

## Supporting Information

### A Macrocyclic-Assisted Nanoparticlization Process for Bulk Ag<sub>2</sub>S

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#### General Consideration

All commercially available chemicals were used without further purification. Methylazacalix[6]pyridine (**Py[6]**) was synthesized according to the literature method by the [3+3] fragment coupling protocol between terminal dibrominated and diaminated linear trimers.<sup>[1]</sup> The solvents used in this study were processed by standard procedures. All reactions were carried out under a nitrogen atmosphere unless otherwise noted. <sup>1</sup>H NMR experiments were carried out on a JEOL ECX-400MHz instrument.

**Synthesis of [Ag<sub>3</sub>(Py[6])](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>•(H<sub>2</sub>O)<sub>0.5</sub> (1).** In a 25 mL round-bottom flask, AgSO<sub>3</sub>CF<sub>3</sub> (30.8 mg, 0.12 mmol) was dissolved in CH<sub>3</sub>OH (4 ml) at room temperature. Then a CH<sub>2</sub>Cl<sub>2</sub> solution (4 mL) of methylazacalix[6]pyridine (**Py[6]**, 25.4 mg, 0.04 mmol) was added dropwisely. The mixture was further stirred for 2 hours at room temperature. The solution was filtered and the filtrate was diffused by diethyl ether in the dark. After several days, colorless crystals of **1** were deposited.

**Synthesis of [Ag<sub>5</sub>S(Py[6])](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>•(CH<sub>3</sub>OH) (2) and [Ag<sub>5</sub>S(Py[6])<sub>2</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> (3).** In a 25 mL round-bottom flask, AgSO<sub>3</sub>CF<sub>3</sub> (205.6 mg, 0.8 mmol) was dissolved in CH<sub>3</sub>OH (4 ml) at room temperature. Then Ag<sub>2</sub>S (49.6 mg, 0.2 mmol) solid was added to the solution under stirring. After an hour, a CHCl<sub>3</sub> solution (4 mL) of methylazacalix[6]pyridine (**Py[6]**, 25.4 mg, 0.04 mmol) was added dropwisely. The mixture was further stirred for 8 hours at 40 °C. The solution was filtered and the filtrate

was diffused by diethyl ether in the dark. In two separate trials, crystals of complex **2** and **3** were deposited.

**Synthesis of [Ag<sub>12</sub>S<sub>2</sub>(Py[6])<sub>2</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>8</sub>•H<sub>2</sub>O•CH<sub>3</sub>OH (**4**).** In a 25 mL round-bottom flask, AgSO<sub>3</sub>CF<sub>3</sub> (205.6 mg, 0.8 mmol) was dissolved in CH<sub>3</sub>OH (4 ml) at room temperature. Then Ag<sub>2</sub>S (49.6 mg, 0.2 mmol) solid was added to the solution under stirring. After 1 hour, a CHCl<sub>3</sub> solution (4 mL) of methylazacalix[6]pyridine (Py[6], 12.7 mg, 0.02 mmol) was added dropwisely. The mixture was further stirred for 8 hours at 40 °C. The solution was filtered and the filtrate was diffused by diethyl ether in the dark. After several days, pale yellow crystals of **4** were deposited.

**Preparation of silver sulfide nanoparticles (D-NP).** Reaction mixture containing silver-sulfide clusters (the condition for complex **2**) was used as a starting material. *In situ* deprotection of Py[6] was conducted by adding CF<sub>3</sub>COOH (0.4 mmol). Two minutes later, oleic amine (8 mmol) was then added to the solution. **D-NP** was precipitated by ethanol and was then washed three times by ethanol. **D-NP** was characterized by TEM after re-dispersion into cyclohexane.

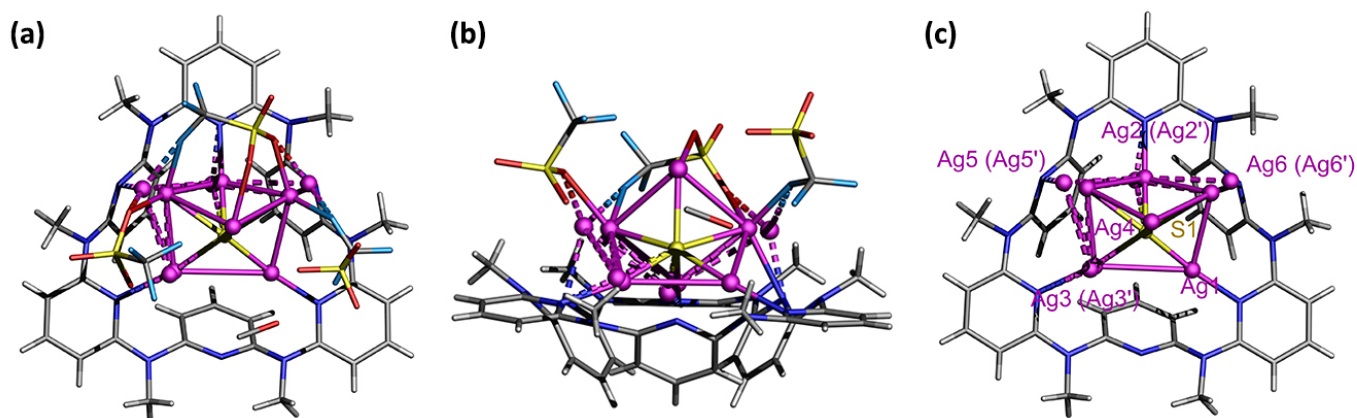
### X-ray Crystallographic Analysis

Data for complexes **1-4** were collected at 173K with Mo-*K*α radiation ( $\lambda = 0.71073 \text{ \AA}$ ) on a Rigaku Saturn 724+ CCD diffractometer with frames of oscillation range 0.5°. All structures were solved by direct methods, and non-hydrogen atoms were located from difference Fourier maps. All non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on  $F^2$  by using the SHELXTL program unless otherwise noticed.<sup>[2]</sup>

Crystal data for [Ag<sub>3</sub>(Py[6])](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>•(H<sub>2</sub>O)<sub>0.5</sub> (**1**) (CCDC-1006732): C<sub>39</sub>H<sub>36</sub>Ag<sub>3</sub>F<sub>9</sub>N<sub>12</sub>O<sub>9.5</sub>S<sub>3</sub>  $M = 1415.59$ , monoclinic, space group  $P2_1/n$  (No. 14),  $a = 13.528(3) \text{ \AA}$ ,  $b = 20.050(4) \text{ \AA}$ ,  $c = 18.260(4) \text{ \AA}$ ,  $\alpha = \gamma = 90^\circ$ ,  $\beta = 107.10(3)^\circ$ ,  $V = 4733.8(16) \text{ \AA}^3$ ,  $Z = 4$ ,  $T = 173 \text{ K}$ ,  $D_c = 1.986 \text{ g cm}^{-3}$ . The structure, refined on  $F^2$ , converged for 10731 unique reflections ( $R_{\text{int}} = 0.0305$ ) and 9612 observed reflections with  $I > 2\sigma(I)$  to give  $R_1 = 0.0529$  and  $wR_2 = 0.1131$  and a goodness-of-fit = 1.095. The triflate groups S2 and S3 both disordered at two positions with site occupancy ratios of 0.049:0.51 and 0.48:0.52, respectively.

