

## Electronic Supplementary Information (ESI)

### A giant 90-nucleus silver cluster templated by hetero-anions

Jia-Wei Liu,<sup>a,#</sup> Hai-Feng Su,<sup>c,#</sup> Zhi Wang,<sup>a</sup>, Yan-An Li,<sup>b</sup> Quan-Qin Zhao,<sup>a</sup> Xing-Po Wang,<sup>a</sup> Chen-Ho Tung,<sup>a</sup> Di Sun<sup>a\*</sup> and Lan-Sun Zheng<sup>c</sup>

<sup>a</sup>*Key Lab of Colloid and Interface Chemistry, Ministry of Education, School of Chemistry and Chemical Engineering, Shandong University, Jinan, 250100, People's Republic of China.*

*E-mail: dsun@sdu.edu.cn. Fax: +86-531-88364218.*

<sup>b</sup>*State Key Laboratory for Physical Chemistry of Solid Surfaces and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, People's Republic of China.*

<sup>c</sup>*College of Chemistry, Chemical Engineering and Materials Science, Shandong Normal University, Jinan 250014, People's Republic of China.*

## Experiment details

The precursors of  $\{(HNEt_3)_2[Ag_{10}(tBuC_6H_4S)_{12}]\}_n$  were prepared according to the literature with some modifications.<sup>1</sup> All chemicals and solvents used in the syntheses were of analytical grade and used without further purification. IR spectra were recorded on a PerkinElmer Spectrum Two in the frequency range of 4000-450 cm<sup>-1</sup>. The elemental analyses (C, H, N contents) were determined on a Vario EL III analyzer. The Raman spectra of compounds in solid state were recorded on a LabRAM HR800 (HORIBA Jobin Yvan) in the frequency range of 300-3000 cm<sup>-1</sup>. 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. 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 93-293 K. Spectra were collected at different temperatures after a 5 min homoiothermy. Time-resolved photoluminescence lifetime measurements were measured on Edinburgh spectrofluorimeter (F920S) using a time-correlated single-photon counting technique. Powder X-ray diffraction (PXRD) data were collected on a Philips X’Pert Pro MPD X-ray diffractometer equipped with an X’Celerator detector using Cu K $\alpha$  radiation. Energy-dispersive X-ray spectrum was measured using an SU-8010 field emission scanning electron microscope (FESEM; Hitachi Ltd., Tokyo, Japan) equipped with an Oxford-Horiba Inca XMax50 energy-dispersive X-ray (EDX; Oxford Instruments Analytical, High Wycombe, England). Mass spectra were recorded on an Agilent 6224 (Agilent Technologies, USA) ESI-TOF-MS spectrometer. Sample solutions are infused by a syringe pump at 4  $\mu$ L/min. Data were acquired using the following settings: ESI capillary voltage was set at 4000 V (+) ion mode and 3500 V (-) ion mode and fragmentor at 200 V. The liquid nebulizer was set to 15 psig and the nitrogen drying gas was set to a flow rate of 4 L/min. Drying gas temperature was maintained at 150 °C. The data analyses of mass spectra were performed based on the isotope distribution patterns using Agilent MassHunter Workstation Data acquisition software (Version B.05.00). The reported m/z values represent monoisotopic mass of the most abundant peak within the isotope pattern.

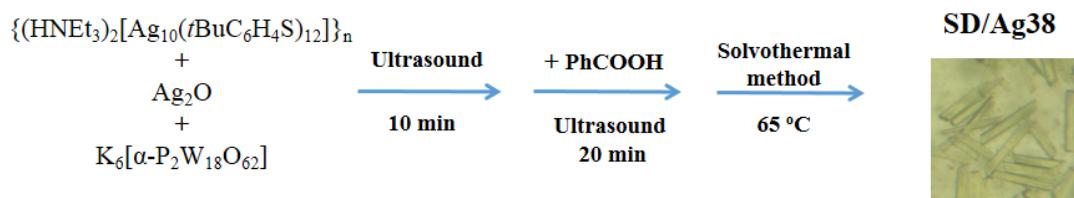
## X-ray Crystallography

Single crystal of **SD/Ag38** with appropriate dimensions was chosen under an optical microscope and quickly coated with high vacuum grease (Dow Corning Corporation) to prevent decomposition. Intensity data and cell parameters were recorded at 100 K for **SD/Ag38** on a Rigaku Oxford Diffraction XtaLAB Synergy diffractometer equipped with a HyPix-6000HE area detector, using a Cu K $\alpha$  radiation ( $\lambda = 1.54184 \text{ \AA}$ ) from PhotonJet micro-focus X-ray source. The diffraction images were processed and scaled using the CrysAlisPro software.<sup>2</sup> The structure was solved using the charge-flipping algorithm, as implemented in the program *SUPERFLIP*<sup>3</sup> and refined by full-matrix least-squares techniques against  $F_o^2$  using the SHELXL program<sup>4</sup> through the OLEX2 interface.<sup>5</sup> Hydrogen atoms at carbon were placed in calculated positions and refined isotropically by using a riding model. All the carbon atoms and several oxygen atoms were refined with isotropic thermal parameters due to their large thermal motion or some unresolved disorder which could not be modeled despite many attempts. Appropriate restraints or constraints were applied to the geometry and the atomic displacement parameters of the atoms in the cluster. All structures were examined using the Addsym subroutine of PLATON<sup>6</sup> to ensure that no additional symmetry could be applied to the models. The highly disordered solvent molecules and additional counter ions were taken into account with the SQUEEZE/PLATON procedure.<sup>6</sup> The residual electron density corresponding to 1958 electrons/cell was found in the voids of the crystal, which were removed by SQUEEZE and assigned to 13 CH<sub>3</sub>OH, 9 CH<sub>2</sub>Cl<sub>2</sub>, 6 DMF and two additional counter ions (63 electrons/PhCOO) per formula unit. These disordered components removed by the SQUEEZE process have been included in the overall formula, formula weight, density, F(000), etc., calculations reported in the crystal-data text and in the CIF. Pertinent crystallographic data collection and refinement parameters are collated in Table S1. Selected bond lengths and angles are collated in Table S2.

