

## Supporting Information

# **Photoinduced Isomerization-Driven Structural Transformation Between Decanuclear and Octadecanuclear Gold(I) Sulfido Clusters**

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## 1. Experimental Section

**Materials and Reagents.** *cis*-[dppee(AuCl)<sub>2</sub>] and *trans*-[dppee(AuCl)<sub>2</sub>] were prepared according to literature procedures.<sup>1,2</sup> All other reagents and solvents were used as received.

**Instrumentation.** <sup>1</sup>H NMR spectra were recorded on a Bruker AVANCE 400 (400 MHz) fourier transform NMR spectrometer with chemical shifts (δ, ppm) relative to tetramethylsilane (Me<sub>4</sub>Si). <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded on a Bruker AVANCE (162 MHz) Fourier transform NMR spectrometer with chemical shifts (δ, ppm) relative to 85% H<sub>3</sub>PO<sub>4</sub>. MALDI-TOF mass spectra were recorded on a Bruker Autoflex II mass spectrometer (Bruker Daltonics, Bremen, Germany) in positive reflection mode. High resolution ESI-MS were performed on LTQ Orbitrap Velos mass spectrometer (Thermo Scientific). Elemental analyses were performed on a Flash EA 1112 elemental analyzer at the Institute of Chemistry, Chinese Academy of Sciences, Beijing.

**Experimental details.** Bubbling of H<sub>2</sub>S gas into a suspension of *cis*-[dppee(AuCl)<sub>2</sub>] (dppee = 1,2-bis(diphenylphosphino)ethene) or *trans*-[dppee(AuCl)<sub>2</sub>] in dichloromethane-ethanol-pyridine (1:1:1, v/v/v) resulted in a clear yellow or red solution, leading to the formation of polynuclear gold(I) μ<sub>3</sub>-sulfido cluster, [Au<sub>10</sub>(μ-*cis*-dppee)<sub>4</sub>(μ<sub>3</sub>-S)<sub>4</sub>]Cl<sub>2</sub> ([**1**]Cl<sub>2</sub>) or [Au<sub>18</sub>(μ-*trans*-dppee)<sub>6</sub>(μ<sub>3</sub>-S)<sub>8</sub>]Cl<sub>2</sub> ([**2**]Cl<sub>2</sub>). The PF<sub>6</sub><sup>−</sup> salt of cluster **2** ([**2**](PF<sub>6</sub>)<sub>2</sub>) was obtained through metathesis reaction with NH<sub>4</sub>PF<sub>6</sub> in methanol. Pure complexes were obtained by recrystallization. The identities of these clusters were confirmed by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy, elemental analysis, HR-MALDI-TOF and ESI mass spectrometry, and X-ray single crystal diffraction.

**Characterization. Complex 1:** Yield, 83 %. [**1**]Cl<sub>2</sub>: <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD, 298 K /ppm): δ 6.36 (dt, 8H, <sup>3</sup>J(HH) = 7.8 Hz, <sup>4</sup>J(HH) = 2.2 Hz, −Ph), 7.02-7.07 (m, 8H, −Ph), 7.19 (dd, 8H, <sup>3</sup>J(PH) = 12.8 Hz, <sup>3</sup>J(HH) = 7.3 Hz, −Ph), 7.28 (dd, 4H, <sup>3</sup>J(PH) = 13.1 Hz, <sup>3</sup>J(HH) = 7.8 Hz, =CH−), 7.35-7.51 (m, 24H, −Ph), 7.53 (dd, 4H, <sup>3</sup>J(PH) = 13.1 Hz, <sup>3</sup>J(HH) = 7.8 Hz, =CH−), 7.61-7.70 (m,

24H, -Ph), 7.82 (dd, 8H,  $^3J(\text{PH}) = 12.8$  Hz,  $^3J(\text{HH}) = 7.3$  Hz, -Ph);  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CD}_3\text{OD}$ , 298 K /ppm):  $\delta$  13.69 (d,  $^3J(\text{PP}) = 56.7$  Hz, *cis*-dppee), 17.03 (d,  $^3J(\text{PP}) = 56.7$  Hz, *cis*-dppee); MALDI-TOF-MS:  $m/z$ : 1841.5 ( $[\text{M}]^{2+}$ ), 3089.8 ( $[\text{M} - \text{AuL}]^+$ ), 2692.6 ( $[\text{M} - \text{AuL}_2]^+$ ), 2266.9 ( $[\text{M} - \text{Au}_3\text{SL}_2]^+$ ), 1415.3 ( $[\text{M} - \text{Au}_7\text{S}_3\text{L}_2]^+$ ); HR-ESI-MS: 1841.51 ( $[\text{M}]^{2+}$ ); elemental analysis calcd for  $[\mathbf{1}]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  (found): C 32.95 (32.66), H 2.45 (2.52), N 0.00 (< 0.30).