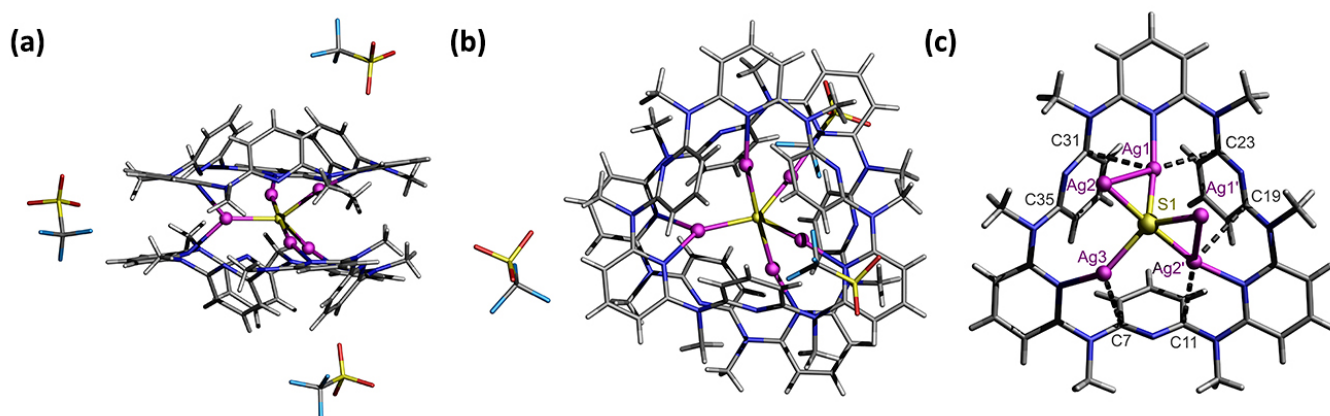
Crystal data for [Ag<sub>5</sub>S(Py[6])](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>•(CH<sub>3</sub>OH) (**2**) (CCDC-1006826): C<sub>40</sub>H<sub>36</sub>Ag<sub>5</sub>F<sub>9</sub>N<sub>12</sub>O<sub>10</sub>S<sub>4</sub>,  $M = 1683.40$ , orthorhombic, space group  $P2_12_12_1$  (No. 19),  $a = 10.570(2) \text{ \AA}$ ,  $b = 21.277(4) \text{ \AA}$ ,  $c = 23.103(5) \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90^\circ$ ,  $V = 5195.6(18) \text{ \AA}^3$ ,  $Z = 4$ ,  $T = 173 \text{ K}$ ,  $D_c = 2.152 \text{ cm}^{-3}$ . The structure, refined on  $F^2$ , converged for 9098 unique reflections ( $R_{\text{int}} = 0.0615$ ) and 7436 observed reflections with  $I > 2\sigma(I)$  to give  $R_1 = 0.1363$  and  $wR_2 = 0.3768$  and a goodness-of-fit = 1.127. On account of the unstable of the crystal and severe disorder in the crystal structure of complex **2**, very weak diffraction pattern at  $2\theta > 45^\circ$  was observed. As a result, large crystal and rapid crystal mounting was needed. Slightly twin crystal was observed and the TWIN command was used. Numerous rigid-body constraints and thermal parameter

restraints were required in the pyridyl rings. Triflate anions S2, S3 and S4 were each disordered at two positions with the occupancy ratio of 0.66:0.34, 0.4:0.6 and 0.51:0.49, respectively. Ag2 and Ag3 were each disordered at two separated position with site-occupancy ratio of 0.8:0.2 and 0.6:0.4. Two silver ions (Ag5 and Ag6) both has a partial occupancy ratio of 0.5 and disordered at two closed position with occupancy ratio of 0.7:0.3. O10 atom in methanol molecule disordered in two different position with occupancy ratio of 0.24:0.76. There is several Alert A in the checkcif file related to the refinement of anisotropic displacement parameter which was a consequence of instability of the crystal (poor diffraction pattern at  $2\theta > 45^\circ$  and slightly twin crystal structure). This resulted in the ADP in different directions has a large disparity (Alert A 1-4) and ADP of certain atom obviously different from the adjacent ones. (Alert A 5-9) For the Alert A 10 (Single Bonded Metal Atom (Unusual !) ..... <Ag5' Check), Ag5' was stabilized by coordination of N11 and two triflates.



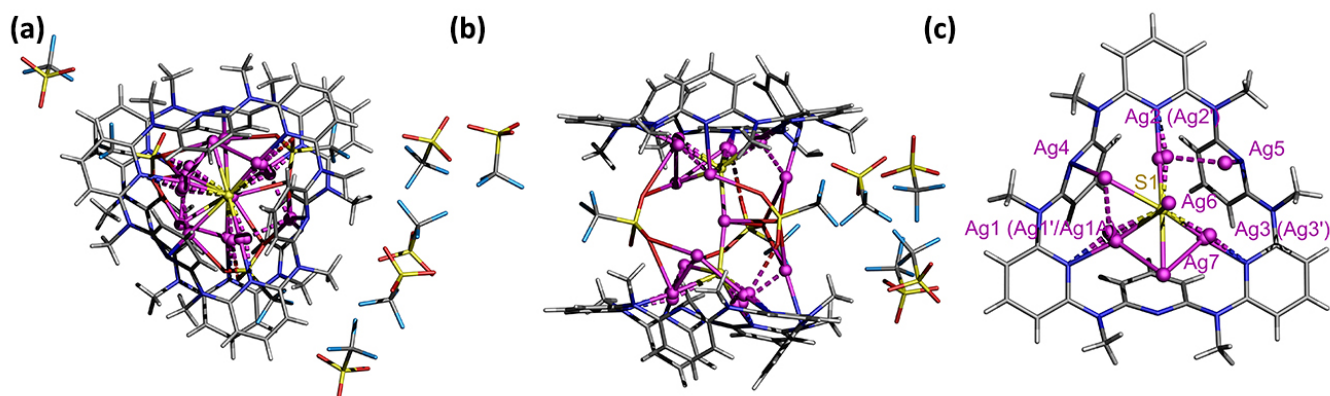
Top view (a) and side view (b) of the crystal structure of complex 2. Bonds related to the disordered silver atoms were represented in dashed line. Anions and solvent molecules were omitted for clarity in (c).

