

Electronic Supplementary Information

Self-promoted solid-state covalent networking of Au₂₅(SR)₁₈ through reversible disulfide bonds. A critical effect of the nanocluster in the oxidation processes

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1. General

Tetrachloroauric (III) acid tetrahydrate (>47.5% for gold) was purchased from TANAKA HOLDINGS Co., Ltd. 1,6-Hexanedithiol (>96%), tetraoctylammonium bromide (>97%), and sodium tetrahydroborate (powder, >95%) were purchased from FUJIFILM Wako Chemicals. Other standard chemicals and solvents were purchased from Kanto chemical and used as received. O₂ gas (>99 %) was purchased from AIR WATER. Visible absorption spectra were recorded on a JASCO V-670 or JASCO V-550 spectrometer at room temperature. Solid-state visible absorption spectra were recorded on a JASCO V-670 at room temperature. Fluorescence spectra were recorded on a JASCO FP-8600 spectrofluorometer and corrected by using rhodamine B and a JASCO ESC-842. Routine ¹H NMR spectra were collected at ambient temperature on a JEOL EX-400 NMR spectrometer, and the chemical shifts (in ppm) were referenced to residual CDHCl₂ ($\delta = 5.30$). Dynamic light scattering (DLS) data were collected on a Malvern Nano-S light scattering system with a 633 nm He/Ne laser at 20 °C. Elemental analysis were performed using an Exeter Analytical CE440 elemental analyzer. Powder X-ray diffraction analysis was performed using a Bruker D8 Advance Diffractometer. Transmission electron microscopy (TEM) images were obtained by JEM-2000FX. Thermogravimetric analysis was performed on a Rigaku Thermo plus TG 8120 at a heating rate of 5 °C/min under air stream. Photoirradiation experiments were conducted on an ASAHI spectra LAX-103 system equipped with a 100 W Xe lamp source and a band-pass filter (520 nm).

2. Experimental procedures

As-synthesized Au₂₅ cluster (2) from 1,6-hexanedithiol

In a 100 mL 2-necked round-bottomed flask containing H₂AuCl₄·4H₂O (400 mg, 0.97 mmol) and tetraoctylammonium bromide (531 mg, 0.97 mmol) was added THF (25 mL) and the solution was stirred at room temperature for 15 min, and then was stirred at 0 °C for 15 min. 1,6-Hexanedithiol (430 μL, 2.91 mmol) was added to the mixture and the solution was stirred for 3 h at 0 °C. After the solution color was changed to colorless, ice cold aqueous solution of NaBH₄ (505 mg, 13.4 mmol/ 6.0 mL Milli-Q water) was added at once under vigorous stirring with the reaction solution kept at 0 °C. After the reaction mixture was stirred for 20 h at room temperature, the aqueous phase was removed by syringe and then the residual THF solution was treated with ice cold water (100 mL), which results in the precipitation of oily solids. After sonication for 3 min, the oily precipitates collected by decantation were washed with methanol (30 mL × 3) and dissolved in dichloromethane (20 mL). The resulting solution was filtered through a PTFE membrane filter (pore size: 0.2 μm) and the filtrate was concentrated and dried *in vacuo* to give **2** as dark brown sticky solids (261 mg, 27% based on Au).

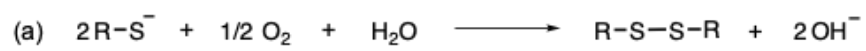
Preparation of Au₂₅ Film (3)

As-synthesized Au₂₅ cluster (**2**) (102 mg) dissolved in dichloromethane (DCM, 20 mL) was evaporated in a 100-mL round-bottomed flask (Figure S3a) and left under O₂ atmosphere for 20-24 h. DCM (15 mL) was added to the flask, where brown films were peeled off from the glass surface (b). The DCM layer was removed by centrifugation and the remaining solid was successively washed with DCM (5 mL × 3) and EtOH (5 mL × 3) and then dried *in vacuo* for 10 min to give **3** as thin curled films (c) (44 mg, 95% based on Au₂₅).