**Complex 2:** Yield: 69 %.  $[\mathbf{2}]\text{Cl}_2$ :  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ , 298 K /ppm):  $\delta$  6.23 (s, 12H, =CH-), 6.50 (br, 24H, -Ph), 6.76 (t, 12H,  $^3J(\text{HH}) = 7.1$  Hz, -Ph), 7.40-7.49 (m, 60H, -Ph), 7.84 (br, 24H, -Ph);  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CD}_3\text{OD}$ , 298 K /ppm):  $\delta$  39.61 (s, *trans*-dppee); elemental analysis calcd for  $[\mathbf{2}]\text{Cl}_2$  (found): C 29.97 (29.93), H 2.13 (2.31), N 0.00 (< 0.30).  $[\mathbf{2}](\text{PF}_6)_2$ :  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K /ppm):  $\delta$  6.32 (s, 12H, =CH-), 6.58 (br, 24H, -Ph), 6.86 (t, 12H,  $^3J(\text{HH}) = 7.1$  Hz, -Ph), 7.46-7.58 (m, 60H, -Ph), 7.92 (br, 24H, -Ph);  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ , 298 K /ppm):  $\delta$  39.55 (s, *trans*-dppee), -144.02 (sept,  $^1J(\text{PF}) = 706.7$  Hz,  $\text{PF}_6$ ); MALDI-TOF-MS:  $m/z$ : 4793.0 ( $[\text{M} - \text{AuL}_3]^+$ ), 4397.6 ( $[\text{M} - \text{AuL}_4]^+$ ), 3941.3 ( $[\text{M} - \text{Au}_5\text{S}_2\text{L}_3]^+$ ); HR-ESI-MS: 3089.41 ( $[\text{M}]^{2+}$ ); elemental analysis calcd for  $[\mathbf{2}](\text{PF}_6)_2$  (found): C 28.96 (29.36), H 2.06 (2.27), N 0.00 (< 0.30).

## 2. X-Ray Diffraction Measurements.

Single crystals of  $[\mathbf{1}]\text{Cl}_2$  suitable for X-ray analysis were obtained by slow vapour diffusion of diethyl ether into the dichloromethane-methanol solution of the complex at ambient temperature. X-Ray diffraction data of the crystal of complex  $[\mathbf{1}]\text{Cl}_2$  were collected using synchrotron radiation ( $\lambda = 0.74990$  Å) on beamline 3W1A at the Beijing Synchrotron Radiation Facilities (BSRF) in the Institute of High Energy Physics (IHEP), Chinese Academy of Sciences (CAS). The diffraction data reduction and integration were performed by the HKL2000 software. Single crystals of  $[\mathbf{2}](\text{PF}_6)_2$

suitable for X-ray analysis were obtained by vapour diffusion of diethyl ether into the dichloromethane/methanol solution of the complex at ambient temperature. Single-crystal X-ray data of [2](PF<sub>6</sub>)<sub>2</sub> were determined on an Oxford Diffraction Gemini S Ultra X-ray single-crystal diffractometer using graphite-monochromatized Cu-K $\alpha$  radiation ( $\lambda = 1.54178$  Å) in Department of Biology and Chemistry at the City University of Hong Kong. The structures were solved by direct methods and refined employing full-matrix least-squares on  $F^2$  by using SHELXTL NT/2000 program and expanded using Fourier techniques.<sup>3</sup> All non-H atoms of the complexes were refined with anisotropic thermal parameters. The hydrogen atoms were included in idealized positions and refined with fixed geometry with respect to their carrier atoms. The disordered solvent molecules were removed using SQUEEZE routine of PLATON. The non-coordinated counter-anions (Cl<sup>−</sup> for [1]Cl<sub>2</sub> and PF<sub>6</sub><sup>−</sup> for [2](PF<sub>6</sub>)<sub>2</sub>) are isolated and located in the crystal lattice. The counter-anions are omitted in all the schemes and figures both in the manuscript and SI involving crystal structures.

*Crystal data for [1]Cl<sub>2</sub>*; C<sub>104</sub>H<sub>88</sub>Au<sub>10</sub>P<sub>8</sub>S<sub>4</sub>Cl<sub>2</sub>,  $M_r = 3754.31$ , orthorhombic, space group  $Pna2_1$ ,  $T = 100$  K,  $Z = 4$ ,  $a = 17.973(4)$ ,  $b = 32.859(7)$ ,  $c = 18.607(4)$  Å,  $\alpha = \beta = \gamma = 90^\circ$ ,  $V = 10989(4)$  Å<sup>3</sup>,  $\rho_c = 2.269$  g cm<sup>−3</sup>,  $\mu = 15.473$  mm<sup>−1</sup>,  $F(000) = 6880$ . Total reflections 9316, unique 9316 ( $R_{\text{int}} = 0.000$ ).  $R_1 = 0.0483$  ( $I > 2\sigma(I)$ ) and  $wR_2 = 0.1259$ , GOF = 1.02 (all data).

*Crystal data for [2](PF<sub>6</sub>)<sub>2</sub>•2CH<sub>2</sub>Cl<sub>2</sub>*; C<sub>158</sub>H<sub>136</sub>Au<sub>18</sub>Cl<sub>4</sub>F<sub>12</sub>P<sub>14</sub>S<sub>8</sub>,  $M_r = 6639.93$ , monoclinic, space group  $C2/c$ ,  $T = 173$  K,  $Z = 4$ ,  $a = 32.9628(7)$ ,  $b = 32.7442(5)$ ,  $c = 20.4118(4)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 109.837(2)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 20724.0(7)$  Å<sup>3</sup>,  $\rho_c = 2.128$  g cm<sup>−3</sup>,  $\mu(\text{CuK}\alpha) = 25.931$  mm<sup>−1</sup>,  $F(000) = 12080$ . Total reflections 40097, unique 19103 ( $R_{\text{int}} = 0.065$ ).  $R_1 = 0.0830$  ( $I > 2\sigma(I)$ ) and  $wR_2 = 0.2471$ , GOF = 1.08 (all data).

