Electronic Supplementary Information (ESI)

Small size yet big action: a simple sulfate anion templated a discrete 78-nuclearity silver sulfur nanocluster with a multishell structure

Li-Ping Cheng,[a,#] Zhi Wang,[b,#] Qiao-Yu Wu,[a] Hai-Feng Su,[d] Tao Peng,[a] Geng-Geng Luo,[a*] Yan-An Li,[c] Di Sun[b*] and Lan-Sun Zheng[d]

[a] *Key Laboratory of Environmental Friendly Function Materials, Ministry of Education, College of Materials Science and Engineering, Huaqiao University, Xiamen 361021, P.R. China; E-mail: ggluo@hqu.edu.cn.*

[b] *Key Lab of Colloid and Interface Chemistry, Ministry of Education, School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, P.R. China; E-mail: dsun@sdu.edu.cn*

[c] *College of Chemistry, Chemical Engineering and Materials Science, Shandong Normal University, Jinan 250014, P.R. China.*

[d] *State Key Laboratory for Physical Chemistry of Solid Surface and Department of Chemistry, Xiamen University, Xiamen 361005, P.R. China*

#These authors contributed equally to this work.

Materials and Instruments

All reagents employed were commercially available and used as received without further purification. Solvents were dried and distilled using common techniques unless otherwise mentioned. IR spectra were recorded on a Nicolet iS50 FT-IR spectrometer as KBr pellets in the frequency range of 4000-400 cm^{-1}. The elemental analyses (C and H contents) were determined on a Vario EL III analyzer. 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). The experimental powder X-ray diffraction (PXRD) data were collected on a Panalytical X-Pert Pro diffractometer with CuKα radiation equipped with an X'Celerator detector. Solid-state reflectance spectra were recorded on a Perkin Elmer Lambda 19 UV/Vis spectrometer at 298K. $BaSO_4$ was used as a 100% reflectance substance for the detected solid state reflectance spectra. 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.

X-ray Crystallography

Single crystal of **SD/Ag39** 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 173 K on a Bruker Apex II single crystal diffractometer, employing a Mo K_α radiation (λ = 0.71073 Å) and a CCD area detector. The raw frame data were processed using SAINT and SADABS to yield the reflection data file.[1] The structure was solved using the charge-flipping algorithm, as implemented in the program *SUPERFLIP*[2] and refined by full-matrix least-squares techniques against F_o^2 using the SHELXL program[3] through the OLEX2 interface.[4] Hydrogen atoms at carbon were placed in calculated positions and refined isotropically by using a riding model. 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[5] to ensure that no additional symmetry could be applied to the models. Pertinent crystallographic data collection and refinement parameters are collated in Table S2. Selected bond lengths and angles are collated in Table S3.

Fig. S1 The experimental and simulated powder X-ray diffraction patterns of **SD/Ag39.**

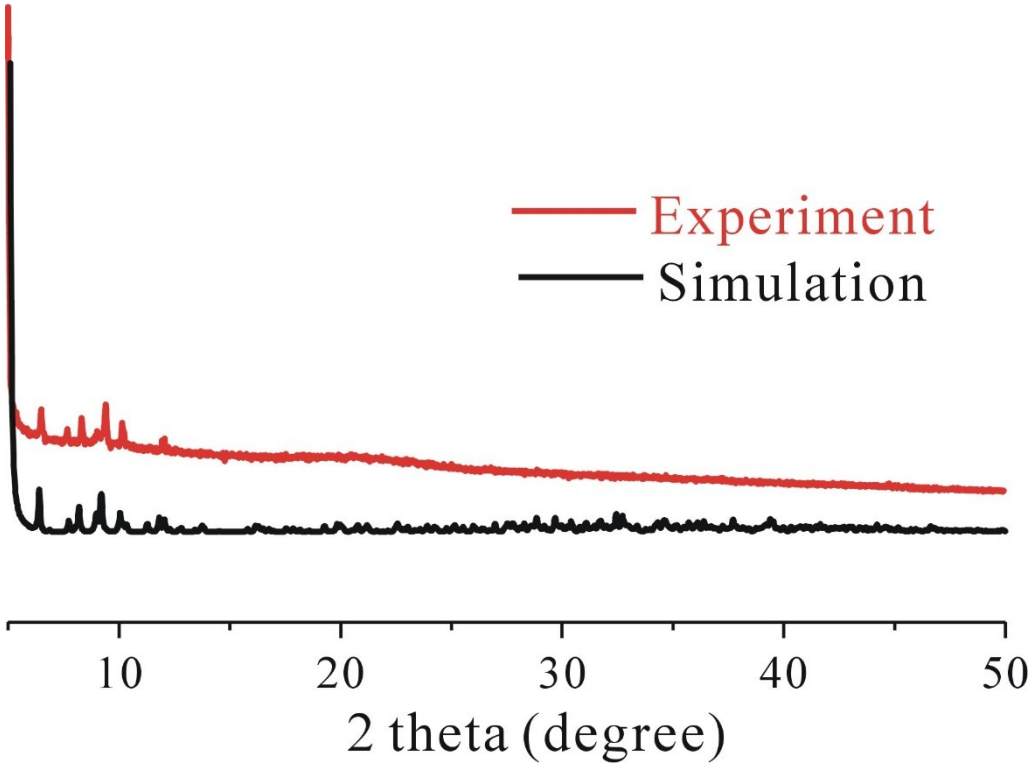


Fig. S2 The IR spectrum of **SD/Ag39**.

