

Electronic Supplementary Information
for
**Colorimetric Response to Mercury-induced Abstraction of
Triethylene Glycol Ligand from Gold Nanoparticle Surface**

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Figure S1. UV-vis spectra of Au:S-EG_n (n = 2, 3, and 4) before and after the reaction with Hg²⁺.

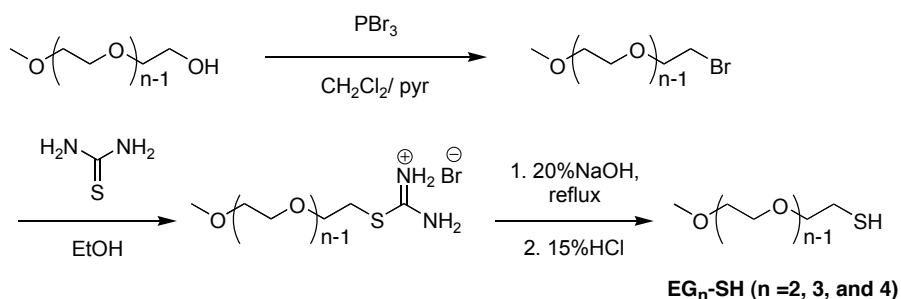
Figure S2. ESI-MS of the reaction products between Au:S-EG₃ and Hg²⁺.

1. Synthesis

General. All chemicals used in this study were commercial products of the highest available purity and were further purified by the standard methods, if necessary.¹ ¹H-NMR spectra were recorded with a JEOL JNM-EX-270 (270 MHz) or a JEOL alpha-500 (500 MHz) using TMS as the internal standard. TLC analyses were carried out by using Silica gel 60 F₂₅₄ (Merck). Flash chromatography was performed on silica gel (Merck Silica Gel 60).

EG_n-SH (*n* = 2, 3, and 4)

Scheme S1. Synthesis of EG_n-SH.



Ethyleneglycol ligands were synthesized by reported procedure.^{2,3} In brief, synthesis of EG₃-SH is described here as typical example. To a ice-cooled solution of tri(ethyleneglycol) monomethyl ether (10 g, 61 mmol) and pyridine (3.5 mL) in CH₂Cl₂ (40 mL) was added dropwise PBr₃ (16 g, 61 mmol) in CH₂Cl₂ with stirring over 30 minutes. The reaction mixture immediately turned cloudy and the resulting suspension was stirred overnight. After reaction, the mixture was washed with 10% aqueous sodium carbonate (50 mL), 5% sulfuric acid (50 mL), water (50 mL × 2), and brine (40 mL). The organic phase was dried over MgSO₄, and the solvent was evaporated to obtain CH₃O(CH₂CH₂O)₂CH₂CH₂Br (7.39 g, 32.6 mmol, 54%). The crude product was used without further purification.

A solution of 1-bromo-2-[2-(2-methoxyethoxy)ethoxy]ethane (7.39 g, 32.6 mmol) and thiourea (5.0 g, 65.2 mmol) in ethanol (50 mL) was stirred for 5 h, and then the solvent was evaporated. To the resultant gum, 20% NaOH_{aq} (40 mL) was added, and the mixture was refluxed for 3 h. After cooling to room temperature, pH of the resultant mixture was adjusted to ≈ 2 by addition of 6 M HCl_{aq}. The aqueous solution was extracted by ether (50 mL × 3), and the organic phase was washed by water (30 mL × 2). After dried over MgSO₄, the solvent was evaporated. The crude product was distilled under

reduced pressure (62-64 °C, 1.2 mmHg) to obtain EG₃-SH (1.4 g, 24%). ¹H-NMR (270 MHz, CDCl₃): δ 1.59 (1 H, t, *J* = 8.1 Hz), 2.72 (2 H, dt, *J* = 8.1 and 6.3 Hz), 3.38 (3 H, s), 3.53-3.67 (10 H, m).

EG₂SH: Synthesis was started with 1-bromo-2-(2-methoxyethoxy)ethane, and purification was done by distillation at 40-42 °C under 1.2 mmHg pressure. Yield: 2.71 g, 60%. ¹H NMR (270 MHz, CDCl₃): δ 1.58 (1 H, t, *J* = 8.1 Hz), 2.71 (2 H, dt, *J* = 8.1 and 6.3 Hz), 3.39 (3 H, s), 3.54-3.65 (10 H, m).