**Table S1.** Selected bond distances (Å) and angles (°) for [1]Cl<sub>2</sub>

Au1-Au2	2.8797(8)	Au2-Au3	2.9635(6)
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Au3-Au4	2.9163(8)	Au4-Au5	3.1125(7)
Au5-Au6	2.9897(8)	Au6-Au7	3.0227(7)
Au7-Au8	2.9581(8)	Au8-Au10	3.0215(8)
Au8-Au1	3.0871(7)	Au9-Au2	3.1098(8)
Au9-Au10	3.0110(8)	Au10-Au4	3.1573(8)
Au1-S2	2.286(3)	Au2-S1	2.345(2)
Au3-S1	2.320(2)	Au4-S4	2.348(2)
Au5-S4	2.370(2)	Au6-S3	2.345(2)
Au7-S3	2.352(2)	Au8-S2	2.331(2)
Au9-S2	2.329(2)	Au9-S4	2.288(2)
Au10-S1	2.352(2)	Au10-S	2.259(2)
Au1-P1	2.307(3)	Au2-P2	2.297(2)
Au3-P3	2.269(3)	Au4-P4	2.272(2)
Au5-P5	2.210(3)	Au6-P6	2.237(3)
Au7-P7	2.274(3)	Au8-P8	2.277(2)
S4-Au4-P4	168.20(9)	S1-Au10-S3	170.94(8)
S1-Au2-P2	161.95(9)	S2-Au9-S4	174.66(8)
P5-Au5-S4	174.73(9)	S1-Au3-P3	168.36(9)
P7-Au7-S3	176.05(9)	S2-Au8-P8	164.98(9)
S3-Au6-P6	161.82(9)	S2-Au1-P1	171.74(9)
Au10-S1-Au3	97.38(8)	Au10-S3-Au7	101.89(9)
Au10-S1-Au2	107.56(9)	Au10-S3-Au6	104.49(9)

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Au3-S1-Au2	78.87(7)	Au7-S3-Au6	80.11(7)
Au9-S2-Au8	101.74(9)	Au9-S4-Au4	107.13(9)
Au9-S2-Au1	99.97(9)	Au9-S4-Au5	96.30(8)
Au8-S2-Au1	83.93(8)	Au4-S4-Au5	82.57(7)

**Table S2.** Selected bond distances (Å) and angles (°) for [2](PF<sub>6</sub>)<sub>2</sub>

Au1-Au6	3.0071(5)	Au2-Au4	2.9469(5)
Au3-Au5	2.9578(4)	Au5-Au9	3.0804(4)
Au6-Au9	3.1738(4)	Au7-Au1	3.1356(4)
Au7-Au2	3.1478(4)	Au7-Au9	2.9559(4)
Au8-Au3	3.1734(4)	Au8-Au4	3.1329(4)
Au8-Au7	2.9574(5)	Au8-Au9	2.9620(4)
Au9-Au7	2.9559(4)	Au9-Au5	3.0804(4)
Au1-S1	2.326(2)	Au2-S4	2.336(2)
Au3-S2	2.343(2)	Au4-S4	2.337(2)
Au5-S2	2.342(2)	Au6-S1	2.333(2)
Au7-S2	2.362(2)	Au7-S3	2.334(2)
Au8-S1	2.363(2)	Au8-S3	2.335(2)
Au9-S3	2.355(2)	Au9-S4	2.355(2)
Au1-P1	2.270(3)	Au2-P2	2.254(3)
Au3-P3	2.252(2)	Au4-P4	2.266(2)
Au5-P5	2.259(2)	Au6-P6	2.265(2)

S1-Au1-P1	175.01(7)	S1-Au6-P6	172.54(7)
S2-Au2-P4	173.03(8)	S2-Au7-S3	175.04(6)
S2-Au3-P3	173.89(6)	S1-Au8-S3	174.65(6)
S4-Au4-P4	173.43(7)	S3-Au9-S4	174.85(6)
S2-Au5-P5	173.35(7)	Au1-S1-Au6	80.40(6)
Au8-S1-Au1	103.67(7)	Au8-S1-Au6	103.29(7)
Au3-S2-Au5	78.29(6)	Au7-S2-Au3	104.35(7)
Au7-S2-Au5	102.65(7)	Au7-S3-Au9	99.87(7)
Au8-S3-Au9	99.82(7)	Au8-S3-Au7	100.80(7)
Au9-S4-Au2	104.36(7)	Au9-S4-Au4	103.11(7)
Au4-S4-Au2	78.20(6)		

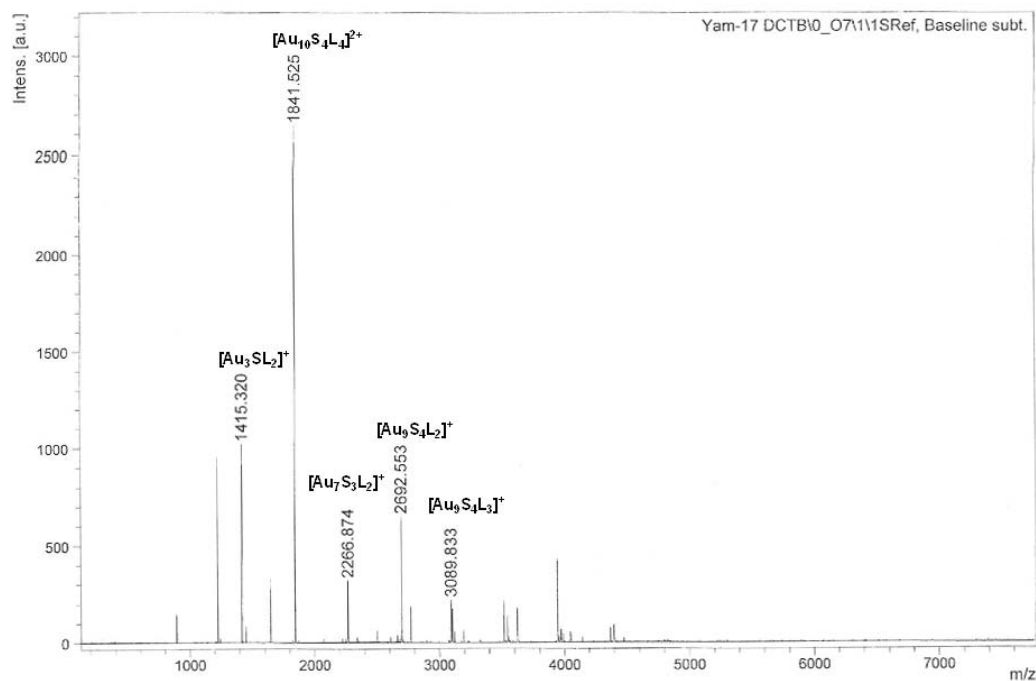
### 3. Photophysical Studies.

