

## Supporting Information

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### Self-assembly of an all-thiol-stabilized {Ag<sub>28</sub>S<sub>23</sub>} high-nuclearity luminescent nanocluster with a “crab-like” shape

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## 1. Synthetic procedures

**General comments:** AgS<sup>t</sup>Bu was prepared by using Et<sub>3</sub>N as organic solvent and reacted with equivalent amounts of AgNO<sub>3</sub> with HS<sup>t</sup>Bu according to the literature.<sup>1</sup> Other reagents and solvents for synthesis were obtained from commercial sources and used without further purification.

### 5 [Ag<sub>28</sub>(S<sup>t</sup>Bu)<sub>23</sub>](CF<sub>3</sub>COO)<sub>5</sub>·8CH<sub>3</sub>OH (**1**):

Compound **1** can be obtained through four methods, which are detailly listed below.

Method 1 (Br<sup>-</sup>): AgS<sup>t</sup>Bu (0.0558 g, 0.2832 mmol) was dissolved in methanol (20 mL) under stir at room temperature. CF<sub>3</sub>COOH (0.1 mL) and Et<sub>3</sub>N (0.3 mL) were in turn added to the above solution with stir, and then KBr (0.0009 g, 0.0076 mmol) was added to the mixture after several minutes. The light pink solution was stirred  
10 at room temperature for one week and then was filtered. The filtrate was evaporated slowly in air at room temperature. Compound **1** was deposited as lightyellow block crystals. Yield: ca. 13% (based on Ag). Elemental analysis (%) calcd for C<sub>110</sub>H<sub>239</sub>O<sub>18</sub>F<sub>15</sub>S<sub>23</sub>Ag<sub>28</sub>: C, 22.42; H, 4.09; Ag, 51.25. Found: C, 22.53; H, 3.96; Ag, 51.19.

Method 2 (I<sup>-</sup>): AgS<sup>t</sup>Bu (0.0593 g, 0.3010 mmol) was dissolved in methanol (20 mL) under stir at room  
15 temperature. CF<sub>3</sub>COOH (0.1 mL) and Et<sub>3</sub>N (0.3 mL) were in turn added to the above solution with stir, and then KI (0.0008 g, 0.0048 mmol) was added to the mixture after several minutes. The light pink solution was stirred at room temperature for one week and then was filtered. The filtrate was evaporated slowly in air at room temperature. Compound **1** was deposited as lightyellow block crystals. Yield: ca. 13% (based on Ag). Elemental analysis (%) calcd for C<sub>110</sub>H<sub>239</sub>O<sub>18</sub>F<sub>15</sub>S<sub>23</sub>Ag<sub>28</sub>: C, 22.42; H, 4.09; Ag, 51.25. Found: C, 22.53; H, 3.96; Ag, 51.19.

20 **Table S1** Synthesis methods contrasted

	T	CH <sub>3</sub> OH	AgS <sup>t</sup> Bu	CF <sub>3</sub> COOH	Et <sub>3</sub> N	KBr	KI
1	RT	20 mL	0.0558 g	0.1 mL	0.3 mL	0.0009 g	
2	RT	20 mL	0.0593 g	0.1 mL	0.3 mL		0.0008 g
3	50 °C	20 mL	0.0590 g	0.1 mL	0.3 mL	0.0013 g	
4	50 °C	20 mL	0.0598 g	0.1 mL	0.3 mL		0.0006 g

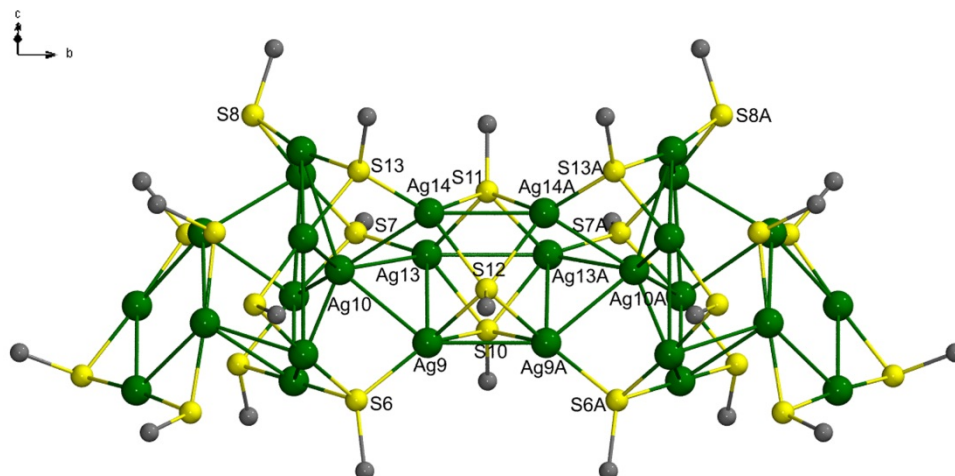
Notes: These synthesis methods are similar to the method 1 (Br<sup>-</sup>) and method 2 (I<sup>-</sup>), and there are only slight difference as listed in Table S1.

