Electronic Supplementary Information (ESI)

Anion-Templated Nanosized Silver Clusters Protected by Mixed Thiolate and Diphosphine

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Experiment details

The precursors, $\{(HNEt_3)_2[Ag_{10}(SC_6H_4{}^tBu)_{12}]\}_n$ and $[MeC_6H_4SAg]_n$ were prepared by slight modifications to those in the literature.[1] All chemicals and solvents used in the syntheses were of analytical grade and used without further purification. $AgCF_3SO_3$ and $AgBF_4$ was purchased from Nanjing luxury Catalytic materials Co., Ltd. IR spectra were recorded on a PerkinElmer Spectrum Two in the frequency range of 4000-400 cm^{-1}. The diffuse-reflectance spectra were performed on UV−Vis spectrophotometer (Evolution 220, ISA-220 accessory, Thermo Scientific) using a built-in 10 mm silicon photodiode with a 60 mm Spectralon sphere. The excitation spectra were recorded on Lumina Fluorescence Spectrometer (Thermo Fisher). Temperature-dependent photoluminescence measurements were carried out in an Edinburgh spectrofluorimeter (F920S) coupled with an Optistat DN cryostat (Oxford Instruments), and the ITC temperature controller and a pressure gauge were used to realize the variable temperature measurement in the range of 88-298 K. Spectra were collected at different temperatures after a 3 min homoiothermy. Time-resolved photoluminescence lifetime and the quantum yield measurements were measured on the same instrument. The high-resolution electrospray mass spectrometry was performed on an Agilent (Santa Clara, CA, USA) ESI-TOF mass spectrometer (6224). The instrument was calibrated with an Agilent tune mixture before mass analysis. The data analyses of mass spectra were processed on a Bruker DataAnalysis (Version 4.0) software and the simulations were performed on a Bruker Isotope Pattern software.

X-ray Crystallography

Single crystals of **1**-**6** with appropriate dimensions were chosen under an optical microscope and quickly coated with high vacuum grease (Dow Corning Corporation) before being mounted on a glass fiber for data collection. Single-crystal X-ray diffraction data were collected using a Bruker SMART APEX II diffractometer with a CCD area detector (graphite monochromatic Mo Kα radiation, λ = 0.71073 Å, ω-scans with a 0.5° step in ω) for **1**-**6**. Indexing was performed using APEX2 (Difference Vectors method).[2] Data integration and reduction were performed using Saint Plus 6.01.[3] Absorption correction was performed by multi-scan method implemented in SADABS.[4] Space groups were determined using XPREP implemented in APEX2. Structures of **1**-**6** were solved using SHELXS-97 (direct methods) and refined using SHELXL-97 (full-matrix least-squares on F^2).[5] Hydrogen atoms were placed in calculated positions and included as riding atoms with isotropic displacement parameters 1.2-1.5 times U_{eq} of the attached C atoms. Furthermore, it was necessary to use constraints to control the geometry of the aromatic rings and restraints to enforce chemically sensible bond lengths and angles in the ^{t}Bu- groups. Vibrational restraints were also used to control atomic displacement parameters of various atoms. All structures were examined using the Addsym subroutine of PLATON[6] to assure that no additional symmetry could be applied to the models. Pertinent crystallographic data collection and refinement parameters of **1**-**6** are collated in Table S2. Selected bond lengths and angles are collated in Table S3.

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Synthesis of $[S@Ag_{18}(^tBuC_6H_4S)_{16}(dppp)_4]\cdot DMF\cdot {}_5CH_3CN\cdot 3CH_3OH$ (1)

$\{(HNEt_3)_2[Ag_{10}(SC_6H_4{}^tBu)_{12}]\}_n$ (54.8 mg, 0.20 mmol), dppp (41.2 mg, 0.10 mmol) and $K_2Cr_2O_7$ (5.8 mg, 0.02 mmol) were added into 5 mL CH_3OH-CH_3CN-DMF (v:v:v = 6:4:1) and treated under the ultrasonic condition for 10 min (160 W, 40 kHz, 25 ^oC). To this solution CF_3SO_3Ag (12.8 mg, 0.05 mmol) was added. The reaction continued for further 20 min under the same ultrasonic condition. Then, the reaction mixture was sealed in a 25 mL Teflon-lined reaction vessel and kept at 70 °C for 33 hours. After cooling to room temperature, the solution was filtered and the filtrate was evaporated slowly in darkness at room temperature. The product **1** crystallized as yellow rod crystals for two weeks, which were isolated by filtration, washed with ethanol and dried at room temperature (Yield: 60%).

Synthesis of $[MoO_4@Ag_{24}(MeC_6H_4S)_{12}(dppm)_6(MoO_4)_4]\cdot 2BF_4\cdot C_2H_5NO$ (2)

$[MeC_6H_4SAg]_n$ (23.1 mg, 0.10 mmol), dppm (19.2 mg, 0.05 mmol) and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (6.2 mg, 0.005 mmol) were added into 5 mL CH_3OH-CH_3CN (v:v = 3:2) and treated under the ultrasonic condition for 10 min (160 W, 40 kHz, 25 ^oC). To this solution $AgBF_4$ (19.6 mg, 0.10 mmol) was added. The reaction continued for further 20 min under the same ultrasonic condition. Then, the reaction mixture was sealed in a 25 mL Teflon-lined reaction vessel and kept at 75 °C for 33 hours. After cooling to room temperature, the solution was filtered and the filtrate was evaporated slowly in darkness at room temperature. The product **2** crystallized as yellow hexagon crystals were collected after ten days (Yield: ~15 %).

Synthesis of $[MoO_4@Ag_{24}(MeC_6H_4S)_{12}(dppm)_6(MoO_4)_4]\cdot 2CF_3SO_3$ (3)

The synthesis of complex **3** was similar to that of **2** except for using $(^nBu_4N)_4Mo_8O_{26}$ (8.7 mg, 0.004 mmol) and CF_3SO_3Ag (25.7 mg, 0.10 mmol) instead of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and $AgBF_4$. The product **3** crystallized as yellow hexagon crystals for one week (Yield: ~10 %).

Synthesis of $[MoO_4@Ag_{24}(MeC_6H_4S)_{12}(dppf)_6(MoO_4)_4]\cdot 2CF_3SO_3$ (4)

The synthesis of complex **4** was similar to that of **2** except for using dppf (27.7 mg, 0.05 mmol), Na_2MoO_4 (2.4 mg, 0.01 mmol) and CF_3SO_3Ag (25.7 mg, 0.10 mmol) instead of dppm, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and $AgBF_4$. Additionally, the reaction mixture was kept at 70 °C instead of 75 °C for 33 hours. The product **4** crystallized as yellow block crystals for two weeks (Yield: 30%)

Synthesis of $[MoO_4@Ag_{24}(MeC_6H_4S)_{12}(dppb)_6(MoO_4)_4]\cdot 2CF_3SO_3$ (5)

The synthesis of complex **5** was similar to that of **2** except for using dppb (21.3 mg, 0.05 mmol), $(^nBu_4N)_4Mo_8O_{26}$ (6.5 mg, 0.003 mmol) and CF_3SO_3Ag (25.7 mg, 0.10 mmol) instead of dppm, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and $AgBF_4$. Additionally, the reaction mixture was kept at 70 °C instead of 75 °C for 33 hours. The product **5** crystallized as yellow block crystals for three weeks, which were isolated by filtration, washed with ethanol and dried at room temperature (Yield: 50%).

