$[\{AgL\}_2Mo_8O_{26}]^{n-}$ complexes: combined experimental and theoretical study

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Supporting Information

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Part A. Synthesis and characterization.

General information. $(NBu_4)_4[\beta\text{-}Mo_8O_{26}]$ and $(NBu_4)_2[Mo_6O_{19}]$ were synthesized according to the standard procedures. All another reagents were of commercial purity (Sigma Aldrich) and were used without any purification. Elemental analysis was carried out on a Eurovector EA 3000 CHN analyzer. ESI-MS spectra were recorded on an Agilent (6130 Quadrupole MS, 1260 infinity LC) in m/z 400–3000 diapason in the mixture of $CH_3CN/H_2O/CH_3COOH$.

Complex $(NBu_4)_2[\{AgPPh_2Py\}_2Mo_8O_{26}]\cdot DMF$ (1): 0.016 g (0.095 mmol) of solid $AgNO_3$ was added to the solution of 0.100 g (0.046 mmol) $(NBu_4)_4[Mo_8O_{26}]$ in 5 mL DMF. After that 0.024 g (0.091 mmol) of PPh_2Py was added to the reaction mixture under stirring. 30 minutes later reaction media was transferred into the Et_2O atmosphere at 5 °C. A crop of colorless crystals of $(NBu_4)_2[\{AgPPh_2Py\}_2Mo_8O_{26}]\cdot DMF\cdot Et_2O$ was collected after 2 days. Crystals were washed several times with Et_2O and dried in air. Ether molecules of crystallization were lost during drying according to the EA. Yield 0.109 g (98% based on POM). IR (ATR, cm^{-1}): 1659 (m), 1567 (w), 1477 (w), 1433 (w), 1383 (w), 1092 (w), 947 (s), 928 (s), 897 (vs), 885 (vs), 826 (s), 772 (m), 741 (m), 692 (vs), 644 (vs). Analysis: calcd for $(NBu_4)_2[\{AgPPh_2Py\}_2Mo_8O_{26}]\cdot DMF$ C, H, N (%): 33.2, 4.3, 2.8; found C, H, N (%): 33.6, 4.5, 3.0.

Complex $(NBu_4)_2[\{AgPPh_3\}_2Mo_8O_{26}]\cdot 2DMF$ (2): 0.028 g (0.166 mmol) of solid $AgNO_3$ was added to the solution of 0.179 g (0.083 mmol) $(NBu_4)_4[Mo_8O_{26}]$ in 9 mL DMF. After that 0.043 g (0.164 mmol) of PPh_3 was added to the reaction mixture under stirring. 30 minutes later reaction media was transferred into the Et_2O atmosphere at 5 °C. A crop of colorless crystals of $(NBu_4)_2[\{AgPPh_3\}_2Mo_8O_{26}]\cdot 2DMF$ was collected after 2 days. Crystals were washed several times with Et_2O and dried in air.

Yield 0.184 g (92% based on POM). IR (ATR, cm^{-1}): 1477 (m), 1378 (w), 1300 (w), 1157 (w), 930 (vs), 888 (vs), 826 (s), 771 (m), 685 (vs), 644 (vs), 570 (s). Analysis, calcd for **2** C, H, N (%): 34.6, 4.5, 2.2; found C, H, N (%): 34.8, 4.5, 2.3.

Complex $(NBu_4)_2[\{AgAsPh_3\}_2Mo_8O_{26}]\cdot 2DMF$ (3): 0.027 g (0.16 mmol) of solid $AgNO_3$ was added to the solution of 0.173 g (0.08 mmol) $(NBu_4)_4[Mo_8O_{26}]$ in 8 mL DMF. After that 0.049 g (0.16 mmol) of $AsPh_3$ was added to the reaction mixture under stirring. 30 minutes later reaction media was transferred into the Et_2O atmosphere at 5 °C. A crop of colorless crystals of $(NBu_4)_2[\{AgAsPh_3\}_2Mo_8O_{26}]\cdot 2DMF$ was collected after 2 days. Crystals were washed several times with Et_2O and dried in air.

Yield 0.181 g (90.5% based on POM). IR (ATR, cm^{-1}): 1661 (s), 1483 (w), 1434 (m), 1384 (m), 1248 (w), 1089 (w), 947 (s), 926 (s), 897 (vs), 885 (vs), 828 (s), 740 (m), 692 (vs), 682 (vs), 648 (vs), 571 (m). Analysis, calcd for **3** C, H, N (%): 33.4, 4.4, 2.1; found C, H, N (%): 33.5, 4.4, 2.3.

Complex $(NBu_4)_2[\{Ag(SbPh_3)\}_2Mo_8O_{26}]\cdot DMF$ (4): 0.016 g (0.095 mmol) of solid $AgNO_3$ was added to the solution of 0.1 g (0.046 mmol) $(NBu_4)_4[Mo_8O_{26}]$ in 5 mL DMF. After that 0.032 g (0.91 mmol) of $SbPh_3$ was added to the reaction mixture under stirring. 30 minutes later reaction media was transferred into the Et_2O atmosphere at 5 °C. A crop of colorless crystals of $(NBu_4)_2[\{Ag(SbPh_3)(DMF)\}_2Mo_8O_{26}]$ was collected after 2 days. Crystals were washed several times with Et_2O and dried in air. One DMF molecule of crystallization was lost during drying according to the EA. Yield 0.077 g (65% based on POM). IR (ATR, $см^{-1}$): 1478 (m), 1431 (m), 1378 (w), 1066 (w), 997 (w), 960 (m), 927 (s), 887 (vs), 829 (s), 731 (s), 679 (vs), 644 (s), 575

(s). Analysis, calcd for $(NBu_4)_2[\{Ag(SbPh_3)\}_2Mo_8O_{26}]\cdot DMF$ C, H, N (%): 31.8, 4.1, 1.6; found C, H, N (%): 31.5, 4.0, 1.2.

Complex $(NBu_4)_2[\{AgC_5H_4NCl\}_2Mo_8O_{26}]\cdot 2DMF$ (5): 0.016 g (0.095 mmol) of solid $AgNO_3$ was added to the solution of 0.1 g (0.046 mmol) $(NBu_4)_4[Mo_8O_{26}]$ in 5 mL DMF. After that 9 μL (0.096 mmol) of C_5H_4NCl was added to the reaction mixture under stirring. 30 minutes later reaction media was transferred into the Et_2O atmosphere at 5 °C. A crop of colorless crystals of **5** was collected after 2 days. Crystals were washed several times with Et_2O and dried in air. Yield 0.095 g (98% based on POM). IR (ATR, cm^{-1}): 1655 (m), 1472 (m), 1422 (w), 1379 (m), 1124(w), 1107 (m), 1027 (w), 954 (m), 934 (vs), 892 (vs), 827(s), 797 (s), 736 (m), 677 (vs), 648(vs), 570 (s). Analysis, calcd for **5** C, H, N (%): 25.4, 4.1, 3.7; found C, H, N (%): 25.2, 3.9, 4.0.

Complex $(NBu_4)_2[\{AgC_5H_4NBr\}_2Mo_8O_{26}]\cdot 2DMF$ (6): 0.016 g (0.095 mmol) of solid $AgNO_3$ was added to the solution of 0.1 g (0.046 mmol) $(NBu_4)_4[Mo_8O_{26}]$ in 5 mL DMF. After that 9 μL (0.096 mmol) of C_5H_4NBr was added to the reaction mixture under stirring. 30 minutes later reaction media was transferred into the Et_2O atmosphere at 5 °C. A crop of colorless crystals of **6** was collected after 2 days. Crystals were washed several times with Et_2O and dried in air. Yield 0.093 g (92% based on POM). IR (ATR, cm^{-1}): 1652 (m), 1478 (m), 1420 (m), 1380 (m), 1097 (m), 1025 (m), 954 (m), 934 (vs), 893 (vs), 828 (s), 794 (m), 771(s), 683 (vs), 650 (vs), 570 (s). Analysis, calcd for **6** C, H, N (%): 24.4, 4.0, 3.6; found C, H, N (%): 24.6, 3.8, 3.9.

Complex $(NBu_4)_2[\{AgC_5H_4NI\}_2Mo_8O_{26}]\cdot 2DMF$ (7): 0.016 g (0.095 mmol) of solid $AgNO_3$ was added to the solution of 0.1 g (0.046 mmol) $(NBu_4)_4[Mo_8O_{26}]$ in 5 mL DMF. After that 0.019 g (0.092 mmol) of C_5H_4NI was added to the reaction mixture under stirring. 30 minutes later reaction media was transferred into the Et_2O atmosphere at 5 °C. A crop of colorless crystals of **7** was collected after 2 days. Crystals were washed several times with Et_2O and dried in air. Yield 0.102 g (97% based on POM). IR (ATR, cm^{-1}): 1650 (s), 1479 (m), 1416 (m), 1379 (m), 1092 (m), 1024 (m), 954 (m), 932 (s), 892 (vs), 827 (s), 791 (m), 701 (s), 685 (vs), 677 (vs), 646 (vs), 634 (vs), 596 (m), 570 (s). Analysis, calcd for **7** C, H, N (%): 23.5, 3.9, 3.4; found C, H, N (%): 23.1, 3.3, 3.5.

Complex $(NBu_4)_2[\{AgC_5H_4NNH_2\}_2Mo_8O_{26}]$ (8): 0.032 g (0.189 mmol) of solid $AgNO_3$ was added to the solution of 0.2 g (0.092 mmol) $(NBu_4)_4[Mo_8O_{26}]$ in 10 mL DMF. After that 0.017 g (0.18 mmol) of $C_5H_4NNH_2$ was added to the reaction mixture under stirring. 30 minutes later reaction media was transferred into the Et_2O atmosphere at 5 °C. A crop of colorless crystals of **8** was collected after 2 days. Crystals were washed several times with Et_2O and dried in air. Yield 0.185 g (97% based on POM). IR (ATR, cm^{-1}): 1630 (m), 1561 (w), 1487 (m), 1474 (m), 1447 (m), 1409 (w), 1384 (w), 1289 (w), 1159 (w), 1053 (w), 959 (m), 943 (s), 930 (s), 889 (vs), 827 (s), 783 (m), 681 (vs), 647 (vs), 565 (s). Analysis, calcd for **8** C, H, N (%): 24.3, 4.1, 4.0; found C, H, N (%): 24.8, 4.0, 4.3.

Complex $(NBu_4)_2[\{AgC_5H_4NCH_3\}_2Mo_8O_{26}]$ (9): 0.016 g (0.095 mmol) of solid $AgNO_3$ was added to the solution of 0.1 g (0.046 mmol) $(NBu_4)_4[Mo_8O_{26}]$ in 5 mL DMF. After that 9 μL (0.097 mmol) of $C_5H_4NCH_3$ was added to the reaction mixture under stirring. 30 minutes later reaction media was transferred into the Et_2O atmosphere at 5 °C. A crop of colorless crystals of **9** was collected after 2 days. Crystals were washed several times with Et_2O and dried in air. Yield: 0.95 g (99% based on POM). IR (ATR, cm^{-1}): 1601 (w), 1477 (m), 1451 (m), 1378 (w), 1300 (w), 1157 (w), 953 (m), 930 (vs), 888 (vs), 826 (s), 771 (m), 685 (vs), 644 (vs), 570 (s). Analysis, calcd for **9** C, H, N (%): 25.5, 4.2, 2.7; found C, H, N (%): 25.8, 4.0, 3.1.

Complex $(NBu_4)_2[\{AgC_5H_2N(CH_3)_3\}_2Mo_8O_{26}]\cdot 2DMF$ (10): 0.016 g (0.095 mmol) of solid $AgNO_3$ was added to the solution of 0.1 g (0.046 mmol) $(NBu_4)_4[Mo_8O_{26}]$ in 5 mL DMF. After that 12 μL (0.091 mmol) of $C_5H_4N(CH_3)_2$ was added to the reaction mixture under stirring. 30 minutes later reaction media was transferred into the Et_2O atmosphere at 5 °C. A crop of colorless crystals of **10** was collected after 2 days. Crystals were washed several times with Et_2O and dried in air. Yield 0.095 g (97% based on POM). IR (ATR, cm^{-1}): 1665 (m), 1617 (m), 1477 (m), 1456 (m), 1377 (m), 1088 (w), 1024 (w), 956 (m), 930 (s), 887 (vs), 832 (s), 681 (s), 648 (s), 573 (s). Analysis, calcd for **10** C, H, N (%): 27.6, 4.7, 3.7; found C, H, N (%): 28.2, 4.7, 3.7.

Complex $(NBu_4)_2[\{AgC_5H_3N(NH_2)_2\}_2Mo_8O_{26}]$ (11): 0.032 g (0.189 mmol) of solid $AgNO_3$ was added to the solution of 0.2 g (0.092 mmol) $(NBu_4)_4[Mo_8O_{26}]$ in 10 mL DMF. After that 0.02 g (0.183 mmol) of $C_5H_4N(NH_2)_2$ was added to the reaction mixture under stirring. 30 minutes later reaction media was transferred into the Et_2O atmosphere at 5 °C. A crop of colorless crystals of **11** was collected after 2 days. Crystals were washed several times with Et_2O and dried in air. Yield 0.133 g (69% based on POM). IR (ATR, cm^{-1}): 2152 (w), 1660 (m), 1622 (m), 1580 (m), 1469 (s), 1384 (w), 1302 (w), 1096 (w), 940 (s), 924 (s), 900 (vs), 885 (vs), 837 (s), 784 (m), 685 (vs), 650 (vs). Analysis, calcd for **11** C, H, N (%): 23.8, 4.1, 5.3; found C, H, N (%): 24.1, 4.0, 5.9.

Complex $[Ag_2(PPh_2Py)_2(DMF)_4][Mo_6O_{19}]$ (12):

0.025 g (0.148 mmol) of solid $AgNO_3$ was added to the solution of 0.1 g (0.073 mmol) $(NBu_4)_2[Mo_6O_{19}]$ in 5 mL DMF. After that 0.038 g (0.144 mmol) of PPh_2Py was added to the reaction mixture under stirring. 30 minutes later reaction media was transferred into the Et_2O atmosphere at 5 °C. A crop of colorless crystals of **13** was collected after 2 days. Crystals were washed several times with Et_2O and dried in air. Yield 0.074 g (53% based on POM). IR (ATR, cm^{-1}): 1644 (vs), 1580 (w), 1480 (w), 1455 (w), 1435 (m), 1381 (m), 1253 (w), 1096 (m), 950 (vs), 790 (vs), 747 (s), 693 (s), 661 (s), 596 (m). Analysis, calcd for 13 C, H, N (%): 28.6, 3.0, 4.3; found C, H, N (%): 28.0, 2.7, 3.8.

X-ray diffraction. Crystallographic data and refinement details for **1 – 8**, **10 – 12** are given in Table S10 (see Electronic supplementary information). The diffraction data were collected on a New Xcalibur (Agilent Technologies) diffractometer with MoK_α radiation (λ = 0.71073) by doing φ scans of narrow (0.5°) frames at 130 K. Absorption correction was done empirically using SCALE3 ABSPACK (CrysAlisPro, Agilent Technologies, Version 1.171.37.35 (release 13-08-2014 CrysAlis171 .NET)). Structure was solved by SHELXT[1] and refined by full-matrix least-squares treatment against $|F|^2$ in anisotropic approximation with SHELX 2014/7[2] in ShelXle[3] program. Hydrogen atoms were refined in geometrically added positions. The crystallographic data have been deposed in the Cambridge Crystallographic Data Centre under the deposition codes CCDC 1959363-1959373.