Crystal data for  $[\text{Ag}_5\text{S}(\text{Py}[\mathbf{6}])_2](\text{CF}_3\text{SO}_3)_3$  (**3**) (CCDC-1006827):  $\text{C}_{75}\text{H}_{72}\text{Ag}_5\text{F}_9\text{N}_{24}\text{O}_9\text{S}_4$ ,  $M = 2292.16$ , monoclinic, space group  $C2/c$  (No. 15),  $a = 23.725(5)$  Å,  $b = 19.387(4)$  Å,  $c = 18.732(4)$  Å,  $\beta = 90.71(3)^\circ$ ,  $V = 8615(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 173$  K,  $D_c = 1.767$  g cm<sup>-3</sup>. The structure, refined on  $F^2$ , converged for 7575 unique reflections ( $R_{\text{int}} = 0.0912$ ) and 6244 observed reflections with  $I > 2\sigma(I)$  to give  $R_1 = 0.1143$  and  $wR_2 = 0.2169$  and a goodness-of-fit = 1.236. Several highly disordered additional solvents could not be located in the difference map. The SQUEEZE procedure of PLATON was used in the processing of **3**.<sup>[3]</sup> The triflate group S2 is disordered at two positions with a refined site-occupancy ratio of 0.52:0.48. Disordered triflate anion S3 is arranged at two totally reversed anti-parallel orientations. Thus only half parts of the triflate is shown in the crystal asymmetric unit.



Side view (a) and top view (b) of the crystal structure of complex **3**. Anions and one **Py[6]** were omitted for clarity in (c).

Crystal data for  $[\text{Ag}_{12}\text{S}_2(\text{Py}[\mathbf{6}])_2](\text{CF}_3\text{SO}_3)_8 \cdot (\text{H}_2\text{O}) \cdot (\text{CH}_3\text{OH})$  (**4**) (CCDC-1006830):  $\text{C}_{81}\text{H}_{78}\text{Ag}_{12}\text{F}_{24}\text{N}_{24}\text{O}_{26}\text{S}_9$   $M = 3829.12$ , orthorhombic, space group  $Pbcn$  (No. 60),  $a = 12.772(3) \text{ \AA}$ ,  $b = 35.464(7) \text{ \AA}$ ,  $c = 25.664(5) \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90^\circ$ ,  $V = 11624(4) \text{ \AA}^3$ ,  $Z = 4$ ,  $T = 173 \text{ K}$ ,  $D_c = 2.208 \text{ g cm}^{-3}$ . The structure, refined on  $F^2$ , converged for 10222 unique reflections ( $R_{\text{int}} = 0.0552$ ) and 9794 observed reflections with  $I > 2\sigma(I)$  to give  $R_1 = 0.1258$  and  $wR_2 = 0.3558$  and a goodness-of-fit = 1.154. Triflate groups S5 was arranged at two positions according to the  $C_2$  rotation axis. Thus only half parts of this triflate is shown in the crystal asymmetric unit. The triflate groups S3 is disordered at two positions with a refined site-occupancy ratio of 0.57:0.43. Ag1 is disordered at three positions with a site-occupancy ratio of 0.8:0.1:0.1. Ag2 and Ag3 were both disordered at two separated position with same constraint occupancy of 0.85:0.15, respectively after refinement. Ag6 and Ag7 each has a partial occupancy ratio of 0.5, respectively. There are several Alert A mainly resulted from oxygen atoms O2w to O10w. These peaks were suspected to be a half triflate group but in a severe disorder, which thus hindered the identification of the atoms of the half triflate.



Top view (a) and side view (b) of the crystal structure of complex **4**. Bonds related to the disordered silver atoms were represented in dashed line. (c) Asymmetric unit of complex **4** with anions and solvent molecules omitted for clarity.

### **TEM Characterization**

The morphology and size distribution of as-prepared Ag-S nanoclusters was determined on a Hitachi H-7650 transmission electron microscope. The SAED pattern, EDX and trials for searching lattice fringe of **D-NP** were taken by a JEOL JEM-2011 and a FEI Tecnai G<sup>2</sup> 20 high-resolution transmission electron microscope.

### **X-ray photoelectron spectroscopy (XPS) Characterization**

(XPS) was performed on the Thermo Scientific ESCALab 250Xi using 200 W monochromated Al K $\alpha$  radiation. The 500  $\mu\text{m}$  X-ray spot was used for XPS analysis. The base pressure in the analysis chamber was about  $3 \times 10^{-10}$  mbar. Typically the hydrocarbon C1s line at 284.8 eV from adventitious carbon is used for energy referencing.