Synthesis of $[Mo_6O_{22}@Ag_{46}(^tBuC_6H_4S)_{32}(dppm)_4(CH_3CN)_8]\cdot 6CF_3SO_3$ (6)

The synthesis of complex **6** was similar to that of **1** except for using dppm (19.2 mg, 0.05 mmol) and $(^nBu_4N)_2Mo_6O_{19}$ (4.1 mg, 0.003 mmol) instead of dppp and $K_2Cr_2O_7$. Particularly, the reaction solution system was C_2H_5OH-CH_3CN (5 mL, v:v = 3:2) instead of CH_3OH-CH_3CN (5 mL, v:v = 3:2). The product **6** crystallized as yellow rectangular crystals for one month (Yield: ~10 %), which were isolated by filtration, washed with ethanol and dried at room temperature.

Table S1. The geometry and coordination mode of $Mo_6O_{22}^{8-}$ polyoxoanion templates found in the Ag clusters in the literature and this work.

Structures of $Mo_6O_{22}^{8-}$ in silver clusters	Numbers of Ag ligated by POM	Reference
$Mo_6O_{22}@Ag_{58}S_2(SC_6H_4{}^tBu)_{36}(CF_3COO)_{10}(H_2O)_8$ 	24	[7]
$Mo_6O_{22}@Ag_{40}(C{\equiv}C{}^tBu)_{20}(CF_3COO)_{12}$ 	24	[8]
$[(Mo_6O_{22})_2@Ag_{60}(C{\equiv}C{}^tBu)_{38}](CF_3SO_3)_6$ 	22	[9]
$[Mo_6O_{22}@Ag_{46}({}^tBuC_6H_4S)_{32}(dppm)_4(CH_3CN)_8](CF_3SO_3)_6$ 	28	This work

Table S2. Crystal data for 1-6.

Compound	1	2	3	4	5	6
Empirical formula	$C_{283}H_{343}Ag_{18}N_6O_3P_8S_{17}$	$C_{240}H_{231}Ag_{24}B_2F_8Mo_5N_3O_{23}P_{12}S_{12}$	$C_{236}H_{216}Ag_{24}F_6Mo_5O_{26}P_{12}S_{14}$	$C_{290}H_{255}Ag_{24}Fe_6Mo_5NO_{20}P_{12}S_{12}$	$C_{252}H_{252}Ag_{24}Mo_5O_{20}P_{12}S_{12}$	$C_{438}H_{522}Ag_{46}F_6Mo_6N_8O_{28}P_8S_{34}$
Formula weight	6611.05	7523.84	7471.15	8233.99	7425.48	13336.06
Temperature/K	173(2)	100(2)	100(2)	100(2)	173(2)	173(2)
Crystal system	triclinic	trigonal	trigonal	triclinic	cubic	triclinic
Space group	$P\bar{1}$	$R\bar{3}$	$R\bar{3}$	$P\bar{1}$	$Pn\bar{3}$	$P\bar{1}$
a/Å	21.510(4)	21.9874(6)	22.0680(14)	22.7887(18)	24.9678(11)	26.730(8)
b/Å	26.990(5)	21.9874(6)	22.0680(14)	27.962(2)	24.9678(11)	26.938(8)
c/Å	34.102(6)	93.887(5)	94.137(6)	33.377(3)	24.9678(11)	27.226(8)
α/°	69.368(2)	90.00	90.00	69.6918(7)	90.00	107.058(3)
β/°	72.781(2)	90.00	90.00	88.7509(8)	90.00	105.040(3)
γ/°	66.700(2)	120.00	120.00	84.3460(8)	90.00	112.696(3)
Volume/Å^3	16732(5)	39308(3)	39703(4)	19848(3)	15564.7(12)	15671(8)
Z	2	6	6	2	2	1
ρ_{calc} g/cm^3	1.312	1.907	1.875	1.378	1.584	1.413
μ/mm^{-1}	1.215	2.208	2.201	1.669	1.854	1.691
F(000)	6690.0	22008.0	21816.0	8056.0	7268.0	6562.0
Radiation	MoKα	MoKα	MoKα	MoKα	MoKα	MoKα
Reflections collected	144730	38707	31359	97197	34650	130324
Independent reflections	57254	15276	15426	68124	5998	53916
Data/parameters	57254/2929	15276/993	15426/962	68124/3337	5998/255	53916/2440
GOF	0.920	1.013	1.090	0.973	1.091	0.885
Final R indexes [I>=2σ (I)]	R_1 = 0.0716, wR_2 = 0.1636	R_1 = 0.0332, wR_2 = 0.0784	R_1 = 0.0746, wR_2 = 0.1563	R_1 = 0.0701, wR_2 = 0.1806	R_1 = 0.0369, wR_2 = 0.0908	R_1 = 0.0992, wR_2 = 0.2292
Final R indexes [all data]	R_1= 0.1431, wR_2 = 0.1866	R1 = 0.0488, wR_2 = 0.0874	R_1 = 0.0893, wR_2 = 0.1621	R_1 = 0.1181, wR_2 = 0.2048	R_1 = 0.0519, wR_2 = 0.0975	R_1 = 0.1912, wR_2 = 0.2685

Table S3: Selected bond distances (Å) and angles (°) for 1-6

Compound 1			
Ag1—Ag3	2.9188 (11)	Ag10—S6	2.412 (2)
Ag1—P1	2.407 (3)	Ag10—S13	2.419 (3)
Ag1—S1	2.494 (3)	Ag10—S16	2.658 (2)
Ag1—S2	2.495 (3)	Ag11—Ag13	3.3416 (11)
Ag2—Ag3	3.1289 (11)	Ag11—S9	2.459 (3)
Ag2—S2	2.430 (3)	Ag11—S12	2.652 (3)
Ag2—S3	2.639 (2)	Ag11—S15	2.612 (2)
Ag2—S6	2.462 (3)	Ag11—S16	2.675 (2)
Ag3—Ag4	3.0486 (12)	Ag12—Ag13	3.1009 (12)
Ag3—S1	2.453 (3)	Ag12—S8	2.651 (3)
Ag3—S5	2.427 (3)	Ag12—S11	2.436 (3)
Ag4—P8	2.412 (3)	Ag12—S13	2.461 (3)
Ag4—S1	2.965 (3)	Ag13—Ag14	2.9541 (11)
Ag4—S3	2.577 (2)	Ag13—Ag15	3.0525 (12)
Ag4—S4	2.564 (3)	Ag13—S8	2.937 (2)
Ag5—Ag6	3.0635 (12)	Ag13—S10	2.452 (3)
Ag5—S4	2.904 (3)	Ag13—S12	2.399 (3)
Ag5—S5	2.483 (3)	Ag14—P5	2.407 (3)
Ag5—S16	2.840 (2)	Ag14—S10	2.517 (3)
Ag5—S17	2.411 (3)	Ag14—S11	2.475 (3)
Ag6—Ag7	3.1151 (11)	Ag15—P4	2.446 (3)
Ag6—Ag8	3.0689 (12)	Ag15—S8	2.768 (3)
Ag6—S4	2.392 (3)	Ag15—S9	2.560 (2)
Ag6—S15	2.421 (3)	Ag15—S10	2.774 (3)
Ag7—S3	2.446 (2)	Ag16—Ag17	3.2933 (12)
Ag7—S14	2.424 (2)	Ag16—S7	2.411 (3)
Ag7—S16	2.769 (3)	Ag16—S8	2.436 (3)
Ag8—P7	2.389 (3)	Ag16—S16	2.803 (2)
Ag8—S14	2.538 (2)	Ag17—P3	2.440 (3)
Ag8—S15	2.459 (3)	Ag17—S7	2.768 (3)
Ag9—P6	2.425 (3)	Ag17—S9	2.793 (3)
Ag9—S12	2.624 (3)	Ag17—S17	2.505 (3)
Ag9—S13	2.653 (2)	Ag18—P2	2.429 (3)
Ag9—S14	2.656 (2)	Ag18—S5	2.630 (3)
Ag10—Ag12	3.1858 (12)	Ag18—S6	2.614 (3)
Ag10—Ag16	3.3100 (13)	Ag18—S7	2.643 (3)
P1—Ag1—S1	135.90 (9)	S9—Ag11—S15	134.56 (8)
P1—Ag1—S2	117.58 (9)	S9—Ag11—S16	107.75 (8)
S1—Ag1—S2	106.37 (8)	S12—Ag11—S16	102.29 (8)