Computational Details. The molecular geometry of the ground state of $[Ag\{Mo_4O_{13}\}PPh_2Py]_2^{2-}$, $[Ag\{Mo_4O_{13}\}AsPh_3]_2^{2-}$, and $[Ag\{Mo_4O_{13}\}\{SbPh_3\}(DMF)]_2^{2-}$ was fully optimized in the gas phase at the Density Functional Theory (DFT) level. The B3LYP [4–7] functional was used coupled with the triple-ζ 6-311++G** basis set for light elements (*viz.* H, C, N and O) the double-ζ LANL2DZ[8–11] basis set for the valence shell of the heavy elements (*viz.* Mo and Ag) whose inner electrons were model using the LANL2DZ pseudo-potential, whereas for the pnictogens the triple-ζ 6-311+G* basis set was used for P and As, and the LANL2DZ basis/pseudo for Sb. Empirical dispersion GD3 with Becke-Johnson damping (GD3BJ)[12] was also included.

The optimized structures were submitted to vibrational frequencies calculations in harmonic approximation; the stationary points were checked to be "genuine" minima. The IR intensities were also computed.

Natural Bond Orbital (NBO)[13–19] analysis was performed on the Hartree-Fock (HF) density computed for the optimized geometries with the aforementioned basis sets. Analysis of possible dispersive interactions was performed using Non-Covalent Interaction (NCI) index along with Reduced Density Gradient (RDG).[20–23]

To investigate the presence and location of critical points, the Bader analysis based on the quantum atoms in molecules (QAIM) theory [24–26] was applied to the electron densities of the optimized structures.

The integration grid was set up to 250 radial shells and 974 angular points on each centre. Accuracy for 2-electron integrals calculation was set up to 10^{-14} a.u. The convergence criteria for the self-consistent field were set to 10^{-12} for the RMS change in the density matrix and 10^{-10} for the maximum change in the density matrix. The convergence criteria for optimizations were set to 2×10^{-6} a.u. for the maximum force, 1×10^{-6} a.u. for the RMS force, 6×10^{-6} a.u. for the maximum displacement and 4×10^{-6} a.u. for the RMS displacement.

All calculations were performed using the GAUSSIAN G09.D01 package[27], except for the research of the critical points, for which the AIMPAC code[28] was employed, and for the NCI investigation, for which a homemade code was used.

Computational details (X…O interactions). The single point calculations based on the experimental X-ray geometries of **5-7** have been carried out at the DFT level of theory using the M06 functional[29] with the help of Gaussian-09[27] program package. The Douglas–Kroll–Hess 2nd order scalar relativistic calculations requested relativistic core Hamiltonian were carried out using the DZP-DKH basis sets[30–33] for all atoms. The topological analysis of the electron density distribution with the help of the atoms in molecules (QTAIM) method developed by Bader[24] has been performed by using the Multiwfn program.[34] The Wiberg bond indices were computed by using the Natural Bond Orbital (NBO) partitioning scheme.[35] The Cartesian atomic coordinates for model supramolecular associates are presented in Supporting Information, **Table S1**.

HPLC-ICP-AES. Separations were performed with HPLC system Milichrom A-02 (EcoNova, Russia) equipped with a two-beam spectrophotometric detector at the wavelength range of 190−360 nm in ion-pair mode of reversed phase chromatography (ProntoSIL 120-5-C18AQ, 2x75 mm). Reversed-phase C18 column was preliminary coated using solution of 1.5 mM tetrabutylammonium hydroxide (TBAOH). Good quality separation in terms of efficiency, peak shape and retention time was achieved in gradient mode (DI water (eluent A) and acetonitrile (eluent B) with gradual increase in acetonitrile concentration. The gradient mode conditions: 0–2 min, 0–40% B; 2–12.2 min, 40–100% B; flow rate – 0.18 mL min^{-1}. Detection wavelength: 250 nm. An ICP-AES spectrometer iCap 6500 Duo (ThermoFisher Scientific, USA) with concentric nebulizer was applied as detector in hyphenated HPLC-ICP-AES mode. For quantitative estimations the Ag 328.0 nm, Mo 281.6 nm spectral lines were selected. All measurements were performed in three replicates. The data acquisition and processing was carried out with iTEVA (Thermo Scientific, USA) software. The ICP-AES working parameters: power supply – 1150 W, nebulizer Ar flow rate – 0.70 L min^{-1}, auxiliary – 0.50 L min^{-1}, cooling – 12 L min^{-1}. In order to eliminate plasma quenching we diluted the liquid coming out of the column into the spray chamber with deionized water. The steady state of the plasma and the optimal values of analytical signals were finally achieved at the eluent flow rate of 0.18 mL min^{-1}, and the eluent

velocity of 3 mL min^{-1} (peristaltic pump speed – 75 rpm). Under these conditions, stable plasma burning was observed even when the share of acetonitrile in the gradient profile attained 65%.

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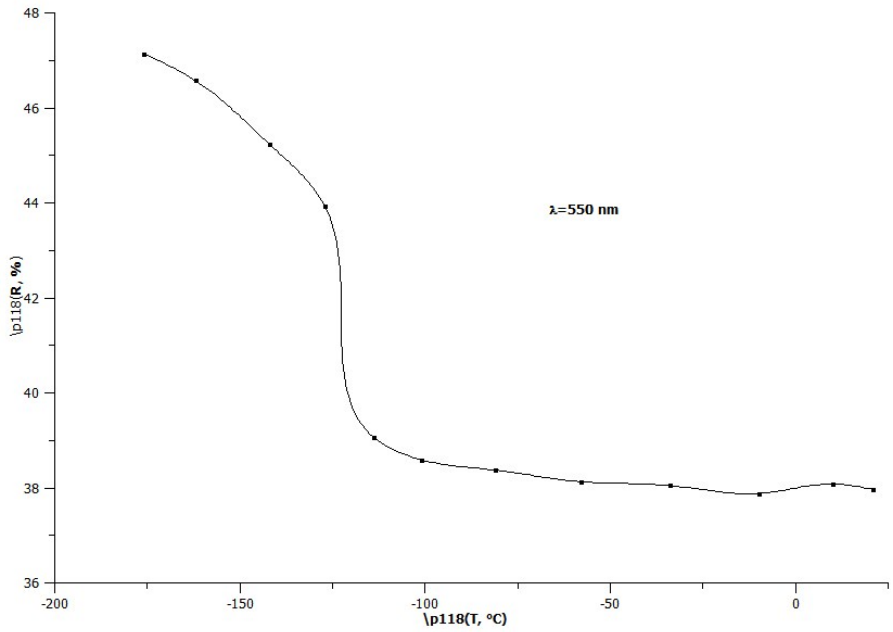


Fig. S1. The dependence of reflectance coefficient on temperature at 550 nm for 11.

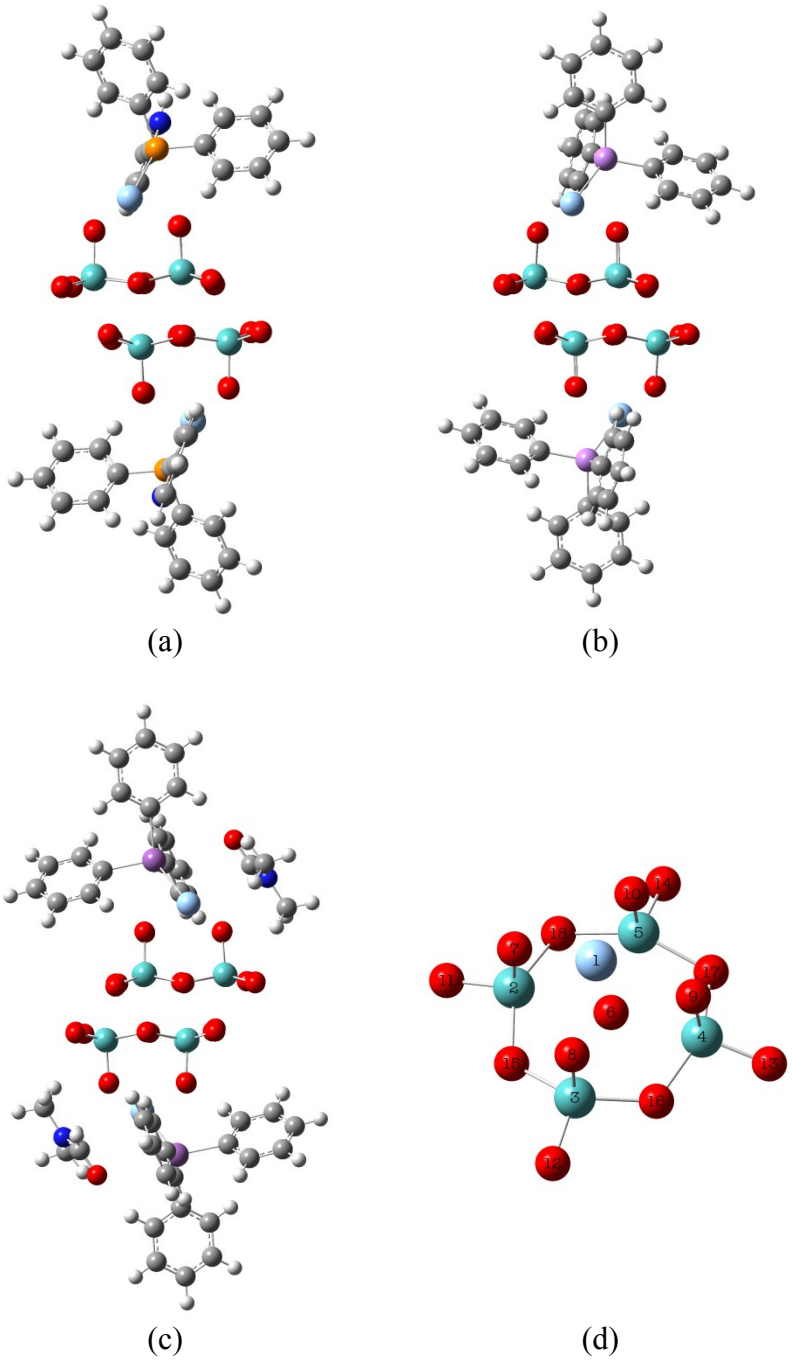
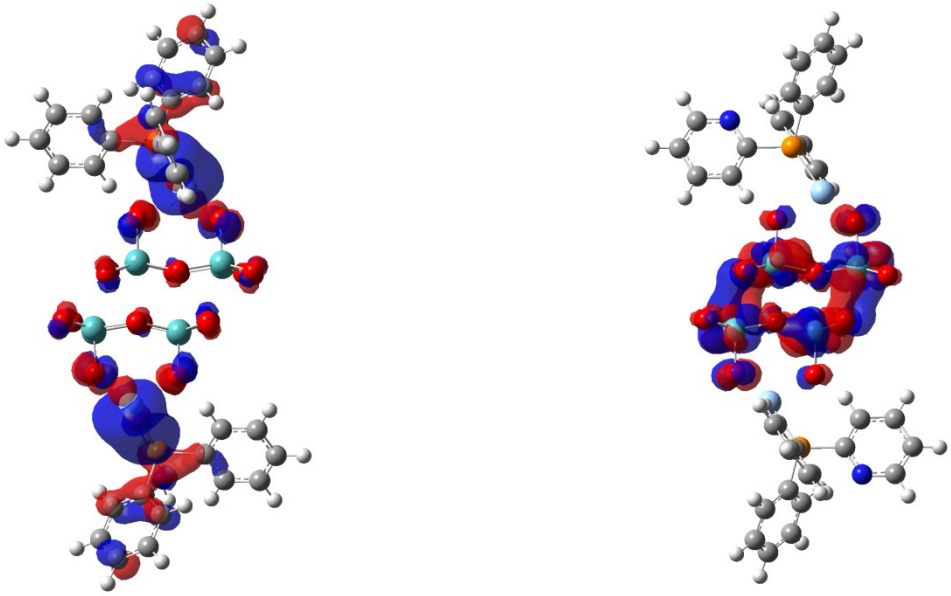
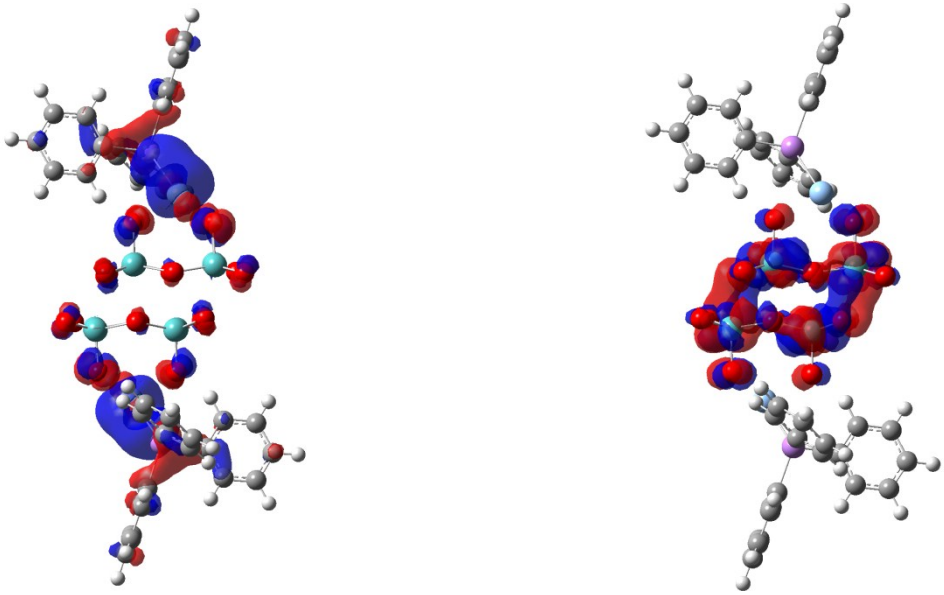


Fig. S2. Optimized molecular geometries of the three compounds investigated computationally, *viz.* $[Ag\{Mo_4O_{13}\}\{PPh_2Py\}]_2^{2-}$ (a), $[Ag\{Mo_4O_{13}\}\{AsPh_3\}]_2^{2-}$ (b), and $[Ag\{Mo_4O_{13}\}\{SbPh_3\}(DMF)]_2^{2-}$ (c). Labels of the atoms forming the $Ag\{Mo_4O_{13}\}$ moiety (d). Legend of colors: white (Hydrogen), grey (Carbon), blue (Nitrogen), red (Oxygen), orange (Phosphorus), lilac (Arsenic), violet (Antimony), light blue (Silver), and teal green (Molybdenum).