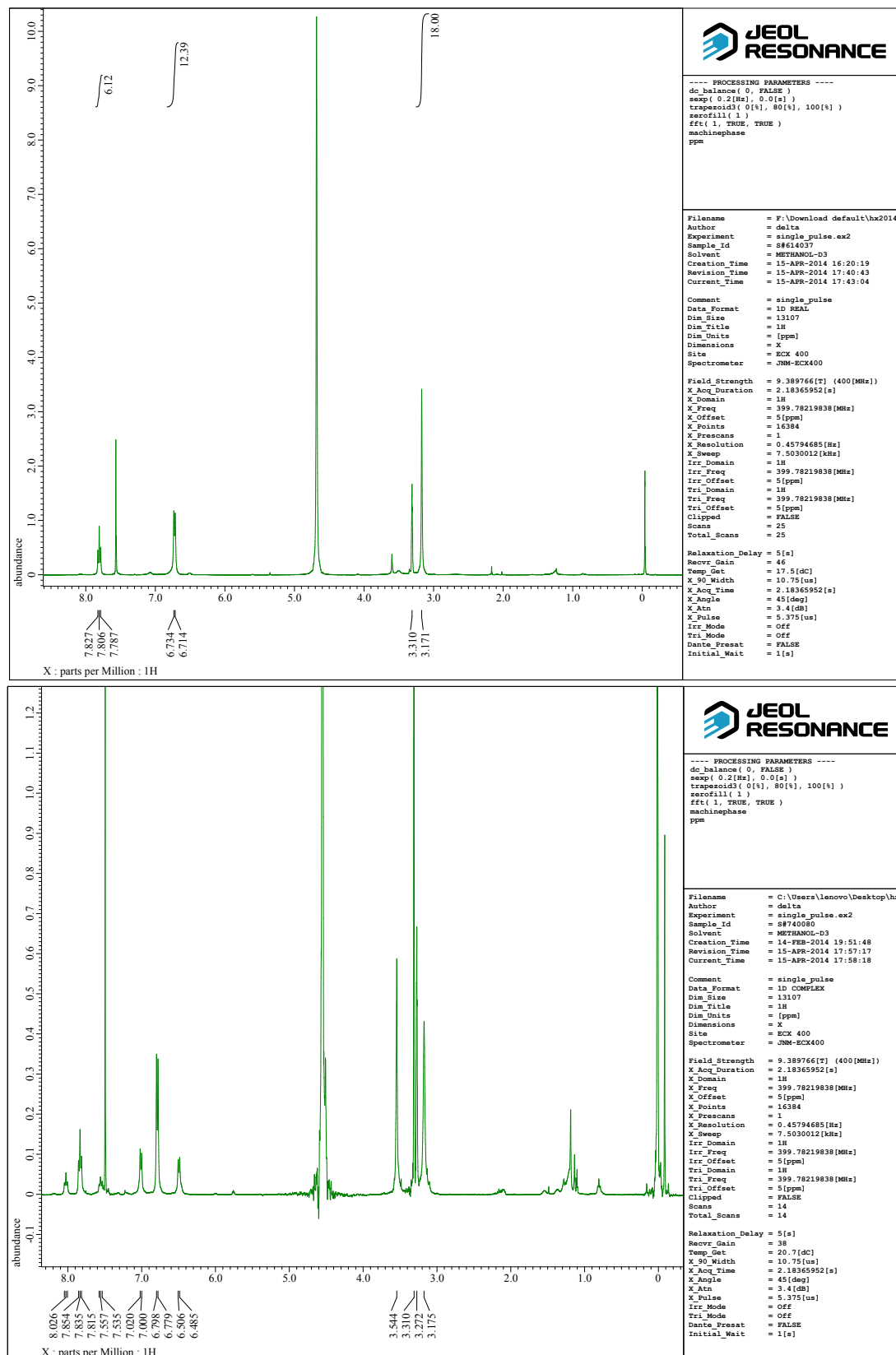
### **Band gap Determination**

Bardeen or Tauc equation:<sup>[4]</sup>

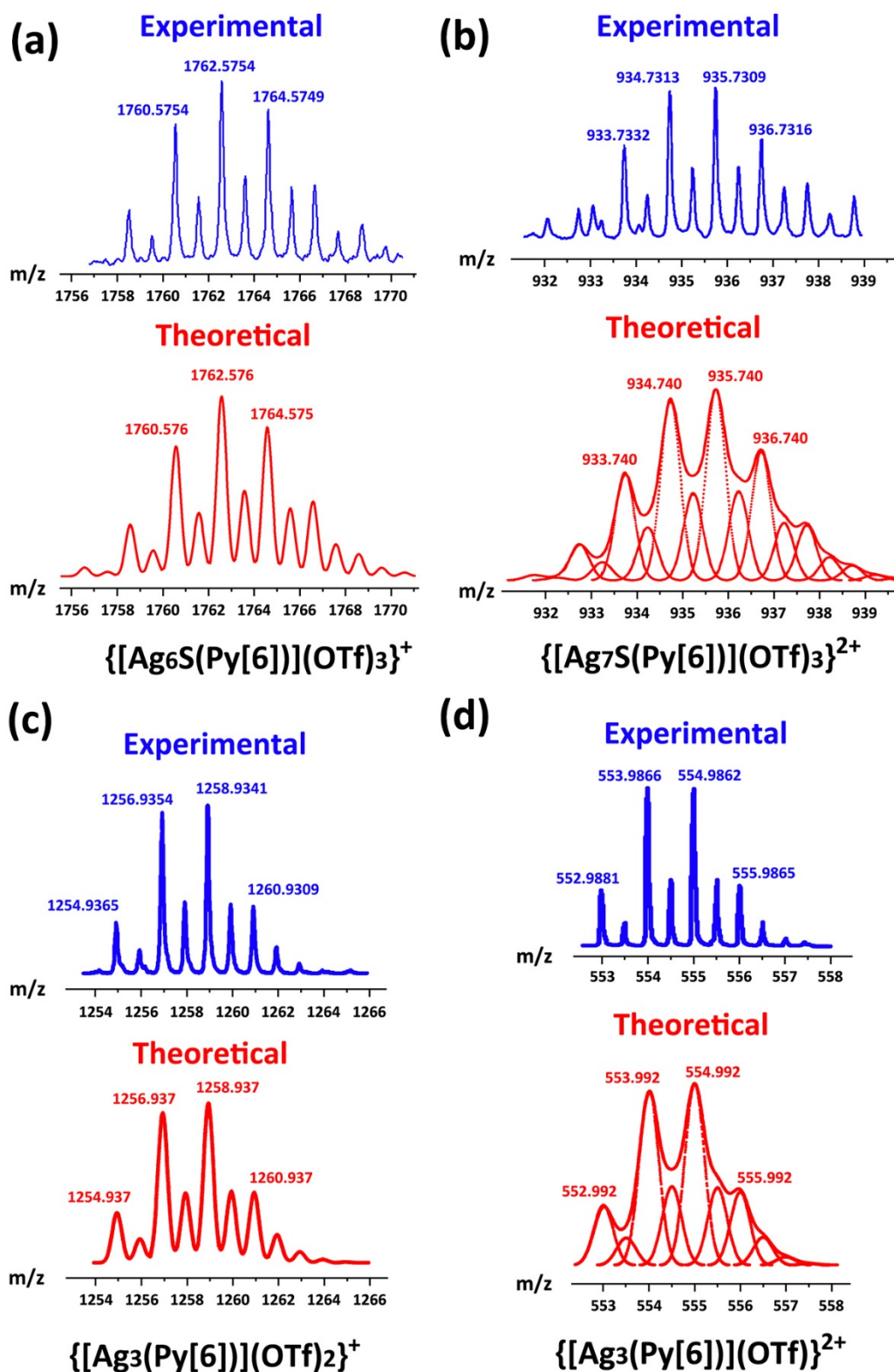
$$\alpha h\nu = A(h\nu - E_g)^n$$

$\alpha$ : Absorption coefficient;  $h\nu$ : Photon energy; A: Constant factor determined by the transition probability;  $E_g$ : Gap energy;  $n= 1/2$  for allowed direct and 2 for allowed indirect electronic transitions. Plots of  $(\alpha h\nu)^{1/2}$  or  $(\alpha h\nu)^2$  versus  $h\nu$  gives the linear version of the Bardeen or Tauc equation. The optical band gap was determined by the x-intercept of the line fit to the data.