**Instrumentation.** UV-Vis absorption spectra were recorded using a Cary 50 Bio UV-Visible spectrophotometer. Photoirradiation experiments were carried out using a 300 W Oriel Corporation model 60011 Xe (ozone-free) lamp.

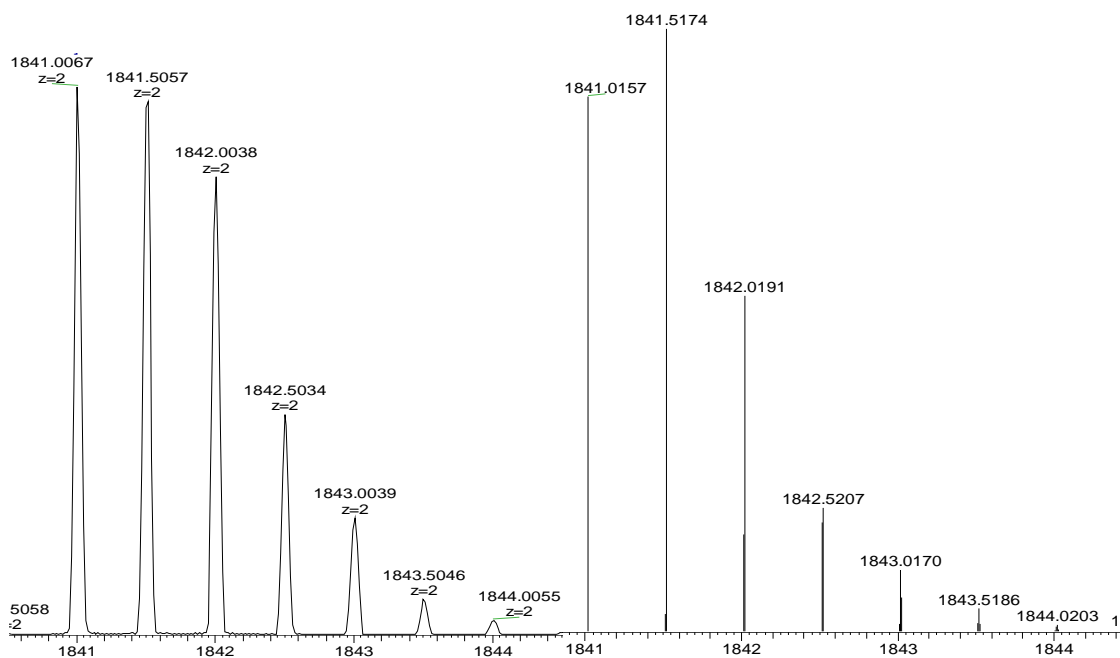
Steady-state emission and excitation spectra at room temperature were recorded on a Spex Fluorolog-3 Model FL3-211 fluorescence spectrophotometer equipped with a R2658P PMT detector. For solution emission and excitation spectra, samples were degassed on a high-vacuum line in a degassing cell with a 10 cm<sup>3</sup> Pyrex round-bottomed flask connected by a side-arm to a 1 cm quartz fluorescence cuvette and sealed from the atmosphere by a Rotaflo HP6/6 quick release Teflon stopper. Solutions were rigorously degassed with no fewer than four freeze-pump-thaw cycles. Solid-state emission and excitation spectra at room temperature were recorded with solid samples

loaded in a quartz tube inside a quartz-walled Dewar flask.