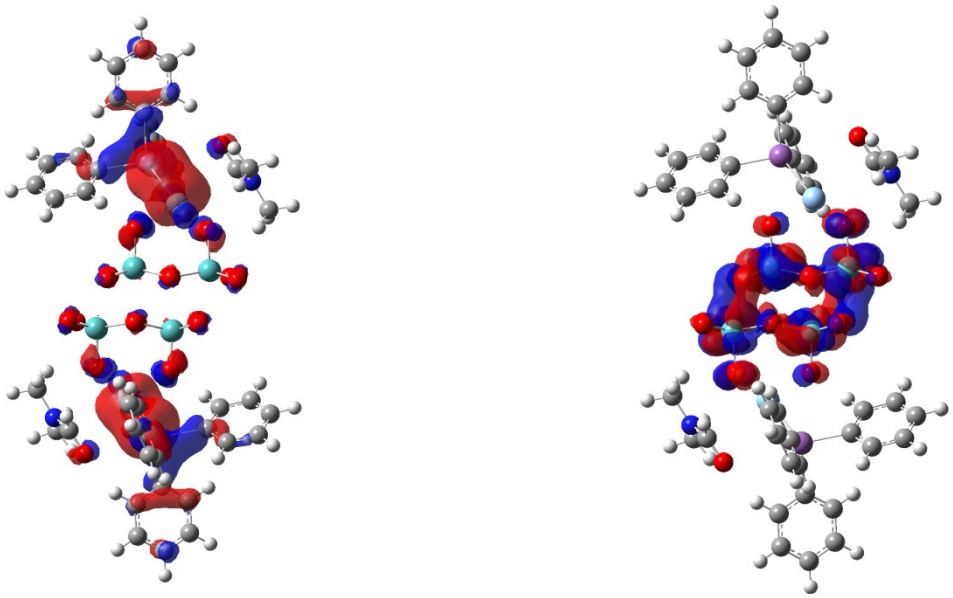
HOMO LUMO



(a) $[Ag\{Mo_4O_{13}\}\{PPh_2Py\}]_2^{2-}$

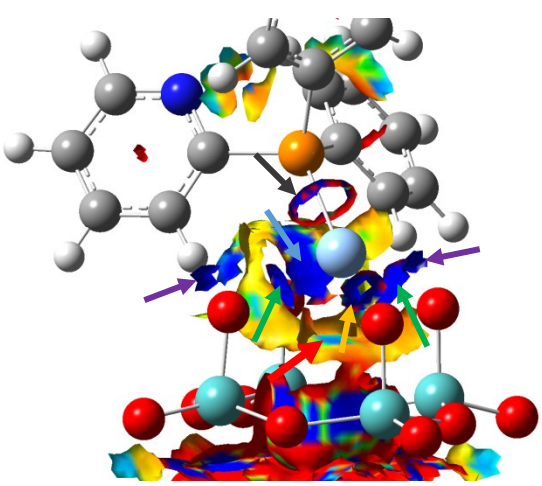


(b) $[Ag\{Mo_4O_{13}\}\{AsPh_3\}]_2^{2-}$

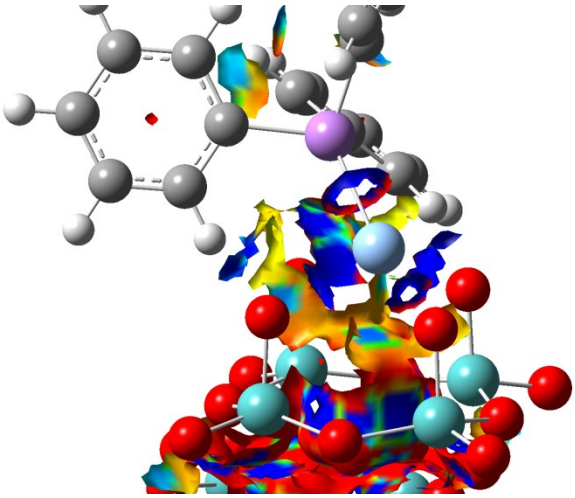


(c) $[Ag\{Mo_4O_{13}\}\{SbPh_3\}(DMF)]_2^{2-}$

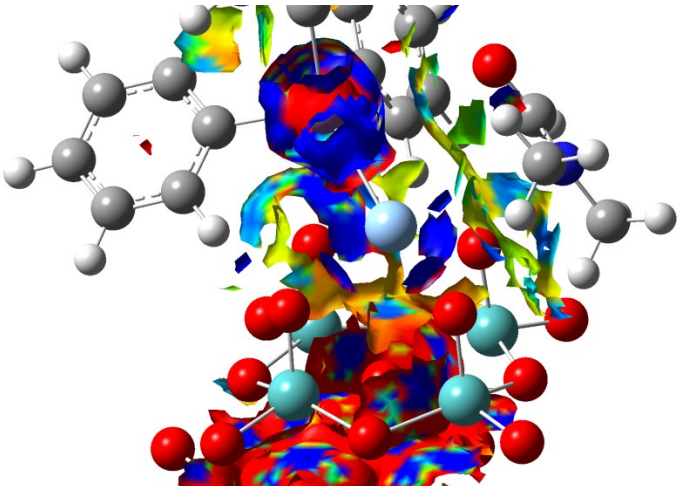
Fig. S3. Plot of the isosurface of the frontier molecular orbitals (HOMO on the left and LUMO on the right) of $[Ag\{Mo_4O_{13}\}\{PPh_2Py\}]_2^{2-}$ (a), $[Ag\{Mo_4O_{13}\}\{AsPh_3\}]_2^{2-}$ (b), and $[Ag\{Mo_4O_{13}\}\{SbPh_3\}(DMF)]_2^{2-}$ (c). | Isovalue | = 0.02 a.u..

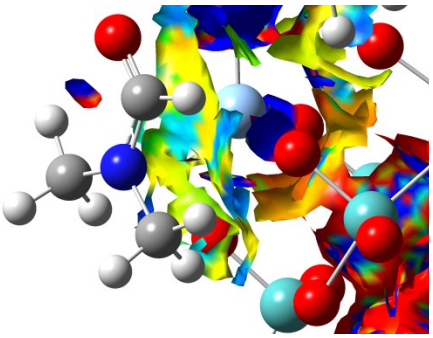


(a) $[Ag\{Mo_4O_{13}\}\{PPh_2Py\}]_2^{2-}$



(b) $[Ag\{Mo_4O_{13}\}\{AsPh_3\}]_2^{2-}$





(c) $[Ag\{Mo_4O_{13}\}\{SbPh_3\}(DMF)]_2^{2-}$

Fig. S4. Plot of the Non-Covalent Interaction (NCI) isosurfaces of $[Ag\{Mo_4O_{13}\}\{PPh_2Py\}]_2^{2-}$ (a), $[Ag\{Mo_4O_{13}\}\{AsPh_3\}]_2^{2-}$ (b), and $[Ag\{Mo_4O_{13}\}\{SbPh_3\}(DMF)]_2^{2-}$ (c) around the coordination sphere of Ag atom. *s* = 0.5 a.u.; colour scale from –0.012 a.u. (blue) < sign (λ_2) ρ(r) < +0.012 a.u. (red).

Table S1. Some geometrical parameters of the optimized structures: *r* (interatomic distance in 10^{-10} m) and α (bond angle in degrees). Atoms numbers refer to Fig. S2(d). Asterisks refer to atoms belonging to the other sub-unit.

							X		
							P	As	Sb
r	Ag	(1)	X				2.454	2.547	2.689
r	Ag	(1)	O_c	(6)			3.274	3.221	3.219
r	Ag	(1)	O_a	(7)			2.567	2.530	2.554
r	Ag	(1)	O_a	(8)			2.292	2.289	2.306
r	Ag	(1)	O_a	(9)			2.563	2.519	2.524
r	Ag	(1)	O_a	(10)			2.812	2.817	2.770
r	Mo	(2)	O_a	(7)			1.741	1.744	1.730
r	Mo	(3)	O_a	(8)			1.759	1.759	1.756
r	Mo	(4)	O_a	(9)			1.741	1.741	1.747
r	Mo	(5)	O_a	(10)			1.725	1.725	1.734
r	Mo	(2)	O_e	(11)			1.709	1.711	1.708
r	Mo	(3)	O_e	(12)			1.711	1.711	1.708
r	Mo	(4)	O_e	(13)			1.714	1.712	1.714
r	Mo	(5)	O_e	(14)			1.774	1.771	1.769
r	Mo	(2)	O_c	(6)			2.524	2.382	2.095
r	Mo	(3)	O_c	(6)			2.598	2.620	2.367
r	Mo	(4)	O_c	(6)			2.300	2.362	2.592
r	Mo	(5)	O_c	(6)			2.086	2.100	2.400
r	Mo	(2)	O_b	(18)			1.973	1.997	1.966
r	Mo	(2)	O_b	(15)			1.901	1.911	1.974
r	Mo	(3)	O_b	(15)			1.938	1.924	1.987
r	Mo	(3)	O_b	(16)			1.917	1.920	1.907
r	Mo	(4)	O_b	(16)			1.921	1.915	1.937
r	Mo	(4)	O_b	(17)			1.990	1.993	1.917
r	Mo	(5)	O_b	(17)			1.965	1.976	1.919
r	Mo	(5)	O_b	(18)			1.984	1.963	1.999
r	Mo	(4)	O_e*				2.248	2.253	2.373
r	Mo	(2)	O_c*				2.403	2.390	2.402
r	O_a	(7)	H’				3.772	2.106	2.247
r	O_a	(10)	H’				2.411	2.895	2.730
r	O_a	(9)	H”				3.609	2.336	2.303
r	O_a	(10)	H”				2.639	2.364	2.462
α	X		Ag	(1)	O_c	(6)	129.1	125.6	126.9

Part B. Optimized Geometries

The Cartesian coordinates of the atomic positions for the optimized structures are reported in units of 10^{-10} m.

(1) $[Ag\{Mo_4O_{13}\}\{PPh_2Py\}]_2^{2-}$

47	-4.107232	0.131600	-1.765984
47	4.107232	-0.131600	1.765984
42	-1.300413	2.520356	-0.979117
42	-0.956589	0.363963	-3.576810
42	-1.218092	-2.209968	-1.459560
42	-1.474846	-0.138730	1.003948
42	1.300413	-2.520356	0.979117
42	0.956589	-0.363963	3.576810
42	1.218092	2.209968	1.459560
42	1.474846	0.138730	-1.003948
15	-6.060165	0.060052	-0.280960
15	6.060165	-0.060052	0.280960
8	-3.026956	2.377289	-1.149880
8	-2.715142	0.351143	-3.573664
8	-2.952181	-2.150163	-1.603357
8	-3.195314	-0.149422	0.879242
8	-0.765179	2.109173	-2.756720
8	-0.997063	4.196329	-0.839301
8	-1.135270	1.810706	0.854395
8	-0.925613	0.024593	-1.001605
8	-0.502333	0.557029	-5.215250
8	-0.713691	-1.492777	-3.168441
8	-0.786078	-3.856161	-1.660860
8	-1.062085	-1.995750	0.512794
8	-1.127039	-0.299156	2.736020
8	3.026956	-2.377289	1.149880
8	2.715142	-0.351143	3.573664
8	2.952181	2.150163	1.603357
8	3.195314	0.149422	-0.879242
8	0.765179	-2.109173	2.756720
8	0.997063	-4.196329	0.839301
8	1.135270	-1.810706	-0.854395
8	0.925613	-0.024593	1.001605
8	0.502333	-0.557029	5.215250
8	0.713691	1.492777	3.168441
8	0.786078	3.856161	1.660860
8	1.062085	1.995750	-0.512794
8	1.127039	0.299156	-2.736020
7	-7.266097	1.546078	1.683246
7	7.266097	-1.546078	-1.683246
6	-6.121299	1.407629	0.991079
6	-4.991054	2.198941	1.215726
6	-5.044844	3.162631	2.223568
6	-7.304748	2.477791	2.640761
6	-7.701194	0.220448	-1.087302
6	-6.207003	-1.469175	0.718703
6	-6.222468	3.305793	2.955071
6	-8.166060	1.489208	-1.466041
6	-8.446532	-0.910391	-1.447370
6	-5.212625	-2.449303	0.608864
6	-7.279379	-1.655527	1.606702
6	-9.359015	1.624283	-2.175245

6	-9.640262	-0.774423	-2.160560
6	-5.289515	-3.608710	1.386163
6	-7.351936	-2.816571	2.375719
6	-10.102416	0.492243	-2.525295
6	-6.355020	-3.794078	2.268019
6	6.121299	-1.407629	-0.991079
6	4.991054	-2.198941	-1.215726
6	5.044844	-3.162631	-2.223568
6	7.304748	-2.477791	-2.640761
6	7.701194	-0.220448	1.087302
6	6.207003	1.469175	-0.718703
6	6.222468	-3.305793	-2.955071
6	8.166060	-1.489208	1.466041
6	8.446532	0.910391	1.447370
6	5.212625	2.449303	-0.608864
6	7.279379	1.655527	-1.606702
6	9.359015	-1.624283	2.175245
6	9.640262	0.774423	2.160560
6	5.289515	3.608710	-1.386163
6	7.351936	2.816571	-2.375719
6	10.102416	-0.492243	2.525295
6	6.355020	3.794078	-2.268019
1	-4.097602	2.070667	0.615096
1	-4.170735	3.781081	2.425779
1	-8.248497	2.563809	3.185142
1	-6.308557	4.041159	3.755240
1	-7.592781	2.376921	-1.199331
1	-8.095667	-1.901425	-1.162647
1	-4.374254	-2.311364	-0.070341
1	-8.039580	-0.882027	1.700830
1	-9.708982	2.618148	-2.457320
1	-10.209781	-1.664653	-2.431157
1	-4.499927	-4.355324	1.304398
1	-8.183098	-2.955179	3.069125
1	-11.034521	0.598205	-3.081899
1	-6.407059	-4.695841	2.880089
1	4.097602	-2.070667	-0.615096
1	4.170735	-3.781081	-2.425779
1	8.248497	-2.563809	-3.185142
1	6.308557	-4.041159	-3.755240
1	7.592781	-2.376921	1.199331
1	8.095667	1.901425	1.162647
1	4.374254	2.311364	0.070341
1	8.039580	0.882027	-1.700830
1	9.708982	-2.618148	2.457320
1	10.209781	1.664653	2.431157
1	4.499927	4.355324	-1.304398
1	8.183098	2.955179	-3.069125
1	11.034521	-0.598205	3.081899
1	6.407059	4.695841	-2.880089
1	-4.413267	1.144015	4.785461
1	-4.407178	-0.198107	5.973664
1	-3.346525	-0.250039	4.530111
1	3.960704	1.458672	2.332495
1	7.724751	-0.474463	3.192760
1	9.015506	-1.121926	0.985683
1	5.137672	-2.152057	-0.605497
1	8.863429	0.837840	-1.356220
1	7.917858	2.347664	2.569062
1	3.363611	1.363043	4.722152
1	7.127893	-0.559692	5.593972
1	9.757390	-3.465384	0.689795
1	5.877638	-4.483887	-0.905026

1	11.068736	1.967388	-1.255476
1	10.103945	3.503765	2.657051
1	4.943416	0.356389	6.372057
1	8.194739	-5.161132	-0.260678
1	11.699797	3.311434	0.749245
1	6.113911	-1.187579	-3.460785
1	4.419853	2.424483	-3.810185
1	5.577108	2.432807	-5.179730
1	6.188914	2.401103	-3.493741
1	4.413267	-1.144015	-4.785461
1	4.407178	0.198107	-5.973664
1	3.346525	0.250039	-4.530111