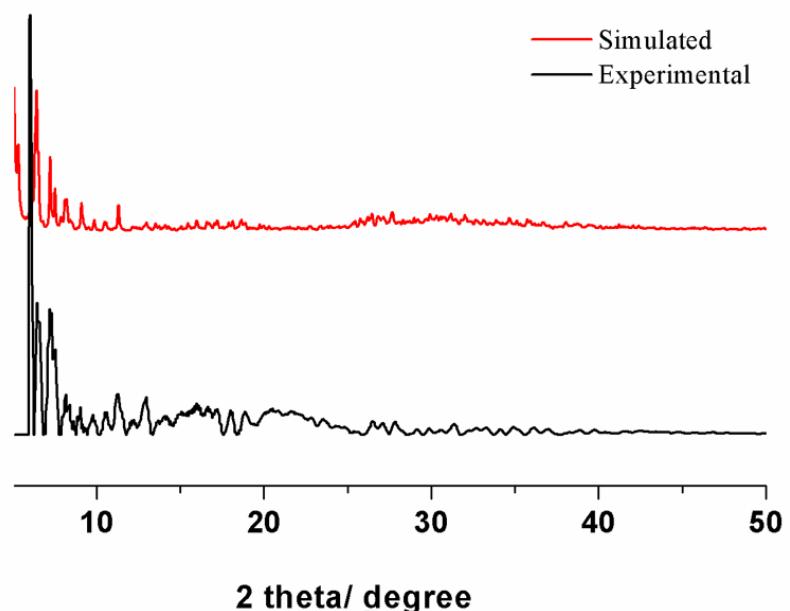
## Synthesis of SD/Ag38

$\{(HNEt_3)_2[Ag_{10}(SC_6H_4fBu)_{12}]\}_n$  (0.025 mmol, 6.9 mg), Ag<sub>2</sub>O (0.025 mmol, 5.8 mg) and K<sub>6</sub>[ $\alpha$ -P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>] (0.01 mmol, 4.6 mg) were mixed in CH<sub>3</sub>OH/CH<sub>2</sub>Cl<sub>2</sub>/DMF (5.5 mL, v: v: v = 5:5:1) under the ultrasound condition (160 W, 40 kHz) at room temperature. After ten minutes, PhCOOH (0.05 mmol, 6.1 mg) was added into above mixture. After reacting for another 20 min under the same ultrasonic condition, the mixture was sealed in 25 mL Teflon-lined stainless steel vessel and kept at 65°C for 33 hours. After cooling to room temperature, the yellow solution was filtrated and left at room temperature for slow evaporation in the darkness. Yellow block crystals of **SD/Ag38** were collected with a yield of ~5 %. Elemental analyses calc. (found) for **SD/Ag38**: C<sub>668</sub>H<sub>828</sub>Ag<sub>90</sub>N<sub>8</sub>O<sub>121</sub>S<sub>46</sub>W<sub>10</sub>Cl<sub>18</sub> C, 32.66 (32.32); H, 3.39 (3.25); N, 0.45 (0.39) %. Selected IR peaks (cm<sup>-1</sup>): 2962 (w), 1585 (w), 884 (w), 1526 (m), 1487 (m), 1114 (m), 1002 (m), 1373 (s), 714 (s), 672 (s)

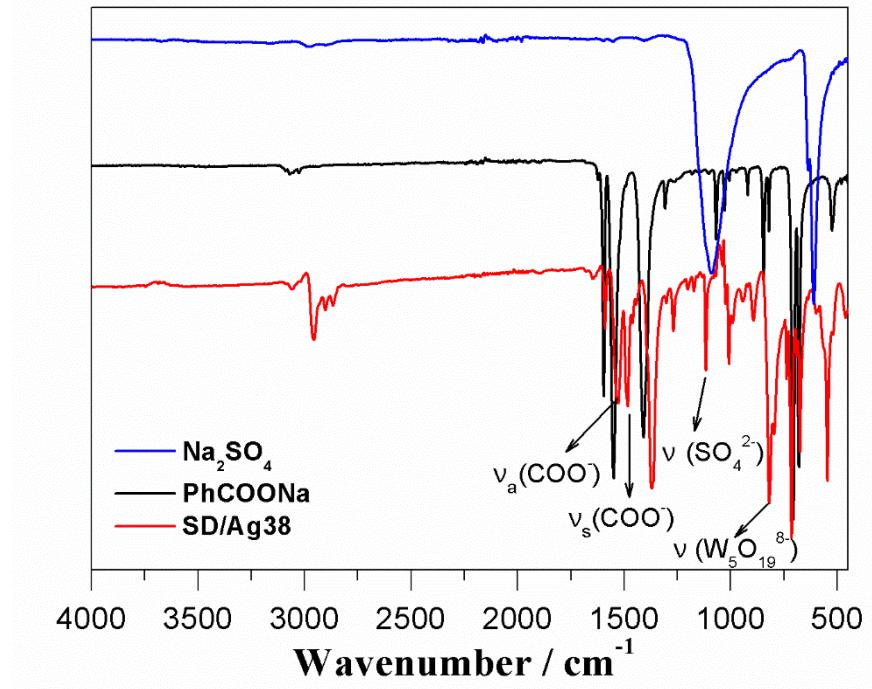
**Scheme S1: Synthetic Route for SD/Ag38**