#### 4. Figure S1–S12.

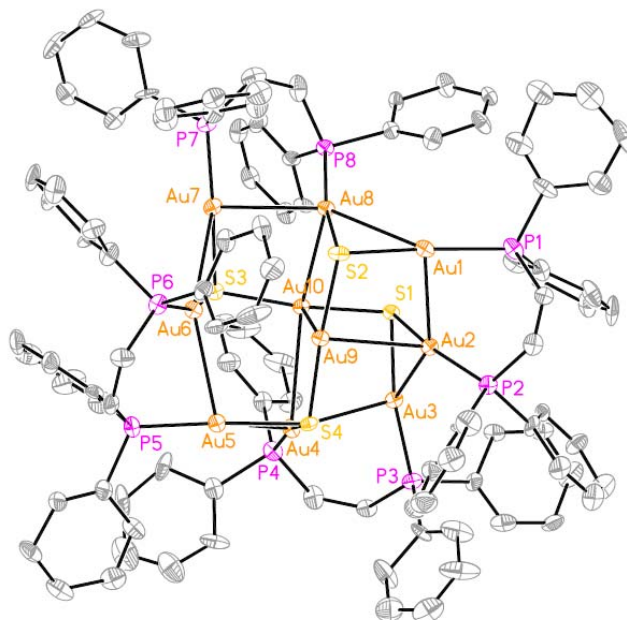


**Figure S1.** MALDI-TOF mass spectrum of complex **1**.

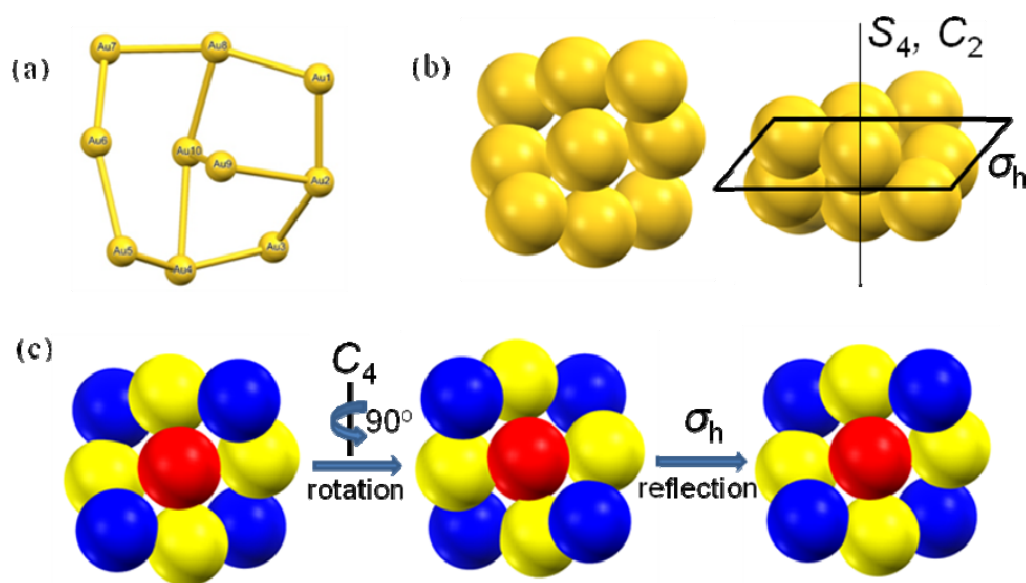


**Figure S2.** Comparison of the experimentally observed high-resolution molecular peak (left) with the simulation (right) of the dication of cluster **1** in ESI mass spectrum.

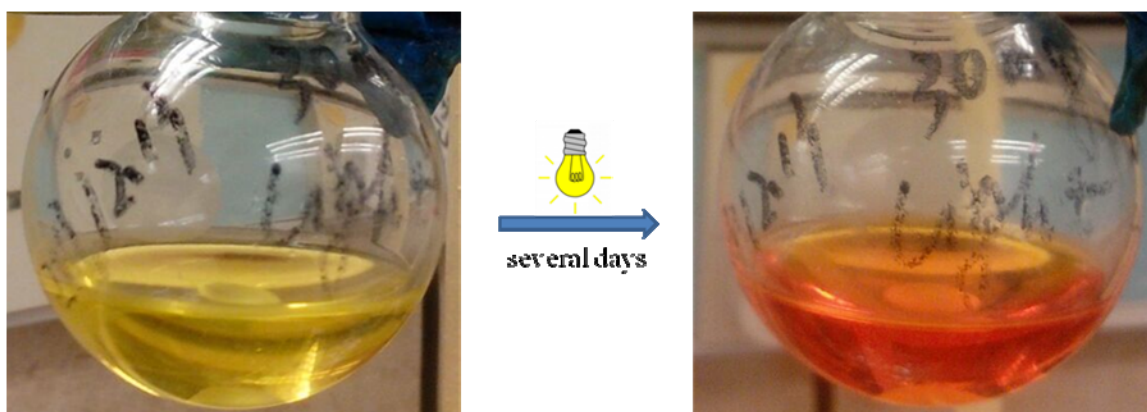




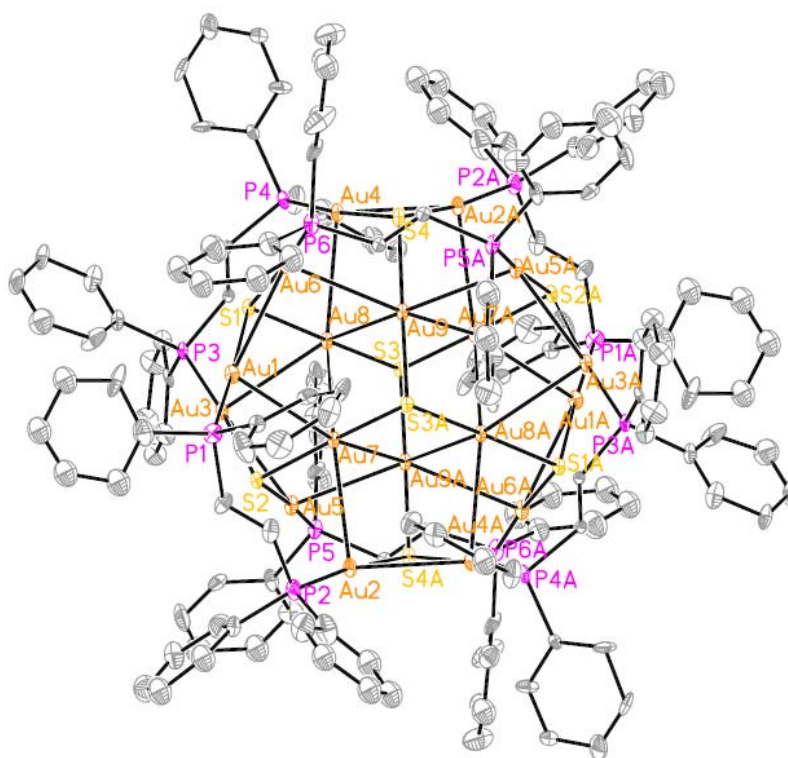
**Figure S3.** Perspective view of the cluster cation of **1**. Thermal ellipsoids are shown at the 30% probability level. The counter-anions and hydrogen atoms are omitted for clarity.