## 2. Crystallographic studies

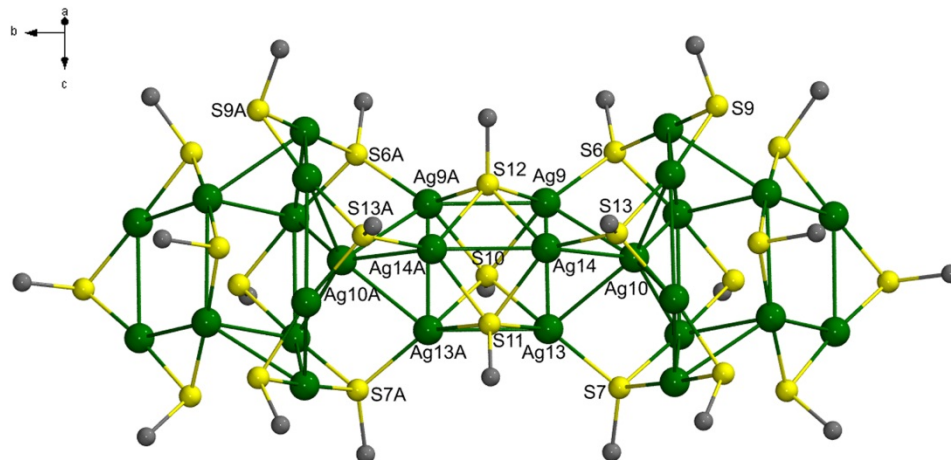
Single-crystal X-ray diffraction data for **1** was recorded on a Bruker Apex CCD II area-detector diffractometer with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 293(2) K. Absorption corrections were applied using multi-scan technique and performed by using the SADABS program. The structure of compound **1** was solved by direct methods and refined on  $F^2$  by full-matrix least squares methods using the SHELXTL package.<sup>2</sup>

Crystal data for **1**:  $C_{110}H_{239}O_{18}F_{15}S_{23}Ag_{28}$ ;  $P2_1/m$ ;  $a = 14.416(5) \text{ \AA}$ ,  $b = 40.031(5) \text{ \AA}$ ,  $c = 15.177(5) \text{ \AA}$ ;  $\alpha = 90.000(5)^\circ$ ;  $\beta = 93.276(5)^\circ$ ;  $\gamma = 90.000(5)^\circ$ ;  $V = 8744(4) \text{ \AA}^3$ ;  $Z = 4$ ; 30781 reflns measured, 9277 unique ( $R_{\text{int}} = 0.0730$ ); final  $R_1 = 0.0610$ ,  $wR_2 = 0.1466$  for 5664 observed reflections [ $I > 2\sigma(I)$ ]. CCDC-991113 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif) for **1**.

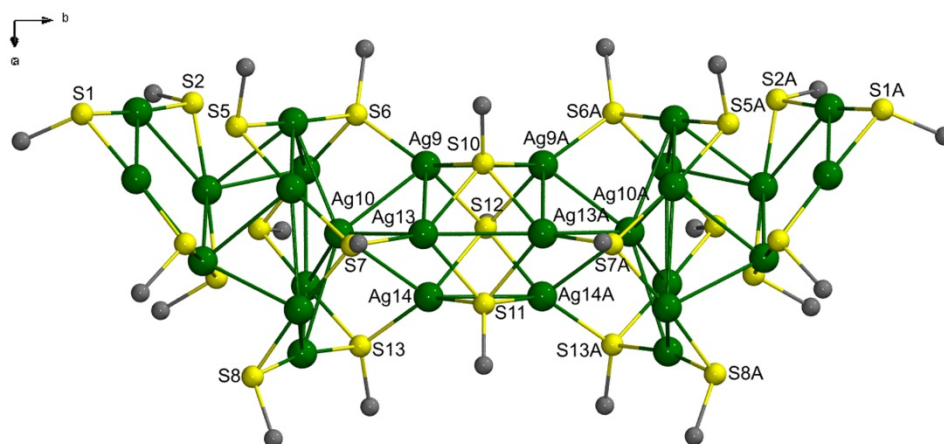
## 3. The structure models of the “crab-like” $\{Ag_{28}S_{23}\}$ cluster in **1**



**Fig. S1** (a) The first kind of direction observation of the “crab-like” shape of the  $\{Ag_{28}S_{23}\}$  cluster in **1**.  $CH_3$  moieties are omitted for clarity. Symmetry code: A,  $x, y, z$ ; B,  $x, 0.5-y, z$ . Color code: Ag, green; S, yellow; C, gray-50%.