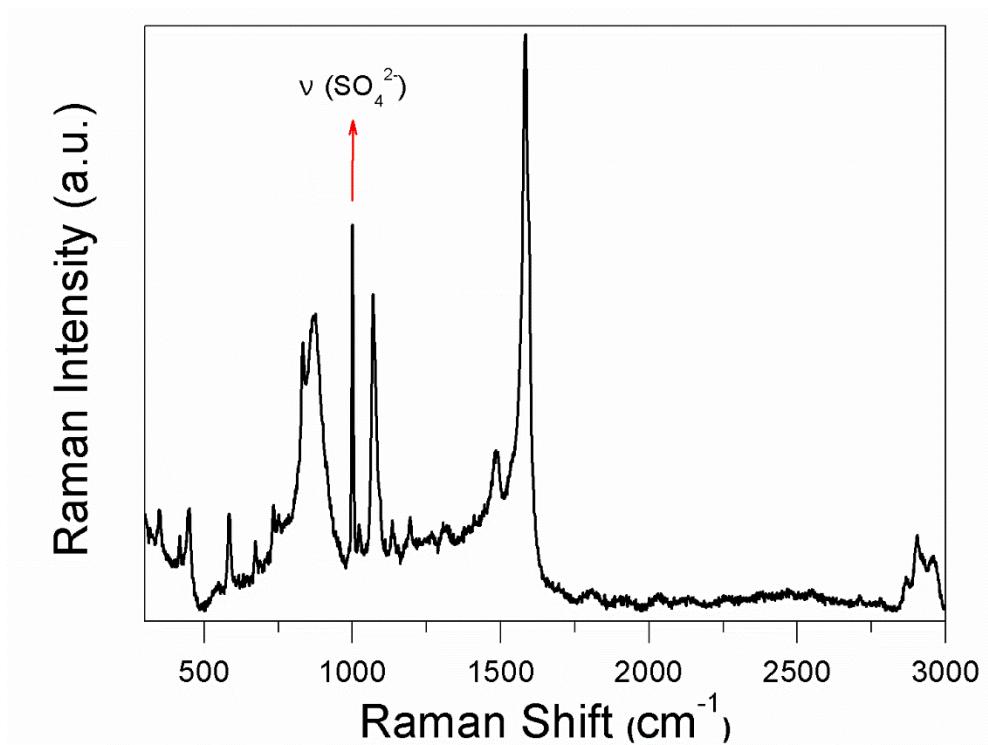
**Figure S1: The PXRD pattern of SD/Ag38.**



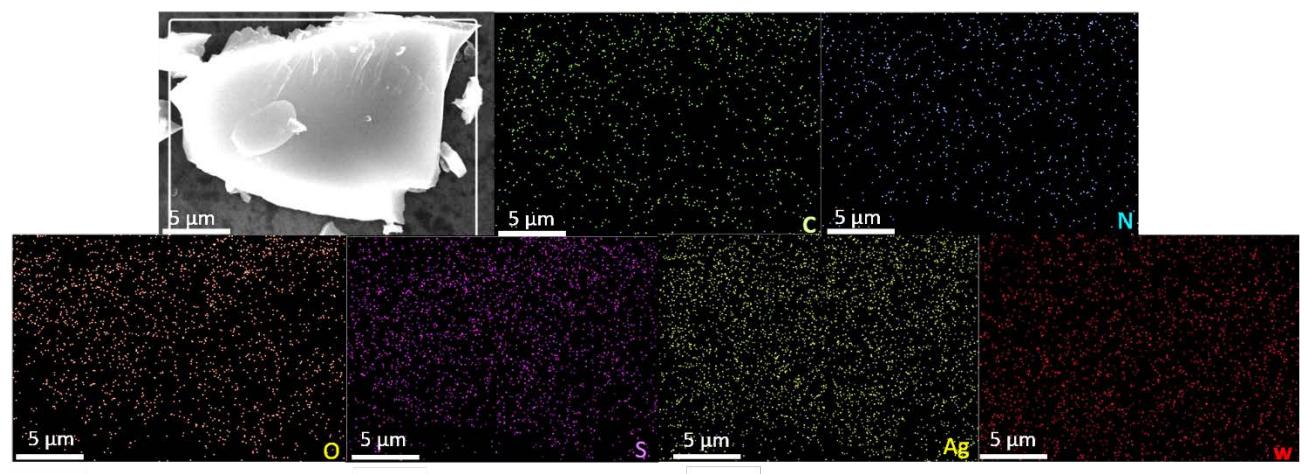
**Figure S2: The IR spectra of SD/Ag38, Na<sub>2</sub>SO<sub>4</sub> and PhCOONa.**



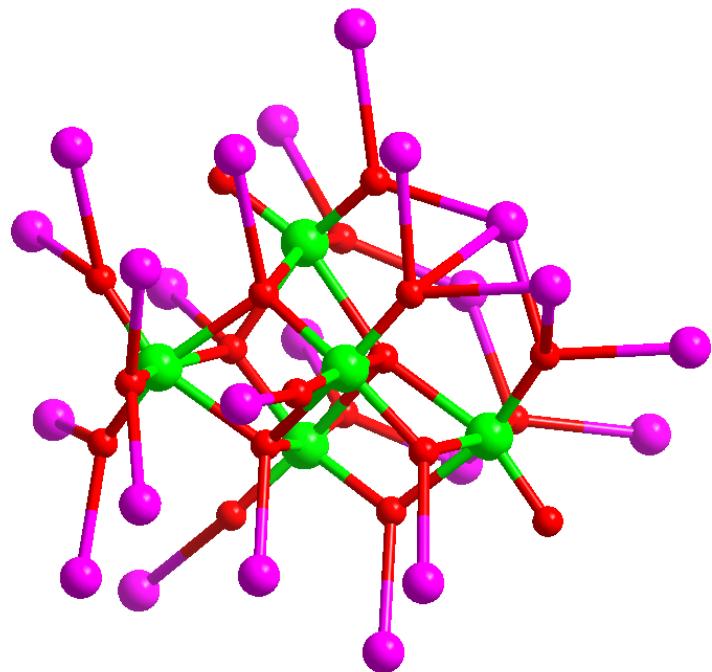
**Figure S3: The Raman spectrum of SD/Ag38. Experimental conditions: laser excitations 632.81 nm, 100- $\mu$ m slits, 298 K.**



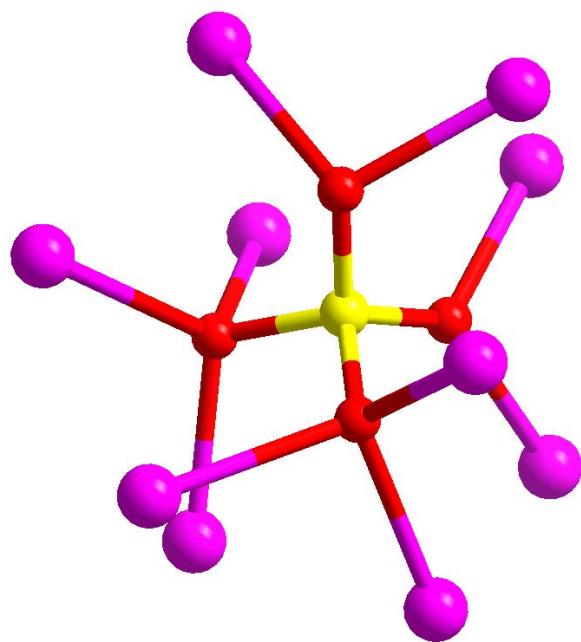
**Figure S4:** The energy dispersive spectroscopy (EDS) mapping of SD/Ag38.