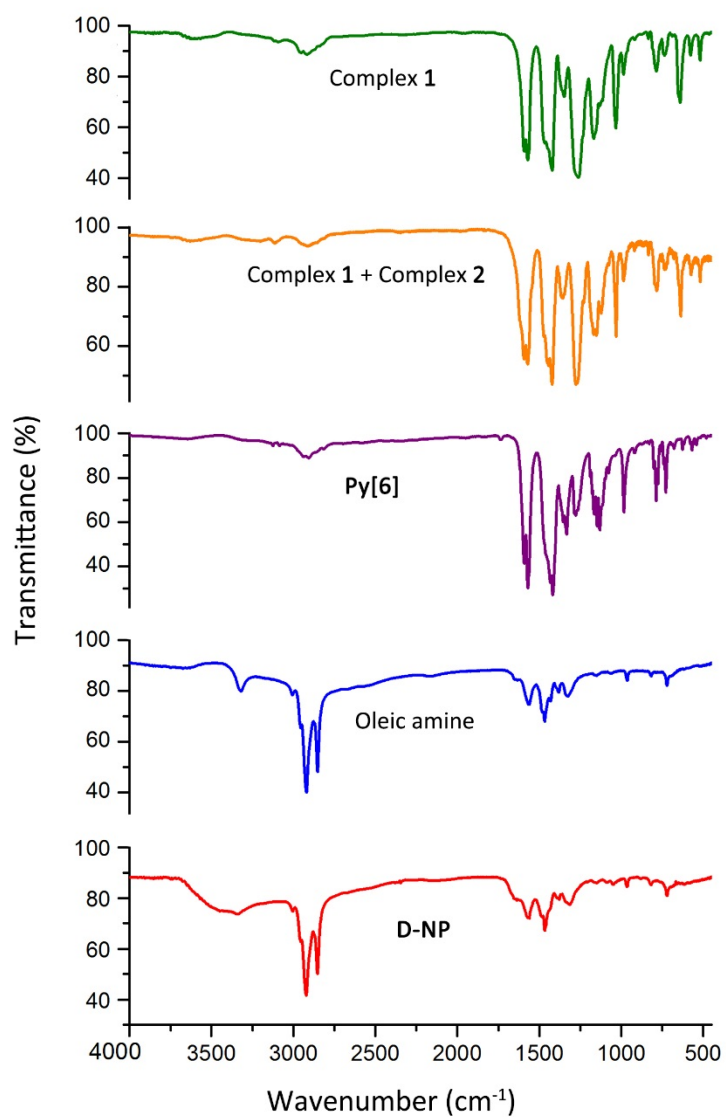
## Supporting Figures



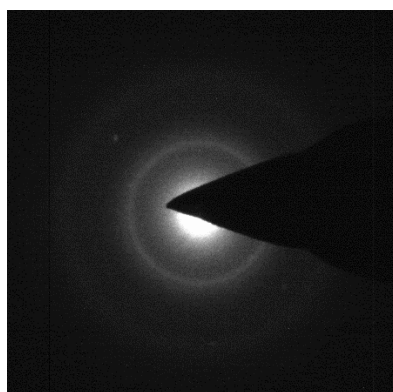
**Figure S1.** (up)  $^1\text{H-NMR}$  spectrum (400MHz, methanol- $d_4$ : $\text{CDCl}_3$ ,  $\nu : \nu = 1 : 1$ ) of complex **1**. (bottom)  $^1\text{H-NMR}$  spectrum (400MHz, methanol- $d_4$ : $\text{CDCl}_3$ ,  $\nu : \nu = 1 : 1$ ) of reaction mixture containing complexes **1** and **2**.



**Figure S2.** Theoretical (red) and experimental (blue) ESI-MS spectra of the charged species in the reaction mixture of  $Ag_2S$ ,  $AgCF_3SO_3$  and **Py[6]**.

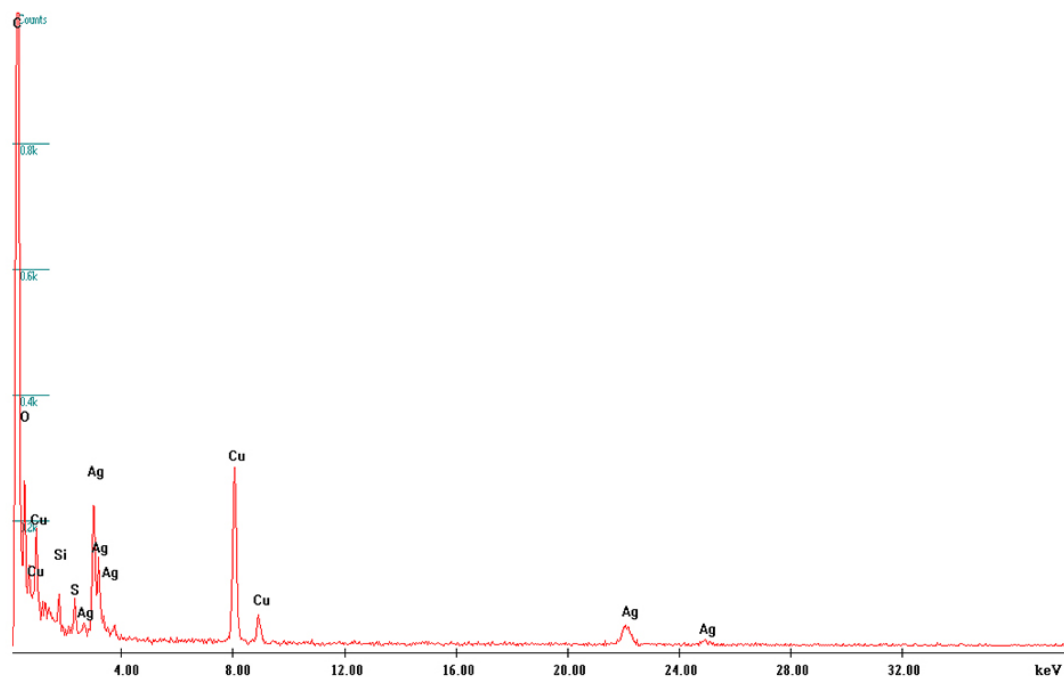


**Figure S3.** FT-IR spectra of (1) **D-NP** (2) oleic amine (3) **Py[6]** (4) complex **1** and complex **2** and (5) complex **1**.

