Supporting Information

Electron Transfer through Coordination Bond Interaction between Single Molecules: Conductance Switching by Metal Ion

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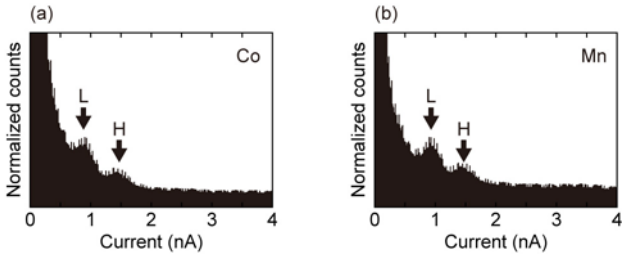

Figure S1. Current histograms from *I*–*z* curves obtained by measurements with C_2COOH tip and C_1COOH-modified substrate in the presence of (a) Co^{2+} and (b) Mn^{2+} ions. Bias voltage: 0.2 V; initial set-point current: 7.5 nA; bin size: 10 pA.

Table S1. Peak current values in the current histograms[a]

Added ion	Peak current (nA)	
	L peak	*H* peak
None	1.1	–
Zn^{2+}	0.99	1.6
Co^{2+}	0.92	1.5
Mn^{2+}	0.95	1.5
Na^{+}	1.1	–

[a]Measurements were performed using the C_2COOH tip and C_1COOH-modified substrate.

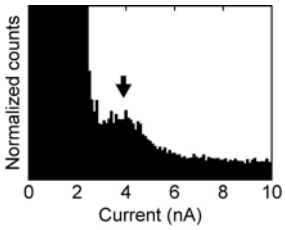

Figure S2. Current histogram from *I*–*z* curves obtained by measurements with 4-mercaptobenzoic acid (4MBA) tips and 4MBA-modified substrate in 0.1 M $NaClO_4$ solution containing 10 mM $ZnBr_2$ and 10 mM ethylenediaminetetraacetic acid (EDTA). Bias voltage: 0.2 V; initial set-point current 75 nA; bin size: 100 pA.

Experimental procedure

Reagents. The reagents were of the highest grade available. De-ionized water purified through a Milli-Q water purification system (Japan Millipore, Tokyo, Japan) was used in all experiments.

Tip Preparation. Small pieces of gold wire (0.25 mm diameter, 99.95%) were electrochemically etched in 3 M NaCl at AC 10 V. They were then washed by sonication in pure water and 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*.) Finally, they were thoroughly washed with pure water. To prepare molecular tips, either aliphatic (C_nCOOH) or aromatic (4MBA or 4MP) thiol was dissolved in EtOH typically at 7.5 mM, and the gold tips sharpened by the electrochemical etching were immersed in the thiol solution overnight. The modified tips were then rinsed with EtOH and water prior to use. For the current measurements in aqueous solutions, the gold tips were insulated with poly(dimethylsiloxane) except for their apices to reduce ionic and polarization currents.[1] The tips were then modified

using the thiol molecule as above.

Sample Preparation. Ultraflat gold films epitaxially grown on mica were used as Au(111) substrates.[2] The gold substrate was immersed in a 50 μM EtOH solution of thiol (C_nCOOH, 4MBA or 4MP) for 1 h. After washing with a pure EtOH solution, the substrate was placed on an STM sample plate. The cell was filled with either 1,2,4-trichlorobenzene or 0.1 M $NaClO_4$ aqueous solution for the current measurements. Alternatively, $ZnBr_2$, $MnBr_2$, $CoBr_2$, or NaBr was dissolved in each solution at a concentration of 10 mM. Ultrasonication was applied to dissolve these reagents in 1,2,4-trichlorobenzene. Control experiments were performed using 0.1 M $NaClO_4$ solution containing 10 mM $ZnBr_2$ and 10 mM ethylenediaminetetraacetic acid.

Current Measurements. The tunneling current measurements were performed on an SPM 5100 with a 1 nA/V pre-amplifier (Agilent Technologies, Santa Clara, CA, USA). Before each measurement, the STM was equilibrated with the room temperature for 30 min to reduce the thermal drift. The piezo scanner of the STM was allowed to settle under feedback control without being driven during the equilibration. This procedure suppresses unwanted hysteresis and creep of the piezo scanner. The molecular tip was then brought in close proximity to, but not in contact with, the modified Au(111) surface. This procedure was achieved by applying a large set-point current (7.5 nA) under the STM feedback control. A bias voltage of 0.2 V was employed for all the measurements. After a short delay time of 100 ms, the molecular tip was pulled up at a velocity of 20 nm/s with the feedback loop disabled, and *I*–*z* traces were recorded at a 20 kHz sampling frequency using a data acquisition unit (NR-500; Keyence, Osaka, Japan). This measurement was repeated several thousand times.

Data Analyses. The current histograms were constructed from the *I*–*z* traces that

exhibited the plateaus. Plateaus were observed in ~10% of the obtained *I*–*z* traces. Other traces exhibited either simple exponential or noisier decays. This ratio is comparable to that observed in our previous work, in which the electron transfer through a hydrogen bond interaction between single molecules was measured.[3] The two-dimensional (2D) current histograms were created according to the reported procedure[4] as follows. Using the 1D histogram, the current peaks and their widths were calculated to determine the minimum and maximal current values of the plateau. Then, the *I*–*z* traces with a current plateau longer than 0.02 nm, having a slope greater than −5, were selected. For each of the selected traces, the end of the current plateau was determined, and this point was set to the origin in the displacement axis. Finally, the 2D histograms were constructed using these traces.

References

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