S2—Ag2—S3	103.61 (8)	S15—Ag11—S12	92.81 (8)
S2—Ag2—S6	140.95 (8)	S15—Ag11—S16	96.90 (8)
S6—Ag2—S3	114.32 (8)	S11—Ag12—S8	101.48 (9)
S5—Ag3—S1	159.54 (9)	S11—Ag12—S13	138.78 (9)
P8—Ag4—S1	102.64 (9)	S13—Ag12—S8	118.54 (8)
P8—Ag4—S3	134.16 (10)	S10—Ag13—S8	93.30 (8)
P8—Ag4—S4	126.82 (9)	S12—Ag13—S8	108.25 (8)
S3—Ag4—S1	90.97 (7)	S12—Ag13—S10	158.10 (9)
S4—Ag4—S1	102.02 (8)	P5—Ag14—S10	125.49 (9)
S4—Ag4—S3	91.38 (8)	P5—Ag14—S11	121.42 (9)
S5—Ag5—S4	89.93 (8)	S11—Ag14—S10	113.09 (9)
S5—Ag5—S16	101.47 (8)	P4—Ag15—S8	129.19 (9)
S16—Ag5—S4	90.88 (7)	P4—Ag15—S9	123.04 (9)
S17—Ag5—S4	111.83 (8)	P4—Ag15—S10	105.36 (9)
S17—Ag5—S5	154.73 (10)	S8—Ag15—S10	90.41 (8)
S17—Ag5—S16	91.25 (8)	S9—Ag15—S8	87.06 (8)
S4—Ag6—S15	166.51 (8)	S9—Ag15—S10	118.15 (8)
S3—Ag7—S16	95.05 (8)	S7—Ag16—S8	151.05 (9)
S14—Ag7—S3	147.96 (9)	S7—Ag16—S16	109.00 (8)
S14—Ag7—S16	116.58 (8)	S8—Ag16—S16	99.95 (8)
P7—Ag8—S14	118.67 (9)	P3—Ag17—S7	100.02 (10)
P7—Ag8—S15	138.75 (9)	P3—Ag17—S9	117.92 (10)
S15—Ag8—S14	102.43 (8)	P3—Ag17—S17	130.03 (10)
P6—Ag9—S12	127.74 (8)	S7—Ag17—S9	110.51 (8)
P6—Ag9—S13	122.58 (8)	S17—Ag17—S7	110.08 (9)
P6—Ag9—S14	118.81 (8)	S17—Ag17—S9	87.96 (8)
S12—Ag9—S13	93.59 (8)	P2—Ag18—S5	118.37 (9)
S12—Ag9—S14	91.93 (8)	P2—Ag18—S6	123.04 (9)
S13—Ag9—S14	93.43 (7)	P2—Ag18—S7	117.22 (9)
S6—Ag10—S13	158.45 (9)	S5—Ag18—S7	90.78 (8)
S6—Ag10—S16	97.47 (8)	S6—Ag18—S5	97.33 (8)
S13—Ag10—S16	100.91 (8)	S6—Ag18—S7	104.00 (8)
S9—Ag11—S12	117.32 (8)		
Compound 2			
Ag1—Ag2	3.1781 (6)	Ag4—S3	2.4912 (13)
Ag1—Ag3	3.2901 (5)	Ag5—Ag2^{ii}	3.3313 (6)
Ag1—O2	2.376 (3)	Ag5—O5^{ii}	2.450 (4)
Ag1—P2	2.3872 (13)	Ag5—S2	2.4382 (13)
Ag1—S3	2.7212 (13)	Ag5—S4^{ii}	2.4460 (13)
Ag1—S4	2.5910 (13)	Ag6—Ag7	3.0819 (6)
Ag2—Ag5^{i}	3.3313 (6)	Ag6—O8^{ii}	2.348 (4)
Ag2—O5	2.312 (3)	Ag6—P4	2.4020 (15)
Ag2—P1	2.3850 (14)	Ag6—S1	2.7124 (15)

Ag2—S3	2.5760 (14)	Ag6—S2	2.6276 (13)
Ag2—S4	2.9612 (13)	Ag7—O7	2.298 (4)
Ag3—Ag4	3.0313 (6)	Ag7—P3	2.3790 (16)
Ag3—Ag5	3.0783 (6)	Ag7—S1	2.5508 (15)
Ag3—O2	2.496 (4)	Ag7—S2	2.9320 (14)
Ag3—O3	2.597 (2)	Ag8—Ag8^{ii}	3.1056 (7)
Ag3—S3	2.4833 (13)	Ag8—Ag8^{i}	3.1056 (7)
Ag3—S4^{ii}	2.4681 (14)	Ag8—O4^{ii}	2.521 (3)
Ag4—Ag5	3.1946 (6)	Ag8—O8	2.460 (4)
Ag4—O4^{ii}	2.501 (3)	Ag8—S1	2.4831 (15)
Ag4—O7	2.431 (4)	Ag8—S1^{i}	2.5093 (15)
Ag4—S2	2.4735 (14)		
O2—Ag1—P2	134.34 (9)	S3—Ag4—O4^{ii}	104.58 (8)
O2—Ag1—S3	96.71 (9)	S2—Ag5—O5^{ii}	105.21 (9)
O2—Ag1—S4	90.48 (9)	S2—Ag5—S4^{ii}	141.66 (5)
P2—Ag1—S3	123.09 (4)	S4^{ii}—Ag5—O5^{ii}	103.28 (9)
P2—Ag1—S4	113.84 (5)	O8^{ii}—Ag6—P4	134.82 (10)
S4—Ag1—S3	82.91 (4)	O8^{ii}—Ag6—S1	93.10 (10)
O5—Ag2—P1	134.87 (10)	O8^{ii}—Ag6—S2	89.31 (9)
O5—Ag2—S3	93.01 (10)	P4—Ag6—S1	127.80 (5)
O5—Ag2—S4	92.60 (9)	P4—Ag6—S2	111.10 (5)
P1—Ag2—S3	130.42 (5)	S2—Ag6—S1	83.53 (4)
P1—Ag2—S4	106.02 (4)	O7—Ag7—P3	130.59 (10)
S3—Ag2—S4	78.55 (4)	O7—Ag7—S1	97.45 (10)
O2—Ag3—O3	88.48 (14)	O7—Ag7—S2	89.62 (10)
S3—Ag3—O2	100.05 (8)	P3—Ag7—S1	129.73 (5)
S3—Ag3—O3	114.85 (6)	P3—Ag7—S2	109.44 (5)
S4^{ii}—Ag3—O2	100.61 (8)	S1—Ag7—S2	80.58 (4)
S4^{ii}—Ag3—O3	99.37 (3)	O8—Ag8—O4^{ii}	89.00 (11)
S4^{ii}—Ag3—S3	140.18 (5)	O8—Ag8—S1	109.43 (9)
O7—Ag4—O4^{ii}	90.08 (12)	O8—Ag8—S1^{i}	95.64 (9)
O7—Ag4—S2	98.41 (9)	S1—Ag8—O4^{ii}	106.11 (9)
O7—Ag4—S3	104.52 (9)	S1^{i}—Ag8—O4^{ii}	114.12 (9)
S2—Ag4—O4^{ii}	115.18 (8)	S1—Ag8—S1^{i}	132.60 (7)
S2—Ag4—S3	133.68 (5)		
symmetry codes: (i) −*x*+*y*, −*x*+1, *z*; (ii) −*y*+1, *x*−*y*+1, *z*.			
Compound 3			
Ag1—Ag1^{i}	3.0920 (17)	Ag4—S6^{i}	2.443 (3)
Ag1—Ag1^{ii}	3.0920 (17)	Ag5—Ag6	2.9993 (12)
Ag1—Ag2	3.3277 (14)	Ag5—O4^{ii}	2.438 (8)
Ag1—O2	2.464 (9)	Ag5—O6	2.509 (8)
Ag1—O6^{i}	2.491 (7)	Ag5—S4	2.474 (3)
Ag1—S3	2.486 (3)	Ag5—S5	2.477 (3)