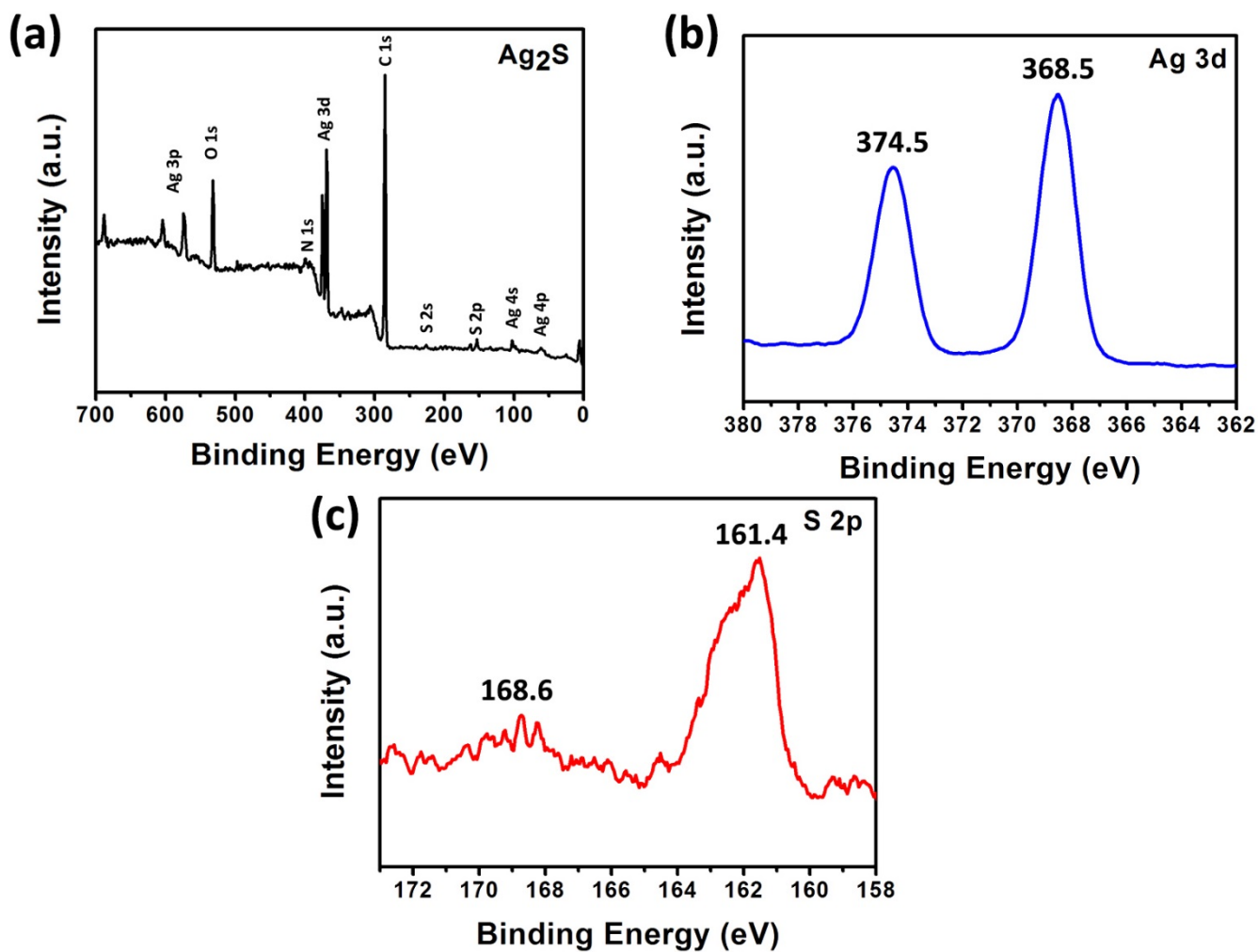


**Figure S4.** SAED pattern of **D-NP** corresponding to the (-103) and (232) facets of  $\alpha$ - $\text{Ag}_2\text{S}$ .

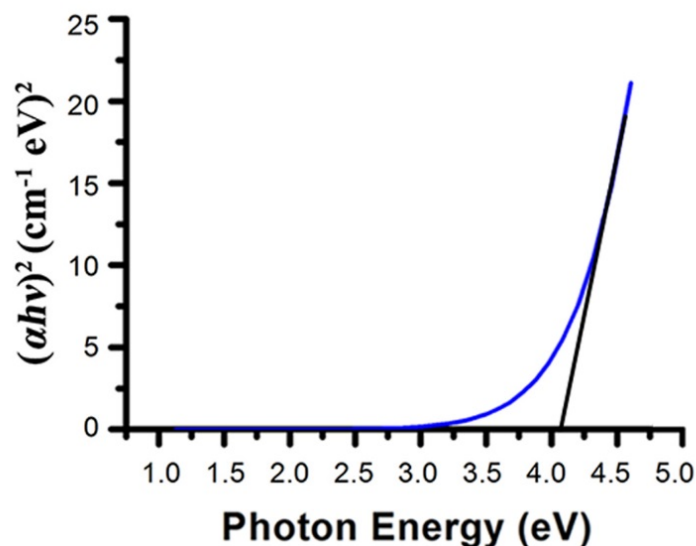




**Figure S5.** EDX of D-NP. Ag-77.6%, S-22.4% (Ag/S elemental ratio equals 3.46).



**Figure S6.** (a) XPS survey spectra of **D-NP**. (b) Ag 3d signals recorded for **D-NP**. (c) S 2p signals recorded for **D-NP**. Two peaks corresponding to the core levels of S2p may result from two types of sulfur atoms in **D-NP**: S<sup>2-</sup> (161.4 eV) and SO<sub>3</sub>CF<sub>3</sub><sup>-</sup> (168.6 eV). The Ag/S atomic ratio was determined to be 3.7:1 for **D-NP**.