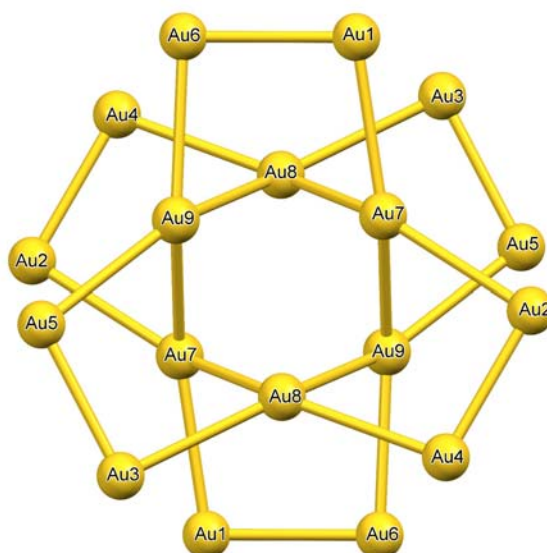
**Figure S4.** (a) Ball and stick view of the metallic skeleton of **1** in the solid state (view from the top), showing the atomic numbering scheme; (b) proposed structure model of the cluster cation with  $S_4$  symmetry in solution (left, top view; right, side view) on the NMR timescale; (c) anti-clockwise rotation of the proposed structure in solution along  $C_4$  axis (the axis along Au9 and Au10) followed by reflection about  $\sigma_h$ , and the three colors (red, yellow, and blue) represent the three different Au environments.



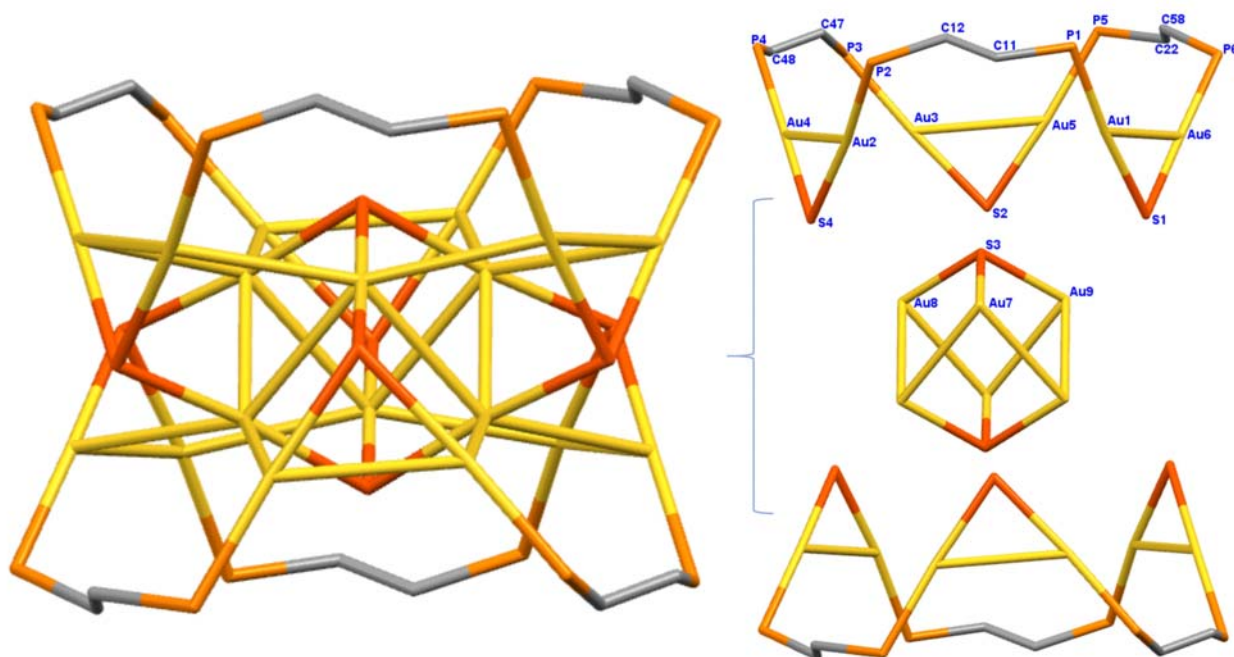
**Figure S5.** The color of the methanol solution of cluster **1** before (left) and after (right) being placed under ambient light for several days.