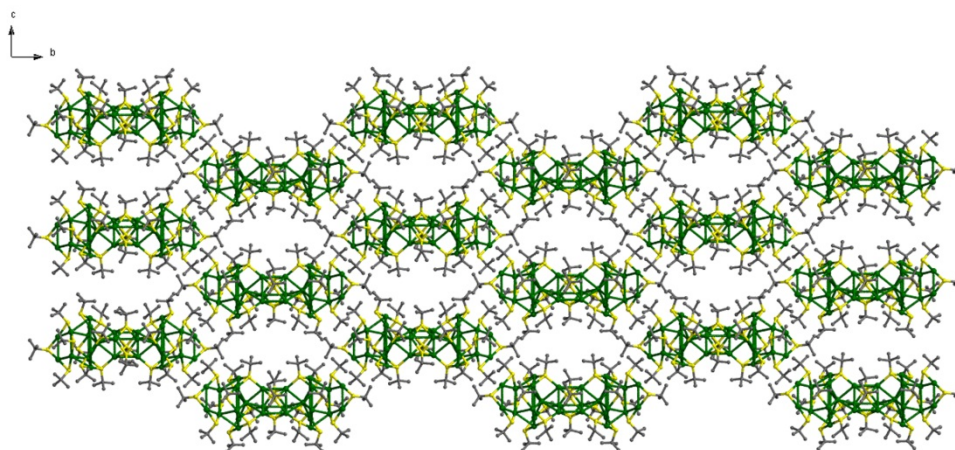


**Fig. S1** (b) The second kind of direction observation of the “crab-like” shape of the  $\{Ag_{28}S_{23}\}$  cluster in **1**.  $CH_3$  moieties are omitted for clarity. Symmetry code: A,  $x, y, z$ ; B,  $x, 0.5-y, z$ . Color code: Ag, green; S, yellow; C, gray-50%.



**Fig. S1** (c) The third kind of direction observation of the “crab-like” shape of the  $\{Ag_{28}S_{23}\}$  cluster in **1**.  $CH_3$  moieties are omitted for clarity. Symmetry code: A,  $x, y, z$ ; B,  $x, 0.5-y, z$ . Color code: Ag, green; S, yellow; C, gray-50%.

The similar “crab-like” shapes of the  $\{Ag_{28}S_{23}\}$  cationic cluster viewed along three directions are shown in Fig. S1. We only select one of these directions to spread our detailed description below as shown in Fig. S1a (Fig. 1c in the main text), and the other two directions are illustrated in Fig. S1b and Fig. S1c.



**Fig. S2** Ball-and-stick view of the 3D structure of **1** along the  $a$  axis. All hydrogen atoms, dissociative  $CF_3COO^-$  and  $CH_3OH$  molecules are omitted for clarity. Symmetry code: A,  $x, y, z$ ; B,  $x, 0.5-y, z$ . Color code: Ag, green; S, yellow; C, gray-50%.

#### 4. Physical Measurements

Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. Ag was analyzed on a PLASMA-SPEC(I) ICP atomic emission spectrometer. The FT-IR spectra were recorded from KBr pellets in the range of  $4000-400\text{ cm}^{-1}$  on a Mattson Alpha-Centauri spectrometer. XPS analysis was performed on a thermo ECSALAB 250 spectrometer with an Al  $K\alpha$  (1486.6 eV) achromatic X-ray source running at 15 kV. The XPS binding energy (BE) was internally referenced to the aliphatic C(1s) peak (BE, 284.6 eV). NMR data were recorded on a Bruker AV spectrometer (500 MHz). TEM was performed on a JEOL-2100F transmission electron microscope under 200 Kv accelerating voltage. Diffuse reflectivity was measured from 200 to 800 nm using barium sulfate ( $BaSO_4$ ) as a standard with 100% reflectance on a Varian Cary 500 UV-Vis spectrophotometer. Luminescence was measured on an F-4500 FL Spectrophotometer.