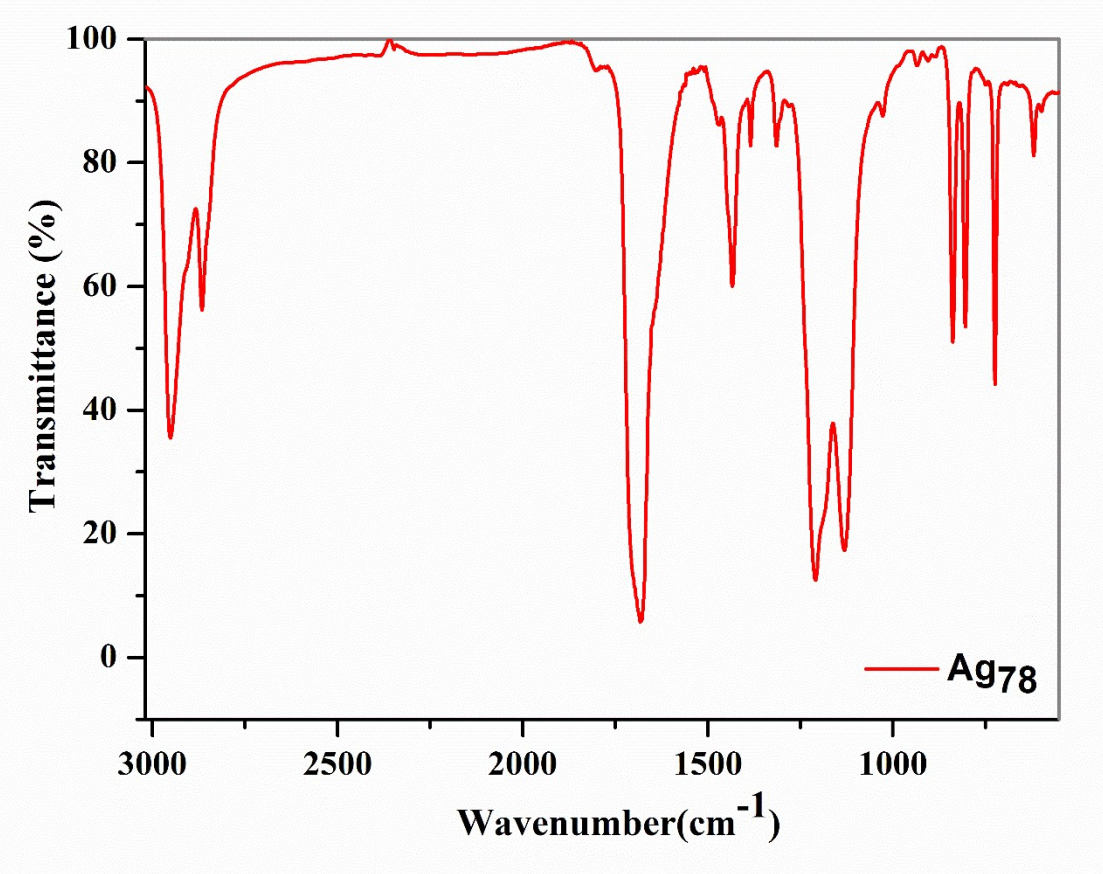
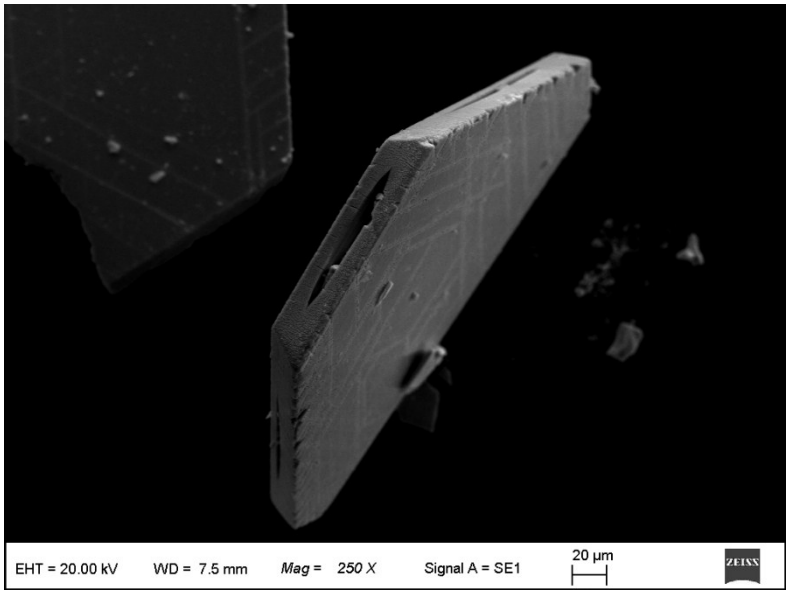


Fig. S3 (a) FESEM image of **SD/Ag39**; (b) FESEM/EDX spectrum of cluster **SD/Ag39** showing the expected elements.