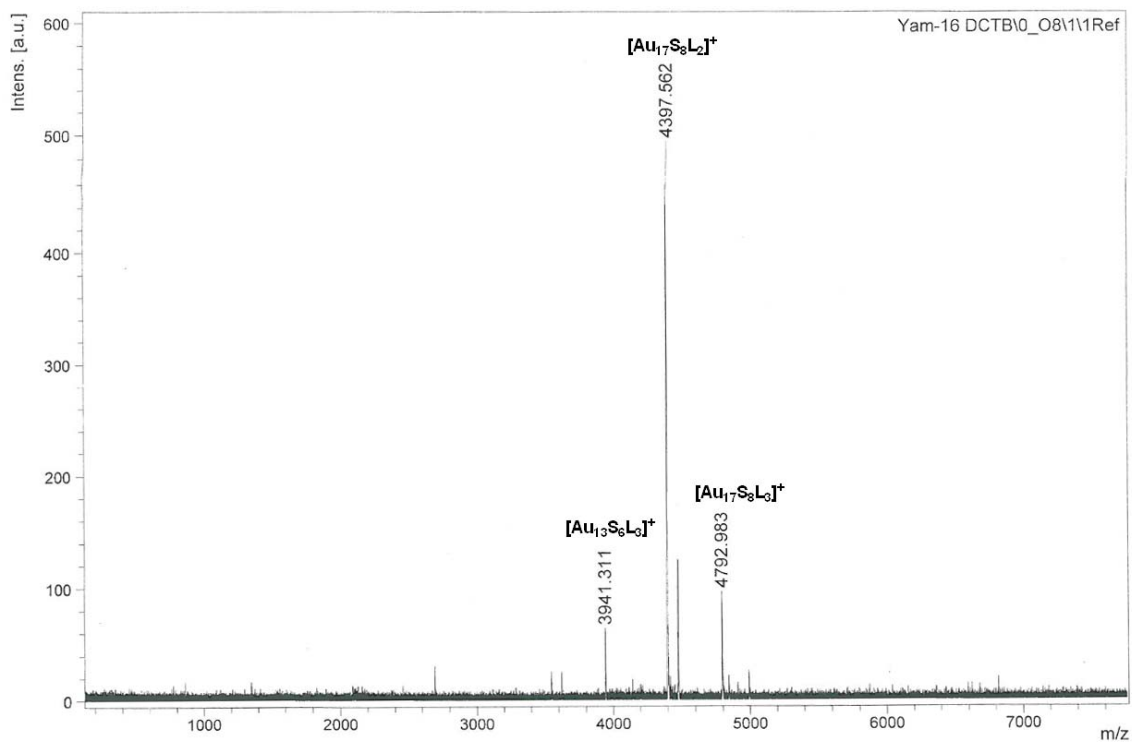
**Figure S6.** Perspective view of the cluster cation of **2**. Thermal ellipsoids are shown at the 30% probability level. The counter-anions, solvent molecules, and hydrogen atoms are omitted for clarity.



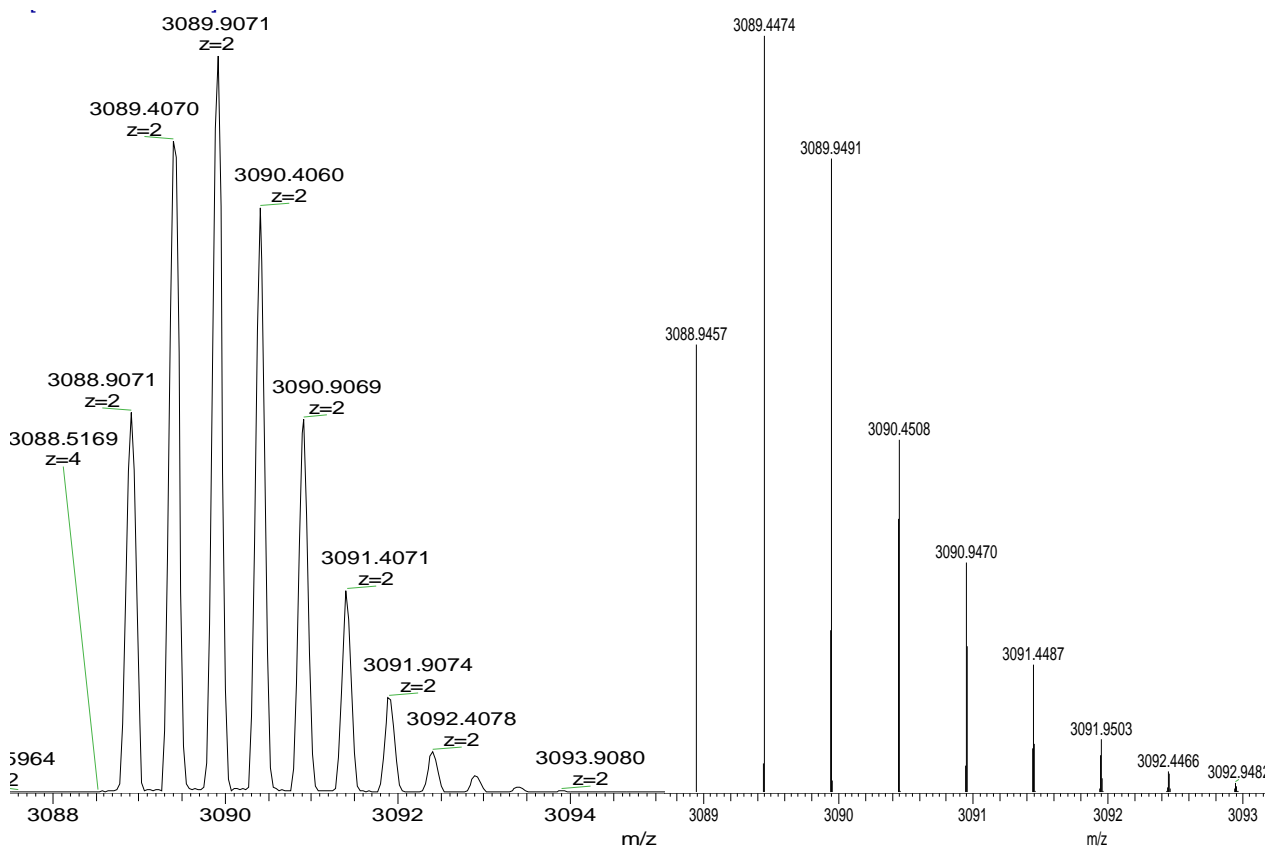
**Figure S7.** Ball and stick view of the metallic skeleton of **2**, showing the atomic numbering scheme.