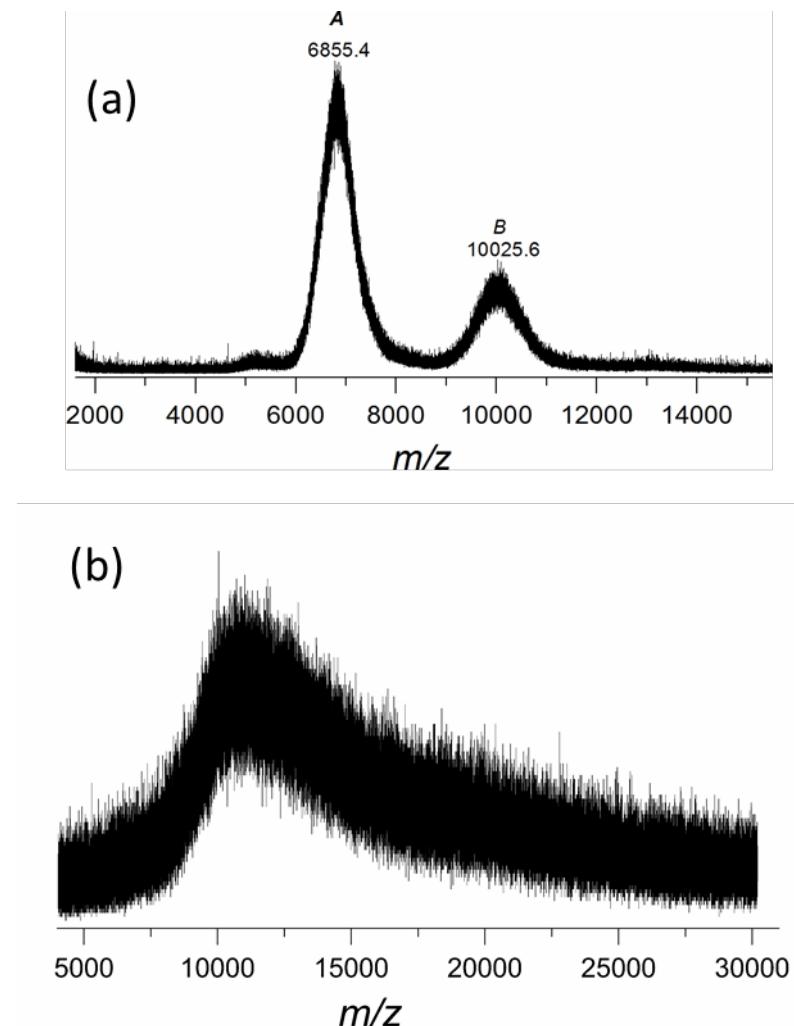
**Figure S5:** The binding mode of  $\text{W}_5\text{O}_{19}^{8-}$  towards Ag atoms.



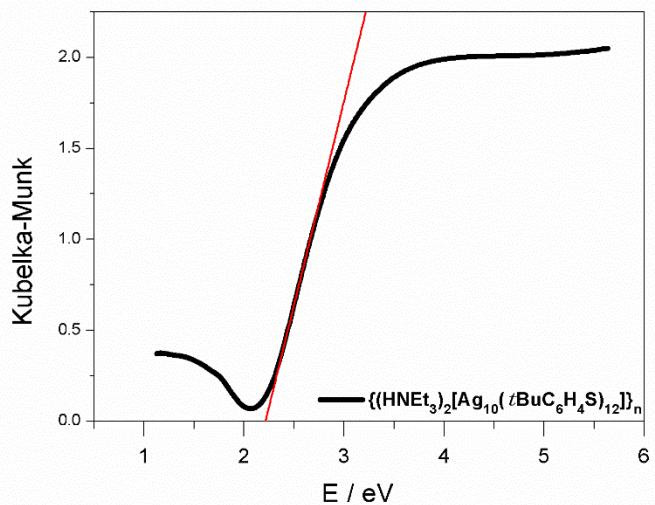
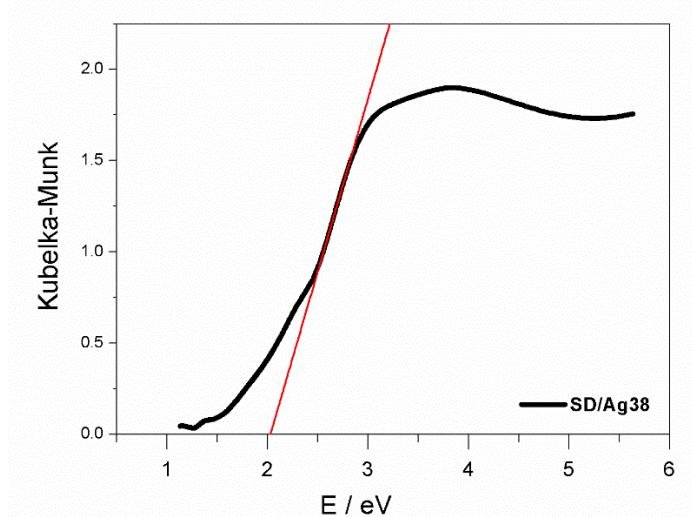
**Figure S6:** The binding mode of  $\text{SO}_4^{2-}$  towards Ag atoms.