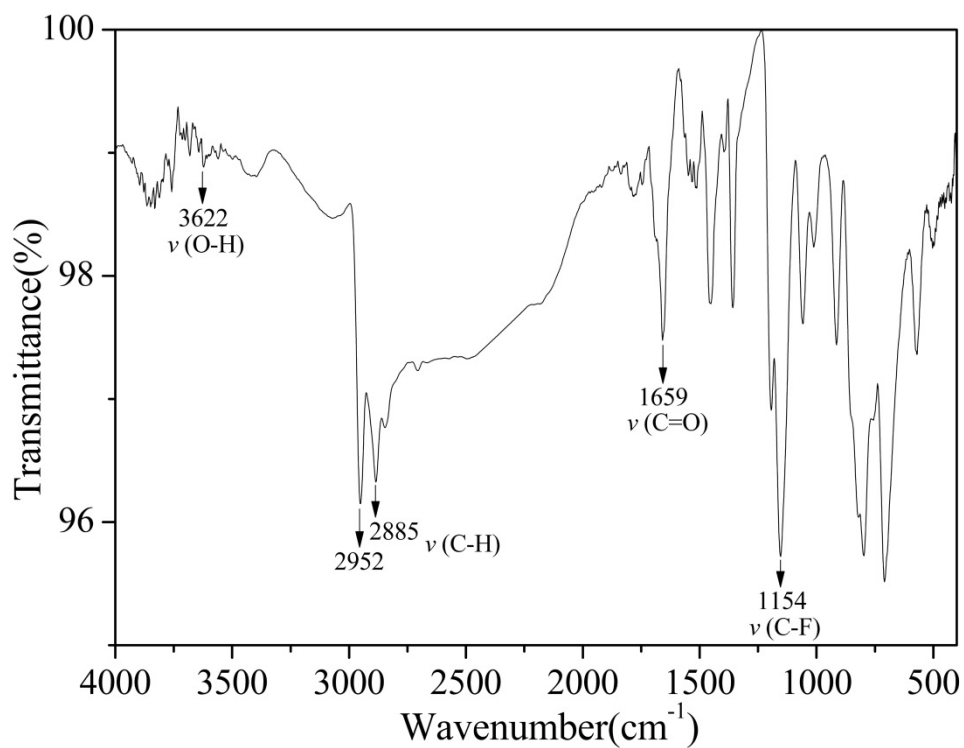


Fig. S3 The IR spectrum of **1**.

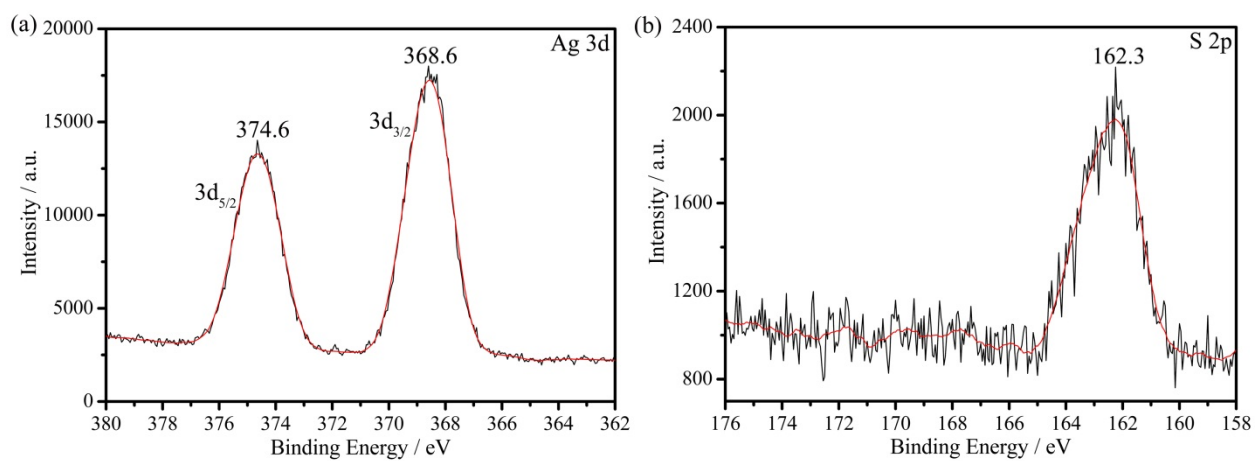


Fig. S4 XPS analysis of Ag (a) and S (b) for **1**.