(a)



(b)

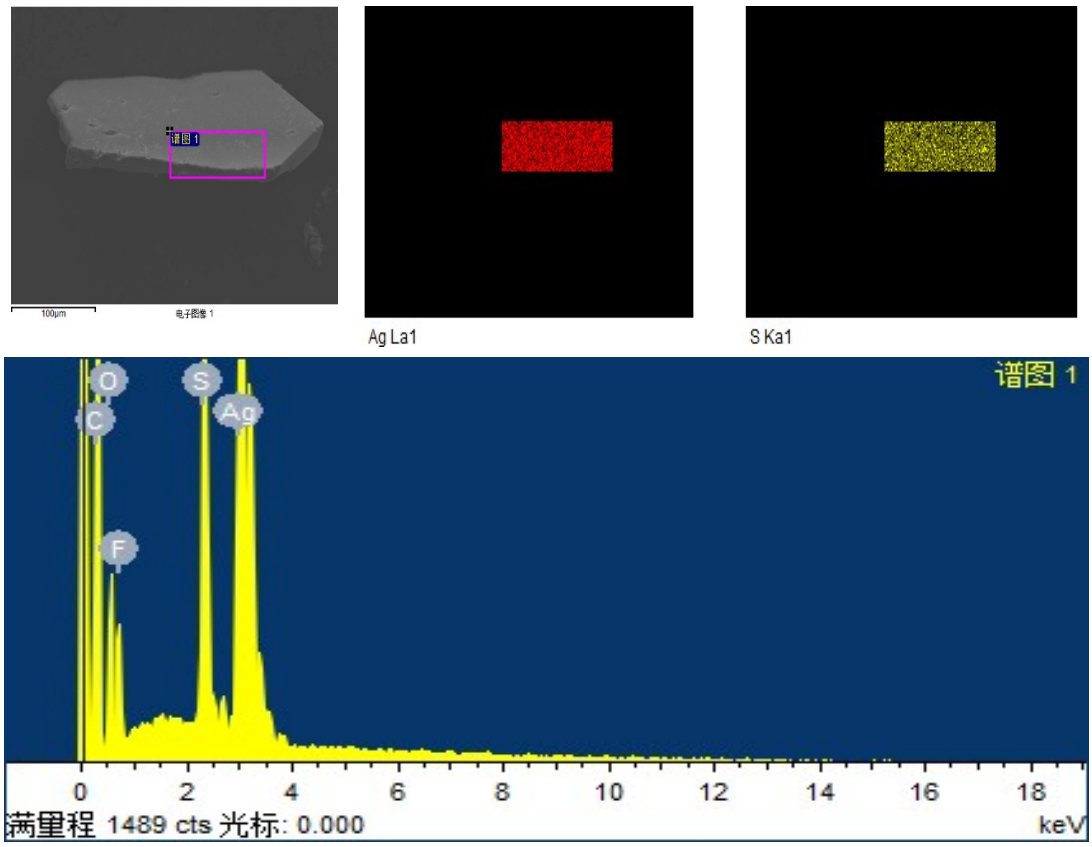


Fig. S4 The coordination modes of CpS^- and CF_3COO^- ligands in **SD/Ag39**.

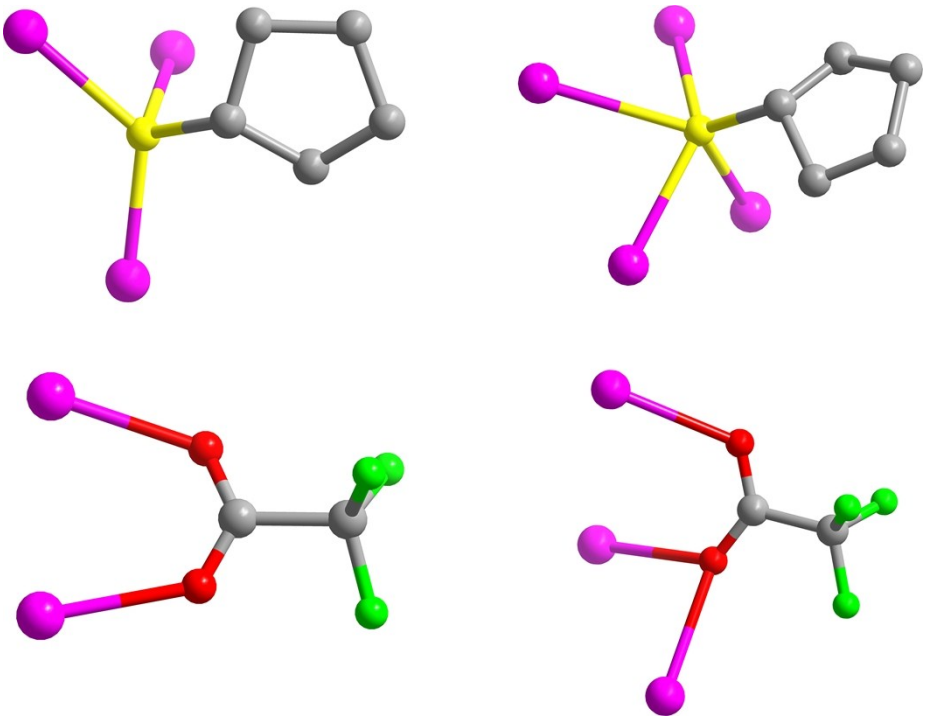


Fig. S5 Crystal packing of **SD/Ag39**.

