
3. P. Wagner, M. Hegner, H.-J. Guentherodt and G. Semenza, *Langmuir*, 1995, **11**, 3867-3875.