(2) $[Ag\{Mo_4O_{13}\}\{AsPh_3\}]_2^{2-}$

47	4.114985	1.635923	-0.072565
47	-4.114984	-1.635928	0.072572
42	1.259805	1.295961	2.280260
42	1.088536	3.577037	-0.185912
42	1.422119	-1.082670	0.068621
42	1.285595	1.048569	-2.399082
42	-1.259800	-1.295953	-2.280251
42	-1.088530	-3.577030	0.185920
42	-1.422117	1.082679	-0.068614
42	-1.285595	-1.048559	2.399086
33	5.996937	-0.079668	-0.053841
33	-5.996938	0.079659	0.053831
8	2.997349	1.327658	2.176328
8	2.847508	3.539158	-0.174566
8	3.143613	-1.000872	0.130037
8	3.024172	1.114981	-2.282257
8	0.898564	1.440410	3.947043
8	0.843085	3.054411	1.645507
8	1.001097	-0.652383	1.950416
8	0.964565	0.964348	-0.039866
8	0.861992	2.859080	-1.956364
8	0.673506	5.234673	-0.277360
8	1.028250	-2.807008	0.162568
8	1.065302	-0.858498	-1.848212
8	0.953579	1.001048	-4.076403
8	-2.997344	-1.327653	-2.176319
8	-2.847503	-3.539158	0.174571
8	-3.143610	1.000881	-0.130028
8	-3.024172	-1.114969	2.282263
8	-0.898559	-1.440401	-3.947035
8	-0.843076	-3.054402	-1.645497
8	-1.001093	0.652392	-1.950408
8	-0.964564	-0.964338	0.039874
8	-0.861993	-2.859071	1.956370
8	-0.673495	-5.234664	0.277369
8	-1.028247	2.807018	-0.162559
8	-1.065299	0.858508	1.848219
8	-0.953576	-1.001038	4.076407
6	5.727312	-1.614562	-1.225657
6	7.842817	0.439344	-0.470668
6	6.269651	-0.926179	1.688608
6	6.328262	-2.851292	-0.966944
6	4.839677	-1.474143	-2.298398
6	8.624169	-0.217037	-1.427988
6	8.375215	1.546620	0.205179
6	7.523150	-1.395437	2.102127
6	5.158611	-1.063022	2.531746

6	6.048549	-3.945508	-1.789340
6	4.555763	-2.573702	-3.111425
6	9.925533	0.221119	-1.696944
6	9.676188	1.978533	-0.055793
6	7.662920	-2.012592	3.348395
6	5.303712	-1.683133	3.774746
6	5.159835	-3.807955	-2.860255
6	10.455812	1.315636	-1.010230
6	6.551761	-2.160477	4.184203
6	-5.727333	1.614548	1.225657
6	-7.842819	-0.439366	0.470635
6	-6.269641	0.926178	-1.688616
6	-6.328287	2.851275	0.966944
6	-4.839707	1.474130	2.298406
6	-8.624192	0.217017	1.427938
6	-8.375198	-1.546652	-0.205210
6	-7.523139	1.395435	-2.102141
6	-5.158597	1.063027	-2.531748
6	-6.048590	3.945489	1.789348
6	-4.555809	2.573686	3.111442
6	-9.925556	-0.221148	1.696878
6	-9.676171	-1.978574	0.055745
6	-7.662904	2.012596	-3.348406
6	-5.303693	1.683143	-3.774746
6	-5.159886	3.807936	2.860272
6	-10.455815	-1.315676	1.010165
6	-6.551740	2.160486	-4.184208
1	6.988218	-2.973758	-0.108419
1	4.325839	-0.529401	-2.469738
1	8.216583	-1.072722	-1.964599
1	7.766559	2.074053	0.941636
1	8.393951	-1.274958	1.457836
1	4.187575	-0.682021	2.227089
1	6.504593	-4.913398	-1.575443
1	3.829810	-2.466811	-3.917104
1	10.524502	-0.296751	-2.447646
1	10.079526	2.838873	0.479931
1	8.641702	-2.377414	3.664897
1	4.432049	-1.785722	4.420886
1	4.916448	-4.670942	-3.481220
1	11.470325	1.656660	-1.221169
1	6.660158	-2.643054	5.156698
1	-6.988235	2.973741	0.108414
1	-4.325863	0.529391	2.469746
1	-8.216621	1.072709	1.964547
1	-7.766526	-2.074087	-0.941654
1	-8.393943	1.274951	-1.457855
1	-4.187562	0.682026	-2.227087
1	-6.504638	4.913378	1.575452
1	-3.829863	2.466796	3.917127
1	-10.524542	0.296723	2.447566
1	-10.079494	-2.838922	-0.479978
1	-8.641685	2.377417	-3.664912
1	-4.432027	1.785736	-4.420881
1	-4.916511	4.670922	3.481244
1	-11.470329	-1.656707	1.221091
1	-6.660133	2.643067	-5.156701
1	3.960704	1.458672	2.332495
1	7.724751	-0.474463	3.192760
1	9.015506	-1.121926	0.985683
1	5.137672	-2.152057	-0.605497
1	8.863429	0.837840	-1.356220
1	7.917858	2.347664	2.569062

1	3.363611	1.363043	4.722152
1	7.127893	-0.559692	5.593972
1	9.757390	-3.465384	0.689795
1	5.877638	-4.483887	-0.905026
1	11.068736	1.967388	-1.255476
1	10.103945	3.503765	2.657051
1	4.943416	0.356389	6.372057
1	8.194739	-5.161132	-0.260678
1	11.699797	3.311434	0.749245
1	6.113911	-1.187579	-3.460785
1	4.419853	2.424483	-3.810185
1	5.577108	2.432807	-5.179730
1	6.188914	2.401103	-3.493741
1	4.413267	-1.144015	-4.785461
1	4.407178	0.198107	-5.973664
1	3.346525	0.250039	-4.530111

(3) $[Ag\{Mo_4O_{13}\}\{SbPh_3\}(DMF)]_2^{2-}$

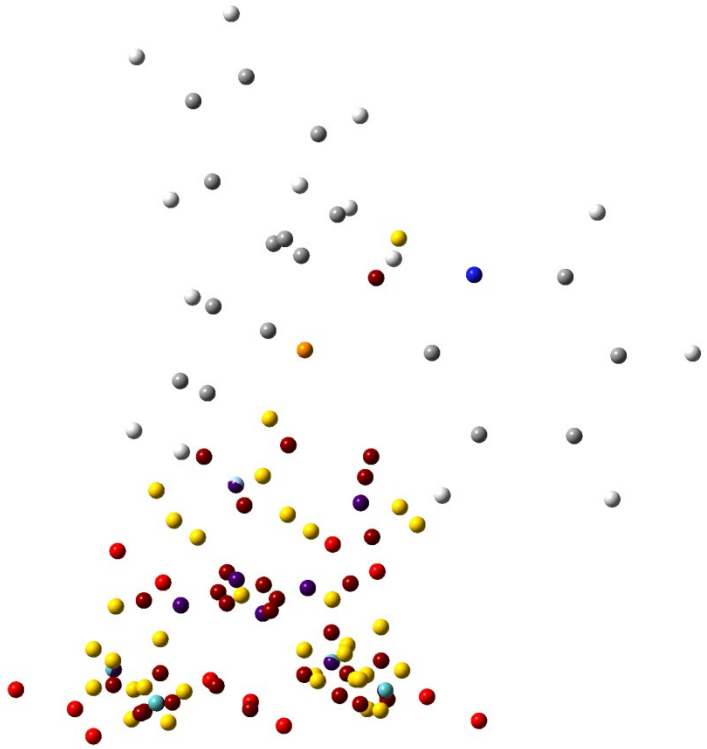
51	-6.316264	-0.528448	-0.494393
51	6.316264	0.528448	0.494393
47	-4.129772	-1.045257	0.983816
47	4.129772	1.045257	-0.983816
42	-0.924558	-1.346877	-0.736608
42	-2.164766	1.653318	-1.066395
42	-0.915057	-1.146950	2.511660
42	-2.213322	1.953331	2.264077
42	0.924558	1.346877	0.736608
42	2.164766	-1.653318	1.066395
42	0.915057	1.146950	-2.511660
42	2.213322	-1.953331	-2.264077
8	0.023640	-2.344894	-1.848306
8	-1.175794	0.166678	-1.965250
8	-0.163000	-2.082943	0.928974
8	-1.199712	0.233415	0.610388
8	-2.509022	-2.042099	-0.719213
8	-2.250454	2.737868	0.514870
8	-3.716416	0.886911	-0.957539
8	-2.320395	2.821977	-2.301934
8	-1.322135	0.556616	3.266863
8	-2.532628	-1.828477	2.451623
8	-0.163407	-1.926811	3.832146
8	-3.765130	1.156181	2.163424
8	-2.445363	3.236888	3.376279
8	-7.191799	-0.397606	2.748757
8	-0.023640	2.344894	1.848306
8	1.175794	-0.166678	1.965250
8	0.163000	2.082943	-0.928974
8	1.199712	-0.233415	-0.610388
8	2.509022	2.042099	0.719213
8	2.250454	-2.737868	-0.514870
8	3.716416	-0.886911	0.957539
8	2.320395	-2.821977	2.301934
8	1.322135	-0.556616	-3.266863
8	2.532628	1.828477	-2.451623
8	0.163407	1.926811	-3.832146
8	3.765130	-1.156181	-2.163424
8	2.445363	-3.236888	-3.376279
8	7.191799	0.397606	-2.748757
7	-5.390324	-0.599757	4.158646
7	5.390324	0.599757	-4.158646
6	-5.896029	-0.522762	-2.598810

6	-7.018357	1.479320	-0.229367
6	-8.240984	-1.502479	-0.604095
6	-4.671787	-1.039964	-3.042683
6	-6.776729	0.049521	-3.525242
6	-8.318908	1.858290	-0.584004
6	-6.146187	2.432904	0.312858
6	-9.139458	-1.408581	0.470906
6	-8.600931	-2.265778	-1.723746
6	-4.332645	-0.984147	-4.397249
6	-6.440563	0.100966	-4.880828
6	-8.741832	3.179625	-0.409244
6	-6.569980	3.752640	0.486758
6	-10.378710	-2.052601	0.414182
6	-9.838996	-2.915108	-1.777017
6	-5.216046	-0.414789	-5.317311
6	-7.866448	4.129239	0.125312
6	-10.732678	-2.807283	-0.708644
6	-6.279664	0.097651	3.421499
6	-5.393409	-2.054853	4.160543
6	-4.329082	0.059170	4.904710
6	5.896029	0.522762	2.598810
6	7.018357	-1.479320	0.229367
6	8.240984	1.502479	0.604095
6	4.671787	1.039964	3.042683
6	6.776729	-0.049521	3.525242
6	8.318908	-1.858290	0.584004
6	6.146187	-2.432904	-0.312858
6	9.139458	1.408581	-0.470906
6	8.600931	2.265778	1.723746
6	4.332645	0.984147	4.397249
6	6.440563	-0.100966	4.880828
6	8.741832	-3.179625	0.409244
6	6.569980	-3.752640	-0.486758
6	10.378710	2.052601	-0.414182
6	9.838996	2.915108	1.777017
6	5.216046	0.414789	5.317311
6	7.866448	-4.129239	-0.125312
6	10.732678	2.807283	0.708644
6	6.279664	-0.097651	-3.421499
6	5.393409	2.054853	-4.160543
6	4.329082	-0.059170	-4.904710
1	-3.960704	-1.458672	-2.332495
1	-7.724751	0.474463	-3.192760
1	-9.015506	1.121926	-0.985683
1	-5.137672	2.152057	0.605497
1	-8.863429	-0.837840	1.356220
1	-7.917858	-2.347664	-2.569062
1	-3.363611	-1.363043	-4.722152
1	-7.127893	0.559692	-5.593972
1	-9.757390	3.465384	-0.689795
1	-5.877638	4.483887	0.905026
1	-11.068736	-1.967388	1.255476
1	-10.103945	-3.503765	-2.657051
1	-4.943416	-0.356389	-6.372057
1	-8.194739	5.161132	0.260678
1	-11.699797	-3.311434	-0.749245
1	-6.113911	1.187579	3.460785
1	-4.419853	-2.424483	3.810185
1	-5.577108	-2.432807	5.179730
1	-6.188914	-2.401103	3.493741
1	-4.413267	1.144015	4.785461
1	-4.407178	-0.198107	5.973664
1	-3.346525	-0.250039	4.530111

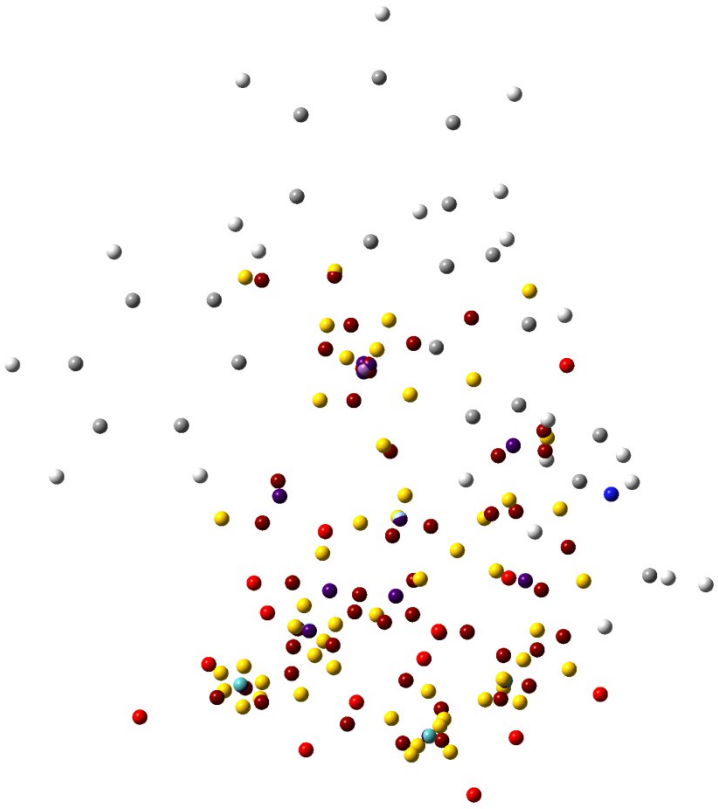
1	3.960704	1.458672	2.332495
1	7.724751	-0.474463	3.192760
1	9.015506	-1.121926	0.985683
1	5.137672	-2.152057	-0.605497
1	8.863429	0.837840	-1.356220
1	7.917858	2.347664	2.569062
1	3.363611	1.363043	4.722152
1	7.127893	-0.559692	5.593972
1	9.757390	-3.465384	0.689795
1	5.877638	-4.483887	-0.905026
1	11.068736	1.967388	-1.255476
1	10.103945	3.503765	2.657051
1	4.943416	0.356389	6.372057
1	8.194739	-5.161132	-0.260678
1	11.699797	3.311434	0.749245
1	6.113911	-1.187579	-3.460785
1	4.419853	2.424483	-3.810185
1	5.577108	2.432807	-5.179730
1	6.188914	2.401103	-3.493741
1	4.413267	-1.144015	-4.785461
1	4.407178	0.198107	-5.973664
1	3.346525	0.250039	-4.530111

Part C. Bader's QAIM Analysis

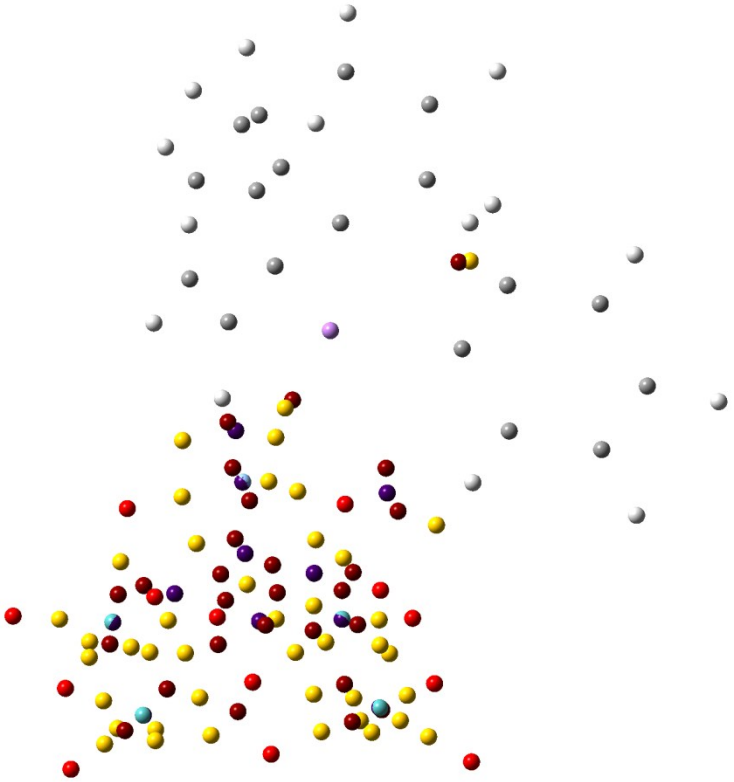
For the sake of clarity, only the non-trivial CPs are shown for one sub-unit.