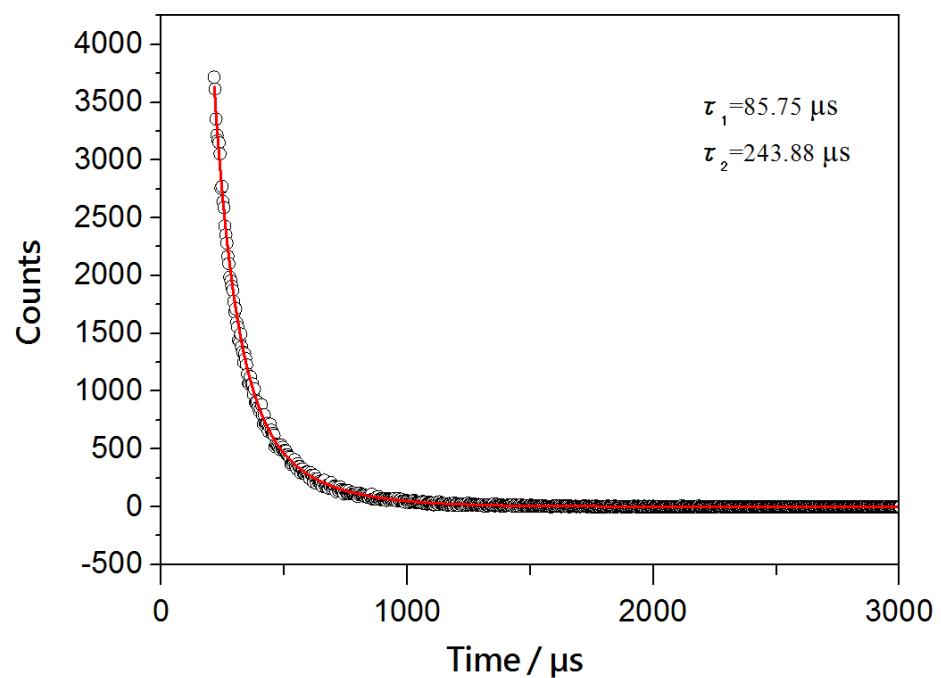
**Figure S7: The positive-mode electrospray-ionization mass spectrometry (a) and matrix-assisted laser desorption/ ionization time of flight mass spectrometry (b) for SD/Ag38.**



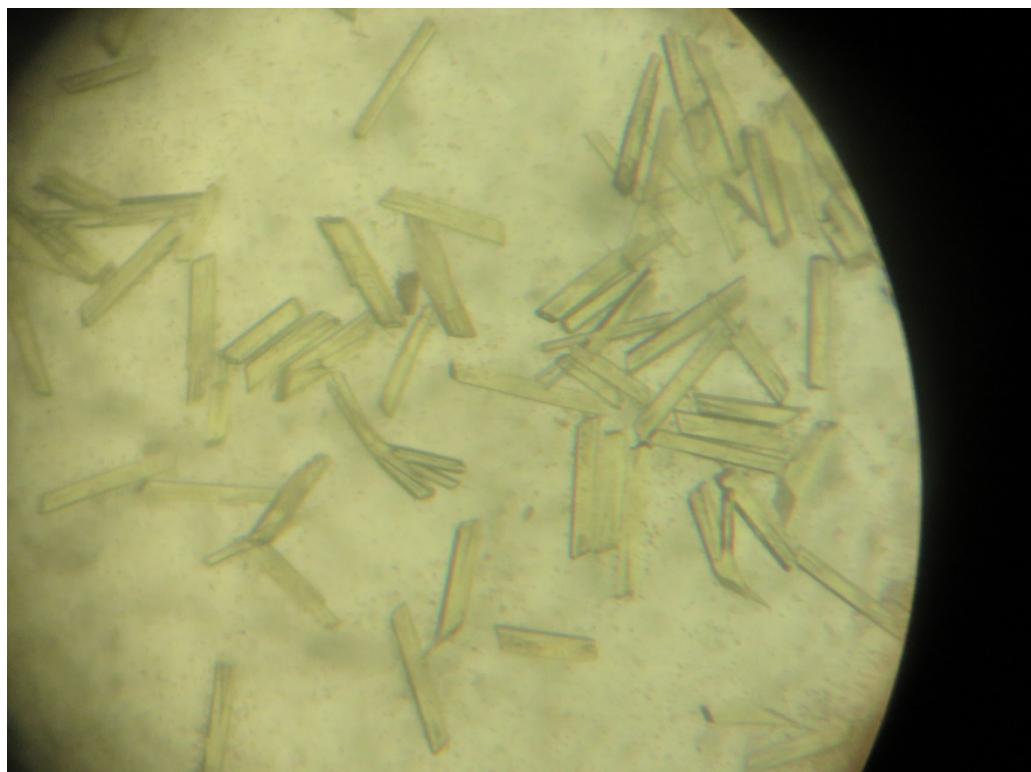
**Figure S8: Diffuse reflectance UV-Vis spectra of the Kubelka-Munk function *vs* energy (eV) of SD/Ag38 (top) and the precursor  $\{(HNEt_3)_2[Ag_{10}(tBuC_6H_4S)_{12}]\}_n$  (down).**



**Figure S9: The emission decay curve of SD/Ag38 measured at 93K.**



**Figure S10: Microscope photograph of crystals of SD/Ag38.**



**Table S1: Crystal Data Collection and Structure Refinement for SD/Ag38.**

Compound	<b>SD/Ag38</b>
Empirical formula	C <sub>668</sub> H <sub>828</sub> Ag <sub>90</sub> N <sub>8</sub> O <sub>121</sub> S <sub>46</sub> W <sub>10</sub> Cl <sub>18</sub>
Formula weight	24564. 99
Temperature/K	100(2)
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /n
a/Å	24. 0308(11)
b/Å	35. 6613(19)
c/Å	45. 039(2)
α/°	90
β/°	92. 815(5)
γ/°	90
Volume/Å <sup>3</sup>	38551(3)
Z	2
ρ <sub>calc</sub> g/cm <sup>3</sup>	2. 116
μ/mm <sup>-1</sup>	22. 779
F(000)	23744. 0
Reflections collected	229505
Independent reflections	68154 [R <sub>int</sub> = 0. 1900, R <sub>sigma</sub> = 0. 1406]
Data/restraints/parameters	68154/643/1997
Goodness-of-fit on F <sup>2</sup>	1. 082
Final R indexes [I>=2σ (I)]	R <sub>1</sub> = 0. 1206, wR <sub>2</sub> = 0. 3328
Final R indexes [all data]	R <sub>1</sub> = 0. 2006, wR <sub>2</sub> = 0. 3960
Largest diff. peak/hole / e Å <sup>-3</sup>	2. 51/-2. 03