Singlet-oxygen generation experiments

To a methanol solution of 9,10-dimethylanthracene (DMA) (20 μM, 3 mL) was added **1** (2.1 mg,) or **3** (3.0 mg), each of which contains 2.7 μmol Au₂₅. After the mixture was purged with O₂, the solution was stirred for 30 min under the irradiation of 520-nm light from a 100W Xe lamp coupled with a band-path filter. The solution was centrifuged (10000 rpm, 5 min) and was subjected to the fluorescence measurements with an excitation of 360 nm. In the recycling experiments, the cluster films (**3**) collected by centrifugation were used for the next reaction batches after washing with methanol.

3. Scheme and Figures



Scheme S1. (a) Thiolate oxidation and (b) thiolate-disulfide exchange reactions.

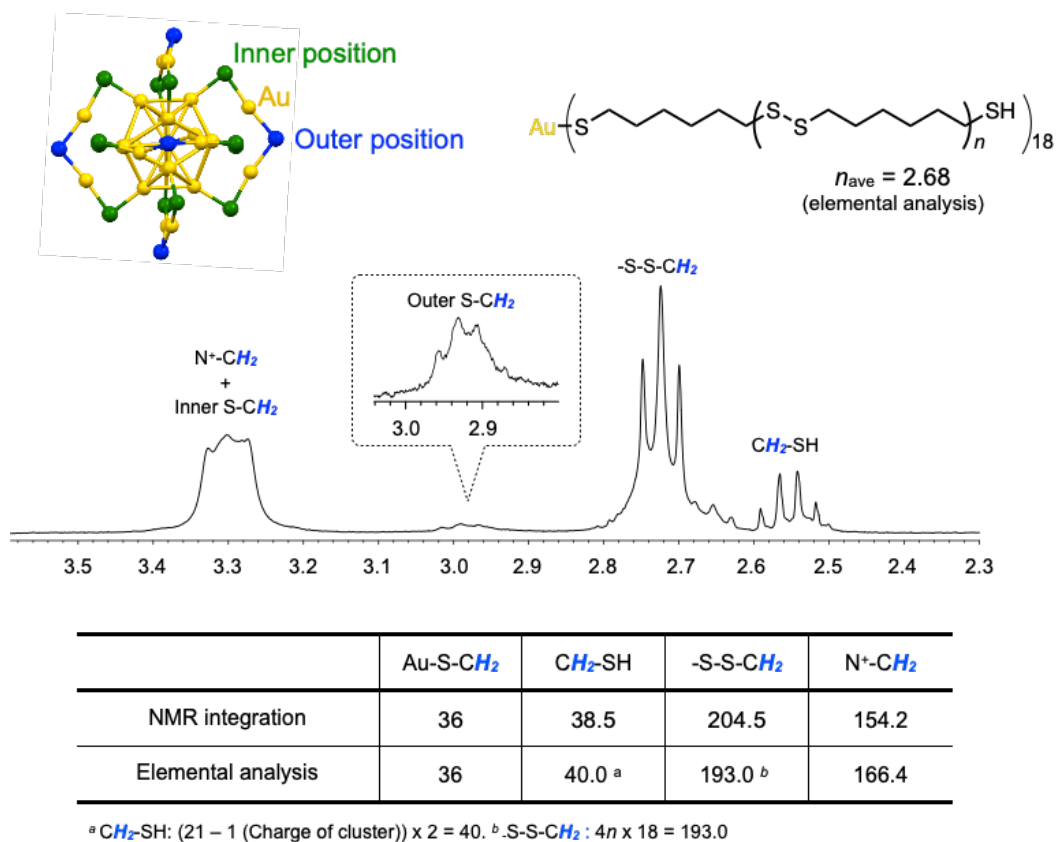


Figure S1. ¹H-NMR spectrum of as-synthesized Au₂₅ cluster (**2**) in the region of α-protons of thiolate, thiol, disulfide and TOA⁺ (CD₂Cl₂, 400 MHz, 298 K). The quartet signal assignable to CH₂SH may be due to the protonation of CH₂S⁻ with residual water. The table shows the numbers of the protons with respect to Au-SCH₂ (36H) estimated from the NMR integration and from the elemental-analysis chemical composition (Au₂₅(S₂C₆H₁₂)₆₆(N(C₈H₁₇)₄)₂₁). The two results accord with each other within experimental errors.