(a) $[Ag\{Mo_4O_{13}\}\{PPh_2Py\}]_2^{2-}$



(b) $[Ag\{Mo_4O_{13}\}\{AsPh_3\}]_2^{2-}$



(c) $[Ag\{Mo_4O_{13}\}\{SbPh_3\}(DMF)]_2^{2-}$

Fig. S5. Critical Points (CPs) of $[Ag\{Mo_4O_{13}\}\{PPh_2Py\}]_2^{2-}$ (a), $[Ag\{Mo_4O_{13}\}\{AsPh_3\}]_2^{2-}$ (b), and $[Ag\{Mo_4O_{13}\}\{SbPh_3\}(DMF)]_2^{2-}$ (c). Legend of colors: Yellow (BCP), Wine (RCP), and Violet (CCP).

Part D. Natural Bond Orbital Analysis

Table S2. Natural Bond Orbital (NBO) analysis for $[Ag\{Mo_4O_{13}\}\{PPh_2Py\}]_2^{2-}$. Values of delocalization energy $E^{(2)}$ shown above 100.00 kcal/mol.

donor						acceptor					$E^{(2)}$ / (kcal/mol)
242	LP	(	1	) P	→	248	LP*	(	6	) Ag	213.91
248	LP*	(	6	) Ag	→	369	RY*	(	11	) C	213.94
248	LP*	(	6	) Ag	→	371	RY*	(	13	) C	172.06
248	LP*	(	6	) Ag	→	401	RY*	(	1	) P	619.04
248	LP*	(	6	) Ag	→	406	RY*	(	6	) P	1465.28
248	LP*	(	6	) Ag	→	416	RY*	(	16	) P	535.86
248	LP*	(	6	) Ag	→	417	RY*	(	17	) P	403.51
248	LP*	(	6	) Ag	→	481	RY*	(	2	) Ag	739.19
248	LP*	(	6	) Ag	→	483	RY*	(	4	) Ag	454.00
248	LP*	(	6	) Ag	→	564	RY*	(	2	) O	659.28
248	LP*	(	6	) Ag	→	567	RY*	(	5	) O	556.53
248	LP*	(	6	) Ag	→	577	RY*	(	1	) O	1149.09
248	LP*	(	6	) Ag	→	606	RY*	(	2	) O	245.52
248	LP*	(	6	) Ag	→	607	RY*	(	3	) O	130.23
248	LP*	(	6	) Ag	→	608	RY*	(	4	) O	156.18
248	LP*	(	6	) Ag	→	609	RY*	(	5	) O	116.79
248	LP*	(	6	) Ag	→	788	RY*	(	5	) O	139.72
248	LP*	(	6	) Ag	→	798	RY*	(	1	) O	166.91

Table S3. Natural Bond Orbital (NBO) analysis for $[Ag\{Mo_4O_{13}\}\{PPh_2Py\}]_2^{2-}$. Nature, occupancy and composition of the NBOs.

	orbital				occup.	%s	%p	%d
242	LP	(	1	) P	1.80480	42.77	57.20	0.03
248	LP*	(	6	) Ag	0.19046	92.48	6.37	1.15
369	RY*	(	11	) C	0.00016	12.42	4.83	82.75
371	RY*	(	13	) C	0.00008	84.28	2.44	13.28
401	RY*	(	1	) P	0.00678	0.89	82.53	16.58
406	RY*	(	6	) P	0.00176	14.65	59.97	25.38
416	RY*	(	16	) P	0.00019	43.51	47.66	8.83
417	RY*	(	17	) P	0.00014	57.00	36.04	6.96
481	RY*	(	2	) Ag	0.00106	83.98	14.35	1.66
483	RY*	(	4	) Ag	0.00037	7.55	63.68	28.77
564	RY*	(	2	) O	0.00150	4.84	94.79	0.37
567	RY*	(	5	) O	0.00030	58.70	37.41	3.90
577	RY*	(	1	) O	0.00238	8.15	91.49	0.36
606	RY*	(	2	) O	0.00246	4.46	95.38	0.16
607	RY*	(	3	) O	0.00198	8.90	90.97	0.13
608	RY*	(	4	) O	0.00104	86.48	13.11	0.41
609	RY*	(	5	) O	0.00044	68.62	29.81	1.57
788	RY*	(	5	) O	0.00090	74.95	23.75	1.31
798	RY*	(	1	) O	0.00645	9.51	90.21	0.28

Table S4. Natural Bond Orbital (NBO) analysis for $[Ag\{Mo_4O_{13}\}\{AsPh_3\}]_2^{2-}$. Values of delocalization energy $E^{(2)}$ shown above 100.00 kcal/mol.

donor						acceptor					$E^{(2)}$ / (kcal/mol)
266	LP*	(	6	) Ag	→	377	RY*	(	1	) Ag	2557.98
266	LP*	(	6	) Ag	→	380	RY*	(	4	) Ag	403.96
266	LP*	(	6	) Ag	→	381	RY*	(	5	) Ag	526.95
266	LP*	(	6	) Ag	→	382	RY*	(	6	) Ag	2612.62
266	LP*	(	6	) Ag	→	389	RY*	(	2	) O	221.25
266	LP*	(	6	) Ag	→	391	RY*	(	4	) O	2373.95
266	LP*	(	6	) Ag	→	392	RY*	(	5	) O	405.09
266	LP*	(	6	) Ag	→	393	RY*	(	6	) O	162.96
266	LP*	(	6	) Ag	→	402	RY*	(	1	) O	1391.05
266	LP*	(	6	) Ag	→	494	RY*	(	7	) Mo	102.33
266	LP*	(	6	) Ag	→	418	RY*	(	3	) O	163.44
266	LP*	(	6	) Ag	→	431	RY*	(	2	) O	542.42
266	LP*	(	6	) Ag	→	432	RY*	(	3	) O	175.65
266	LP*	(	6	) Ag	→	433	RY*	(	4	) O	1134.55
266	LP*	(	6	) Ag	→	434	RY*	(	5	) O	161.24
266	LP*	(	6	) Ag	→	435	RY*	(	6	) O	2503.06
266	LP*	(	6	) Ag	→	674	RY*	(	14	) O	111.48
266	LP*	(	6	) Ag	→	444	RY*	(	1	) As	1202.96
266	LP*	(	6	) Ag	→	448	RY*	(	5	) As	238.33
266	LP*	(	6	) Ag	→	605	RY*	(	1	) O	190.45
266	LP*	(	6	) Ag	→	611	RY*	(	7	) O	511.18
279	LP*	(	1	) Mo	→	268	LP*	(	8	) Ag	106.61
282	LP*	(	1	) Mo	→	377	RY*	(	1	) Ag	976.20
278	LP	(	1	) As	→	266	LP*	(	6	) Ag	223.87

Table S5. Natural Bond Orbital (NBO) analysis for $[Ag\{Mo_4O_{13}\}\{AsPh_3\}]_2^{2-}$. Nature, occupancy and composition of the NBOs.

	orbital				occup.	%s	%p	%d
266	LP*	(	6	) Ag	0.19751	89.87	9.20	0.93
268	LP*	(	8	) Ag	0.04048	0.00	99.83	0.16
278	LP	(	1	) As	1.80717	51.36	48.57	0.07
279	LP*	(	1	) Mo	0.59031	8.20	3.29	88.51
282	LP*	(	1	) Mo	0.30068	73.50	3.67	22.83
377	RY*	(	1	) Ag	0.00134	37.99	61.22	0.79
380	RY*	(	4	) Ag	0.00036	8.29	69.77	21.94
381	RY*	(	5	) Ag	0.00024	57.58	4.61	37.81
382	RY*	(	6	) Ag	0.00019	10.68	14.09	75.23
389	RY*	(	2	) O	0.00156	16.02	83.46	0.53
391	RY*	(	4	) O	0.00070	64.78	34.57	0.65
392	RY*	(	5	) O	0.00029	51.31	45.54	3.15
393	RY*	(	6	) O	0.00029	32.36	50.73	16.90
402	RY*	(	1	) O	0.00242	4.83	94.84	0.33
418	RY*	(	3	) O	0.00204	2.09	97.77	0.14
431	RY*	(	2	) O	0.00165	4.87	94.65	0.48
432	RY*	(	3	) O	0.00132	27.31	72.44	0.26
433	RY*	(	4	) O	0.00071	63.51	35.45	1.04
434	RY*	(	5	) O	0.00027	40.79	37.13	22.09
435	RY*	(	6	) O	0.00228	7.51	92.45	0.04
444	RY*	(	1	) As	0.00203	6.41	72.55	21.04
448	RY*	(	5	) As	0.00193	62.45	18.35	19.19
494	RY*	(	7	) Mo	0.00054	60.47	36.92	2.61
605	RY*	(	1	) O	0.00641	8.81	90.95	0.24
611	RY*	(	7	) O	0.00063	31.32	68.16	0.52
674	RY*	(	14	) O	0.00004	7.07	3.45	89.48

Table S6. Natural Bond Orbital (NBO) analysis for $[Ag\{Mo_4O_{13}\}\{SbPh_3\}(DMF)]_2^{2-}$. Values of delocalization energy $E^{(2)}$ shown above 100.00 kcal/mol.

donor						acceptor					$E^{(2)}$ / (kcal/mol)
277	LP*	(	5	) Mo	→	316	LP*	(	7	) Ag	606.00
279	LP*	(	1	) Mo	→	318	LP*	(	9	) Ag	136.79
315	LP*	(	6	) Ag	→	441	RY*	(	9	) Mo	302.51
315	LP*	(	6	) Ag	→	480	RY*	(	1	) O	1062.50
315	LP*	(	6	) Ag	→	483	RY*	(	4	) O	998.49
315	LP*	(	6	) Ag	→	484	RY*	(	5	) O	116.98
315	LP*	(	6	) Ag	→	485	RY*	(	6	) O	471.61
315	LP*	(	6	) Ag	→	487	RY*	(	8	) O	644.23
315	LP*	(	6	) Ag	→	405	RY*	(	1	) O	213.92
315	LP*	(	6	) Ag	→	550	RY*	(	1	) O	349.42
315	LP*	(	6	) Ag	→	554	RY*	(	5	) O	118.68
315	LP*	(	6	) Ag	→	602	RY*	(	3	) O	360.09
315	LP*	(	6	) Ag	→	589	RY*	(	1	) Ag	801.35
315	LP*	(	6	) Ag	→	592	RY*	(	4	) Ag	217.42
315	LP*	(	6	) Ag	→	593	RY*	(	5	) Ag	220.84
315	LP*	(	6	) Ag	→	595	RY*	(	7	) Ag	5280.31
315	LP*	(	6	) Ag	→	597	RY*	(	9	) Ag	438.63
315	LP*	(	6	) Ag	→	598	RY*	(	10	) Ag	298.62
315	LP*	(	6	) Ag	→	628	RY*	(	1	) Sb	398.56
323	LP	(	1	) Sb	→	315	LP*	(	6	) Ag	176.36

Table S7. Natural Bond Orbital (NBO) analysis for $[Ag\{Mo_4O_{13}\}\{SbPh_3\}(DMF)]_2^{2-}$. Nature, occupancy and composition of the NBOs.

	orbital				occup.	%s	%p	%d
277	LP*	(	5	) Mo	0.17971	13.56	85.51	0.94
279	LP*	(	1	) Mo	0.46414	0.99	32.86	66.15
315	LP*	(	6	) Ag	0.22217	87.97	11.42	0.61
316	LP*	(	7	) Ag	0.08999	9.23	90.74	0.03
318	LP*	(	9	) Ag	0.04506	1.72	98.13	0.15
323	LP	(	1	) Sb	1.78983	56.84	43.16	0.00
405	RY*	(	1	) O	0.00468	12.65	86.88	0.47
441	RY*	(	9	) Mo	0.00093	79.38	20.16	0.46
480	RY*	(	1	) O	0.00201	3.65	96.11	0.23
483	RY*	(	4	) O	0.00075	67.52	31.94	0.55
484	RY*	(	5	) O	0.00026	42.21	57.60	0.19
485	RY*	(	6	) O	0.00020	12.42	80.35	7.23
487	RY*	(	8	) O	0.00012	3.11	91.06	5.83
550	RY*	(	1	) O	0.00321	10.41	89.33	0.26
554	RY*	(	5	) O	0.00048	27.12	69.14	3.74
589	RY*	(	1	) Ag	0.00173	56.23	43.48	0.29
592	RY*	(	4	) Ag	0.00053	63.65	29.81	6.54
593	RY*	(	5	) Ag	0.00043	32.97	65.69	1.34
595	RY*	(	7	) Ag	0.00024	6.02	1.12	92.86
597	RY*	(	9	) Ag	0.00017	29.36	2.68	67.96
598	RY*	(	10	) Ag	0.00015	55.59	4.20	40.21
602	RY*	(	3	) O	0.00221	46.08	53.72	0.20
628	RY*	(	1	) Sb	0.00286	0.34	99.66	0.00

Table S8. Natural Atomic Charges (NAC), in units of elementary charge.