EG₄SH: Synthesis was started with tetra(ethyleneglycol)monomethyl ether, and purification was done by silica gel column chromatography (AcOEt : Hexane = 1:1). Yield: 565 mg, 17%. ¹H-NMR (270 MHz, CDCl₃): δ 1.60 (1 H, t, *J* = 8.1 Hz), 2.70 (2 H, dt, *J* = 8.1 and 6.3 Hz), 3.38 (3 H, s), 3.53-3.73 (14 H, m).

Au:S-EG_n (n = 2, 3, and 4)

Au:S-EG_n were synthesized by modified previous procedure.² To a solution of HAuCl₄•4H₂O (200 mg, 0.49 mmol) in pre-mixed MeOH-AcOH (6:1, 35 mL), 0.5 eq of EG_n-SH (0.25 mmol) was added. An aqueous solution (5 mL) of NaBH₄ (186 mg, 6.1 mmol) was added dropwise to the mixture, and immediately the color turned from yellow to brown. After rapid stirring for 2 h, the solvent was evaporated below 45 °C. Ethanol was added, and the mixture was filtered through a membrane filter (pore size = 0.1 μm) to remove an insoluble salt. After evaporation, the residue was re-suspended in MilliQ water and purified by size-exclusion chromatography (Sephadex G-25). The collected fraction was then lyophilized for 3 days to obtain pure Au:S-EG_n as a dark purple powder.

2. UV-vis Absorption Spectroscopy

The UV absorption spectra of Au:S-EG_n (n = 2, 3, and 4) were recorded on a Hewlett-Packard 8453 spectrometer. The path length was 1 cm with a cell volume of 3.0 mL. Au:S-EG_n (n = 2, 3, and 4) was dissolved in a 10 mM HEPES buffer (pH 7.20) to give the final concentration of 50 μg mL⁻¹. 15 μL of Hg²⁺ stock solution (0.1 M) in water was added to the 3 mL of Au:S-EG_n solutions (final Hg²⁺ conc. = 500 μM), and the solutions were incubated under ambient conditions for 1 h and measured. Time course measurements of Au:S-EG_n were carried out under the same condition as described above. While the measurement, the solution was kept stirring. The absorbance at 580 nm was recorded at every 60 seconds.

3. Electrospray Ionization Mass Spectroscopy (ESI-MS)

ESI-mass measurement was performed on PE SCIEX API 150EX. 0.1 mg mL⁻¹ Au:S-EG₃ was incubated with 0.5 mM Hg²⁺ in water for 1 h. As the color changed to blue, the resultant was applied to an ultrafiltration with a filter of 10 kDa MWCO. The filtrate was diluted with methanol (1:10) prior to ESI-mass measurement. Control experiments were performed under the same procedures except Hg²⁺-addition.

4. Transmission Electron Microscopy (TEM)

TEM images were obtained with JEOL JEM-2100 by operating at 100 kV. 0.1 mg mL⁻¹ Au:S-EG₃ in water was prepared, and a 5 μL drop of the solution was placed on a carbon-coated Cu grid (JEOL). The Au:S-EG₃ solution was then incubated with 0.5 mM Hg²⁺ for 1 h, and then placed on the grid.

5. References

1. W. L. F. Armarego and C. L. L. Chai, *Purification of Laboratory Chemicals*, 5th ed.; Butterworth-Heinemann: Boston, 2003.
2. M. Zheng, F. Davidson and X. Y. Huang, *J. Am. Chem. Soc.*, 2003, **125**, 7790; M. Zheng, Z. G. Li and X. Y. Huang, *Langmuir*, 2004, **20**, 4226.