**Table S2: Selected bond distances (Å) and angles (°) for SD/Ag38.**

Ag1—Ag26	3.225(6)	Ag23—Ag26 <sup>i</sup>	3.070(3)
Ag1—S4	2.399(8)	Ag23—S2 <sup>i</sup>	2.554(7)
Ag1—S22 <sup>i</sup>	2.367(9)	Ag23—S22	2.448(8)
Ag1—O6	2.512(16)	Ag23—S23	2.780(7)
Ag2—Ag4	3.031(9)	Ag23—O42	2.354(15)
Ag2—Ag42	2.577(9)	Ag24—Ag6 <sup>i</sup>	3.072(3)
Ag2—S3	2.598(10)	Ag24—Ag25	3.105(3)
Ag2—S10	2.740(12)	Ag24—Ag26	2.981(3)
Ag2—O19	1.94(3)	Ag24—Ag28	3.002(3)
Ag2—O20	2.17(3)	Ag24—O30	2.48(2)
Ag3—Ag12	3.10(2)	Ag24—O44 <sup>i</sup>	2.286(17)
Ag3—Ag40	3.199(17)	Ag24—O44	2.398(17)
Ag3—S7	2.59(2)	Ag25—Ag16 <sup>i</sup>	3.243(3)
Ag3—S15	2.895(18)	Ag25—Ag22 <sup>i</sup>	3.196(3)
Ag3—O5	2.24(3)	Ag25—S2	2.478(7)
Ag3—O39	2.02(3)	Ag25—S13 <sup>i</sup>	2.473(6)
Ag4—Ag10	2.828(4)	Ag25—O41	2.41(2)
Ag4—Ag11	3.213(3)	Ag26—Ag23 <sup>i</sup>	3.070(3)
Ag4—Ag42	3.270(4)	Ag26—Ag27	3.171(2)
Ag4—S8	2.521(8)	Ag26—S2	2.508(6)
Ag4—S10	2.498(9)	Ag26—S4	2.563(7)
Ag4—O20	2.50(3)	Ag26—O29	2.56(2)
Ag4—O46	2.373(16)	Ag26—O43 <sup>i</sup>	2.443(17)
Ag5—Ag6	3.313(4)	Ag27—Ag28	3.347(4)
Ag5—Ag10	3.264(3)	Ag27—Ag29	3.020(3)
Ag5—S10	2.599(9)	Ag27—Ag30	2.968(3)
Ag5—S12	2.543(8)	Ag27—Ag45	3.035(3)
Ag5—S22 <sup>i</sup>	2.514(7)	Ag27—S4	2.509(7)
Ag5—O3	2.466(14)	Ag27—S9	2.479(8)
Ag6—Ag23 <sup>i</sup>	3.262(4)	Ag27—O28	2.27(2)
Ag6—Ag24 <sup>i</sup>	3.072(3)	Ag28—S9	2.481(6)
Ag6—Ag44	3.077(3)	Ag28—S23	2.487(8)
Ag6—S12	2.426(7)	Ag28—O29	2.48(2)
Ag6—S23 <sup>i</sup>	2.611(7)	Ag28—O43 <sup>i</sup>	2.491(16)
Ag6—O42 <sup>i</sup>	2.295(19)	Ag29—Ag30	3.303(3)
Ag7—Ag8	3.182(3)	Ag29—Ag45	2.982(2)

Ag7—Ag44	2.963(3)	Ag29—S9	2.506(7)
Ag7—O3	2.259(18)	Ag29—S20	2.484(6)
Ag7—O13	2.410(12)	Ag29—O15	2.420(17)
Ag7—O41 <sup>i</sup>	2.225(18)	Ag30—Ag31	2.868(3)
Ag8—Ag15	2.961(3)	Ag30—Ag32	3.209(3)
Ag8—Ag44	3.114(3)	Ag30—Ag45	3.376(3)
Ag8—S13	2.473(6)	Ag30—S4	2.485(6)
Ag8—S14	2.525(6)	Ag30—S5	2.671(8)
Ag8—O13	2.557(14)	Ag30—O15	2.424(19)
Ag8—O49	2.494(17)	Ag30—O27	2.47(3)
Ag9—Ag10	2.821(4)	Ag31—Ag42	2.892(3)
Ag9—Ag13	3.080(3)	Ag31—Ag43	2.851(4)
Ag9—Ag44	2.981(3)	Ag31—S3	2.449(8)
Ag9—S11	2.794(8)	Ag31—S5	2.474(6)
Ag9—S12	2.484(7)	Ag31—O7	2.569(16)
Ag9—O37	2.34(3)	Ag32—Ag33	3.248(3)
Ag9—O49	2.362(14)	Ag32—Ag38	3.110(4)
Ag10—Ag11	2.948(3)	Ag32—S5	2.586(7)
Ag10—S10	2.446(8)	Ag32—S20	2.501(8)
Ag10—S11	2.461(7)	Ag32—O27	2.55(3)
Ag10—O4	2.496(15)	Ag32—O47	2.21(4)
Ag11—Ag12	3.199(4)	Ag33—Ag34	3.000(3)
Ag11—S8	2.542(9)	Ag33—Ag38	2.879(5)
Ag11—S11	2.514(8)	Ag33—S20	2.531(7)
Ag11—O5	2.358(16)	Ag33—S21	2.580(7)
Ag11—O40	2.35(2)	Ag33—O2A	2.49(3)
Ag12—Ag13	2.926(4)	Ag33—O26	2.25(4)
Ag12—Ag14	2.966(4)	Ag34—Ag35	3.061(3)
Ag12—O17	2.372(15)	Ag34—Ag36	2.952(4)
Ag12—O36	2.28(3)	Ag34—S17	2.484(10)
Ag12—O39	2.31(3)	Ag34—S21	2.676(8)
Ag13—S11	2.512(8)	Ag34—O2	2.35(4)
Ag13—S14	2.472(7)	Ag34—O2A	2.48(4)
Ag13—O36	2.46(2)	Ag34—O11	2.431(12)
Ag13—O37	2.51(3)	Ag35—Ag36	2.887(4)
Ag14—Ag35	3.099(3)	Ag35—S15	2.587(8)
Ag14—S14	2.615(7)	Ag35—S17	2.453(8)
Ag14—S15	2.594(8)	Ag35—O14	2.438(14)
Ag14—O34	2.53(2)	Ag35—O34	2.52(2)

