

ELECTRONIC SUPPLEMENTARY INFORMATION

**Charge-dependent hierarchical self-assembling of fluorinated gold nanoclusters.**

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## General

Tetrachloroauric (III) acid tetrahydrate (>47.5% for gold) was purchased from TANAKA HOLDINGS Co., Ltd. 1-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. Dynamic light scattering (DLS) was collected on a Malvern Zetasizer Nano-S light scattering system with a 633 nm He/Ne laser at 20 °C. Routine <sup>1</sup>H NMR spectra were collected at ambient temperature on a JEOL EX-400 NMR spectrometer. Visible absorption and photoluminescence spectra were recorded at 25°C on a JASCO V-670 and FP-8600 spectrometers, respectively, using a quartz cell with a 1-cm path length. Transmission electron microscopy (TEM) images were obtained by JEM-2000FX at Faculty of Engineering, Hokkaido University. Scanning electron microscopy (SEM) images were obtained by JSM-7001FA at Faculty of Engineering, Hokkaido University. Powder X-ray diffraction (PXRD) profiles were obtained at room temperature on a Bruker D2 PHASER 2<sup>nd</sup> Generation with CuK $\alpha$  radiation. SAXS measurements were conducted on a Rigaku NANOPIX with a Rigaku model HyPix-6000 detector. The sample-to-detector distance was set to be 59.4 cm and exposure time was 2 minutes. The scattering vector  $q$  ( $q = 4\pi \cdot \sin\theta / \lambda$ ;  $\theta$  = scattering angle;  $\lambda$  = wavelength of the incident X-ray beam [1.54 Å]) and the position of the incident X-ray beam on the detector was calibrated using several orders of layer reflections from silver behenate.

### Synthesis of [Au<sub>25</sub>(SC<sub>6</sub>H<sub>13</sub>)<sub>18</sub>]<sup>-</sup>(TOA<sup>+</sup>)

[Au<sub>25</sub>(SC<sub>6</sub>H<sub>13</sub>)<sub>18</sub>]<sup>-</sup>(TOA<sup>+</sup>) was prepared from HAuCl<sub>4</sub>•3H<sub>2</sub>O, 1-hexanethiol, and tetraoctylammonium bromide by using a conventional NaBH<sub>4</sub> reduction method reported for the synthesis of analogous Au<sub>25</sub> clusters (e.g., Z. Wu, J. Suhan, R. Jin, *J. Mater. Chem.*, 2009, **19**, 622–626). Finally, [Au<sub>25</sub>(SC<sub>6</sub>H<sub>13</sub>)<sub>18</sub>]<sup>-</sup>(TOA<sup>+</sup>) was isolated in 31% yield as black powder.

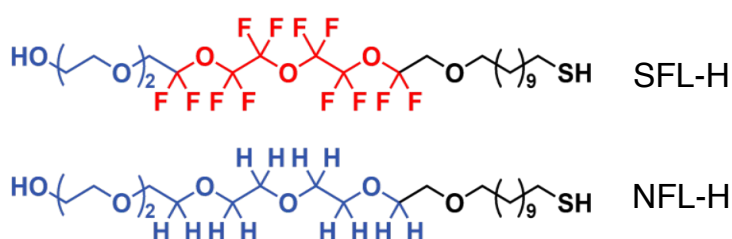
### Synthesis of [Au<sub>25</sub>(SC<sub>6</sub>H<sub>13</sub>)<sub>18</sub>]<sup>0</sup>

[Au<sub>25</sub>(SC<sub>6</sub>H<sub>13</sub>)<sub>18</sub>]<sup>-</sup> was oxidized by following a method for the synthesis of analogous Au<sub>25</sub> cluster (S. Antonello, G. Arrigoni, T. Dainese, M. De Nardi, G. Parisio, L. Perotti, A. Rene, A. Venzo and F. Maran, *ACS Nano*, 2014, **8**, 2788). Briefly, [Au<sub>25</sub>(SC<sub>6</sub>H<sub>13</sub>)<sub>18</sub>]<sup>-</sup>(TOA) was dissolved in DCM and stirred in the presence

of silica gel for column chromatography (Silica gel 60 (spherical, neutral), Merck) at room temperature. UV-Vis absorption spectra were used to monitor the oxidation, where the absorbance increase at 400 nm and the decrease at 450 nm were observed, and the color of solution turned from brown to green as the extent of the oxidation. After the spectral changes reached saturation (~ 1h), the mixture was loaded on a silica gel column using DCM as an eluent to remove and TOA<sup>+</sup>. The green fraction was separated, concentrated by rotary evaporator, and then dried in vacuo for over 3 h to give [Au<sub>25</sub>(SC<sub>6</sub>H<sub>13</sub>)<sub>18</sub>]<sup>0</sup>.