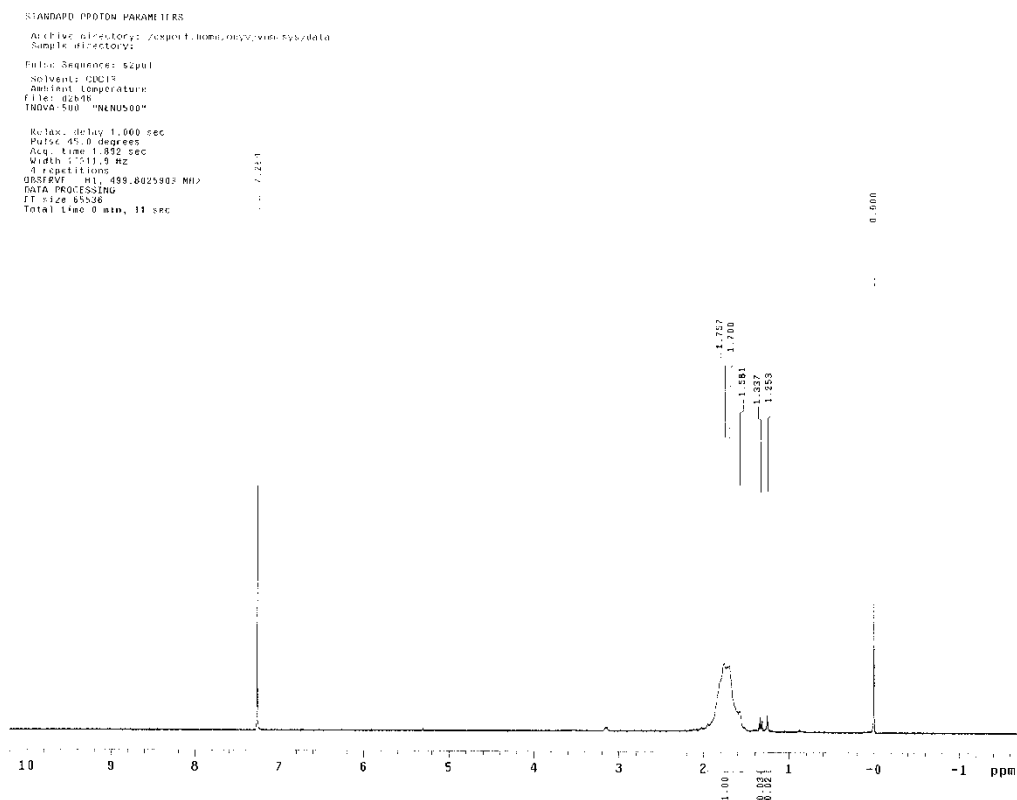


Fig. S5  $^1\text{H}$  NMR spectrum of **1** (500MHz,  $\text{CDCl}_3$ , RT).

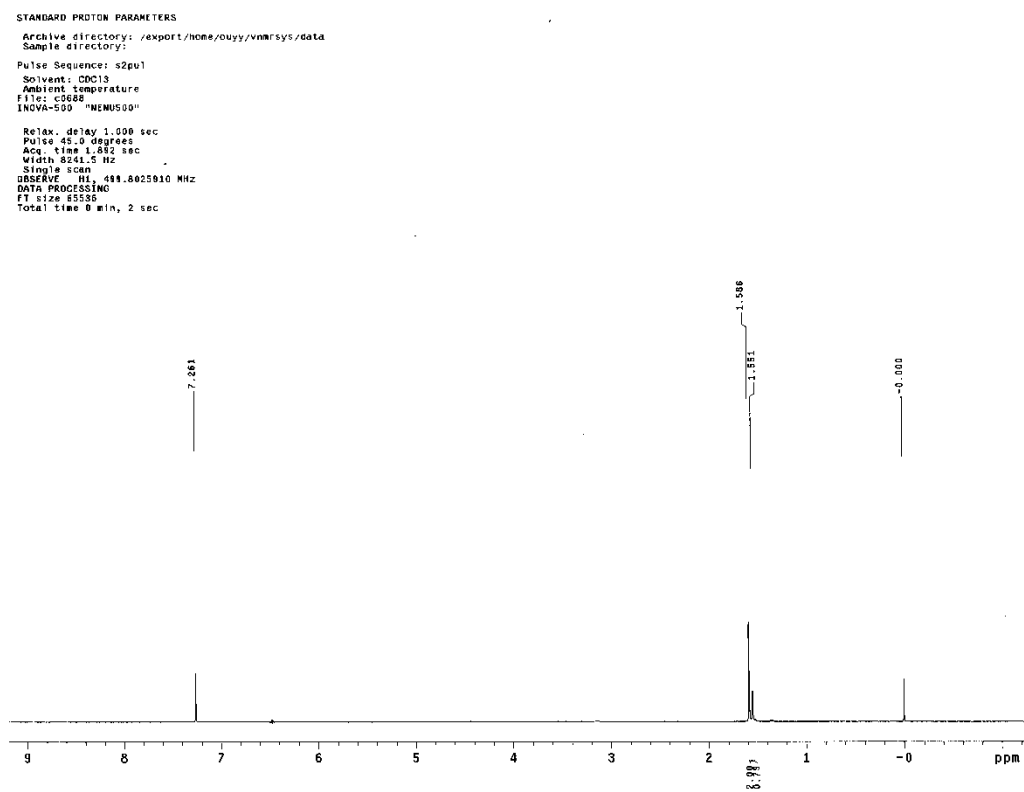
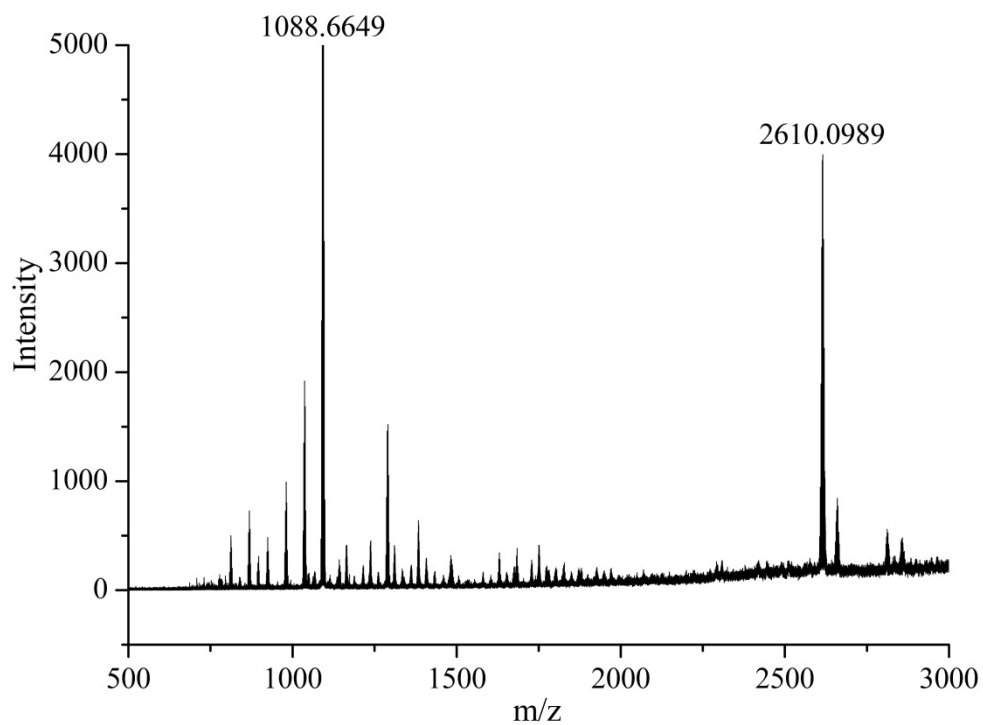