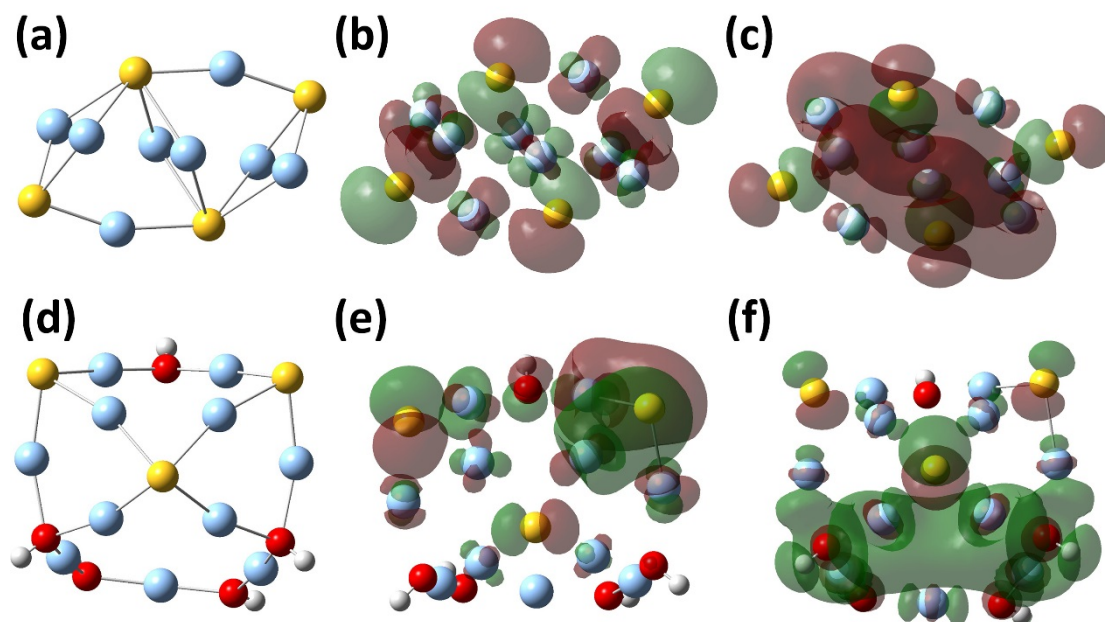
**Figure S7.** Gap energy determination of **D-NP** by using the Bardeen or Tauc equation.

### Computational Details

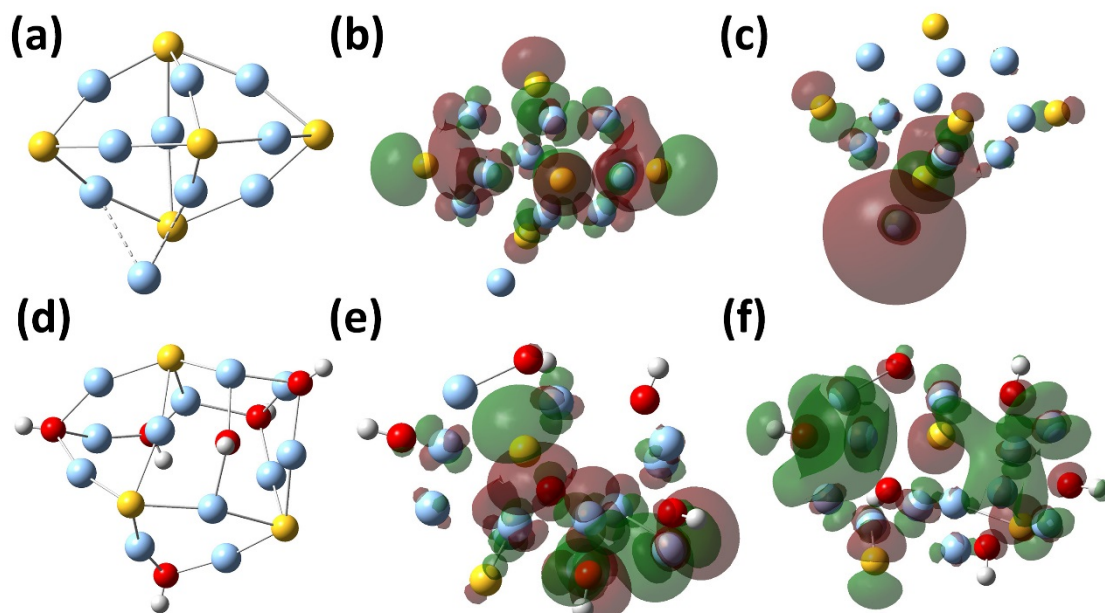
Structural optimizations, frequency and gap energy calculation of Ag-S clusters were performed using the Gaussian 09 program.<sup>[5]</sup> Initial structure of calculated Ag-S clusters were built up based on reported structure motif of  $\alpha$ -Ag<sub>2</sub>S and crystal structure of obtained silver-rich sulfide clusters. Density functional theory B3LYP<sup>[6]</sup> calculations were used to locate the gas phase stationary point of all the Ag-S clusters. The above mentioned hybrid DFT method performed well in reported theoretical works including Ag-S system and HOMO-LUMO gap calculations. The LANL2DZ<sup>[7]</sup> basis set was applied for all atoms. Frequency analysis at the same level was conducted to make sure the optimized structure was minimum. HOMO-LUMO gap calculations were then conducted at the correspond level.

Because of the high silver to sulfide atomic ratio, the cluster model couldn't be constructed by simply adopting structure motif of  $\alpha$ -Ag<sub>2</sub>S. Together with surface reconstruction, built up a model up to 4 nm is exceedingly difficult. Thus, we carried out four calculations on small Ag-S clusters with different Ag:S ratio in order to verify whether the large silver over sulfide elemental ratio would raise up the energy gap or not. Based on the coordination environment of silver and sulfide in the  $\alpha$ -Ag<sub>2</sub>S and herein reported

silver-rich sulfide clusters, four Ag-S clusters was built up. Acting as the standard, two of them owing a Ag:S ratio equals 2 while the ratio of other two was 3.5 and 4.0 which was similar to that in **D-NP**. For the sake of simplification of the optimization and computation, hydroxyl group was used as the substitution of the coordinated peripheral  $\text{CF}_3\text{SO}_3^-$  and  $\text{CF}_3\text{CO}_2^-$  anion.