		X		
		P	As	Sb
Ag	(1)	0.706	0.692	0.622
X		0.922	1.031	1.516
Mo	(2)	2.013	2.014	2.055
Mo	(3)	2.077	2.080	2.021
Mo	(4)	2.066	2.018	2.032
Mo	(5)	2.030	2.024	2.023
O	(6)	-1.064	-1.063	-1.060
O	(7)	-0.726	-0.718	-0.771
O	(8)	-0.779	-0.782	-0.777
O	(9)	-0.736	-0.732	-0.652
O	(10)	-0.653	-0.656	-0.856
O	(11)	-0.590	-0.584	-0.634
O	(12)	-0.627	-0.628	-0.565
O	(13)	-0.599	-0.582	-0.695
O	(14)	-0.706	-0.700	-0.567
O	(15)	-0.855	-0.857	-0.861
O	(16)	-0.865	-0.856	-0.892
O	(17)	-0.912	-0.899	-0.896
O	(18)	-0.898	-0.902	-0.718

Part E. IR data.

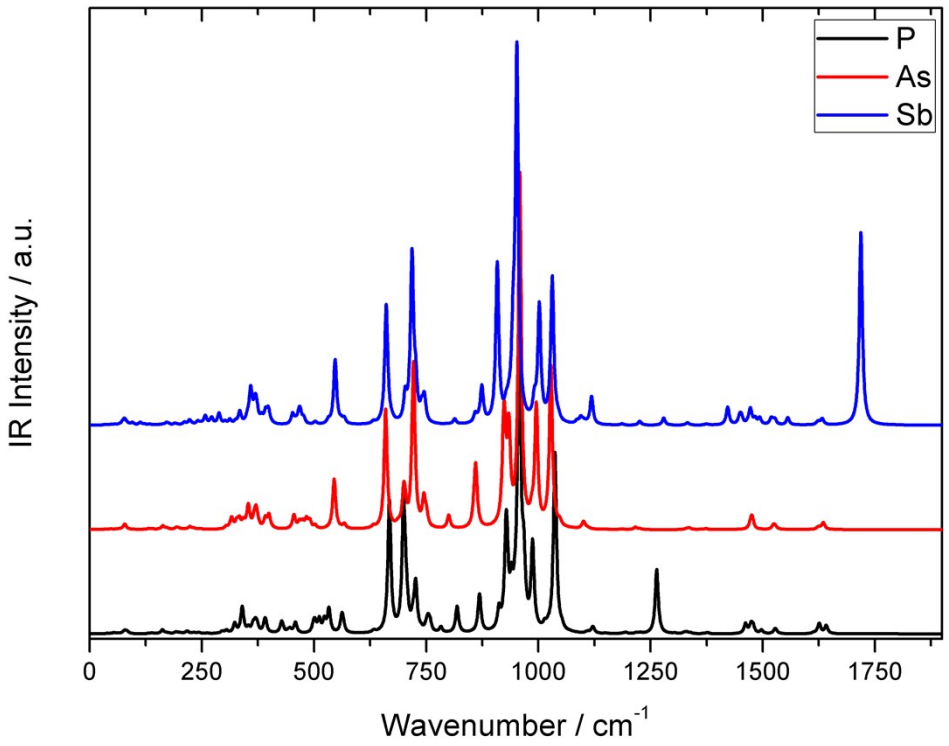


Fig. S6. Computed infrared spectra of $[Ag\{Mo_4O_{13}\}\{PPh_2Py\}]_2^{2-}$ (a), $[Ag\{Mo_4O_{13}\}\{AsPh_3\}]_2^{2-}$ (b), and $[Ag\{Mo_4O_{13}\}\{SbPh_3\}(DMF)]_2^{2-}$ (c) in the near and far region. Harmonic approximation is assumed. No scale factor is applied.

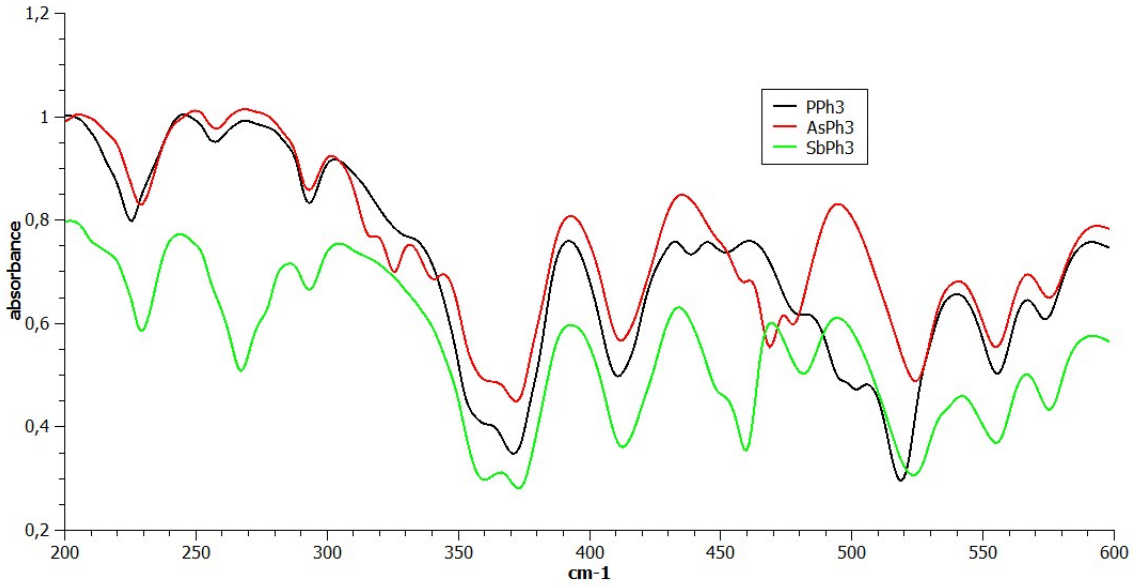
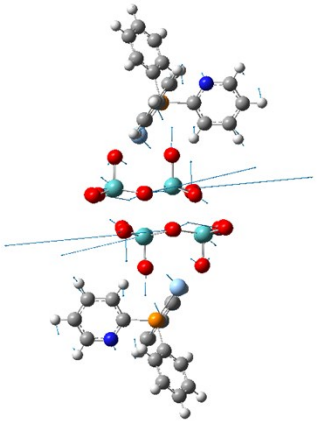
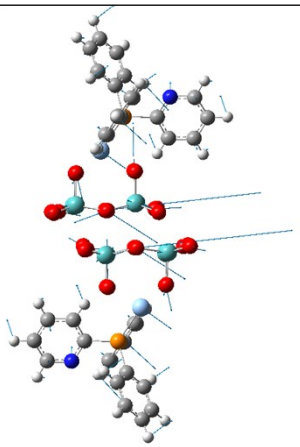
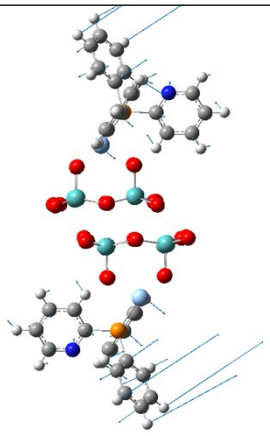
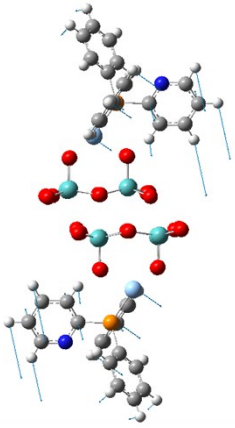
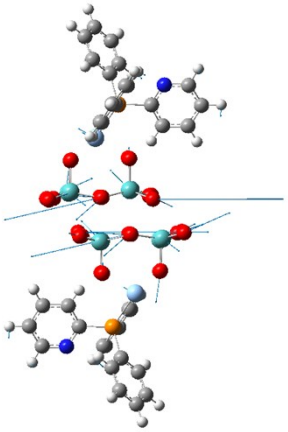
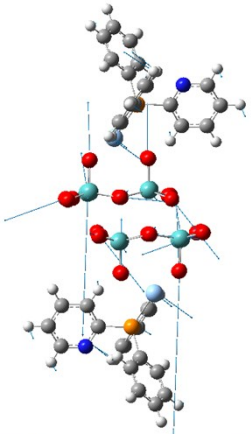
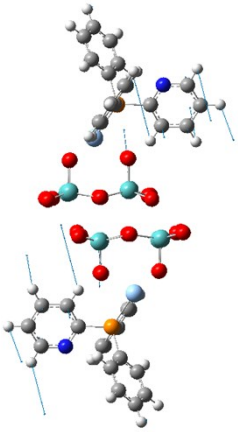
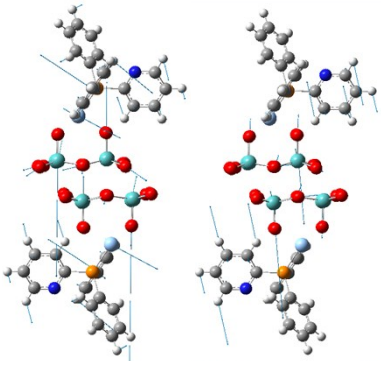
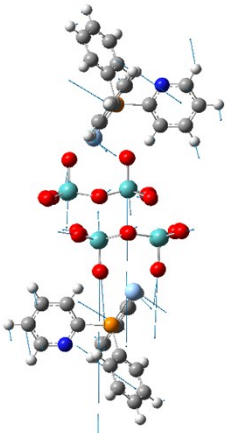
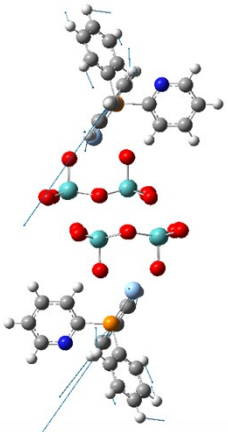
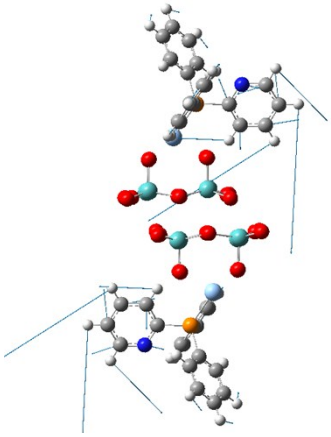
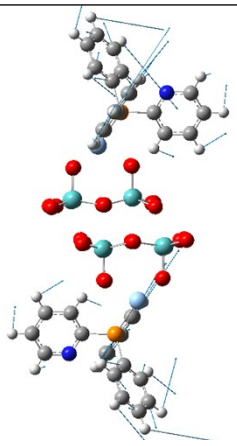
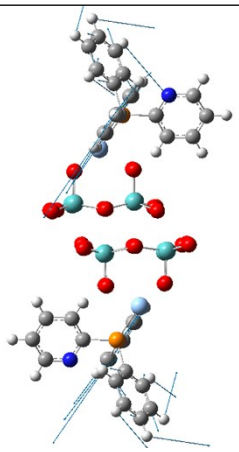
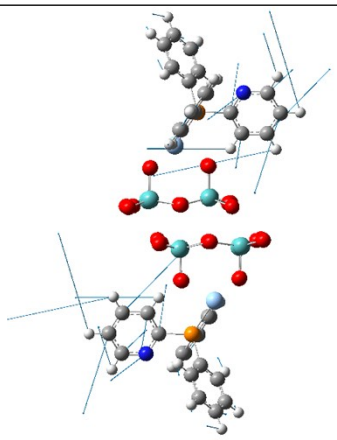
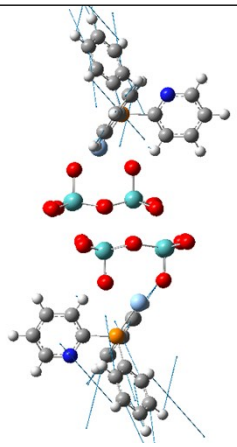


Fig. S7. Experimental IR spectra (200 - 600 cm^{-1}) for 2-4.

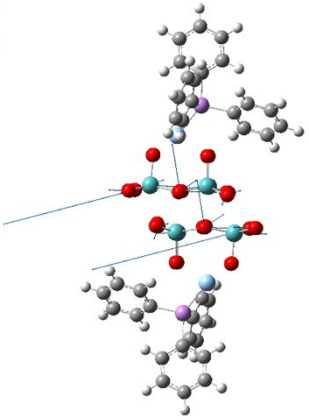
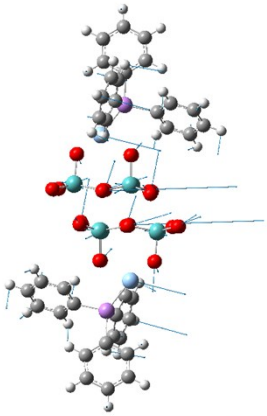
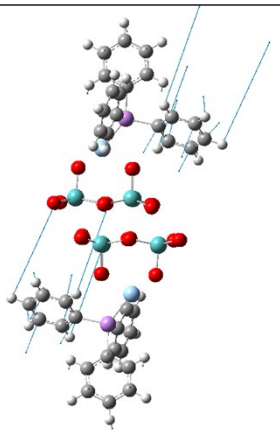
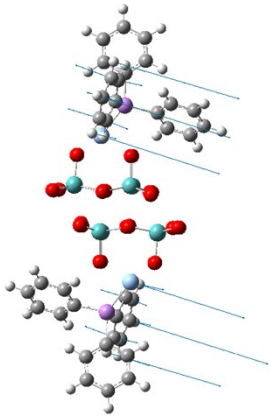
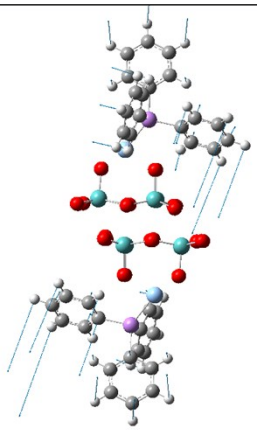
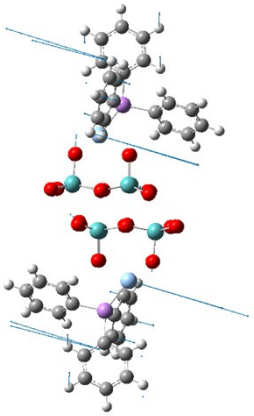
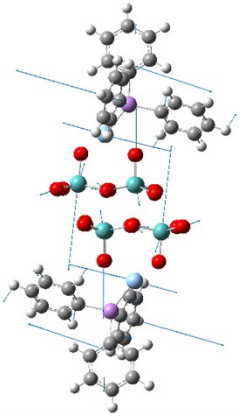
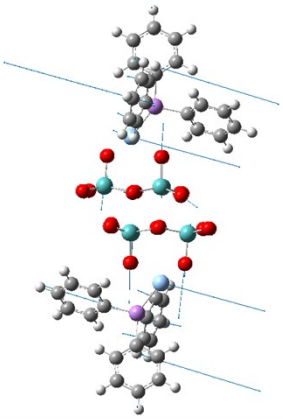
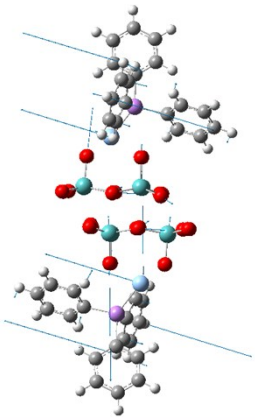
Fig. S8. Comparison between experimental and computed infrared wavenumbers (in cm^{-1}). Computed values are reported in *Italics*. Displacement vectors are depicted on the molecular structure.