Ag1—S3^{ii}	2.506 (3)	Ag6—Ag7	3.3280 (12)
Ag2—Ag3	3.0920 (15)	Ag6—O8	2.380 (7)
Ag2—O2	2.336 (9)	Ag6—S5	2.504 (3)
Ag2—P4	2.396 (4)	Ag6—S6^{i}	2.483 (3)
Ag2—S3^{ii}	2.729 (3)	Ag7—Ag8	3.1998 (13)
Ag2—S4	2.632 (3)	Ag7—O8	2.292 (7)
Ag3—O4^{ii}	2.277 (9)	Ag7—P1	2.375 (3)
Ag3—P3	2.379 (4)	Ag7—S5	2.782 (3)
Ag3—S3^{ii}	2.544 (3)	Ag7—S6	2.619 (3)
Ag3—S4	2.892 (3)	Ag8—Ag4^{ii}	3.3740 (13)
Ag4—Ag5	3.2186 (13)	Ag8—O5^{ii}	2.361 (8)
Ag4—Ag6	3.0524 (12)	Ag8—P2	2.394 (3)
Ag4—Ag8^{i}	3.3740 (13)	Ag8—S5	2.573 (3)
Ag4—O5	2.465 (8)	Ag8—S6	2.857 (3)
Ag4—S4	2.447 (3)		
O2—Ag1—O6^{i}	89.4 (3)	O4^{ii}—Ag5—O6	90.1 (3)
O2—Ag1—S3^{ii}	97.9 (2)	O4^{ii}—Ag5—S4	96.3 (2)
O2—Ag1—S3	107.2 (2)	O4^{ii}—Ag5—S5	106.7 (2)
O6^{i}—Ag1—S3^{ii}	116.43 (19)	S4—Ag5—O6	110.84 (19)
S3—Ag1—O6^{i}	105.30 (19)	S4—Ag5—S5	134.21 (11)
S3—Ag1—S3^{ii}	131.15 (15)	S5—Ag5—O6	108.18 (18)
O2—Ag2—P4	133.8 (2)	O8—Ag6—S5	98.32 (17)
O2—Ag2—S3^{ii}	95.1 (2)	O8—Ag6—S6^{i}	102.64 (18)
O2—Ag2—S4	90.2 (2)	S6^{i}—Ag6—S5	141.56 (10)
P4—Ag2—S3^{ii}	126.82 (12)	O8—Ag7—P1	140.61 (19)
P4—Ag2—S4	111.24 (12)	O8—Ag7—S5	93.01 (19)
S4—Ag2—S3^{ii}	82.79 (10)	O8—Ag7—S6	90.10 (19)
O4^{ii}—Ag3—P3	130.5 (2)	P1—Ag7—S5	120.19 (10)
O4^{ii}—Ag3—S3^{ii}	98.1 (2)	P1—Ag7—S6	113.86 (10)
O4^{ii}—Ag3—S4	89.3 (2)	S6—Ag7—S5	81.21 (9)
P3—Ag3—S3^{ii}	128.78 (12)	O5^{ii}—Ag8—P2	134.2 (2)
P3—Ag3—S4	110.13 (13)	O5^{ii}—Ag8—S5	93.3 (2)
S3^{ii}—Ag3—S4	81.15 (10)	O5^{ii}—Ag8—S6	92.1 (2)
S4—Ag4—O5	106.7 (2)	P2—Ag8—S5	130.18 (11)
S6^{i}—Ag4—O5	100.51 (19)	P2—Ag8—S6	106.65 (10)
S6^{i}—Ag4—S4	140.93 (10)	S5—Ag8—S6	80.56 (9)
Symmetry codes: (i) −*x*+*y*, −*x*, *z*; (ii) −*y*, *x*−*y*, *z*.			
Compound 4			
Ag1—Ag2	3.1756 (12)	Ag12—O14	2.360 (7)
Ag1—S4	2.780 (3)	Ag13—Ag14	3.0232 (11)
Ag1—S5	2.549 (3)	Ag13—S1	2.496 (3)
Ag1—P10	2.392 (3)	Ag13—S2	2.496 (3)
Ag1—O12	2.375 (7)	Ag13—O4	2.356 (7)

Ag2—S4	2.547 (3)	Ag13—O5	2.551 (6)
Ag2—S5	2.737 (3)	Ag14—Ag15	3.2787 (12)
Ag2—P9	2.377 (3)	Ag14—S1	2.481 (3)
Ag2—O15	2.411 (6)	Ag14—S7	2.480 (3)
Ag3—Ag4	3.0179 (11)	Ag14—O6	2.552 (6)
Ag3—Ag5	2.9886 (10)	Ag14—O19	2.400 (6)
Ag3—S5	2.496 (3)	Ag15—Ag16	3.1401 (11)
Ag3—S8	2.521 (3)	Ag15—S1	2.728 (3)
Ag3—O7	2.511 (6)	Ag15—S12	2.526 (2)
Ag3—O11	2.348 (6)	Ag15—P3	2.376 (3)
Ag4—Ag5	3.0108 (11)	Ag15—O19	2.392 (7)
Ag4—S5	2.525 (3)	Ag16—S1	2.519 (3)
Ag4—S6	2.507 (3)	Ag16—S12	2.778 (3)
Ag4—O8	2.564 (7)	Ag16—P4	2.365 (3)
Ag4—O15	2.393 (7)	Ag16—O2	2.363 (6)
Ag5—S6	2.533 (3)	Ag17—Ag18	3.1605 (11)
Ag5—S8	2.489 (3)	Ag17—S9	2.786 (3)
Ag5—O17	2.387 (7)	Ag17—S10	2.562 (3)
Ag6—Ag7	3.1178 (12)	Ag17—P5	2.389 (3)
Ag6—Ag12	3.3153 (12)	Ag17—O3	2.373 (7)
Ag6—S6	2.503 (3)	Ag18—S9	2.522 (3)
Ag6—S7	2.722 (3)	Ag18—S10	2.745 (3)
Ag6—P2	2.367 (3)	Ag18—P6	2.384 (3)
Ag6—O14	2.411 (6)	Ag18—O9	2.384 (7)
Ag7—S6	2.815 (3)	Ag19—Ag20	2.9215 (11)
Ag7—S7	2.522 (3)	Ag19—Ag21	2.9617 (11)
Ag7—P1	2.386 (3)	Ag19—S10	2.509 (2)
Ag7—O17	2.365 (7)	Ag19—S12	2.545 (2)
Ag8—Ag9	3.2778 (11)	Ag19—O2	2.328 (6)
Ag8—Ag21	3.3655 (11)	Ag20—Ag21	3.0670 (10)
Ag8—S8	2.551 (3)	Ag20—S10	2.517 (3)
Ag8—S11	2.718 (3)	Ag20—S11	2.492 (3)
Ag8—P8	2.385 (3)	Ag20—O7	2.568 (7)
Ag8—O20	2.397 (6)	Ag20—O9	2.371 (6)
Ag9—S8	2.905 (3)	Ag21—S11	2.515 (3)
Ag9—S11	2.516 (3)	Ag21—S12	2.492 (3)
Ag9—P7	2.376 (3)	Ag21—O6	2.550 (6)
Ag9—O11	2.367 (7)	Ag21—O20	2.412 (6)
Ag10—Ag11	3.2062 (12)	Ag22—Ag23	2.9273 (12)
Ag10—S2	2.514 (3)	Ag22—Ag24	2.9909 (11)
Ag10—S3	2.773 (3)	Ag22—S3	2.521 (3)
Ag10—P11	2.367 (3)	Ag22—S4	2.483 (3)
Ag10—O16	2.373 (7)	Ag22—O16	2.345 (7)