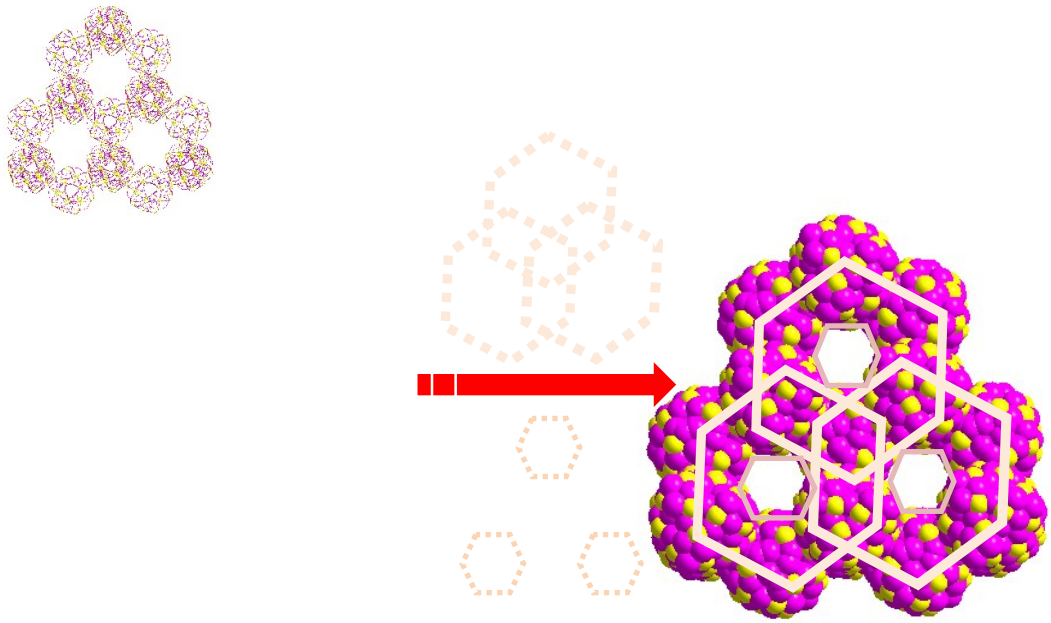
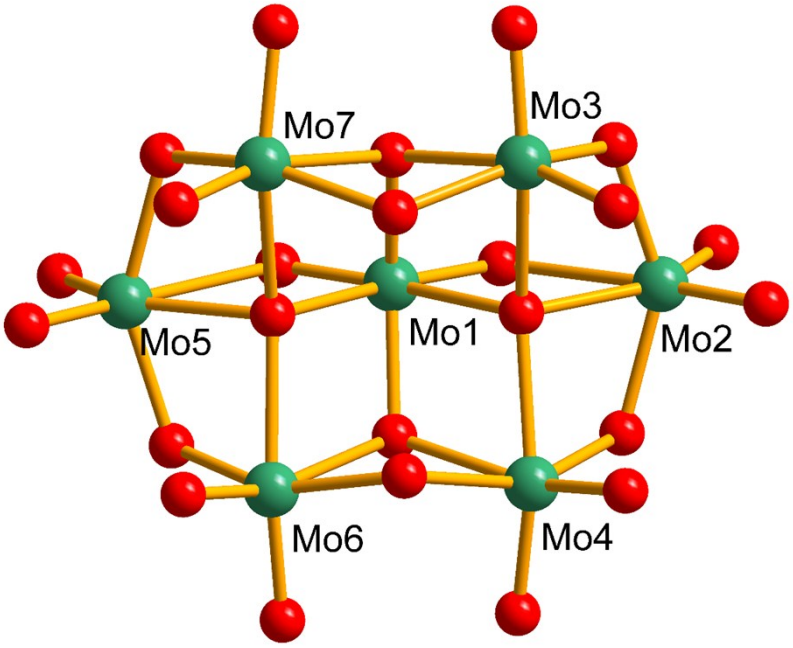


Fig. S6 BVS for seven Mo cations from $[Mo_7O_{24}]^{6-}$ anion.



Comments: Structurally, the $[Mo_7O_{24}]^{6-}$ ion is a regular Anderson-type polyoxometalate and contains a central $\{Mo_3O_8\}$ core built of three edge-shared MoO_6 octahedral units; two MoO_6 units from above and two from below share the equatorial oxygen atoms at the apices of the octahedra in the rectangle. Bond-valence sums for the seven Mo cations, calculated using parameters for the Mo-O bonds are in the range of 5.88-6.09 vu (valence units),[6] confirm that the +VI oxidation state of the Mo atoms is intact (Fig. S5, ESI†). This indicates that no redox reaction occurs under the reaction conditions. Bond valences (*S)* are calculated according to *eq 1* (*eq 1*: $S = \exp[(r_0 - r)/B]$), where $B = 0.37$ and $r_0 = 1.907$ for Mo^{6+}-O. The BVS for a given Mo ion is then the sum of bond valences for each bond made to that Mo ion.