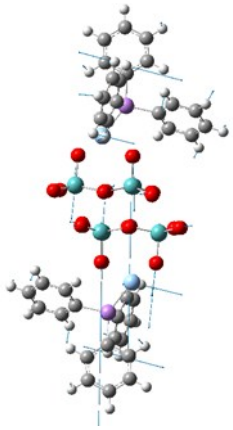
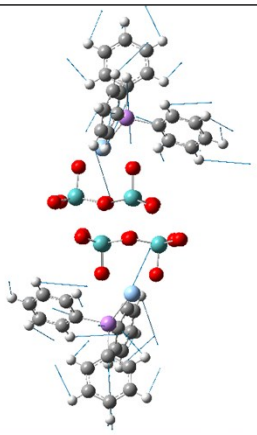
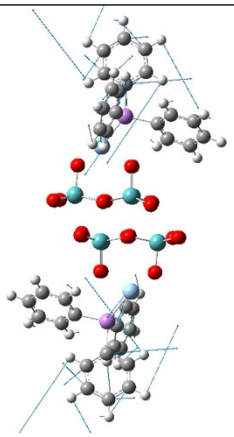
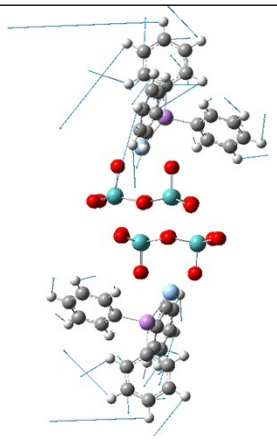
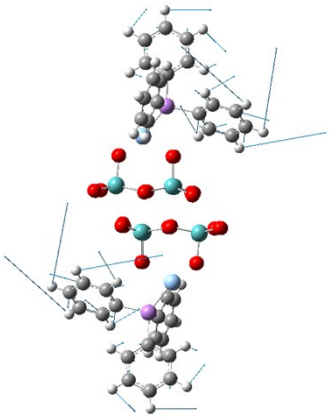
(**1**) $[Ag\{Mo_4O_{13}\}\{PPh_2Py\}]_2^{2-}$

 644 (vs) *668*	 692 (vs) *699*	 741 (m) *751*
 772 (m) *782*	 826 (s) *819*	 885 (vs) *867*
 897 (vs) *912*	 928 (s) *928 & 930*	 947 (s) *957*

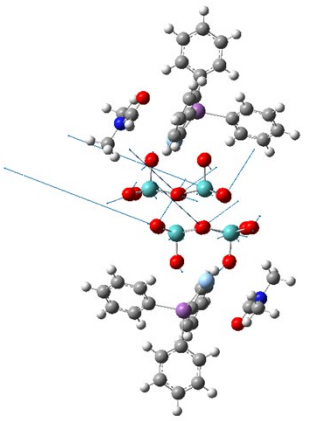
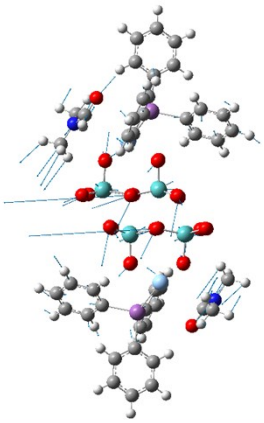
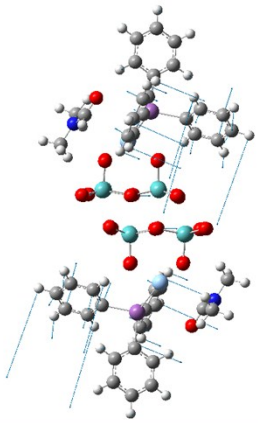
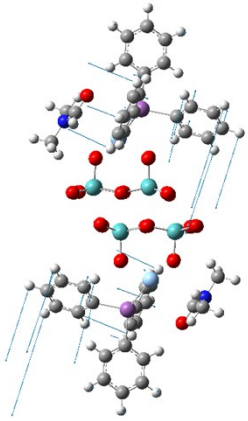
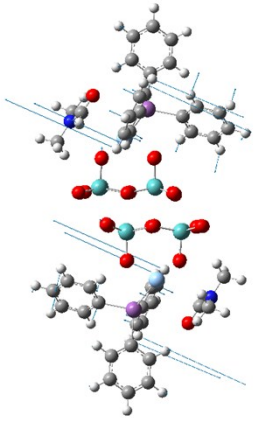
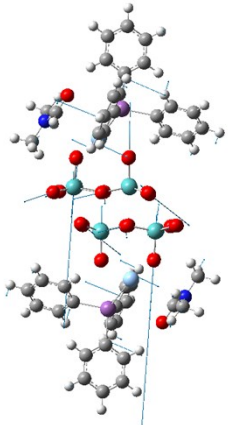
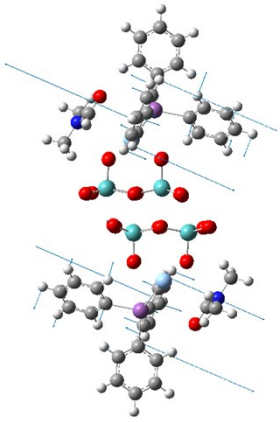
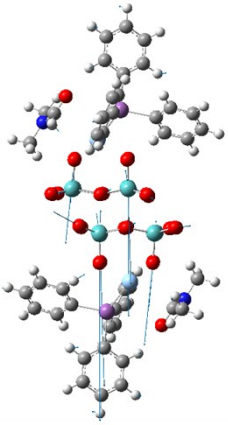
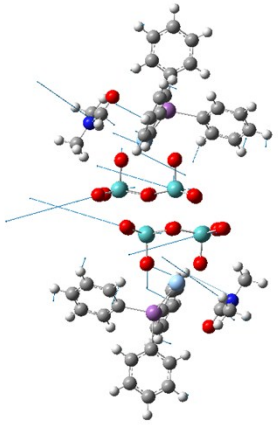
 1092 (w) *1110*	 1383 (w) *1462*	 1433 (w) *1474*
 1477 (w) *1478*	 1567 (w) *1614*	 1659 (m) *1642*

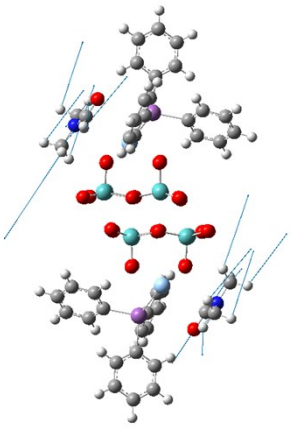
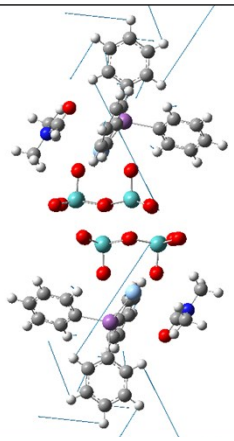
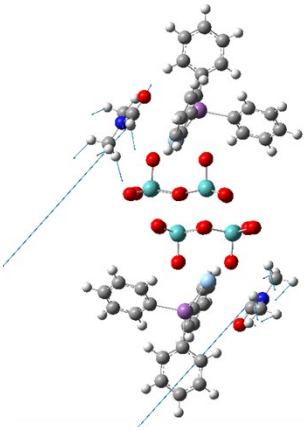
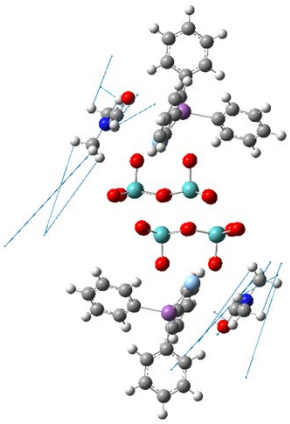
(**3**) $[Ag\{Mo_4O_{13}\}\{AsPh_3\}]_2^{2-}$

 571 (m) *568*	 648 (vs) *660*	 682 (vs) *699*
 692 (vs) *701*	 740 (m) *744*	 828 (s) *856*
 885 (vs) *911*	 897 (vs) *922*	 926 (s) *926*

 947 (s) *958*	 1089 (w) *1099*	 1248 (w) *1331*
 1434 (m) *1473*	 1483 (w) *1477*	

(**4**) $[Ag\{Mo_4O_{13}\}\{SbPh_3\}(DMF)]_2^{2-}$

		
575 (s) *574*	644 (s) *661*	679 (vs) *703*
		
731 (s) *740*	829 (s) *859*	887 (vs) *908*
		
927 (s) *928*	960 (m) *952*	997 (w) *1002*

 1066 (w) *1086*	 1378 (w) *1376*	 1431 (m) *1422*
 1478 (m) *1483*		

Part F. Non-valence contacts.

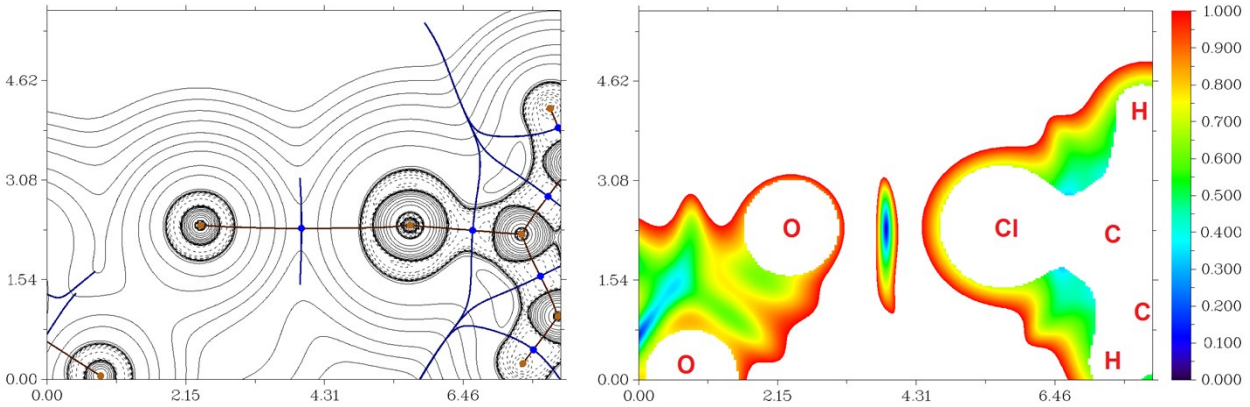


Fig. S9. Contour line diagram of the Laplacian distribution $\nabla^2\rho(r)$, bond paths and selected zero-flux surfaces (left) and RDG isosurface (right) referring to halogen bonding Cl···O in supramolecular structure of Cl. Bond critical points (3, –1) are shown in blue, nuclear critical points (3, –3) – in pale brown. Length units – Å, RDG isosurface values are given in a.u.

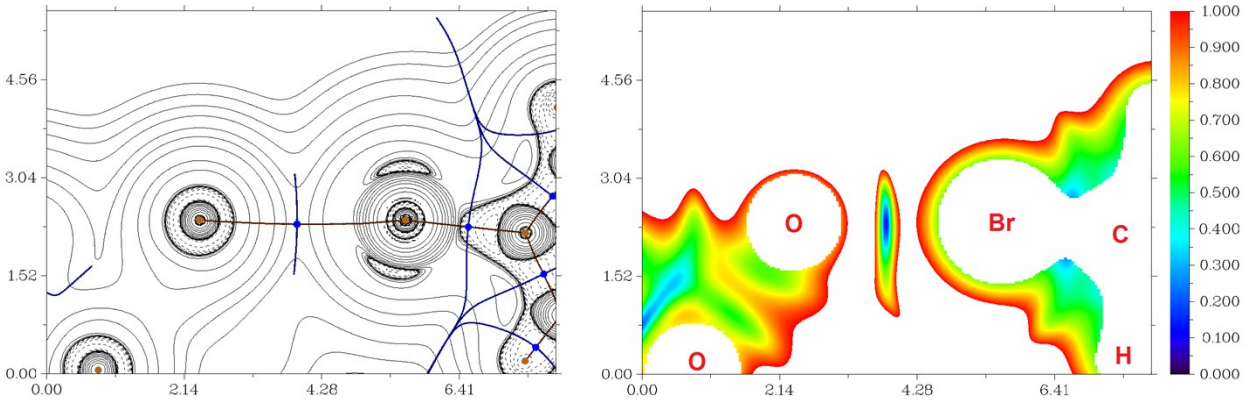


Fig. S10. Contour line diagram of the Laplacian distribution $\nabla^2\rho(r)$, bond paths and selected zero-flux surfaces (left) and RDG isosurface (right) referring to halogen bonding Br···O in supramolecular structure of Br. Bond critical points (3, –1) are shown in blue, nuclear critical points (3, –3) – in pale brown. Length units – Å, RDG isosurface values are given in a.u.

Table S9. Cartesian atomic coordinates for model supramolecular associates.