Ag14—O35	2.32(3)	Ag36—Ag37	2.966(4)
Ag15—Ag17	2.882(3)	Ag36—S15	2.495(7)
Ag15—Ag35	3.205(4)	Ag36—S21	2.461(7)
Ag15—S14	2.503(7)	Ag36—O10	2.378(14)
Ag15—S16	2.494(7)	Ag37—Ag38	3.036(4)
Ag15—O34	2.51(2)	Ag37—S7	2.621(8)
Ag16—Ag25 <sup>i</sup>	3.243(3)	Ag37—S21	2.572(8)
Ag16—S13	2.649(5)	Ag37—O8	2.37(2)
Ag16—S16	2.557(6)	Ag37—O23	2.49(4)
Ag16—S18	2.455(7)	Ag38—Ag43	3.275(5)
Ag16—O13	2.391(15)	Ag38—O16	2.304(15)
Ag17—Ag18	3.015(3)	Ag38—O24	2.36(3)
Ag17—Ag19	3.017(3)	Ag38—O25	2.10(4)
Ag17—S16	2.524(6)	Ag39—Ag40	2.961(4)
Ag17—S17	2.572(9)	Ag39—Ag41	2.962(4)
Ag17—O33	2.34(3)	Ag39—S6	2.610(12)
Ag18—Ag19	2.937(3)	Ag39—S7	2.642(9)
Ag18—S16	2.602(6)	Ag39—O21	2.32(3)
Ag18—S19	2.519(8)	Ag39—O23	2.57(4)
Ag18—O32	2.19(3)	Ag40—Ag41	3.042(4)
Ag19—Ag20	2.950(3)	Ag40—S7	2.508(9)
Ag19—S17	2.569(8)	Ag40—S8	2.559(8)
Ag19—S19	2.601(7)	Ag41—S6	2.513(9)
Ag19—O1	2.38(4)	Ag41—S8	2.565(9)
Ag19—O31	2.42(4)	Ag42—S3	2.558(11)
Ag20—Ag29	3.007(3)	Ag42—S6	2.562(14)
Ag20—Ag34	3.192(3)	Ag42—O20	2.52(3)
Ag20—S19	2.506(9)	Ag42—O46	2.419(16)
Ag20—S20	2.506(8)	Ag43—S5	2.518(7)
Ag20—O2	2.30(4)	Ag43—S6	2.539(9)
Ag21—Ag29	3.352(4)	Ag43—O8	2.377(18)
Ag21—S9	2.555(8)	Ag43—O24	2.45(3)
Ag21—S18	2.523(9)	Ag44—S12	2.519(8)
Ag21—S19	2.540(7)	Ag44—S13	2.483(6)
Ag21—O18	2.393(16)	Ag44—O38	2.33(2)
Ag22—Ag23	2.831(3)	Ag45—O6	2.288(16)
Ag22—Ag25 <sup>i</sup>	3.196(3)	Ag45—O18	2.294(17)
Ag22—Ag28	3.015(4)	Ag45—O43 <sup>i</sup>	2.232(18)
Ag22—S2 <sup>i</sup>	2.800(7)	Ag22—S23	2.547(7)

Ag22—S18	2.420(6)	Ag22—O44 <sup>i</sup>	2.463(19)
Ag23—Ag6 <sup>i</sup>	3.262(4)		
S7—Ag3—S15	122.0(6)	S4—Ag1—O6	83.9(4)
O5—Ag3—S7	83.6(8)	S2 <sup>i</sup> —Ag23—S23	115.7(2)
O5—Ag3—S15	113.1(8)	S22—Ag23—S2 <sup>i</sup>	128.0(3)
O39—Ag3—S7	131.6(11)	S22—Ag23—S23	109.4(2)
O39—Ag3—S15	86.0(11)	O42—Ag23—S2 <sup>i</sup>	111.1(5)
O39—Ag3—O5	123.8(13)	O42—Ag23—S22	97.3(5)
C249—Ag3—S7	110.5(12)	O42—Ag23—S23	84.6(5)
C249—Ag3—S15	119.0(14)	O44—Ag24—O30	131.1(6)
S10—Ag4—S8	154.0(3)	O44 <sup>i</sup> —Ag24—O30	153.1(7)
S10—Ag4—O20	97.8(6)	O44 <sup>i</sup> —Ag24—O44	74.8(6)
O20—Ag4—S8	101.7(6)	S13 <sup>i</sup> —Ag25—S2	140.1(3)
O46—Ag4—S8	84.3(4)	O41—Ag25—S2	121.8(4)
O46—Ag4—S10	111.4(4)	O41—Ag25—S13 <sup>i</sup>	95.5(4)
O46—Ag4—O20	94.4(8)	S2—Ag26—S4	130.0(3)
S12—Ag5—S10	121.3(2)	S2—Ag26—O29	103.1(6)
S22 <sup>i</sup> —Ag5—S10	109.8(3)	S4—Ag26—O29	102.0(6)
S22 <sup>i</sup> —Ag5—S12	128.2(3)	O43 <sup>i</sup> —Ag26—S2	128.2(5)
O3—Ag5—S10	103.6(4)	O43 <sup>i</sup> —Ag26—S4	97.5(5)
O3—Ag5—S12	77.1(4)	O43 <sup>i</sup> —Ag26—O29	82.4(7)
O3—Ag5—S22 <sup>i</sup>	99.5(4)	S9—Ag27—S4	153.9(2)
O42 <sup>i</sup> —Ag6—S12	132.8(5)	O28—Ag27—S4	101.9(6)
O42 <sup>i</sup> —Ag6—S23 <sup>i</sup>	89.8(4)	O28—Ag27—S9	102.6(6)
O3—Ag7—O13	125.0(5)	S9—Ag28—S23	140.5(2)
O41 <sup>i</sup> —Ag7—O3	130.1(7)	S9—Ag28—O29	99.6(6)
O41 <sup>i</sup> —Ag7—O13	89.4(5)	S9—Ag28—O43 <sup>i</sup>	87.0(4)
S13—Ag8—S14	146.5(3)	S23—Ag28—O43 <sup>i</sup>	126.8(5)
S13—Ag8—O13	82.8(3)	O29—Ag28—S23	103.8(6)
S13—Ag8—O49	129.0(4)	O29—Ag28—O43 <sup>i</sup>	83.1(7)
S14—Ag8—O13	114.3(3)	S20—Ag29—S9	141.5(2)
O49—Ag8—S14	84.5(4)	O15—Ag29—S9	133.4(5)
O49—Ag8—O13	72.2(5)	O15—Ag29—S20	84.9(5)
S12—Ag9—S11	138.1(2)	S4—Ag30—S5	139.2(2)
O37—Ag9—S11	88.2(8)	O15—Ag30—S4	128.6(5)
O37—Ag9—S12	106.8(6)	O15—Ag30—S5	84.1(5)
O37—Ag9—O49	103.4(9)	O15—Ag30—O27	95.2(8)
O49—Ag9—S11	84.6(4)	O27—Ag30—S4	107.3(7)
O49—Ag9—S12	126.9(4)	O27—Ag30—S5	90.5(7)