$S_{Mo1} = 0.9965 + 0.4061 + 1.4826 + 1.0541 + 1.5097 + 0.4322 = 5.8812$

$S_{Mo2} = 0.9154 + 1.8123 + 1.6165 + 0.9415 + 0.2072 + 0.5948 = 6.0878$

$S_{Mo3} = 0.5033 + 1.6087 + 0.8508 + 1.7516 + 0.3691 + 0.9229 = 6.0063$

$S_{Mo4} = 1.6478 + 1.5615 + 0.9269 + 0.5358 + 0.3852 + 0.8776 = 5.9348$

$S_{Mo5} = 0.9807 + 0.5691 + 0.1918 + 0.9026 + 1.4846 + 1.7668 = 5.8956$

$S_{Mo6} = 1.6802 + 0.9474 + 0.3889 + 0.4805 + 0.8817 + 1.6135 = 5.9821$

$S_{Mo7} = 0.5428 + 0.8616 + 0.3683 + 1.6452 + 0.8554 + 1.7174 = 5.9906$

Fig. S7 Coordination mode of $[Mo_7O_{24}]^{6-}$anion found in **SD/Ag40**.

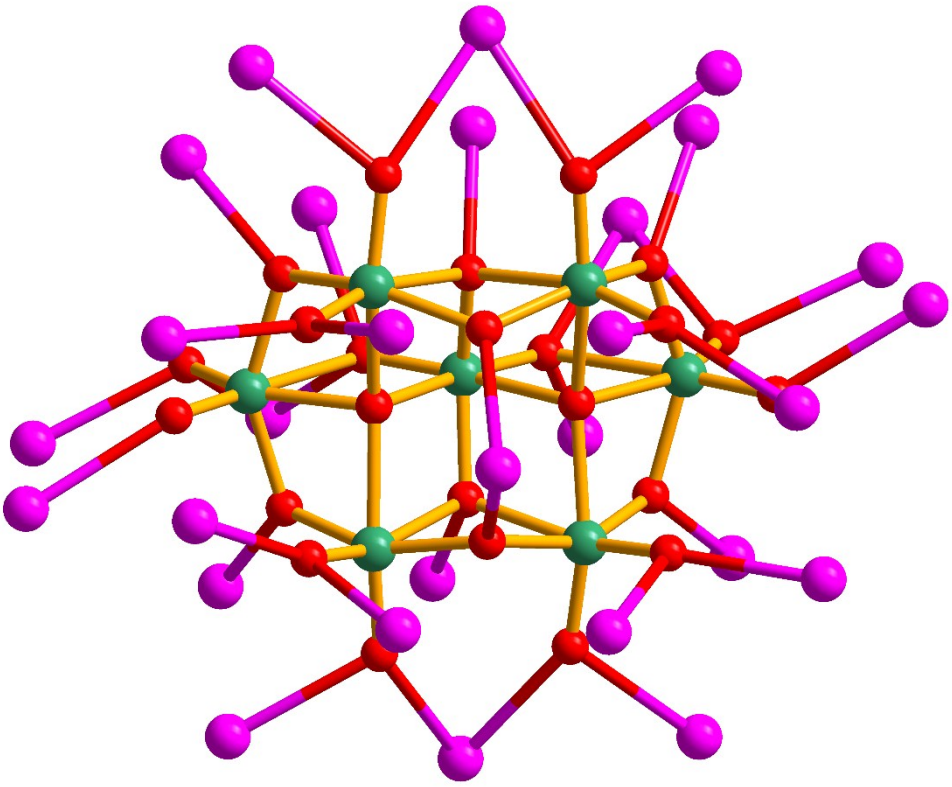


Fig. S8 Diffuse reflectance UV-Vis spectrum of the Kubelka-Munk function *vs* energy (eV) for **SD/Ag39** and $(CpSAg)_n$..