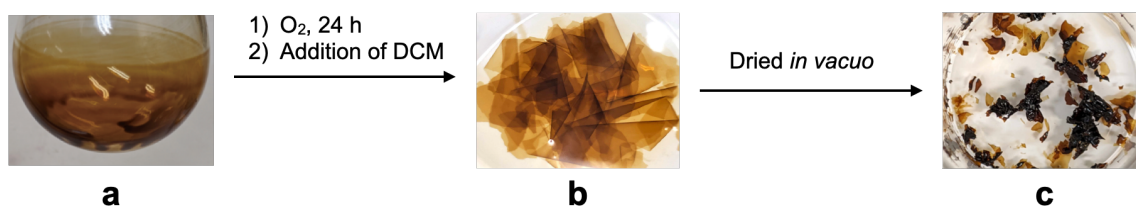


Figure S2. Photographs of thinly deposited precursor **2** on the glass surface of a round-bottom flask by evaporation (a), film **3** soaked in dichloromethane (b) and curled film **3** after dried *in vacuo*.

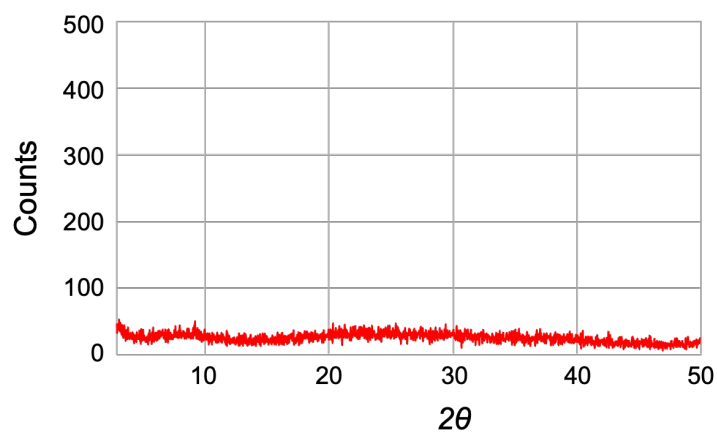


Figure S3. Powder X-ray diffraction profile of Au₂₅ cluster film (**3**).

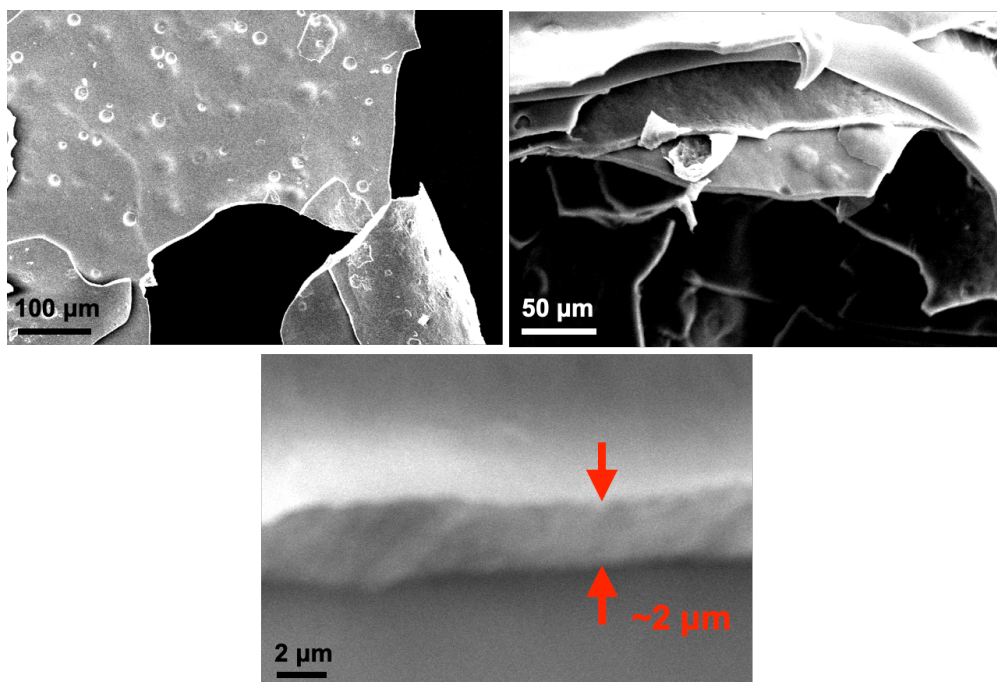


Figure S4. SEM images of the Au₂₅ cluster film **3**.