### Synthesis of semi- and non-fluorinated thiols (SFL-H, and NFL-H)

The precursory thiol for semi-fluorinated ligand (SFL-H) was prepared according to the literature method reported by the group of one of the authors (K. Niikura, N. Iyo, T. Higuchi, T. Nishio, H. Jinnai, N. Fujitani and K. Ijro, *J. Am. Chem. Soc.*, 2012, **134**, 7632). NFL-H was prepared by a standard organic synthesis method (S. Kopitzki, K. J. Jensen, J. Thiem, *Chem. Eur. J.* **2010**, *16*, 7017; N. Bonnet, D. O'Hagan and G. Hähner, *Chem. Commun.*, 2007, **47**, 5066-5068). These thiols were identified by <sup>1</sup>H NMR.



### Synthesis of SFL and NFL-modified Au<sub>25</sub> clusters

Typically, to a 5 mL of THF solution containing 3.0 mg of [Au<sub>25</sub>(SC<sub>6</sub>H<sub>13</sub>)<sub>18</sub>]<sup>-</sup> (TOA<sup>+</sup>) was added 8.0 mg (30 eq.) of SFL-H (30 eq.) was added under air and the mixture was stirred at room temperature for 4.5 h. Then, the resulting solution was partially evaporated to remove THF, and the resulting solution was subjected to size-exclusion chromatography using Bio-Beads S-X1 Beads (Bio-Rad) with THF as eluent to remove residual free ligands. The separated cluster fraction was evaporated and then dried in vacuum for 15 hours, giving modified Au<sub>25</sub> clusters as oily solids.

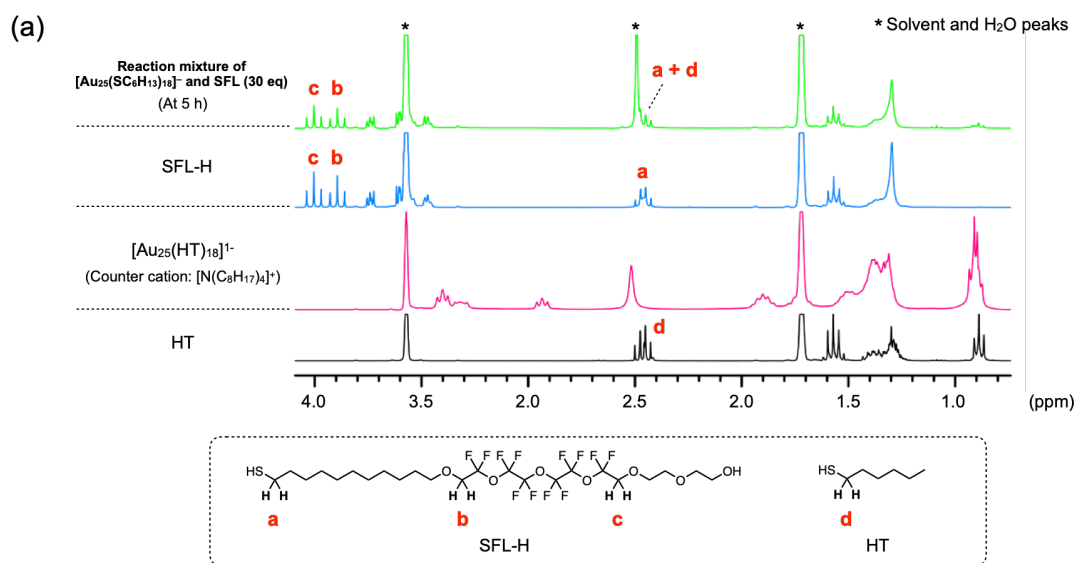
### Preparation of TEM samples

The samples (SFL-Au<sub>25</sub>, NFL-Au<sub>25</sub>) were dissolved in THF and then the solution

was deposited on a TEM grid (Nisshin EM, Fine grid, Cat. 653, 200 mesh, Cu). All grids were dried in vacuo for 24 hours and then subjected to the TEM and measurements.

### **Preparation of SEM samples**

The dried solids of SFL- and NFL-Au<sub>25</sub> clusters were placed on the Carbon double-sided tape for SEM (Nisshin-EM, Cat.No.732) attached to the sample stage of SEM, and air duster was sprayed on it to blow off excess dust. Then the stage was inserted to the SEM chamber.