Ag11—S2	2.792 (3)	Ag23—Ag24	2.9753 (11)
Ag11—S3	2.532 (3)	Ag23—S3	2.503 (3)
Ag11—P12	2.375 (3)	Ag23—S9	2.520 (2)
Ag11—O4	2.364 (6)	Ag23—O3	2.347 (7)
Ag12—Ag13	2.9697 (12)	Ag24—S4	2.522 (3)
Ag12—Ag14	3.0678 (11)	Ag24—S9	2.505 (3)
Ag12—S2	2.500 (3)	Ag24—O7	2.568 (6)
Ag12—S7	2.522 (3)	Ag24—O12	2.351 (6)
Ag12—O8	2.574 (6)		
S5—Ag1—S4	80.87(8)	O14—Ag12—S2	103.22(17)
P10—Ag1—S4	126.09(9)	O14—Ag12—S7	99.80(17)
P10—Ag1—S5	140.35(10)	O14—Ag12—O8	86.2(2)
O12—Ag1—S4	86.50(16)	S1—Ag13—S2	137.06(9)
O12—Ag1—S5	97.90(17)	S1—Ag13—O5	103.67(16)
O12—Ag1—P10	110.90(17)	S2—Ag13—O5	115.05(16)
S4—Ag2—S5	81.75(9)	O4—Ag13—S1	102.51(17)
P9—Ag2—S4	140.84(11)	O4—Ag13—S2	96.66(17)
P9—Ag2—S5	126.68(11)	O4—Ag13—O5	88.3(2)
P9—Ag2—O15	109.72(19)	S1—Ag14—O6	115.92(15)
O15—Ag2—S4	95.20(18)	S7—Ag14—S1	135.42(9)
O15—Ag2—S5	89.31(17)	S7—Ag14—O6	102.14(16)
S5—Ag3—S8	136.99(9)	O19—Ag14—S1	100.81(17)
S5—Ag3—O7	104.56(16)	O19—Ag14—S7	102.19(18)
O7—Ag3—S8	113.50(16)	O19—Ag14—O6	89.1(2)
O11—Ag3—S5	106.14(18)	S12—Ag15—S1	83.84(8)
O11—Ag3—S8	93.78(17)	P3—Ag15—S1	121.37(9)
O11—Ag3—O7	89.5(2)	P3—Ag15—S12	143.52(10)
S5—Ag4—O8	114.82(15)	P3—Ag15—O19	105.13(17)
S6—Ag4—S5	137.73(9)	O19—Ag15—S1	94.33(17)
S6—Ag4—O8	102.55(15)	O19—Ag15—S12	97.93(17)
O15—Ag4—S5	94.96(16)	S1—Ag16—S12	82.96(8)
O15—Ag4—S6	107.10(17)	P4—Ag16—S1	141.35(9)
O15—Ag4—O8	86.0(2)	P4—Ag16—S12	123.71(10)
S8—Ag5—S6	141.80(9)	O2—Ag16—S1	96.23(17)
O17—Ag5—S6	90.61(18)	O2—Ag16—S12	86.58(17)
O17—Ag5—S8	108.87(18)	O2—Ag16—P4	111.40(18)
S6—Ag6—S7	85.14(9)	S10—Ag17—S9	81.40(8)
P2—Ag6—S6	143.93(10)	P5—Ag17—S9	129.36(9)
P2—Ag6—S7	120.83(10)	P5—Ag17—S10	137.70(10)
P2—Ag6—O14	102.01(19)	O3—Ag17—S9	87.54(17)
O14—Ag6—S6	100.83(17)	O3—Ag17—S10	93.75(17)
O14—Ag6—S7	93.19(18)	O3—Ag17—P5	113.19(18)
S7—Ag7—S6	82.89(8)	S9—Ag18—S10	82.95(8)

P1—Ag7—S6	124.15(10)	P6—Ag18—S9	139.98(9)
P1—Ag7—S7	141.04(10)	P6—Ag18—S10	126.24(10)
O17—Ag7—S6	84.50(17)	P6—Ag18—O9	109.30(17)
O17—Ag7—S7	97.67(18)	O9—Ag18—S9	97.58(18)
O17—Ag7—P1	111.22(18)	O9—Ag18—S10	87.21(16)
S8—Ag8—S11	82.12(8)	S10—Ag19—S12	143.95(9)
P8—Ag8—S8	140.41(10)	O2—Ag19—S10	104.14(16)
P8—Ag8—S11	125.51(10)	O2—Ag19—S12	93.00(16)
P8—Ag8—O20	108.06(17)	S10—Ag20—O7	114.77(16)
O20—Ag8—S8	96.63(18)	S11—Ag20—S10	136.33(9)
O20—Ag8—S11	92.97(16)	S11—Ag20—O7	103.75(15)
S11—Ag9—S8	79.05(8)	O9—Ag20—S10	92.99(17)
P7—Ag9—S8	123.43(9)	O9—Ag20—S11	107.12(17)
P7—Ag9—S11	142.73(10)	O9—Ag20—O7	90.2(2)
O11—Ag9—S8	84.19(17)	S11—Ag21—O6	116.52(16)
O11—Ag9—S11	98.86(18)	S12—Ag21—S11	135.40(9)
O11—Ag9—P7	111.74(18)	S12—Ag21—O6	102.49(16)
S2—Ag10—S3	83.17(8)	O20—Ag21—S11	97.89(16)
P11—Ag10—S2	142.23(10)	O20—Ag21—S12	104.42(16)
P11—Ag10—S3	121.68(10)	O20—Ag21—O6	88.2(2)
P11—Ag10—O16	111.33(18)	S4—Ag22—S3	142.56(9)
O16—Ag10—S2	97.36(17)	O16—Ag22—S3	92.50(17)
O16—Ag10—S3	85.86(18)	O16—Ag22—S4	107.10(18)
S3—Ag11—S2	82.45(8)	S3—Ag23—S9	137.69(9)
P12—Ag11—S2	123.95(9)	O3—Ag23—S3	105.68(18)
P12—Ag11—S3	140.54(9)	O3—Ag23—S9	94.72(17)
O4—Ag11—S2	88.97(17)	S4—Ag24—O7	112.62(16)
O4—Ag11—S3	100.73(17)	S9—Ag24—S4	135.10(9)
O4—Ag11—P12	107.78(18)	S9—Ag24—O7	107.42(16)
S2—Ag12—S7	137.69(9)	O12—Ag24—S4	93.25(19)
S2—Ag12—O8	103.09(16)	O12—Ag24—S9	106.27(18)
S7—Ag12—O8	113.50(16)	O12—Ag24—O7	90.2(2)
Compound 5			
Ag1—Ag1^{i}	3.3256 (7)	Ag2—Ag2^{ii}	2.9920 (5)
Ag1—S1^{i}	2.5272 (10)	Ag2—Ag2^{iii}	2.9920 (5)
Ag1—S1	2.7980 (10)	Ag2—S1	2.5110 (10)
Ag1—P1	2.3868 (12)	Ag2—S1^{ii}	2.4890 (10)
Ag1—O2	2.361 (3)	Ag2—O2	2.359 (3)
S1^{i}—Ag1—S1	81.64 (3)	O2—Ag1—P1	109.08 (8)
P1—Ag1—S1^{i}	140.71 (4)	S1^{ii}—Ag2—S1	140.27 (4)
P1—Ag1—S1	122.05 (4)	O2—Ag2—S1	96.04 (8)
O2—Ag1—S1	88.76 (7)	O2—Ag2—S1^{ii}	104.08 (8)
O2—Ag1—S1^{i}	101.65 (7)		