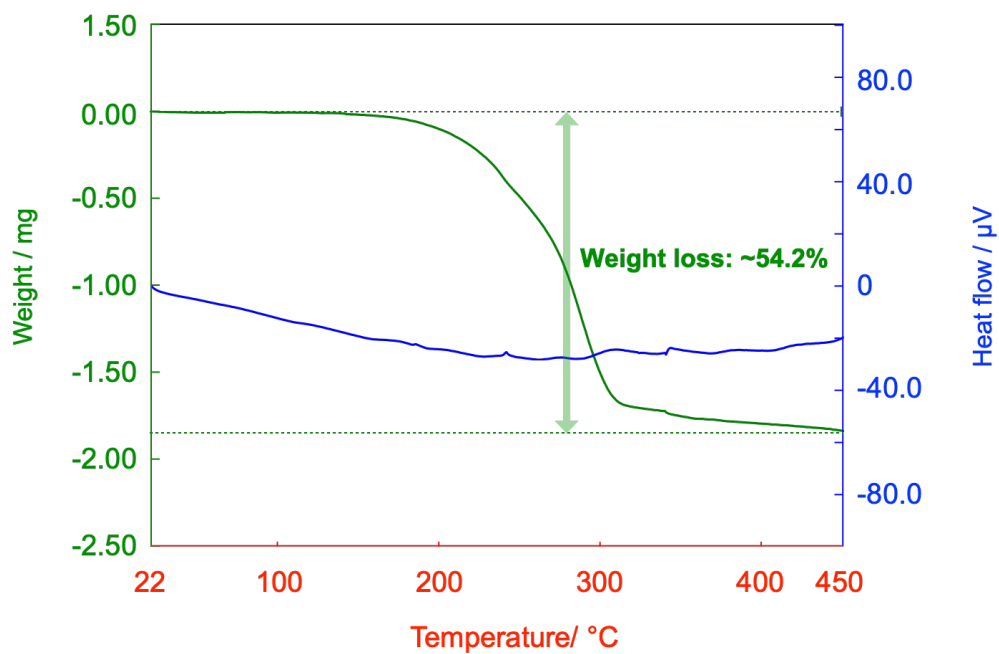


Figure S5. TG-DTA profile of Au₂₅ cluster film **3**. The weight loss expected from the chemical composition Au₂₅(S₂C₆H₁₂)₃₆(N(C₈H₁₇)₄)_{1.8} is 55.6%.

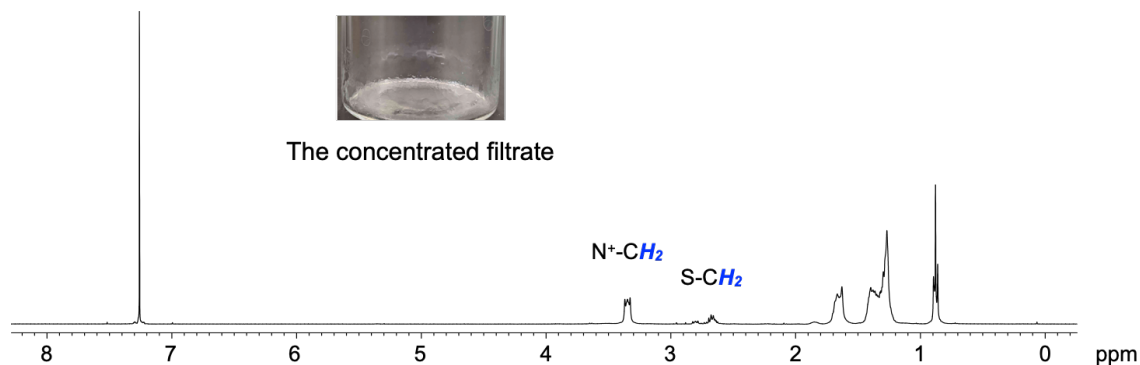


Figure S6. $^1\text{H-NMR}$ spectrum (CDCl_3 , 400 MHz, 298 K) of the filtrate when the film product (**3**) was isolated.