Fig. S6 The  $^1\text{H}$  NMR spectrum of  $\text{AgS}^t\text{Bu}$  ligand (500MHz,  $\text{CDCl}_3$ , RT).

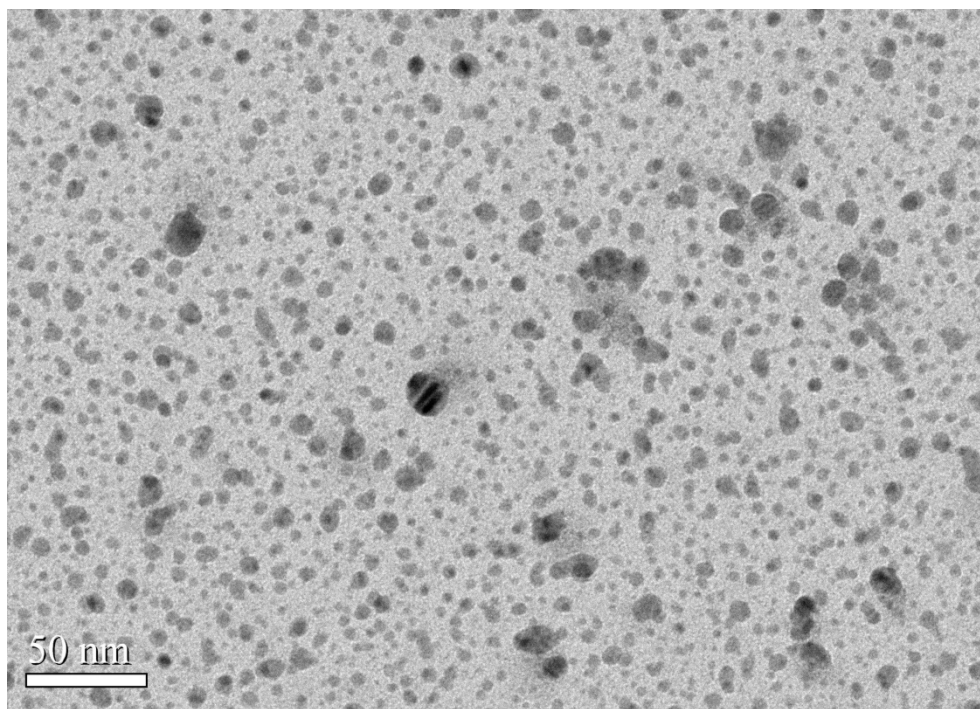


**Fig S7** ESI mass spectrum of nanoparticles in compound **1**.

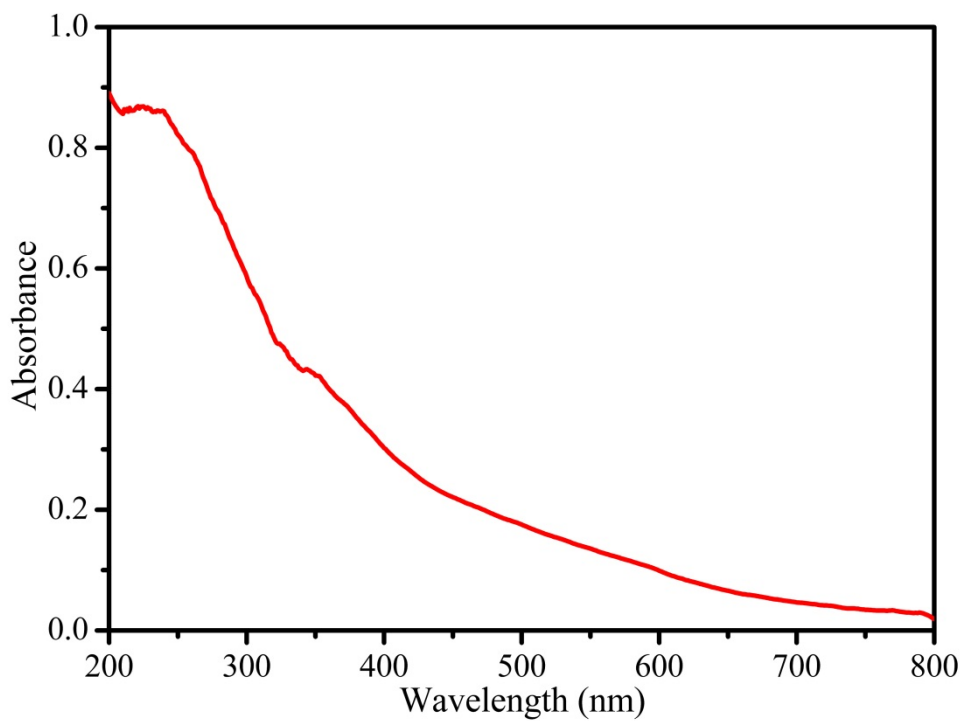
**Table S2.** Detailed assignment of mass spectral data for nanoparticles in compound **1**.

m/z observed	ion set	mass calculated	m/z calculated
1088.6649	$[\text{Ag}_{28}(\text{S}^t\text{Bu})_{23}(\text{CF}_3\text{COO})_3(\text{CH}_3\text{CN})\text{H}_3]^{5+}$	5454.5546	1090.9109
2610.0989	$[\text{Ag}_{28}(\text{S}^t\text{Bu})_{23}(\text{CF}_3\text{COO})(\text{OH})_2]^{2+}$	5218.4627	2609.2314

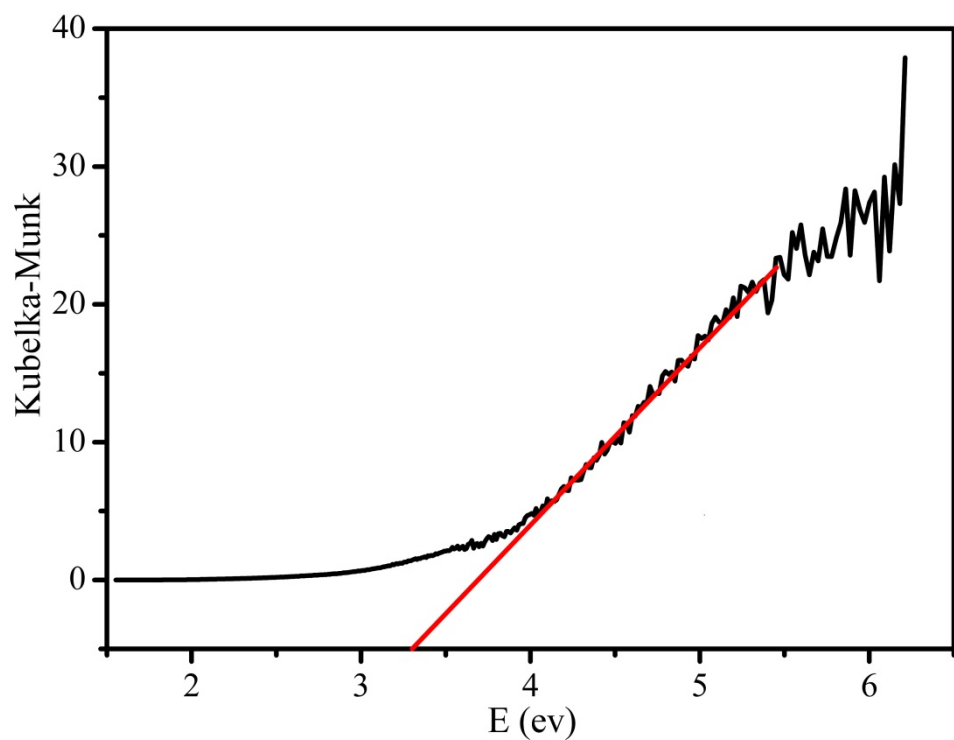
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**Fig. S8** TEM image of **1**.