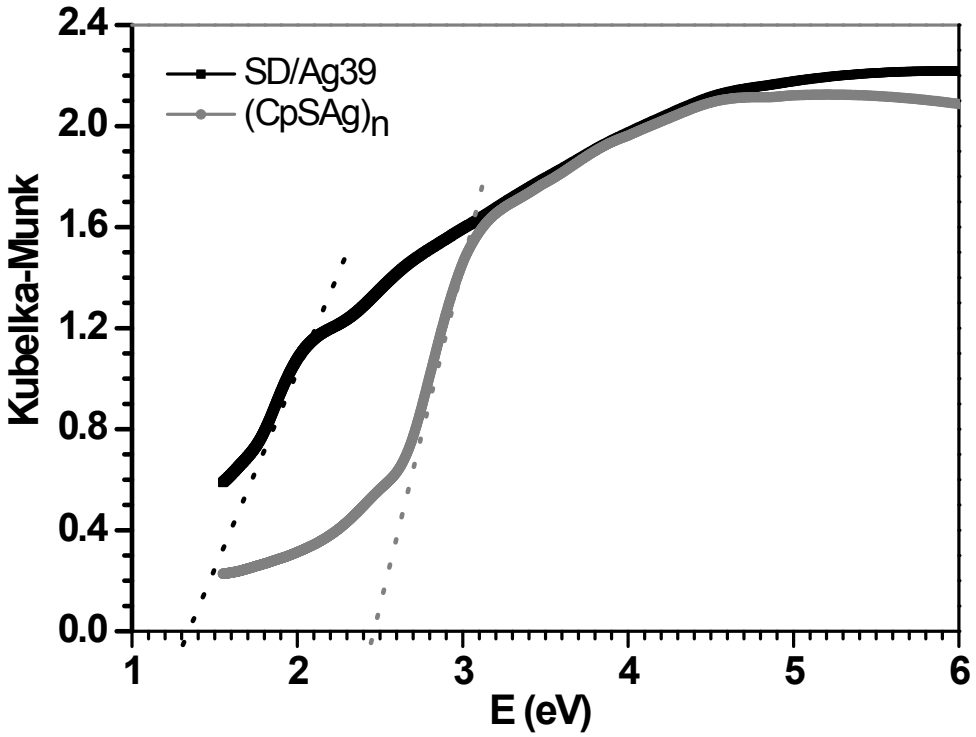


Table S1. The detailed formulae for ionic species **1a-1c**

Species	Assignment	Exp. *m/z*	Cal. *m/z*
1a	$[SO_4@Ag_{76}S_{15}(CpS)_{40}(CF_3COO)_6(H_2O)_8]^{2-}$	6822.03	6822.00
1b	$[SO_4@Ag_{77}S_{15}(CpS)_{20}(CF_3COO)_{26}(OH)]^{2-}$	6931.46	6931.34
1c	$[SO_4@Ag_{78}S_{15}(CpS)_{30}(CF_3CO_2)_{18}(H_2O)]^{2-}$	7039.75	7039.57

Table S2 Crystal data collection and structure refinement for **SD/Ag39.**

Empirical formula	$C_{156}H_{243}Ag_{78}F_{36}O_{25}S_{43}$
Formula weight	12909.57
Temperature/K	173(2)
Crystal system	trigonal
Space group	*P*-3
a/Å	22.8291(14)
b/Å	22.8291(14)
c/Å	38.552(3)
α/°	90.00
β/°	90.00
γ/°	120.00
Volume/Å^3	17400.2(19)
Z	2
ρ_{calc}g/cm^3	2.464
μ/mm^{-1}	4.581
F(000)	12033.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.72 to 50
Index ranges	$-25 \leq h \leq 25$, $-27 \leq k \leq 27$, $-20 \leq l \leq 45$
Reflections collected	52480
Independent reflections	20400 [R_{int} = 0.0384, R_{sigma} = 0.0535]
Data /parameters	20400/877
Goodness-of-fit on F^2	1.532
Final R indexes [I>=2σ (I)]	R_1 = 0.1191, wR_2 = 0.3606
Final R indexes [all data]	R_1 = 0.1659, wR_2 = 0.4106

Table S3 Selected bond lengths (Å) and angles (º) for **SD/Ag39.**

Ag1—Ag1^{i}	3.19 (2)	Ag12—S11^{ii}	2.591 (5)
Ag1—Ag3	1.890 (18)	Ag13—Ag17	2.986 (2)
Ag1—Ag4^{i}	3.107 (18)	Ag13—O1^{ii}	2.57 (2)
Ag1—Ag7	2.935 (11)	Ag13—S9	2.556 (5)
Ag1—S12^{i}	2.558 (13)	Ag13—S11^{ii}	2.573 (5)
Ag2—Ag6^{i}	3.050 (13)	Ag13—S12	2.757 (5)
Ag2—S13^{i}	2.177 (14)	Ag14—Ag15	3.183 (2)
Ag2—S15	2.493 (13)	Ag14—Ag16	3.118 (2)
Ag3—Ag4^{i}	1.413 (16)	Ag14—Ag21	3.079 (3)
Ag3—O11	2.22 (3)	Ag14—S4	2.418 (6)
Ag3—S12^{i}	2.620 (15)	Ag14—S10	2.424 (6)
Ag3—S15^{i}	2.417 (16)	Ag15—Ag16	3.184 (2)
Ag4—Ag6	3.276 (10)	Ag15—Ag17	3.087 (2)
Ag4—Ag7	3.345 (9)	Ag15—Ag21	3.364 (3)
Ag4—S12	2.695 (11)	Ag15—Ag23	3.264 (2)
Ag4—S14	2.719 (11)	Ag15—S3	2.733 (5)
Ag4—S15	2.428 (11)	Ag15—S7	2.547 (5)
Ag5—Ag8	3.022 (2)	Ag15—S9	2.534 (5)
Ag5—Ag9	3.167 (2)	Ag16—Ag21	3.294 (3)
Ag5—Ag10	3.099 (3)	Ag16—S6	2.620 (6)
Ag5—O9	2.36 (3)	Ag16—S7	2.586 (5)
Ag5—S10	2.542 (6)	Ag16—S10	2.468 (6)
Ag5—S11	2.548 (5)	Ag17—Ag18	3.151 (2)
Ag6—Ag10	3.298 (4)	Ag17—Ag19	3.341 (2)
Ag6—Ag11	3.065 (4)	Ag17—Ag20	3.193 (3)
Ag6—S12	2.856 (6)	Ag17—Ag23^{ii}	3.132 (2)
Ag6—S13	2.371 (10)	Ag17—S3	2.835 (5)
Ag6—S14	2.411 (11)	Ag17—S7^{ii}	2.534 (5)
Ag7—Ag7^{ii}	2.953 (3)	Ag17—S9	2.530 (4)
Ag7—Ag9	3.034 (2)	Ag18—Ag19	3.169 (3)
Ag7—Ag13^{i}	3.035 (2)	Ag18—Ag20	3.173 (3)
Ag7—S12^{i}	2.465 (5)	Ag18—S4	2.427 (6)
Ag7—S12	2.460 (5)	Ag18—S5	2.427 (6)
Ag8—Ag9	3.019 (2)	Ag19—Ag20	3.262 (3)
Ag8—Ag12^{i}	2.941 (2)	Ag19—S2	2.612 (8)
Ag8—Ag13^{i}	3.005 (2)	Ag19—S5	2.487 (6)
Ag8—Ag15	2.891 (2)	Ag19—S7^{ii}	2.594 (5)
Ag8—Ag16	3.142 (2)	Ag20—Ag26	2.984 (3)
Ag8—Ag17^{i}	2.895 (2)	Ag20—S2	2.381 (6)
Ag8—Ag19^{i}	3.273 (3)	Ag20—S3	2.443 (5)

