Supporting Information

Self-assembly of an unprecedented polyoxomolybdate anion $[Mo_{20}O_{66}]^{12-}$ in a giant peanut-like 62-core silver-thiolate nanocluster

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Synthetic procedures

Materials: AgS'Bu was prepared by reacting equivalent amounts of AgNO₃ and HS'Bu in the presence of Et_3N .¹ ('Bu₄N)₂[Mo₆O₁₉]² was synthesized with the literature methods. Other reagents and solvents for synthesis were obtained from commercial sources and used without further purification.

Synthesis of $[Ag_{62}(S^{t}Bu)_{40}(Mo_{20}O_{66})(Mo_{6}O_{19})_{3}(CH_{3}CN)_{2}] \cdot (CF_{3}SO_{3})_{4}$ (1)

AgS'Bu (0.0197 g, 0.1 mmol) was dissolved in methanol and acetonitrile (1:1, 4 mL) under stirring. CF₃SO₃Ag (0.0256 g, 0.10 mmol), ('Bu₄N)₂[Mo₆O₁₉] (0.008 g, 0.006 mmol) and CF₃SO₃H (6 μ L) were in turn added to the above solution. The yellow solution was stirred at room temperature for 30 min and then filtered. The filtrate was evaporated slowly in air at room temperature. The resultant yellow solution was allowed to stand in the dark at room temperature for two weeks to give yellow crystals of **1.** The crystals formed were filtered off, washed with diethyl ether and dried at room temperature. Yield: *ca*. 30%. Elemental analysis (%) calcd for C₁₆₈H₃₆₆Ag₆₂F₁₂Mo₃₈N₂O₁₃₅S₄₄: C, 12.18; H, 2.21; N, 0.17; S, 8.51. Found: C, 12.23; H, 2.25; N, 0.18; S, 8.53.

Crystallographic studies

Single-crystal X-ray diffraction data for **1** was collected on OXFORD Diffraction Gemini Single Crystal diffractometer with Mo K α radiation (λ =0.71073 Å) using the ω scan mode at 110K. Empirical absorption corrections were applied to the intensities using the SADABS program.³ The structure was solved using the program *SHELXS-97* ⁴ and refined with the program *SHELXL-97*.⁵ A highly disordered uncoordinated triflate anion and additional solvents could not be located in the difference map. As the structure model contained significant voids and the diffuse residual electron density could not be modeled adequately, the SQUEEZE procedure of PLATON was used.⁶ All nonhydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms of the organic ligands were included in the structure factor calculation at idealized positions using a riding model and refined isotropically.

Some Ag atoms within the cluster were refined with partial occupancies. Large ghost peaks were found from some Ag atoms and these were refined as partial occupancy atoms. In **1**, two silver atoms Ag18 and Ag20 are disordered over three and two closely separated positions in the ratio of 0.55:0.36:0.09 and 0.822:0.178, respectively. The single crystal X-ray diffraction and the selected bond lengths for **1** are gathered in Table S1 and S2, respectively. CCDC-1025476 (**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 for **1**.

Table S1. Crystal data and structure refinement for 1.						
Temperature	110 K					
Formula	$C_{166}H_{366}Ag_{62}F_6Mo_{38}N_2O_{129}S_{42}{}^a$					
Formula weight	16248.68					
Crystal system	Triclinic					
Space Group	P – 1					
Ζ	1					
a (Å)	18.4308(7)					
<i>b</i> (Å)	19.5522(7)					
<i>c</i> (Å)	35.0688(13)					
α (°)	93.065(3)					
$\beta(^{\circ})$	95.734(3)					
$\gamma(^{\circ})$	112.904(4)					
$V(Å^3)$	11523.9(7)					
$D_{ m calcd} ({ m g \ cm^{-3}})$	2.341					
θ range (°)	2.80 to 25.00					
F(000)	7644					
$\mu ({\rm mm^{-1}})$	3.802					
Refln. collected	79169					
Independent reflections	39450					
Completeness	97.2 %					
Refinement Method	Full-matrix least-squares on F ²					
R(int)	0.0814					
GOF	1.055					
${}^{b}R_{I}[I > 2\sigma(I)], wR_{2}$	0.0904, 0.2003					
R_1 [all data], wR_2	0.1517, 0.2325					

^{*a*}The program SQUEEZE was used to model the electron density in the pores from the disordered hydronium ion and crystalline water molecules.