**Fig. S9** UV-vis-NIR absorption spectrum of **1**.

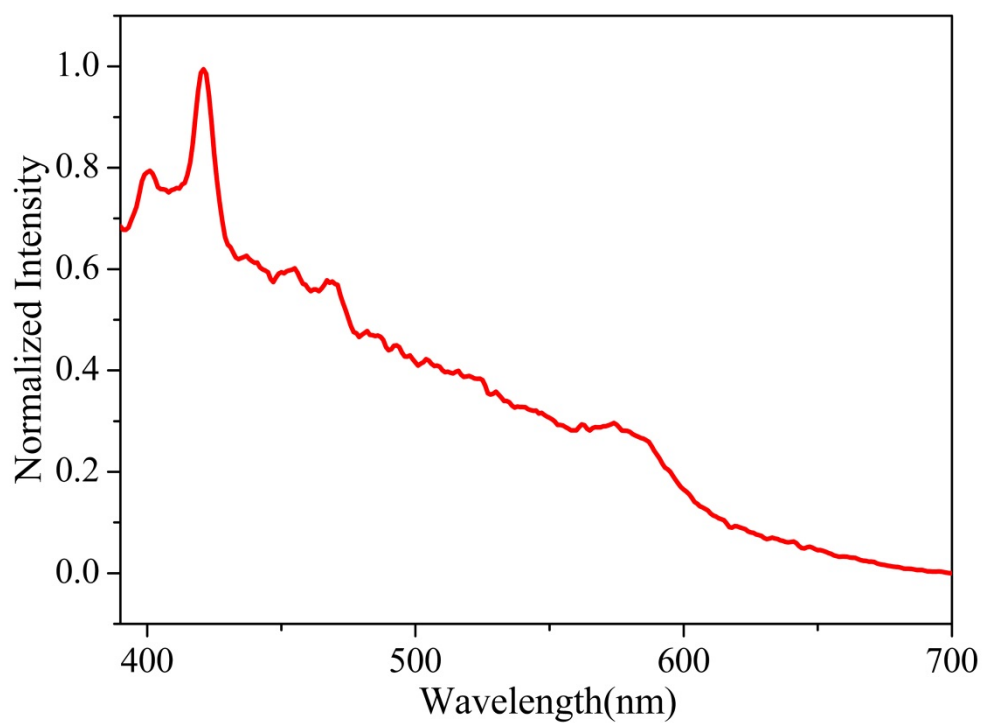


**Fig. S10** Diffuse reflectance UV-vis-NIR spectrum of K-M function vs energy (eV) of **1**.

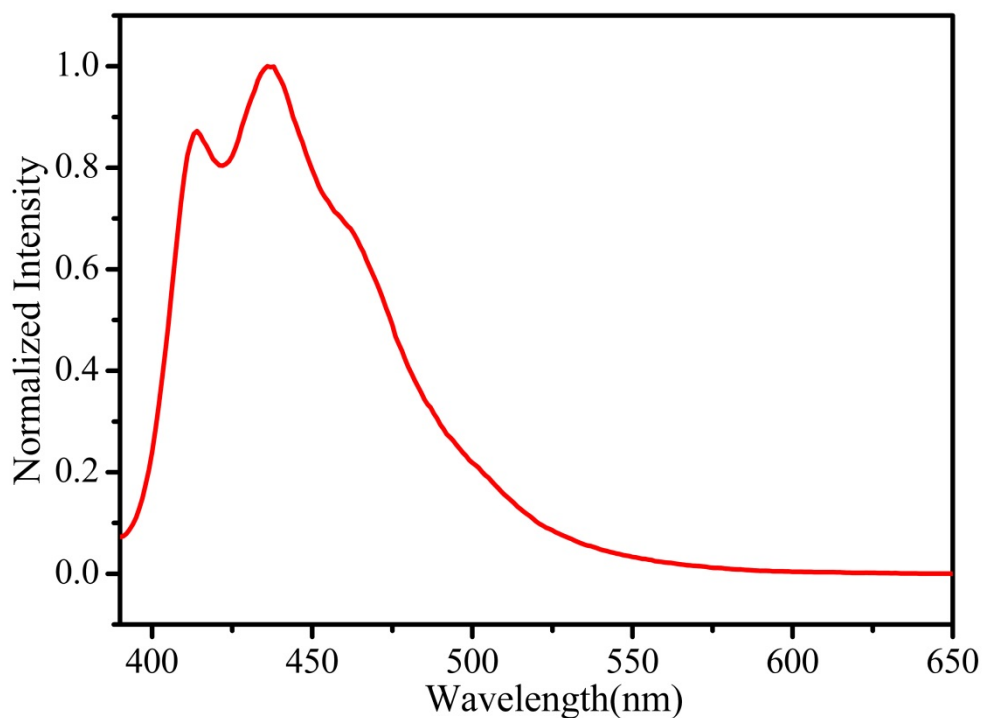
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**Fig. S11** Emission spectrum of **1** upon excitation at 365 nm in the solid state.



**Fig. S12** Emission spectrum of **1** upon excitation at 365 nm in EtOH solution.

**5 Reference:**

1 G. Li, Z. Lei and Q. M. Wang, *J. Am. Chem. Soc.*, 2010, **132**, 17678.

2 (a) G. M. Sheldrick, *SHELX-97, Program for Crystal Structure Refinement*, University of Göttingen, Germany, 1997; (b) G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Solution*, University of Göttingen, Germany, 1997.