S10—Ag10—S11	145.0(2)	S3—Ag31—S5	144.9(3)
S10—Ag10—O4	119.3(4)	S3—Ag31—O7	122.5(4)
S11—Ag10—O4	94.4(4)	S5—Ag31—O7	92.5(4)
S11—Ag11—S8	147.9(3)	S20—Ag32—S5	148.0(2)
O5—Ag11—S8	84.4(5)	S20—Ag32—O27	89.9(7)
O5—Ag11—S11	117.9(4)	O27—Ag32—S5	90.7(7)
O40—Ag11—S8	96.3(7)	O47—Ag32—S5	92.0(8)
O40—Ag11—S11	101.3(7)	O47—Ag32—S20	119.2(8)
O40—Ag11—O5	100.6(8)	O47—Ag32—O27	101.2(11)
O36—Ag12—O17	123.4(8)	S20—Ag33—S21	140.9(2)
O36—Ag12—O39	125.0(9)	O26—Ag33—S20	101.1(9)
O39—Ag12—O17	108.0(8)	O26—Ag33—S21	116.5(9)
S14—Ag13—S11	149.8(2)	S17—Ag34—S21	140.2(2)
S14—Ag13—O37	98.2(9)	O2—Ag34—S17	94.0(10)
O36—Ag13—S11	94.6(6)	O2—Ag34—S21	106.7(11)
O36—Ag13—S14	100.5(6)	O2—Ag34—O11	104.1(9)
O36—Ag13—O37	130.8(10)	O11—Ag34—S17	111.1(5)
O37—Ag13—S11	91.3(9)	O11—Ag34—S21	96.5(4)
S15—Ag14—S14	136.7(2)	S17—Ag35—S15	142.6(2)
O34—Ag14—S14	79.2(6)	S17—Ag35—O34	96.0(6)
O34—Ag14—S15	97.3(6)	O14—Ag35—S15	98.2(4)
O35—Ag14—S14	94.5(7)	O14—Ag35—S17	111.1(4)
O35—Ag14—S15	124.6(7)	O14—Ag35—O34	106.1(7)
O35—Ag14—O34	115.5(9)	O34—Ag35—S15	97.7(6)
S14—Ag15—O34	81.6(6)	S21—Ag36—S15	144.2(2)
S16—Ag15—S14	142.5(2)	O10—Ag36—S15	105.6(4)
S16—Ag15—O34	123.1(6)	O10—Ag36—S21	110.2(4)
S16—Ag16—S13	115.7(2)	S21—Ag37—S7	139.6(3)
S18—Ag16—S13	123.3(2)	O8—Ag37—S7	80.4(4)
S18—Ag16—S16	118.2(2)	O8—Ag37—S21	119.5(5)
O13—Ag16—S13	82.4(3)	O8—Ag37—O23	88.6(10)
O13—Ag16—S16	91.5(4)	O23—Ag37—S7	85.3(9)
O13—Ag16—S18	112.3(4)	O23—Ag37—S21	126.7(9)
S16—Ag17—S17	133.7(3)	O16—Ag38—O24	117.9(9)
O33—Ag17—S16	115.8(10)	O25—Ag38—O16	149.4(10)
O33—Ag17—S17	94.0(10)	O25—Ag38—O24	92.8(12)
S19—Ag18—S16	125.3(2)	S6—Ag39—S7	140.7(3)
O32—Ag18—S16	97.6(12)	O21—Ag39—S6	109.7(8)
O32—Ag18—S19	126.9(13)	O21—Ag39—S7	103.9(8)

S17—Ag19—S19	135.2(2)	O21—Ag39—O23	105.3(12)
O1—Ag19—S17	105.2(8)	O23—Ag39—S6	106.5(9)
O1—Ag19—O31	108.6(15)	O23—Ag39—S7	83.2(9)
O31—Ag19—S17	100.7(9)	S7—Ag40—S8	140.2(3)
O31—Ag19—S19	113.8(10)	S3—Ag42—S6	143.6(3)
S20—Ag20—S19	144.4(2)	O20—Ag42—S3	108.5(6)
O2—Ag20—S19	119.1(10)	O20—Ag42—S6	102.5(7)
O2—Ag20—S20	80.6(11)	O46—Ag42—S3	117.0(5)
S18—Ag21—S9	122.4(2)	O46—Ag42—S6	79.3(5)
S18—Ag21—S19	107.9(3)	O46—Ag42—O20	92.8(7)
S19—Ag21—S9	125.1(2)	S5—Ag43—S6	145.0(3)
O18—Ag21—S9	88.8(4)	O8—Ag43—S5	125.3(5)
O18—Ag21—S18	107.8(4)	O8—Ag43—S6	82.0(5)
O18—Ag21—S19	96.1(4)	O8—Ag43—O24	99.3(9)
S18—Ag22—S2 <sup>i</sup>	109.7(2)	O24—Ag43—S5	93.4(8)
S18—Ag22—S23	132.5(2)	O24—Ag43—S6	104.0(8)
S18—Ag22—O44 <sup>i</sup>	118.7(4)	S13—Ag44—S12	157.4(2)
S23—Ag22—S2 <sup>i</sup>	115.2(2)	O38—Ag44—S12	99.1(6)
O44 <sup>i</sup> —Ag22—S2 <sup>i</sup>	79.4(4)	O38—Ag44—S13	99.9(6)
O43 <sup>i</sup> —Ag45—O18	122.0(6)	O6—Ag45—O18	124.4(6)
O44 <sup>i</sup> —Ag22—S23	84.7(4)	O43 <sup>i</sup> —Ag45—O6	108.3(6)

Symmetry codes: (i)  $-x+2, -y, z$ ; (ii)  $-y+1, x-1, -z+1$ ; (iii)  $y+1, -x+1, -z+1$ .

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