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Ag(3)-Ag(7)	3.199(2)	Ag(9)–S(1)	2.394(9)
Ag(4)-Ag(6)	3.257(3)	Ag(10)-S(16)	2.37(6)
Ag(8)–Ag(12)	3.159(2)	Ag(10)-S(9)	2.389(6)
Ag(9) - Ag(11)	3.177(3)	Ag(11)-S(9)	2.418(6)
Ag(13)-Ag(14)	3.324(2)	Ag(11)-S(10)	2.444(6)
Ag(15)-Ag(25)	3.297(2)	Ag(12)–S(8)	2.387(6)
Ag(16)-Ag(24)	3.181(3)	Ag(12)–S(10)	2.392(5)
Ag(17)–Ag(19)	3.003(2)	Ag(13)–S(4)	2.391(6)
Ag(18)–Ag(26)	2.855(4)	Ag(13)–S(6)	2.447(5)
Ag(19)–Ag(26)	3.232(2)	Ag(14)–S(7)	2.362(7)
Ag(4)–O(23)	2.659(10)	Ag(14)–S(6)	2.38(6)
Ag(5)–O(60)	2.752(15)	Ag(15)–S(6)	2.381(6)
Ag(6)–O(22)	2.51(13)	Ag(15)–S(11)	2.379(6)
Ag(10)–O(21)	2.628(12)	Ag(16)–S(7)	2.398(7)
Ag(11)–O(4)	2.721(5)	Ag(16)–S(14)	2.374(6)
Ag(12)–O(4)	2.614(14)	Ag(17)–S(8)	2.43(5)
Ag(13)–O(7)	2.595(12)	Ag(17)–S(13)	2.46 (5)
Ag(17)–O(6)	2.481(12)	Ag(18)–S(13)	2.662(6)
Ag(18)–O(34)	2.612(12)	Ag(18)–S(11)	2.653(7)
Ag(19)–O(2)	2.673(2)	Ag(19)–S(15)	2.408(6)
Ag(20)–O(20)	2.525(13)	Ag(19)–S(13)	2.433(5)
Ag(23)–O(5)	2.658(10)	Ag(20)–S(14)	2.365(5)
Ag(23)–O(33)	2.606(13)	Ag(20)–S(16)	2.379(6)
Ag(24)–O(24)	2.595(13)	Ag(21)–S(18)	2.355(6)
Ag(25)-O(10)	2.586(13)	Ag(21)–S(16)	2.36(5)
Ag(26)–O(11)	2.375(12)	Ag(22)–S(18)	2.389(5)
Ag(27)–O(24)	2.725(12)	Ag(22)–S(17)	2.415(5)
Ag(27)–O(28)	2.498(12)	Ag(23)–S(17)	2.404(5)
Ag(28)–O(25)	2.676(10)	Ag(23)–S(15)	2.465(5)
Ag(29)–O(31)	2.743(5)	Ag(24)-S(14)	2.409(5)
Ag(1)-S(1)	2.516(10)	Ag(24)–S(12)	2.426(5)
Ag(1)-S(2)	2.422(9)	Ag(25)–S(11)	2.429(5)
Ag(2)-S(1)	2.329(9)	Ag(25)–S(12)	2.427(5)
Ag(2)–S(5)	2.362(9)	Ag(26)–S(13)	2.546(5)
Ag(3)–S(2)	2.395(7)	Ag(26)–S(11)	2.646(6)
Ag(3)–S(3)	2.384(7)	Ag(27)-S(20)	2.408(5)
Ag(4) - S(4)	2.381(6)	Ag(27)–S(12)	2.404(5)
Ag(4)–S(5)	2.398(8)	Ag(28)–S(19)	2.429(4)
Ag(5)–S(3)	2.496(7)	Ag(28)–S(18)	2.433(5)
Ag(5)-S(4)	2.489(6)	Ag(29)-S(20)	2.392(5)
Ag(6)–S(5)	2.347(8)	Ag(29)-S(19)	2.408(5)

 ${}^{b}R_{1} = \Sigma ||F_{o}| - |F_{c}|| \Sigma ||F_{o}|, wR_{2} = [\Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}] \Sigma w(F_{o}^{2})^{2}]^{1/2}$ **Table S2**. Selected bond lengths (Å) for compound **1**.

Ag(6)–S(7) 2	.42 (8)	Ag(30)–S(20)	2.366(5)
Ag(7)–S(8) 2	.394(6)	Ag(30)–S(17)#1	2.378(5)
Ag(7)–S(3) 2	.397(7)	Ag(31)–S(15)#1	2.391(5)
Ag(8)–S(10) 2	.338(6)	Ag(31)–S(19)	2.394(5)
Ag(8)–S(2) 2	.362(7)	S(15)-Ag(31)#1	2.391(5)
Ag(9)–S(9) 2	.386(7)	S(17)-Ag(30)#1	2.378(5)

Symmetry codes: #1 -x+1,-y+1,-z+2.

Fig. S1. The structure of $[Mo_{20}O_{66}]^{12+}$ anions. Color code: blue or orange, Mo; pink or gray, O.

Fig. S2. Stick and polyhedra combined view of compound 1. Hydrogen atoms, CH_3CN and dissociative $CF_3SO_3^-$ are omitted for clarity.

$[Mo_6O_{19}]^{2-}$								
Atom	No	Charge / e	Atom	No	Charge / e	Atom	No	Charge / e
Мо	1	1.173	0	10	-0.499	0	19	-0.833
Мо	2	1.174	0	11	-0.500	0	20	-0.371
Мо	3	1.175	0	12	-0.499	0	21	-0.372
Мо	4	1.176	0	13	-0.500	0	22	-0.371
Мо	5	1.179	0	14	-0.500	0	23	-0.373
Мо	6	1.173	0	15	-0.502	0	24	-0.373
0	7	-0.499	0	16	-0.500	0	25	-0.372
0	8	-0.499	0	17	-0.499			
0	9	-0.497	0	18	-0.501			

Fig. S3. Theoretical calculation model of $[Mo_6O_{19}]^{2-}$.

