Supplementary Information

In-situ Observation of Unique Bianalyte Molecular Behaviors at the Gap of a Single Metal Nanodimer Structure via Electrochemical Surface-Enhanced Rama Scattering Measurements

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1. SEM images of Au dimer structures with various *d* values

It is well known that the optical property of the dimer structure strongly depends on the gap distance. For the optimization of the gap distance (*d* value) to obtain the maximum scattering enhancement, we have prepared various Au dimer structures by changing the *d* values. Figure S1 represents the example of the structures with different *d* values. Through the investigations, we have found the optimized condition for the maximum enhancement as mentioned in the main text.

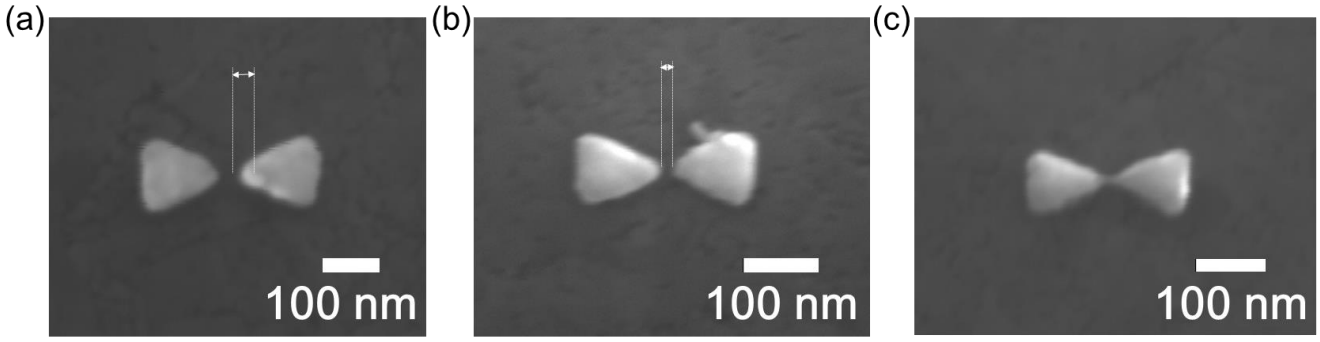

Fig. S1 | (a) SEM images of various Au dimer structures. The *d* values for each figure were 30, 15, and 1.25 nm, respectively.

2. Each value for the calculation of the relative ratio

The calculations shown in Fig. 3b were conducted using each value in below table S1. Peak intensities were estimated from Fig. 3a. Figure 3b was prepared using these values.

Table S1. Values for the calculation of the relative ratio

Potential [V vs. Ag/ AgCl]	Peak intensity of 1480 cm^{-1} (22bpy) [cps]	Peak intensity of 1608 cm^{-1} (44bpy) [cps]	Conversion coefficient by 1 mM 22bpy ($I_{1013cm}{}^{-1}/I_{1480cm}{}^{-1}$)	Conversion coefficient by 1 mM 44bpy ($I_{1021cm}{}^{-1}/I_{1608cm}{}^{-1}$)	Calculated Peak intensity of 1013 cm^{-1} (22bpy) [cps]	Calculated peak intensity of 1021 cm^{-1} (44bpy) [cps]	Relative ratio for 22bpy	Relative ratio for 44bpy
cathodic scan								
−0.8	110	16	0.24	0.91	99.7	4.97	0.95	0.05
−0.75	37	26	0.19	1.05	39.0	8.51	0.82	0.18
−0.7	17	32	0.19	1.26	21.3	11.1	0.66	0.34
−0.6	0	40	0.21	1.16	0.00	13.9	0.00	1.00
−0.4	0	53	0.15	2.60	0.00	16.4	0.00	1.00
0	0	40	0.54	1.19	0.00	11.2	0.00	1.00
anodic scan								
−0.8	110	15	0.24	0.91	99.7	4.66	0.96	0.04
−0.75	75	15	0.19	1.05	79.0	4.91	0.94	0.06
−0.7	56	19	0.19	1.26	70.3	6.57	0.91	0.09
−0.6	20	43	0.21	1.16	23.1	15.0	0.61	0.39
−0.4	11	55	0.15	2.60	28.6	17.0	0.63	0.37
0	4	88	0.54	1.19	4.77	24.7	0.16	0.84