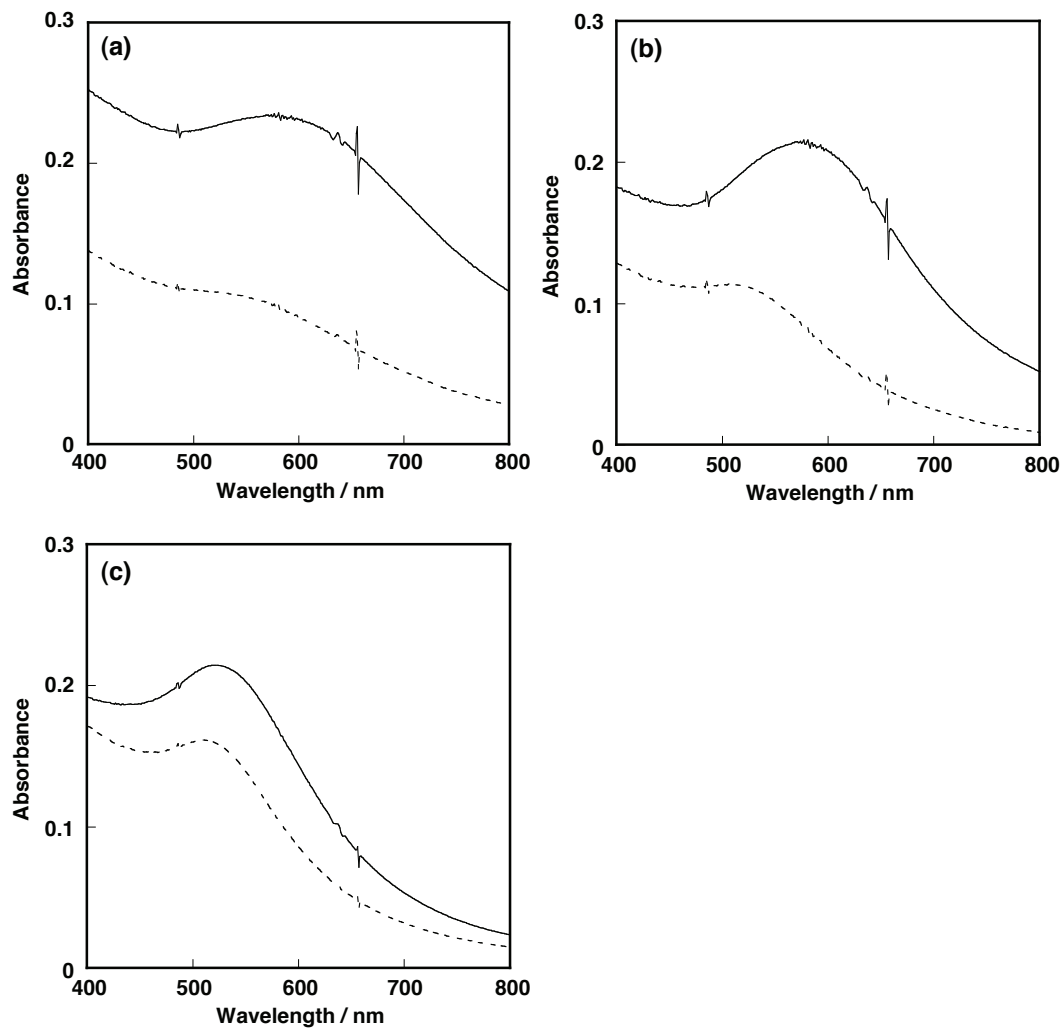


Figure S1. UV-vis spectra of (a) Au:S-EG₂, (b) Au:S-EG₃, and (c) Au:S-EG₄ in the absence (dashed line) and presence of Hg^{2+} (solid line) in 10 mM HEPES (pH 7.20). The spectra were measured after 1 h addition of 500 μM Hg^{2+} to the solution of Au:S-EG_n ($n = 2, 3,$ and 4).

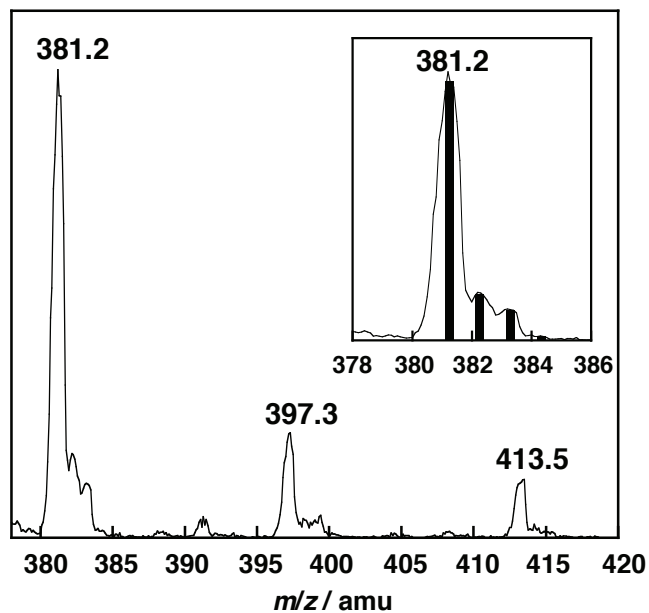


Figure S2. ESI-MS (pos.) of the reaction products between Au:S-EG₃ and Hg²⁺. The sample was separated from the reaction mixture through an ultrafiltration (10 kDa MWCO). The calculated isotope pattern for [EG₃-S-S-EG₃ + Na]⁺ is shown in the inset as black bars.