Symmetry codes: (i) *x*, −*y*+1/2, −*z*+1/2; (ii) −*y*+1/2, −*z*+1/2, *x*; (iii) *z*, −*x*+1/2, −*y*+1/2.			
Compound 6			
Ag1—Ag4	2.804 (11)	Ag12—S12	2.429 (4)
Ag1—Ag15^{i}	2.946 (12)	Ag12—S13	2.405 (5)
Ag1—O6	2.597 (15)	Ag13—Ag4^{i}	3.317 (2)
Ag1—S1^{i}	2.512 (12)	Ag13—Ag14	3.070 (2)
Ag1—S2^{i}	2.706 (10)	Ag13—Ag19	3.0290 (19)
Ag1—S8	2.590 (12)	Ag13—N4	2.524 (18)
Ag2—N2	2.50 (2)	Ag13—S4	2.466 (4)
Ag2—S11	2.882 (13)	Ag13—S13	2.466 (4)
Ag3—Ag23	3.022 (2)	Ag14—Ag4^{i}	3.173 (2)
Ag3—N1	2.202 (18)	Ag14—Ag16	2.977 (2)
Ag3—S7	2.662 (4)	Ag14—O3^{i}	2.500 (10)
Ag3—S8	2.500 (4)	Ag14—S2	2.454 (4)
Ag3—S16^{i}	2.704 (5)	Ag14—S4	2.486 (5)
Ag4—Ag5	3.180 (2)	Ag15—Ag1^{i}	2.946 (12)
Ag4—Ag13^{i}	3.317 (2)	Ag15—Ag16	3.086 (2)
Ag4—Ag14^{i}	3.173 (2)	Ag15—P3	2.373 (6)
Ag4—O6	2.454 (10)	Ag15—S1	2.511 (6)
Ag4—S2^{i}	2.533 (4)	Ag15—S2	2.949 (4)
Ag4—S8	2.923 (4)	Ag15—S10^{i}	2.612 (4)
Ag4—S13^{i}	2.479 (4)	Ag16—P4	2.419 (6)
Ag5—O8	2.511 (10)	Ag16—S2	2.824 (4)
Ag5—S8	2.442 (4)	Ag16—S3	2.667 (4)
Ag5—S9	2.477 (4)	Ag16—S10^{i}	2.573 (5)
Ag6—Ag7	3.040 (2)	Ag17—Ag18	3.0167 (19)
Ag6—O6	2.461 (11)	Ag17—S3	2.470 (4)
Ag6—O10^{i}	2.213 (8)	Ag17—S14^{i}	2.505 (5)
Ag6—S10	2.395 (4)	Ag17—S15^{i}	2.529 (4)
Ag7—Ag21	2.910 (2)	Ag18—O10	2.533 (9)
Ag7—S11	2.437 (5)	Ag18—S3	2.489 (4)
Ag7—S14	2.390 (4)	Ag18—S5	2.426 (4)
Ag8—Ag9	3.0549 (19)	Ag19—O2^{i}	2.525 (10)
Ag8—Ag12	2.943 (2)	Ag19—S4	2.507 (5)
Ag8—S9^{i}	2.477 (4)	Ag19—S5	2.635 (4)
Ag8—S12	2.728 (4)	Ag19—S6	2.441 (5)
Ag8—S14	2.495 (4)	Ag20—Ag21	2.8836 (19)
Ag9—Ag10	2.980 (2)	Ag20—N3	2.323 (18)
Ag9—P1	2.401 (4)	Ag20—S6	2.431 (4)
Ag9—S9^{i}	2.703 (4)	Ag20—S12	2.467 (4)
Ag9—S15	2.446 (4)	Ag21—Ag22	3.3224 (19)
Ag10—Ag11	3.132 (2)	Ag21—O2^{i}	2.538 (9)
Ag10—P2	2.454 (5)	Ag21—O9^{i}	2.281 (9)

Ag10—S9^{i}	2.723 (4)	Ag21—O11	2.353 (9)
Ag10—S16	2.485 (5)	Ag21—S11	2.542 (4)
Ag11—Ag23^{i}	2.939 (2)	Ag22—Ag23	3.015 (2)
Ag11—O8^{i}	2.422 (10)	Ag22—O11	2.434 (9)
Ag11—S5^{i}	2.736 (4)	Ag22—S6	2.405 (4)
Ag11—S15	2.503 (5)	Ag22—S7	2.434 (4)
Ag11—S16	2.523 (4)	Ag23—O7	2.388 (10)
Ag12—Ag13	3.262 (2)	Ag23—S5	2.494 (4)
Ag12—Ag20	3.0367 (19)	Ag23—S7	2.511 (5)
Ag12—Ag21	3.3155 (18)	Ag23—S16^{i}	2.921 (4)
Ag12—O9^{i}	2.543 (9)		
O6—Ag1—S2^{i}	79.8(4)	S13—Ag12—S12	162.55(14)
S1^{i}—Ag1—O6	115.0(5)	S4—Ag13—N4	102.4(5)
S1^{i}—Ag1—S2^{i}	116.5(5)	S4—Ag13—S13	157.32(16)
S1^{i}—Ag1—S8	128.4(4)	S13—Ag13—N4	93.9(5)
S8—Ag1—O6	91.7(5)	S2—Ag14—O3^{i}	110.6(2)
S8—Ag1—S2^{i}	111.0(4)	S2—Ag14—S4	150.07(15)
N2—Ag2—S11	84.3(5)	S4—Ag14—O3^{i}	82.1(2)
S1^{i}—Ag2—N2	127.1(8)	P3—Ag15—S1	135.80(18)
S1^{i}—Ag2—S11	138.8(6)	P3—Ag15—S2	104.19(16)
N1—Ag3—S7	91.0(5)	P3—Ag15—S10^{i}	129.10(17)
N1—Ag3—S8	132.6(5)	S1—Ag15—S2	108.47(15)
N1—Ag3—S16^{i}	103.3(6)	S1—Ag15—S10^{i}	84.90(15)
S7—Ag3—S16^{i}	107.38(15)	S10^{i}—Ag15—S2	81.94(12)
S8—Ag3—S7	125.13(14)	P4—Ag16—S2	104.68(15)
S8—Ag3—S16^{i}	94.45(14)	P4—Ag16—S3	117.47(16)
O6—Ag4—S2^{i}	86.1(3)	P4—Ag16—S10^{i}	134.34(17)
O6—Ag4—S8	87.1(2)	S3—Ag16—S2	112.11(13)
O6—Ag4—S13^{i}	136.6(3)	S10^{i}—Ag16—S2	85.13(13)
S2^{i}—Ag4—Ag1	60.7(2)	S10^{i}—Ag16—S3	98.25(13)
S2^{i}—Ag4—S8	106.08(13)	S3—Ag17—S14^{i}	137.66(14)
S13^{i}—Ag4—S2^{i}	130.84(15)	S3—Ag17—S15^{i}	123.09(15)
S13^{i}—Ag4—S8	100.21(13)	S14^{i}—Ag17—S15^{i}	98.72(14)
S8—Ag5—O8	134.6(2)	S3—Ag18—O10	85.4(2)
S8—Ag5—S9	143.69(13)	S5—Ag18—O10	114.6(2)
S9—Ag5—O8	73.3(2)	S5—Ag18—S3	157.76(15)
O10^{i}—Ag6—O6	114.1(3)	O2^{i}—Ag19—S5	108.5(2)
O10^{i}—Ag6—S10	148.0(3)	S4—Ag19—O2^{i}	102.5(2)
S10—Ag6—O6	97.5(3)	S4—Ag19—S5	99.72(14)
S14—Ag7—S11	160.43(16)	S6—Ag19—O2^{i}	86.9(2)
S9^{i}—Ag8—S12	125.31(14)	S6—Ag19—S4	136.27(15)
S9^{i}—Ag8—S14	136.33(15)	S6—Ag19—S5	117.81(14)
S14—Ag8—S12	98.36(14)	N3—Ag20—S6	102.4(5)