Ag8—S7	2.435 (5)	Ag20—S4	2.858 (6)
Ag8—S11	2.436 (6)	Ag21—Ag24	2.865 (3)
Ag9—Ag10	3.088 (2)	Ag21—O5	2.55 (2)
Ag9—Ag13	3.166 (2)	Ag21—S3	2.591 (5)
Ag9—Ag15	2.984 (2)	Ag21—S4	2.596 (6)
Ag9—O1	2.55 (2)	Ag21—S6	2.543 (6)
Ag9—S9	2.568 (5)	Ag22—Ag24	3.009 (3)
Ag9—S11	2.580 (5)	Ag22—Ag26^{i}	3.120 (3)
Ag9—S12	2.762 (6)	Ag22—S2^{i}	2.494 (7)
Ag10—Ag11	3.264 (3)	Ag22—S6	2.499 (7)
Ag10—Ag14	3.032 (3)	Ag23—Ag17^{i}	3.132 (2)
Ag10—O7	2.359 (19)	Ag23—Ag23^{ii}	2.965 (3)
Ag10—S9	2.681 (5)	Ag23—Ag25	3.179 (2)
Ag10—S10	2.799 (6)	Ag23—S3	2.504 (5)
Ag10—S14	2.459 (8)	Ag23—S7	2.765 (5)
Ag11—Ag12	3.077 (3)	Ag24—Ag25^{ii}	3.122 (3)
Ag11—Ag13	3.048 (2)	Ag24—Ag26^{i}	2.936 (3)
Ag11—Ag18	3.068 (3)	Ag24—S1	2.428 (5)
Ag11—O6	2.33 (2)	Ag24—S6	2.423 (6)
Ag11—S5	2.772 (6)	Ag25—O4^{i}	2.48 (2)
Ag11—S9	2.715 (5)	Ag25—S1	2.633 (6)
Ag11—S13	2.516 (8)	Ag25—S3^{i}	2.545 (5)
Ag12—Ag13	3.275 (2)	Ag26—S1^{ii}	2.543 (6)
Ag12—S5	2.532 (6)	Ag26—S2	2.519 (7)
S13^{i}—Ag2—S15	156.0 (7)	S9—Ag13—S12	99.56 (15)
O11—Ag3—S12^{i}	119.2 (10)	S11^{ii}—Ag13—S12	104.01 (17)
O11—Ag3—S15^{i}	105.0 (10)	S4—Ag14—S10	167.0 (2)
S15^{i}—Ag3—S12^{i}	126.5 (6)	S7—Ag15—S3	92.30 (16)
S12—Ag4—S14	88.2 (3)	S9—Ag15—S3	102.55 (15)
S15—Ag4—S12	122.8 (4)	S9—Ag15—S7	163.88 (16)
S15—Ag4—S14	132.9 (6)	S7—Ag16—S6	88.73 (17)
O9—Ag5—S10	98.6 (8)	S10—Ag16—S6	135.26 (19)
O9—Ag5—S11	127.4 (8)	S10—Ag16—S7	127.81 (18)
S10—Ag5—S11	133.59 (18)	S7^{ii}—Ag17—S3	96.49 (16)
S13—Ag6—S12	99.3 (2)	S9—Ag17—S3	99.90 (15)
S13—Ag6—S14	160.5 (3)	S9—Ag17—S7^{ii}	160.94 (16)
S14—Ag6—S12	90.9 (2)	S5—Ag18—S4	165.7 (2)
S12—Ag7—S12^{i}	164.28 (19)	S5—Ag19—S2	129.1 (2)
S7—Ag8—S11	167.81 (16)	S5—Ag19—S7^{ii}	121.26 (18)
O1—Ag9—S9	100.3 (5)	S7^{ii}—Ag19—S2	94.96 (18)
O1—Ag9—S11	87.7 (5)	S2—Ag20—S3	155.5 (2)
O1—Ag9—S12	97.9 (6)	S2—Ag20—S4	117.3 (2)
S9—Ag9—S11	154.15 (16)	S3—Ag20—S4	86.71 (16)