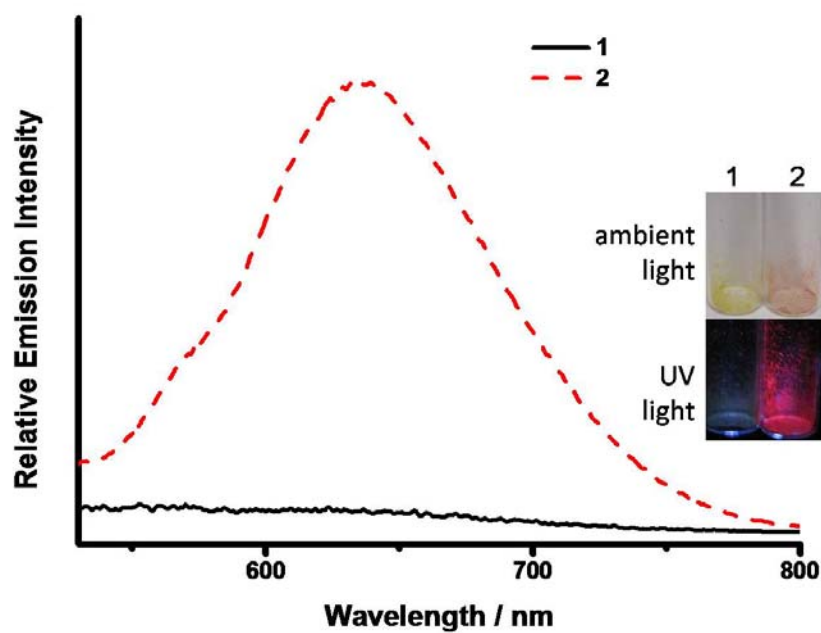
**Figure S8.** Side view and components of the cluster cation of complex **2** in capped stick model (gray, C; orange, P; yellow, Au; red, S; phenyl rings and hydrogen atoms are omitted for clarity).



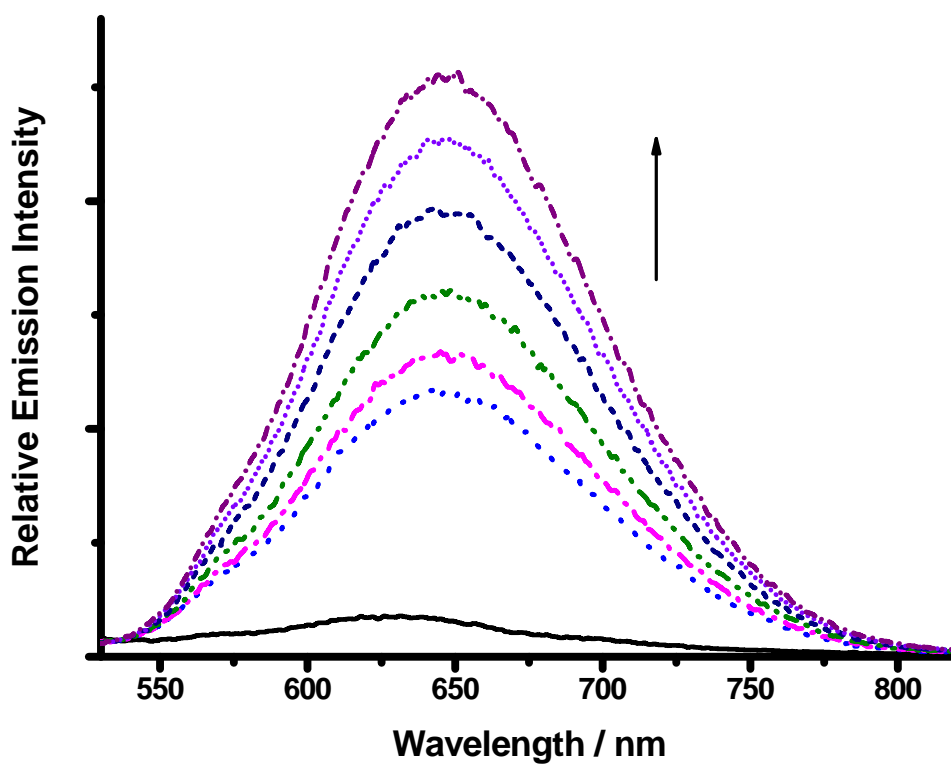
**Figure S9.** MALDI-TOF mass spectrum of complex **2**.



**Figure S10.** Comparison of the experimentally observed high-resolution molecular peak (left) with the simulation (right) of the dication of cluster **2** in ESI mass spectrum.



**Figure S11.** Solid state emission spectra of complexes **[1]**Cl<sub>2</sub> and **[2]**Cl<sub>2</sub> at room temperature. The insets show the color of these two clusters under ambient light and UV light (365 nm).



**Figure S12.** Emission spectral changes of **[1]**Cl<sub>2</sub> in degassed methanol upon photoexcitation.

## 5. References

- [1] Schmidbaur, H.; Reber, G.; Schier, A.; Wagner, F. E.; Müller, G. *Inorg. Chim. Acta* **1988**, *147*, 143–150.
- [2] Bhargava, S.; Kitadai, K.; Masashi, T.; Drumm, D. W.; Russo, S. P.; Yam, V. W.-W.; Lee, T. K.-M.; Wagler, J.; Mirzadeha, N. *Dalton Trans.* **2012**, *41*, 4789.
- [3] G. M. Sheldrick, *SHELXTL NT, Program for Solution and Refinement of Crystal Structures*, version 5.1; University of Göttingen: Göttingen, Germany, **1997**.