(b)

Peaks of free HT and free SFL in the reaction mixture #	a	c	d
NMR integration	2.0	2.0	1.8

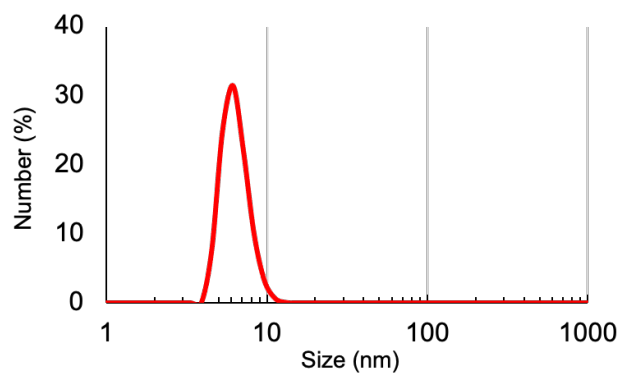
• Free SFL : free 1-hexanethiol = 1 : 0.9  
 • Total free thiolate ligands (Free SFL + free 1-hexanethiol) = 30

$\longrightarrow$  Exchanged 1-hexanethiol (x) =  $(0.9/1.9) \times 30 = 14$

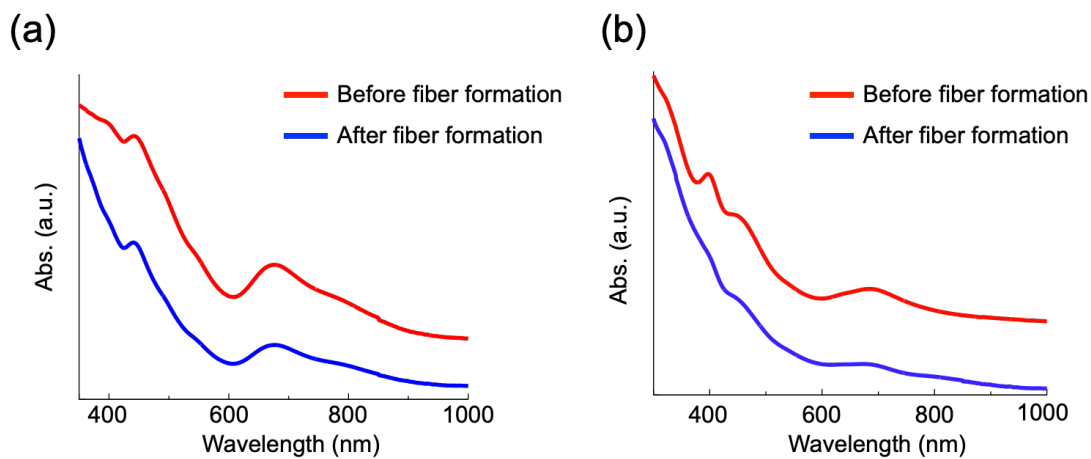
$\downarrow$

$[\text{Au}_{25}(\text{SC}_6\text{H}_{13})_{18-x}(\text{SFL})_x]^{-}$   
 ( $x_{\text{Ave}} = 14$ )

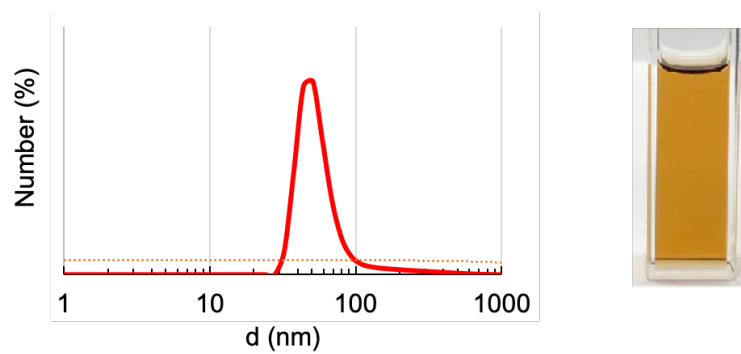
**Figure S1.** (a)  $^1\text{H}$ -NMR spectra of the reaction mixture of  $\text{Au}_{25}(\text{HT})_{18}$  and SFL-H, and individual ones of  $\text{Au}_{25}(\text{HT})_{18}$ , SFL-H, and HT in  $\text{THF-d}^8$  (300 MHz, 298 K). (b) The number of the exchanged SFLs calculated from integrated areas of some characteristic protons. # Coordinated SFL peaks are not seen because the motion of the SFLs was significantly suppressed by bundling of fluorinated units.



**Figure S2.** Number-based DLS profile of  $[\text{Au}_{25}(\text{SFL})_x(\text{HT})_{18-x}]^-$  in THF (25 °C).



**Figure S3.** Changes of the absorption spectra of SFL-modified (a)  $[\text{Au}_{25}]^{1-}$  cluster and (b)  $[\text{Au}_{25}]^0$  cluster before (red line) and after (blue line) the fiber formation in THF. The sample after fiber formation was re-dissolved in THF.



**Figure S4.** DLS profile of re-dissolved solution of **2** in THF.