S9—Ag9—S12	99.14 (16)	O5—Ag21—S3	107.5 (5)
S11—Ag9—S12	104.07 (17)	O5—Ag21—S4	95.3 (7)
O7—Ag10—S9	105.6 (6)	S3—Ag21—S4	89.49 (17)
O7—Ag10—S10	90.6 (6)	S6—Ag21—O5	88.1 (5)
O7—Ag10—S14	117.0 (7)	S6—Ag21—S3	131.36 (19)
S9—Ag10—S10	98.56 (15)	S6—Ag21—S4	135.74 (19)
S14—Ag10—S9	123.5 (2)	S2^{i}—Ag22—S6	126.9 (2)
S14—Ag10—S10	115.5 (3)	S3^{i}—Ag23—S3	167.25 (15)
O6—Ag11—S5	92.0 (7)	S3—Ag23—S7	92.48 (15)
O6—Ag11—S9	107.9 (8)	S3^{i}—Ag23—S7	99.20 (16)
O6—Ag11—S13	114.4 (9)	S6—Ag24—S1	167.3 (2)
S9—Ag11—S5	97.33 (15)	O4^{i}—Ag25—S1^{i}	112.0 (5)
S13—Ag11—S5	109.8 (3)	O4^{i}—Ag25—S1	83.3 (5)
S13—Ag11—S9	127.9 (2)	O4^{i}—Ag25—S3^{i}	97.9 (6)
S5—Ag12—S11^{ii}	132.83 (18)	S1^{i}—Ag25—S1	113.4 (2)
O1^{ii}—Ag13—S11^{ii}	87.5 (5)	S1^{i}—Ag25—S3^{i}	122.67 (18)
O1^{ii}—Ag13—S12	98.2 (6)	S3^{i}—Ag25—S1	117.95 (17)
S9—Ag13—O1^{ii}	101.0 (5)	S2—Ag26—S1^{ii}	137.4 (2)
S9—Ag13—S11^{ii}	153.53 (17)		
Symmetry codes: (i) −*y*+1, *x*−*y*, *z*; (ii) −*x*+*y*+1, −*x*+1, *z*.			

Table S4 The sorted Ag-Ag bond lengths (Å) in **SD/Ag39.**

Ag-Ag bond length (Å) in the inner shell (Ag_{18})			
Ag7—Ag7^{i}	2.953 (3)	Ag9—Ag15	2.984 (2)
Ag7—Ag9	3.034 (2)	Ag15—Ag17	3.087 (2)
Ag7—Ag13^{i}	3.035 (2)	Ag15—Ag23	3.264 (2)
Ag13—Ag17	2.986 (2)	Ag17—Ag23^{ii}	3.132 (2)
Ag9—Ag13	3.166 (2)	Ag23—Ag23^{i}	2.965 (3)
Ag-Ag bond length (Å) in the outer shell (Ag_{60})			
Ag1—Ag1^{i}	3.19 (2)	Ag8—Ag12^{i}	2.941 (2)
Ag1—Ag3	1.890 (18)	Ag8—Ag16	3.142 (2)
Ag1—Ag4^{i}	3.107 (18)	Ag8—Ag19^{i}	3.273 (3)
Ag2—Ag6^{i}	3.050 (13)	Ag10—Ag11	3.264 (3)
Ag3—Ag4^{i}	1.413 (16)	Ag10—Ag14	3.032 (3)
Ag4—Ag6	3.276 (10)	Ag11—Ag12	3.077 (3)
Ag5—Ag8	3.022 (2)	Ag11—Ag18	3.068 (3)
Ag5—Ag10	3.099 (3)	Ag14—Ag16	3.118 (2)
Ag6—Ag10	3.298 (4)	Ag14—Ag21	3.079 (3)
Ag6—Ag11	3.065 (4)	Ag18—Ag20	3.173 (3)
Ag16—Ag21	3.294 (3)	Ag19—Ag20	3.262 (3)
Ag18—Ag19	3.169 (3)	Ag20—Ag26	2.984 (3)
Ag24—Ag25^{ii}	3.122 (3)	Ag21—Ag24	2.865 (3)
Ag24—Ag26^{i}	2.936 (3)	Ag22—Ag24	3.009 (3)
Ag20—Ag21	3.437(3)	Ag22—Ag26^{i}	3.120 (3)
Ag-Ag bond lengths (Å) between the two shells			
Ag1—Ag7	2.935 (11)	Ag17—Ag18	3.151 (2)
Ag3—Ag7^{i}	2.957 (14)	Ag17—Ag19	3.341 (2)
Ag4—Ag7	3.345 (9)	Ag17—Ag20	3.193 (3)
Ag11—Ag13	3.048 (2)	Ag8—Ag17^{i}	2.895 (2)
Ag12—Ag13	3.275 (2)	Ag23—Ag25^{ii}	3.114 (2)
Ag8—Ag13^{i}	3.005 (2)	Ag23—Ag25	3.179 (2)
Ag5—Ag9	3.167 (2)	Ag15—Ag16	3.184 (2)
Ag8—Ag9	3.019 (2)	Ag15—Ag21	3.364 (3)
Ag9—Ag10	3.088 (2)	Ag8—Ag15	2.891 (2)
Ag14—Ag15	3.183 (2)		
Symmetry codes: (i) $-y+1, x-y, z$; (ii) $-x+y+1, -x+1, z$.			

References

(1) *APEX3*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA, 2015.

(2) L. Palatinus, G. Chapuis, G. *J. Appl. Crystallogr.* 2007, **40**, 786.

(3) G. M. Sheldrick, *Acta. Crystallogr. Sect. C* 2015, **71**, 3.

(4) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* 2009, **42**, 339.

(5) A. L. Spek, *Acta. Crystallogr. Sect. D*. 2009, **65**, 148.

(6) W. T. Liu, H. H. Thorp, *Inorg. Chem*., 1993, **32**, 4102.