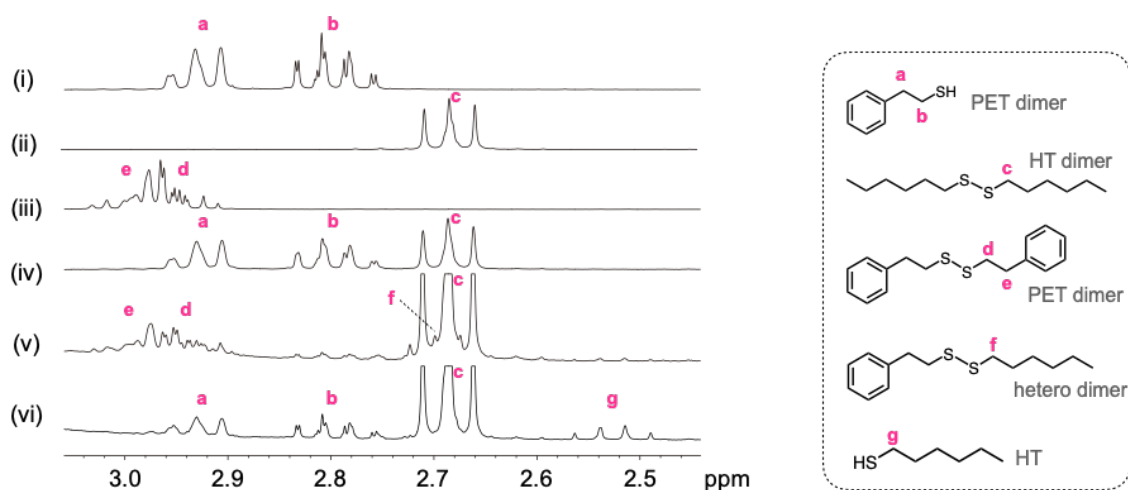


Figure S7. $^1\text{H-NMR}$ spectra (CDCl_3 , 300 MHz) of 2-phenylethanethiol (PET) (i), 1-hexanethiol (HT) dimer (ii), PET dimer (iii), and the reaction mixtures of PET and HT dimer (8.3 and 16 μmol , respectively) under O_2 in the absence (iv) and presence (v) of **1** (0.92 μmol), and under N_2 in the presence of **1** (vi). For (iv)-(vi), neat substrates were treated under the designated conditions without solvent (semi-solid conditions) at 20 $^\circ\text{C}$, and after 46 h, the mixtures were dissolved in CDCl_3 and were immediately subjected to the $^1\text{H NMR}$ and TLC analyses.

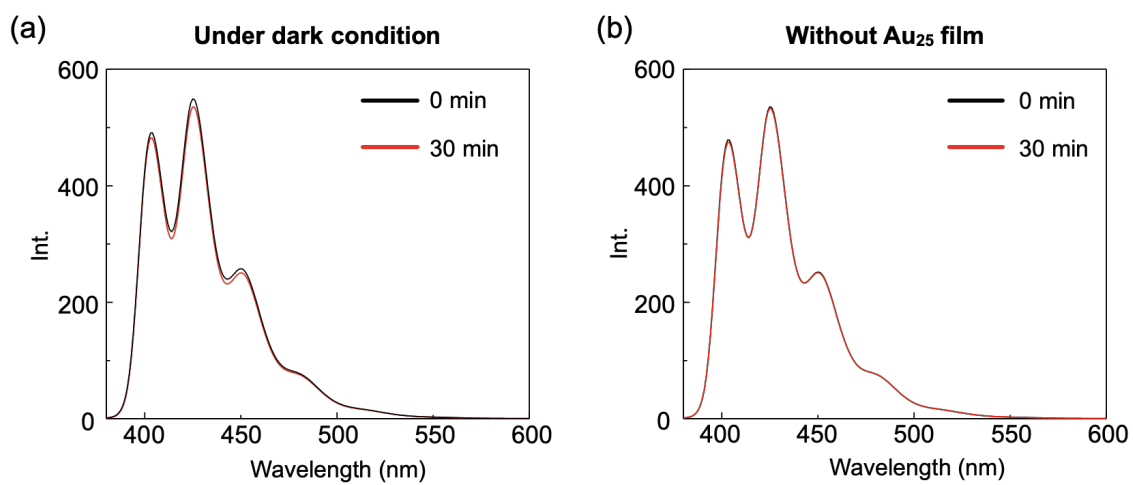


Figure S8. Photoluminescence spectra of DMA in methanol (a) with Au₂₅ cluster film **3** under dark condition and (b) without Au₂₅ film under irradiation at 520 nm.