P1—Ag9—S9^{i}	106.42(15)	N3—Ag20—S12	104.0(5)
P1—Ag9—S15	144.96(17)	S6—Ag20—S12	153.25(14)
S15—Ag9—S9^{i}	105.64(14)	O11—Ag21—O2^{i}	72.5(3)
P2—Ag10—S9^{i}	108.75(15)	O11—Ag21—S11	83.3(2)
P2—Ag10—S16	134.74(15)	O11—Ag22—S7	96.9(2)
S16—Ag10—S9^{i}	114.87(13)	S6—Ag22—O11	101.6(2)
O8^{i}—Ag11—S5^{i}	97.9(2)	S6—Ag22—S7	155.64(16)
O8^{i}—Ag11—S15	89.0(3)	O7—Ag23—S5	105.0(3)
O8^{i}—Ag11—S16	108.3(3)	O7—Ag23—S7	97.1(3)
S15—Ag11—S5^{i}	111.39(14)	O7—Ag23—S16^{i}	85.3(2)
S15—Ag11—S16	130.11(15)	S5—Ag23—S7	142.10(15)
S16—Ag11—S5^{i}	111.88(14)	S5—Ag23—S16^{i}	106.91(14)
S13—Ag12—O9^{i}	107.7(2)	S7—Ag23—S16^{i}	105.23(13)
Symmetry code: (i) −x, −y, −z+1.			

Figure S1. The superimposed picture of Ag_{24} cores in 2-5.

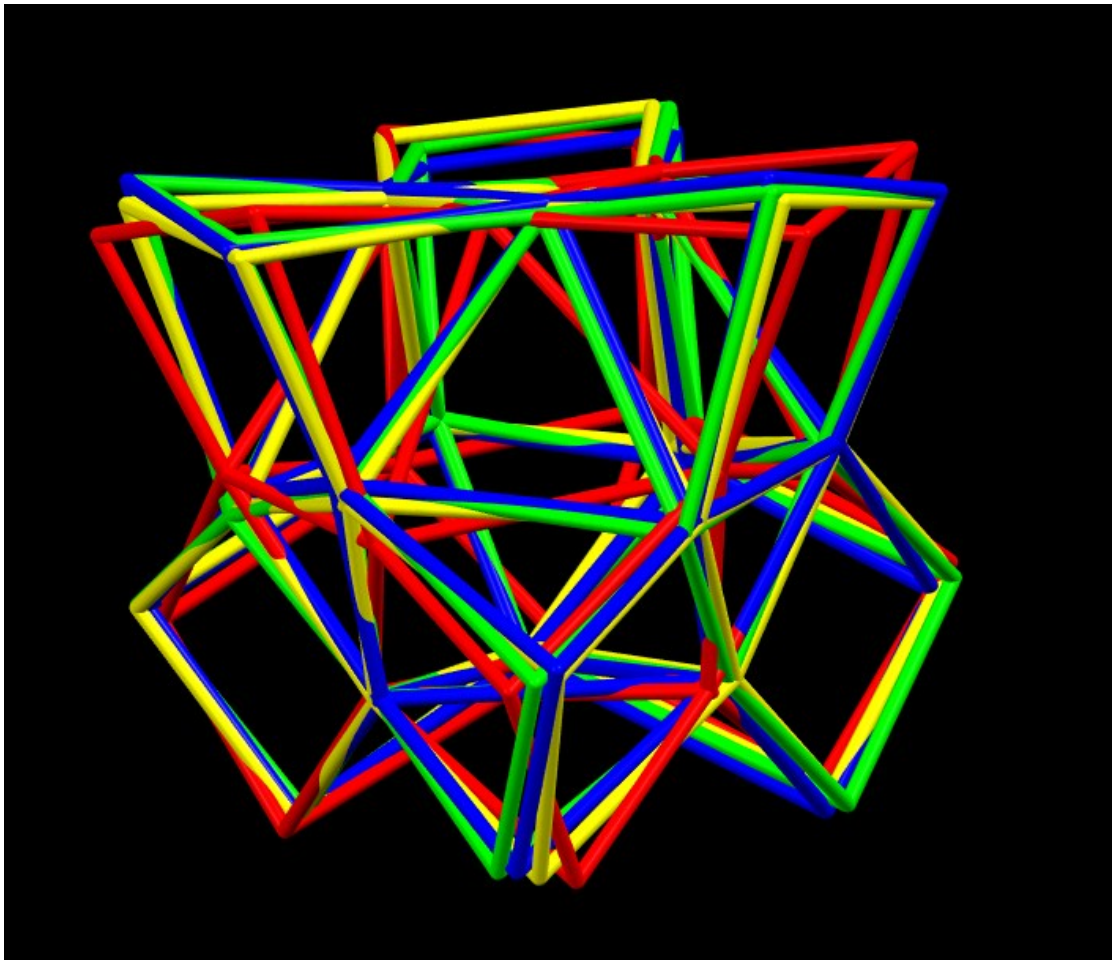


Figure S2. The simulated and experimental isotopic distribution patterns of 6a-6e.