Table S3. The theoretical calculation charge density of $[Mo_6O_{19}]^{2-}$.

Fig. S4. Theoretical calculation model of $[Mo_{20}O_{66}]^{12-}$.

M0 ₂₀ O ₆₆ ¹²⁻								
Atom	No	Charge / e	Atom	No	Charge / e	Atom	No	Charge / e
0	1	-0.489	0	30	-0.616	0	59	-0.438
0	2	-0.460	Мо	31	1.169	0	60	-0.448
0	3	-0.481	0	32	-0.448	0	61	-0.521
0	4	-0.533	0	33	-0.605	Мо	62	1.170
0	5	-0.470	Мо	34	1.163	Мо	63	1.159
0	6	-0.486	0	35	-0.445	Мо	64	1.112
0	7	-0.406	0	36	-0.604	Мо	65	1.081
0	8	-0.441	0	37	-0.431	0	66	-0.409
0	9	-0.523	Мо	38	1.161	0	67	-0.441
Мо	10	1.020	0	39	-0.476	0	68	-0.672
0	11	-0.485	0	40	-0.562	0	69	-0.573
0	12	-0.582	0	41	-0.588	0	70	-0.636
0	13	-0.586	Мо	42	1.142	0	71	-0.470
0	14	-0.581	0	43	-0.467	0	72	-0.556
0	15	-0.558	0	44	-0.430	0	73	-0.731
0	16	-0.731	0	45	-0.586	0	74	-0.587
Мо	17	1.043	Мо	46	1.141	0	75	-0.538
0	18	-0.518	Мо	47	1.163	0	76	-0.482
0	19	-0.520	Мо	48	1.160	0	77	-0.520
Мо	20	1.129	0	49	-0.562	Мо	78	1.128
Мо	21	1.113	0	50	-0.475	Мо	79	1.128
0	22	-0.436	0	51	-0.603	Мо	80	0.911
0	23	-0.672	0	52	-0.468	0	81	-0.470
0	24	-0.637	0	53	-0.603	0	82	-0.580
Мо	25	1.099	0	54	-0.617	0	83	-0.461
0	26	-0.572	0	55	-0.485	0	84	-0.488
0	27	-0.470	0	56	-0.444	0	85	-0.572
Мо	28	1.159	0	57	-0.522	0	86	-0.482
0	29	-0.487	0	58	-0.488			

Table S4. The theoretical calculation charge density of $[Mo_{20}O_{66}]^{12-}$.

Physical Measurements

FT-IR spectra were recorded from KBr pellets in the range from 4000 to 400 cm⁻¹ on a Bruker VECTOR 22 spectrometer. Elemental analyses for C, H, N and S were performed on a Perkin-Elmer 240 elemental analyzer. Transmission electron microscopy (TEM) measurements were performed on JEM-2100 microscope. In the preparation of sample 1 for TEM observation, the crystals were first dispersed in acetone using an ultrasonic bath and then dropped onto cupper grid, which was dried in air at room temperature and kept in vacuum for 20 min before TEM observation. The software NANO MEASURER 1.2 applied to calculate the particle size of nanoclusters. Powder X-ray diffraction (PXRD) data for 1 was collected on a Rigaku D/Max-2500PC diffractometer with Cu-K α radiation ($\lambda = 1.5418$ Å) over the 2 θ range of $3-50^{\circ}$ at room temperature. The light stability of 1 was confirmed by PXRD after simulated sunlight irradiation from a 300 W xenon lamp at room temperature. The XPS spectra were recorded on a Kratos Axis Ultra DLD with an Al Ka X-ray source. The single crystals were put under UHV to reach the 10^{-9} torr range. The nonmonochromatized Al Ka source was used at 15 kV and 10 mA. All binding energies were referenced to the neutral C 1s peak at 284.6 eV to compensate for the surface charging effect. Full spectrum and high resolution narrow-scan spectra were recorded with the electron pass energy of 160eV and 40 eV, respectively. In order to investigate the stoichiometry of states for Ag, Mo, S and O atoms, the software XPSPEAK 4.1 was applied to fit the data. Nonlinear least squares curve fitting was performed using a Gaussian/Lorentzian peak shape after background removal. UVvis diffuse reflectance spectra were recorded on an Agilent Cary5000 UV-VIS-NIR Spectrophotometer with BaSO₄ as the reference. UV-visible absorption spectra were recorded on a TU-1900 double-beam UV-vis spectrophotometer.

Fig. S5. FT-IR spectra of 1 (black) and $({}^{t}Bu_{4}N)_{2}(Mo_{6}O_{19})$ (red).



Fig. S6. X-ray powder diffraction patterns of 1.

Fig. S7. UV-vis absorption spectrum of 1 in acetone solution.

Reference:

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