(a) Optimized structure, localization of the (b) HOMO and (c) LUMO orbitals of  $\text{Ag}_8\text{S}_4$  clusters. (d) Optimized structure, localization of the (e) HOMO and (f) LUMO orbitals of  $\text{Ag}_{11}\text{S}_3(\text{OH})_5$  clusters.



**Figure S8.** (a) Optimized structure, localization of the (b) HOMO and (c) LUMO orbitals of  $\text{Ag}_{10}\text{S}_5$  clusters. (d) Optimized structure, localization of the (e) HOMO and (f) LUMO orbitals of  $\text{Ag}_{12}\text{S}_3(\text{OH})_6$  clusters.

**Table S1.** Sum of electronic and thermal enthalpies ( $H$ , in Hartree), relative energies ( $\Delta H$ , in kcal/mol), HOMO-LUMO gap energies (in eV) and relative HOMO-LUMO gap energies (in eV).

B3LYP/LANL2DZ

Structure	$H$	$\Delta H$	HOMO-LUMO Gap	$\Delta Gap$ Energy
Ag <sub>8</sub> S <sub>4</sub>	-2448.56730	0	2.45154	0
Ag <sub>10</sub> S <sub>5</sub>	-3112.35538	-663.78808	1.86293	-0.58861
Ag <sub>11</sub> S <sub>3</sub> (OH) <sub>5</sub>	-3191.16210	-742.59481	3.11467	0.66314
Ag <sub>12</sub> S <sub>3</sub> (OH) <sub>6</sub>	-3445.85076	-997.28347	3.08611	0.63458

### Coordinates of All Stationary Points

B3LYP/LANL2DZ

Ag<sub>8</sub>S<sub>4</sub>

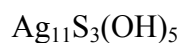
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	47	0	2.866560	-0.727542	1.449781
2	47	0	2.862823	-0.758726	-1.441877
3	47	0	0.000701	-0.007217	-1.431551
4	16	0	4.010623	1.056759	-0.017164
5	16	0	-0.911104	2.161886	-0.004571
6	47	0	1.703688	2.044730	-0.011057
7	16	0	-4.011360	-1.057231	-0.003391
8	47	0	-2.861760	0.739660	-1.450613
9	47	0	-2.867419	0.745768	1.441110
10	47	0	-0.000212	0.007744	1.437693
11	47	0	-1.703882	-2.044277	0.008901
12	16	0	0.910379	-2.161823	0.018110

Ag<sub>10</sub>S<sub>5</sub>

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	47	0	2.538433	0.466996	-1.007064
2	47	0	2.036193	-1.023239	1.832803
3	16	0	3.730174	-1.479359	-0.005641
4	47	0	-2.897081	-1.017329	-0.956236
5	47	0	-0.753936	-1.979593	0.986409
6	16	0	-0.971148	-2.723745	-1.513336
7	47	0	-0.198446	-0.291819	-1.962745
8	16	0	0.647620	2.291342	-1.575133
9	47	0	2.235055	3.142964	0.235877
10	47	0	0.206498	1.138593	0.907302
11	47	0	-1.949556	2.074360	-0.898707
12	47	0	1.573974	-2.495882	-0.922546
13	16	0	-4.060581	1.044362	-0.044501
14	16	0	-0.228486	-0.353623	2.977868
15	47	0	-2.490735	0.400616	1.839628



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	47	0	0.163247	1.663302	-2.136991
2	47	0	-4.585006	0.494972	1.241687
3	47	0	2.769566	1.251957	-0.743576
4	16	0	1.788302	-0.161968	-2.756254
5	47	0	2.373496	-1.850057	-0.814535
6	47	0	0.058370	-3.769555	-0.166165
7	16	0	2.318940	-3.792729	0.810124
8	47	0	-3.201122	-2.431207	-0.062252

9	47	0	-2.626218	3.145329	-0.170404
10	47	0	0.985354	3.661155	0.001474
11	47	0	1.688415	-1.976764	2.364219
12	47	0	-0.260219	-1.525960	-2.201627
13	47	0	2.135413	1.413208	2.452427
14	16	0	3.181162	3.080589	0.957729
15	8	0	-1.702465	-3.081977	-1.443103
16	1	0	-2.016039	-3.724657	-2.111057
17	8	0	-4.306411	2.545218	0.918368
18	1	0	-4.812319	3.200898	1.430830
19	8	0	-4.617396	-1.618134	1.247459
20	1	0	-4.793194	-2.083185	2.086523
21	8	0	-0.859806	3.503576	-1.334233
22	1	0	-0.953482	4.232007	-1.981311
23	8	0	1.249171	-0.220681	3.487431
24	1	0	1.294905	-0.253314	4.461921

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Ag<sub>12</sub>S<sub>3</sub>(OH)<sub>6</sub>

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	47	0	-2.903449	-2.394365	-0.407968
2	47	0	-0.393136	-1.711540	1.836333
3	47	0	-0.753524	-0.736268	-1.621441
4	16	0	-0.509611	-3.107809	-0.349482
5	47	0	0.884536	1.857329	-1.461565
6	47	0	3.476755	0.173211	-1.033376
7	16	0	3.022161	2.546125	0.075609
8	47	0	3.059313	-2.086747	1.157598
9	47	0	-3.382708	-0.584684	1.998055
10	47	0	-3.456582	0.553899	-1.133344
11	47	0	0.903346	3.457280	1.087167

12	47	0	2.369202	0.820578	1.767885
13	47	0	1.652198	-2.527868	-1.702879
14	47	0	-1.717557	3.010054	-0.384101
15	16	0	-1.658194	1.640966	-2.477231
16	8	0	3.813587	-2.147474	-0.867778
17	1	0	4.635499	-2.624823	-1.096913
18	8	0	1.604457	-0.281921	-2.471523
19	8	0	-1.759657	-0.672555	3.330322
20	1	0	-1.457428	0.182547	3.700358
21	8	0	1.872786	-1.114547	2.693755
22	1	0	2.017482	-1.271558	3.648311
23	8	0	-4.538230	-0.902612	0.165471
24	1	0	-5.502939	-1.052111	0.157022
25	8	0	-1.158044	3.959642	1.471951
26	1	0	-1.417757	4.882096	1.664928
27	1	0	1.671714	-0.160281	-3.444696

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