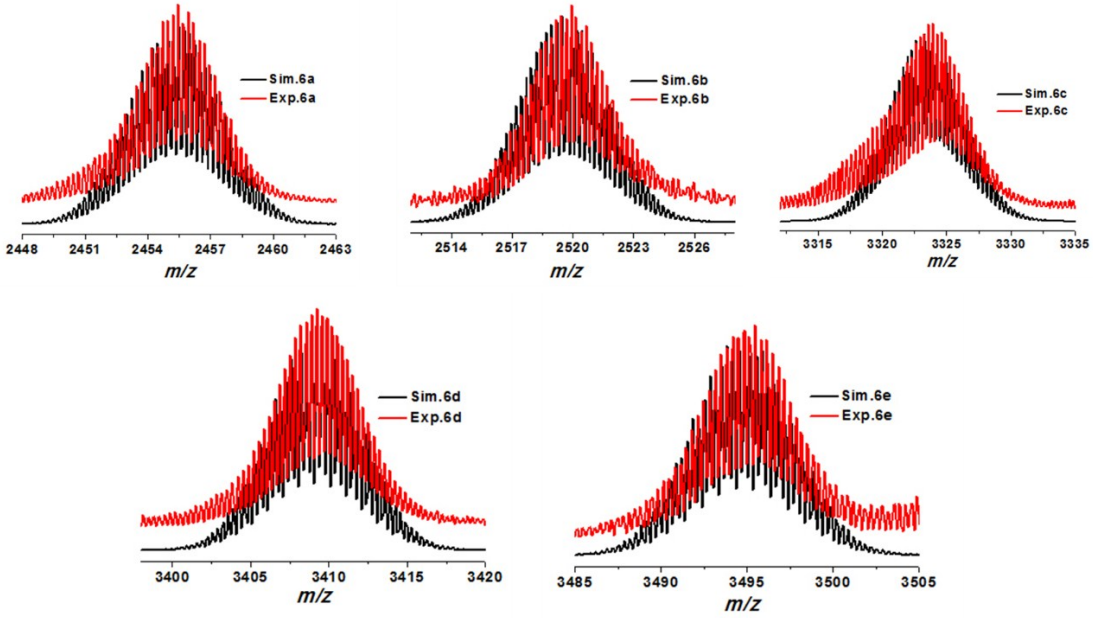


Figure S3. Diffuse reflectance UV-visible spectrum of 1 at room temperature.

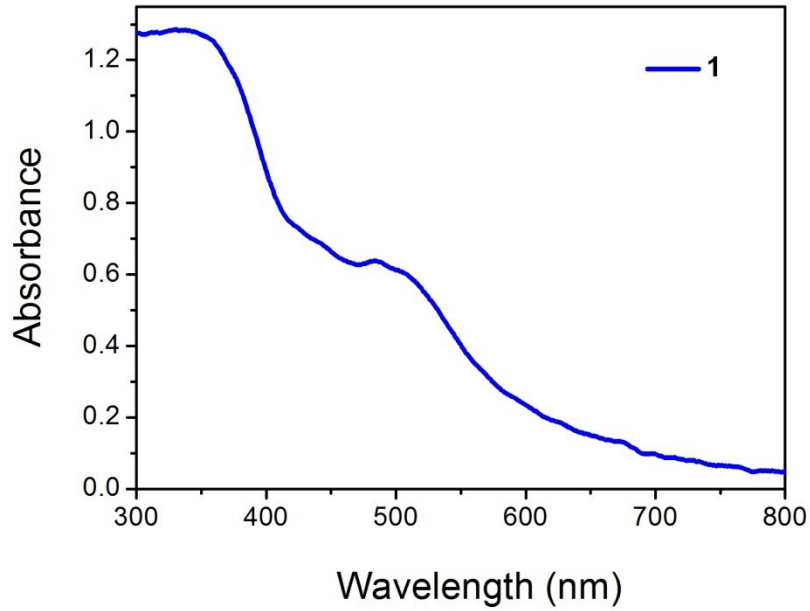


Figure S4. Excitation spectrum of 1 at room temperature.

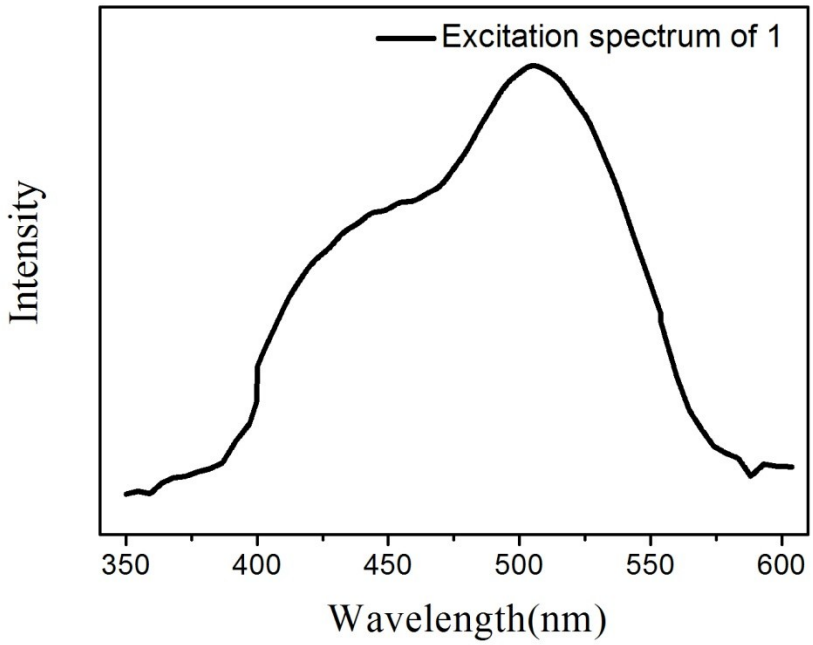
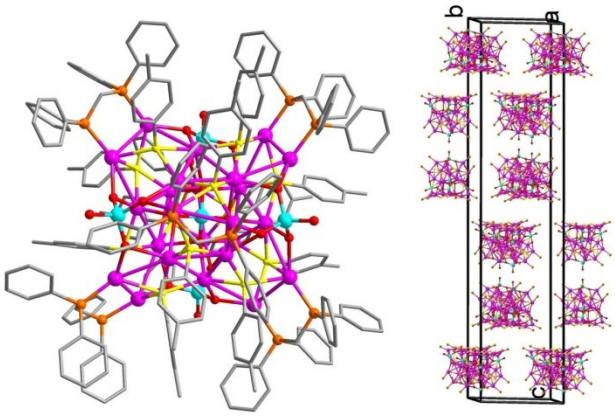
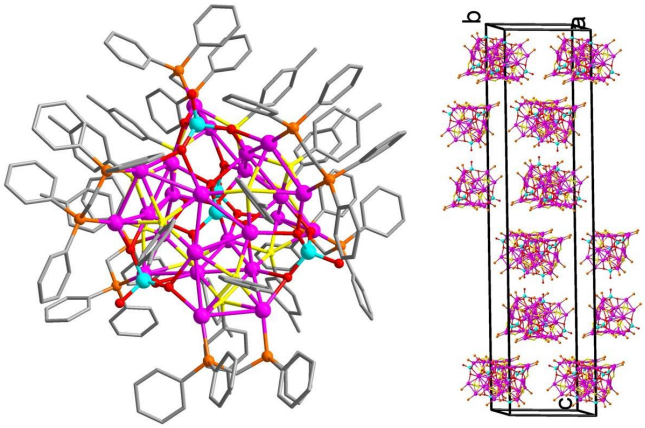


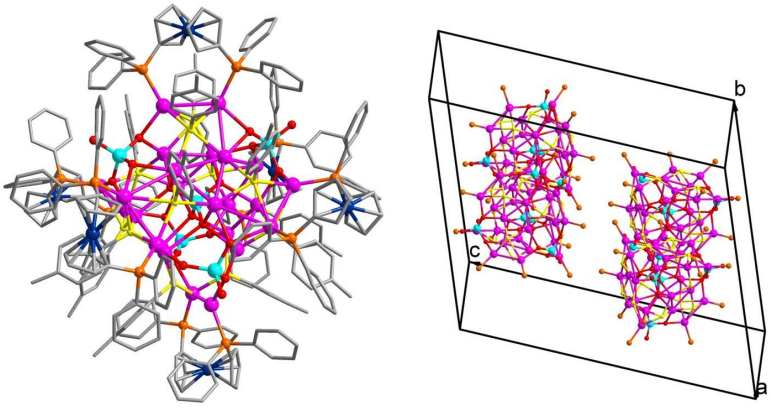
Figure S5. The cluster structure and molecule packing in 2-4.



2



3



4

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