Atom	X	Y	Z
Cl			
C	2.910691	6.368480	1.503831
H	3.407103	6.417109	2.312626
C	3.426245	5.631199	0.454114
H	4.250734	5.168783	0.549532
C	2.727491	5.571210	-0.735746
H	3.048648	5.064828	-1.472542
C	1.557109	6.269789	-0.812554
C	1.093747	6.983848	0.289717
H	0.277896	7.466293	0.219161
C	-2.290675	7.581800	2.991493
H	-2.541727	6.672952	3.100898
C	-2.517302	9.878788	3.743408
H	-3.073672	10.367134	4.385757
H	-1.573891	9.974383	3.988967
H	-2.660381	10.241777	2.844802
C	-3.749607	8.046229	4.845679
H	-4.100278	8.836106	5.307326
H	-4.493527	7.521076	4.484450
H	-3.238664	7.498280	5.477356
O	3.791812	8.700880	3.662557
O	2.293243	6.499294	5.018162
N	1.758333	7.008618	1.429718
N	-2.883683	8.466150	3.760926
O	1.229650	10.341862	3.725891
O	-0.319712	8.074288	5.186602
O	-1.486667	8.570259	7.579796
O	0.079935	10.569819	6.256532
O	1.011208	7.214901	7.392491
O	1.248844	12.755150	4.919793
O	2.364994	9.173243	6.160588
O	3.559309	11.169900	5.021396
O	5.943091	9.755714	4.973694
O	4.516239	7.714743	6.194007
O	3.192544	5.497869	7.369583
O	-1.422390	7.835301	2.125038
Mo	-0.017026	8.704944	6.757270
Mo	1.559210	11.112814	5.218268
Mo	4.248223	9.350113	5.157226
Mo	2.714309	6.949790	6.617802
Ag	0.962468	8.013912	3.247521
Cl	0.635700	6.326294	-2.283237
C	4.076970	12.982720	11.971361
H	3.580559	12.934091	11.162566

C	3.561417	13.720001	13.021078
H	2.736927	14.182417	12.925661
C	4.260171	13.779990	14.210938
H	3.939014	14.286372	14.947734
C	5.430552	13.081411	14.287746
C	5.893915	12.367352	13.185476
H	6.709766	11.884907	13.256032
C	9.278337	11.769400	10.483700
H	9.529388	12.678248	10.374295
C	9.504964	9.472412	9.731784
H	10.061333	8.984066	9.089435
H	8.561552	9.376817	9.486226
H	9.648043	9.109423	10.630391
C	10.737268	11.304971	8.629513
H	11.087940	10.515094	8.167867
H	11.481189	11.830124	8.990743
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O	8.474329	10.780941	5.895397
O	6.907727	8.781381	7.218661
O	5.976453	12.136299	6.082702
O	5.738817	6.596050	8.555400
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O	3.428352	8.181300	8.453797
O	1.044570	9.595486	8.501499
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O	3.795117	13.853331	6.105610
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Ag	6.013790	8.016755	10.279012
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I	13.336713	13.098364	30.005688
C	9.972071	6.426236	15.477176
H	10.435496	6.487757	16.304047
C	10.542081	5.685644	14.454903
H	11.371091	5.241250	14.583809

C	9.885229	5.607892	13.249640
H	10.244026	5.090663	12.537888
C	8.713139	6.286282	13.090039
C	8.184347	6.987997	14.174225
H	7.351729	7.434801	14.070939
C	4.712504	7.641117	16.773246
H	4.470801	6.728732	16.873327
C	4.460091	9.905656	17.545110
H	3.900344	10.381306	18.195113
H	4.307897	10.275932	16.651138
H	5.402966	10.010894	17.787649
C	3.249693	8.066812	18.623793
H	2.893155	8.849739	19.095222
H	3.759832	7.513428	19.250874
H	2.508224	7.543849	18.254069
N	8.809229	7.050199	15.354723
N	4.114507	8.504169	17.550613
O	8.249390	12.799211	18.809536
O	7.106994	10.610676	20.122117
O	5.520040	8.611856	21.422315
O	10.590133	11.224336	18.934740
O	12.987178	9.815852	18.907222
O	11.546015	7.770186	20.100103
O	10.843883	8.770471	17.565748
O	10.219289	5.546662	21.248955
O	9.391008	9.209383	20.043692
O	9.348348	6.539366	18.890712
O	8.027984	7.245552	21.240700
O	8.273462	10.388304	17.611152
O	6.687359	8.122404	19.032427
O	5.573958	7.909363	15.910575
Mo	8.591920	11.163106	19.107412
Mo	11.284101	9.405513	19.066548
Mo	9.737150	6.991885	20.491676
Mo	6.995833	8.742285	20.613028
Ag	7.943697	8.074976	17.103318
I	7.690520	6.339736	11.270449

Part G. Single crystal x-ray diffraction analysis data

Table S10. XRD Experimental details

	(1)	(2)	(3)	(4)
Chemical formula	$C_{73}H_{117}Ag_2Mo_8N_5O_{28}P_2$	$C_{74}H_{116}Ag_2Mo_8N_4O_{28}P_2$	$C_{74}H_{116}Ag_2As_2Mo_8N_4O_{28}$	$C_{74}H_{116}Ag_2Mo_8N_4O_{28}Sb_2$
M_r	2557.91	2554.90	2642.80	2736.46
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
Temperature (K)	130	130	130	130
a, b, c (Å)	16.5619 (3), 16.8748 (2), 16.9072 (2)	13.6714 (6), 14.9284 (5), 22.8407 (10)	13.7196 (4), 15.0038 (4), 22.9225 (7)	16.9154 (8), 18.2535 (6), 16.9286 (8)
α, β, γ (°)	92.027 (1), 100.314 (1), 98.926 (1)	90, 105.875 (4), 90	90, 105.954 (3), 90	90, 118.481 (6), 90
V (Å^3)	4582.84 (11)	4483.8 (3)	4536.8 (2)	4594.4 (4)
Z	2	2	2	2
μ (mm^{-1})	1.58	1.62	2.29	2.12
Crystal size (mm)	0.18 × 0.18 × 0.18	0.32 × 0.20 × 0.08	0.32 × 0.32 × 0.06	0.33 × 0.20 × 0.20
T_{min}, T_{max}	0.980, 1.000	0.896, 1.000	0.692, 1.000	0.949, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	43858, 21452, 17765	27691, 10869, 8298	23821, 10710, 8788	18507, 10216, 8972
R_{int}	0.020	0.034	0.026	0.019
θ values (°)	θ_{max} = 29.6, θ_{min} = 3.3	θ_{max} = 29.5, θ_{min} = 3.4	θ_{max} = 29.5, θ_{min} = 3.4	θ_{max} = 29.7, θ_{min} = 3.5
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.696	0.693	0.693	0.696
Range of h, k, l	$-22 \le h \le 22$, $-23 \le k \le 21$, $-23 \le l \le 23$	$-16 \le h \le 18$, $-20 \le k \le 17$, $-31 \le l \le 20$	$-12 \le h \le 17$, $-19 \le k \le 20$, $-31 \le l \le 28$	$-15 \le h \le 23$, $-21 \le k \le 24$, $-22 \le l \le 15$
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.026, 0.058, 1.04	0.035, 0.076, 1.06	0.030, 0.067, 1.06	0.026, 0.065, 1.05
No. of reflections, parameters, restraints	21452, 1049, 0	10869, 532, 0	10710, 532, 0	10216, 516, 1
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0216P)^2 + 1.8031P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0215P)^2 + 4.8146P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0257P)^2 + 1.6793P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0273P)^2 + 4.2731P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.81, -0.75	0.70, -0.81	0.76, -0.69	1.20, -0.67

	(5)	**(6)**	**(7)**	**(8)**
Chemical formula	$C_{48}H_{94}Ag_2Cl_2Mo_8N_6O_{28}$	$C_{48}H_{94}Ag_2Br_2Mo_8N_6O_{28}$	$C_{48}H_{94}Ag_2I_2Mo_8N_6O_{28}$	$C_{42}H_{84}Ag_2Mo_8N_6O_{26}$
M_r	2257.45	2346.37	2440.35	2072.41
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Orthorhombic, *Pbca*
Temperature (K)	130	130	130	150
a, *b*, *c* (Å)	13.8548 (7), 19.3512 (6), 15.1241 (8)	13.8102 (16), 19.3590 (7), 15.2005 (11)	13.8249 (8), 19.4381 (7), 15.3544 (9)	16.7622 (8), 16.3030 (7), 23.5350 (9)
α, β, γ (°)	90, 117.004 (7), 90	90, 116.826 (12), 90	90, 116.353 (7), 90	90, 90, 90
V (Å^3)	3612.8 (4)	3626.5 (6)	3697.4 (4)	6431.5 (5)
Z	2	2	2	4
μ (mm^{-1})	2.02	3.04	2.74	2.18
Crystal size (mm)	0.26 × 0.26 × 0.04	0.40 × 0.30 × 0.08	0.25 × 0.20 × 0.05	0.30 × 0.30 × 0.03
T_{min}, T_{max}	0.838, 1.000	0.806, 1.000	0.737, 1.000	0.444, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	20290, 8361, 6888	21463, 8647, 6075	22107, 8581, 7258	32403, 7926, 6130
R_{int}	0.030	0.054	0.030	0.050
θ values (°)	θ_{max} = 29.5, θ_{min} = 3.4	θ_{max} = 29.6, θ_{min} = 1.8	θ_{max} = 29.5, θ_{min} = 2.0	θ_{max} = 29.5, θ_{min} = 2.0
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.693	0.695	0.692	0.693
Range of *h*, *k*, *l*	$-17 \le h \le 16$, $-26 \le k \le 18$, $-13 \le l \le 20$	$-18 \le h \le 19$, $-25 \le k \le 24$, $-20 \le l \le 19$	$-18 \le h \le 19$, $-19 \le k \le 26$, $-14 \le l \le 20$	$-22 \le h \le 15$, $-22 \le k \le 20$, $-32 \le l \le 23$
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.036, 0.086, 1.04	0.044, 0.082, 1.02	0.036, 0.097, 1.05	0.038, 0.091, 1.11
No. of reflections, parameters, restraints	8361, 424, 0	8647, 424, 0	8581, 424, 0	7926, 379, 0
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0359P)^2 + 6.721P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0213P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0453P)^2 + 9.204P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0326P)^2 + 9.3863P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.93, -1.54	0.93, -0.83	2.94, -2.19	1.05, -1.03

	(10)	(11)	(12)
Chemical formula	$C_{54}H_{108}Ag_2Mo_8N_6O_{28}$	$C_{45}H_{93}Ag_2Mo_8N_9O_{27}$	$C_{52}H_{70}Ag_2Mo_6N_8O_{25}P_2$
M_r	2272.72	2175.54	2060.48
Crystal system, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
Temperature (K)	150	130	130
a, *b*, *c* (Å)	14.1580 (4), 14.8963 (5), 19.5225 (6)	13.0475 (5), 16.5992 (6), 17.9506 (7)	11.3665 (4), 12.0432 (4), 12.7074 (4)
α, β, γ (°)	88.701 (2), 71.414 (3), 82.710 (2)	88.636 (3), 74.794 (4), 68.719 (4)	94.658 (3), 90.989 (3), 95.871 (3)
V (Å^3)	3870.4 (2)	3484.7 (3)	1724.09 (10)
Z	2	2	1
μ (mm^{-1})	1.82	2.02	1.74
Crystal size (mm)	0.27 × 0.27 × 0.03	0.15 × 0.08 × 0.06	0.22 × 0.20 × 0.12
T_{min}, T_{max}	0.728, 1.000	0.954, 1.000	0.922, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	34496, 18050, 13890	31154, 16091, 9159	13177, 7909, 7078
R_{int}	0.032	0.045	0.018
θ values (°)	θ_{max} = 29.5, θ_{min} = 2.0	θ_{max} = 29.6, θ_{min} = 3.3	θ_{max} = 29.4, θ_{min} = 3.5
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.693	0.694	0.691
Range of *h*, *k*, *l*	$-15 \le h \le 19$, $-13 \le k \le 19$, $-24 \le l \le 26$	$-15 \le h \le 16$, $-16 \le k \le 21$, $-22 \le l \le 21$	$-14 \le h \le 14$, $-13 \le k \le 15$, $-15 \le l \le 12$
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.036, 0.077, 1.01	0.058, 0.130, 0.96	0.024, 0.056, 1.06
No. of reflections, parameters, restraints	18050, 883, 12	16091, 793, 24	7909, 431, 1
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0251P)^2 + 0.957P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0514P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0215P)^2 + 0.4633P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.33, -0.92	1.51, -2.10	0.82, -0.57

Computer programs: *CrysAlis PRO* 1.171.38.41 (Rigaku OD, 2015), *SHELXS2014* (Sheldrick, 2014), *SHELXL2014* (Sheldrick, 2014), ShelXle (Hübschle, 2011), CIFTAB-2014 (Sheldrick, 2014).

Part H. Chromatography and ESI-MS data.

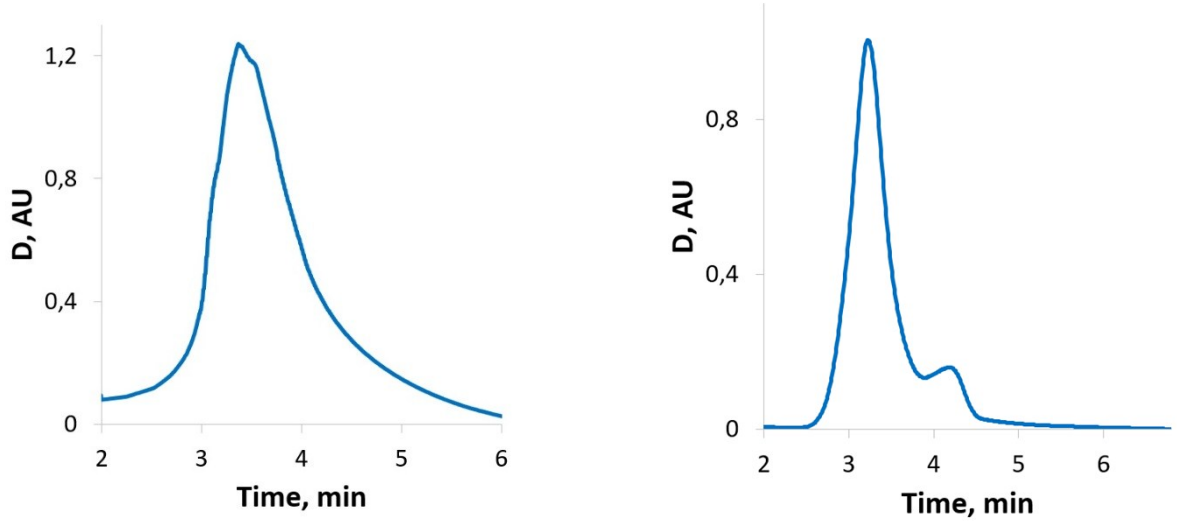

Fig. S11. HPLC-UV chromatograms of $(NBu_4)_4[\beta\text{-}Mo_8O_{26}]$ solutions: fresh (left) and aged (right).

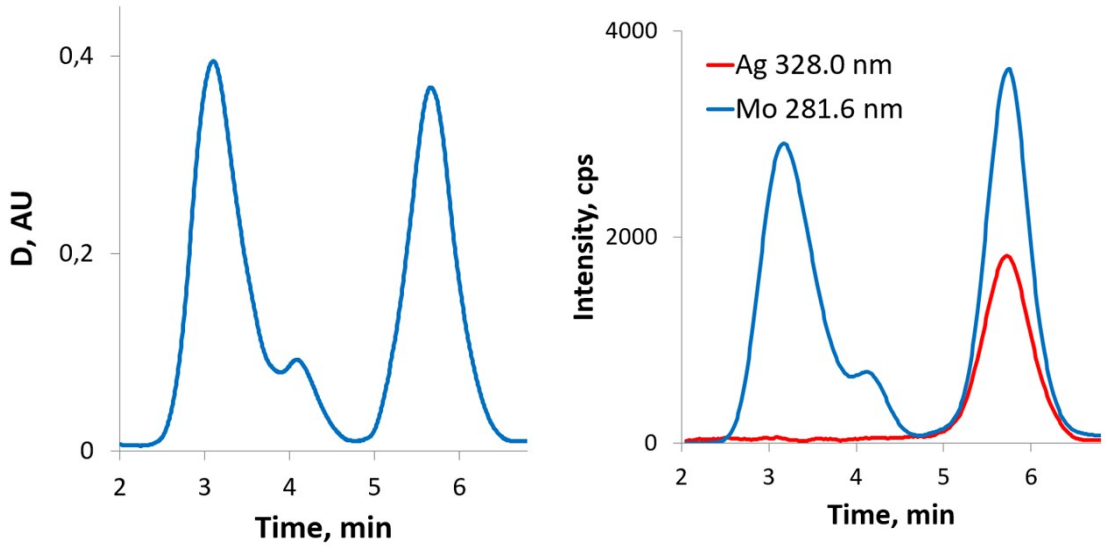

Fig. S12. HPLC-UV (left) and HPLC-ICP-AES (right) chromatograms for 1.

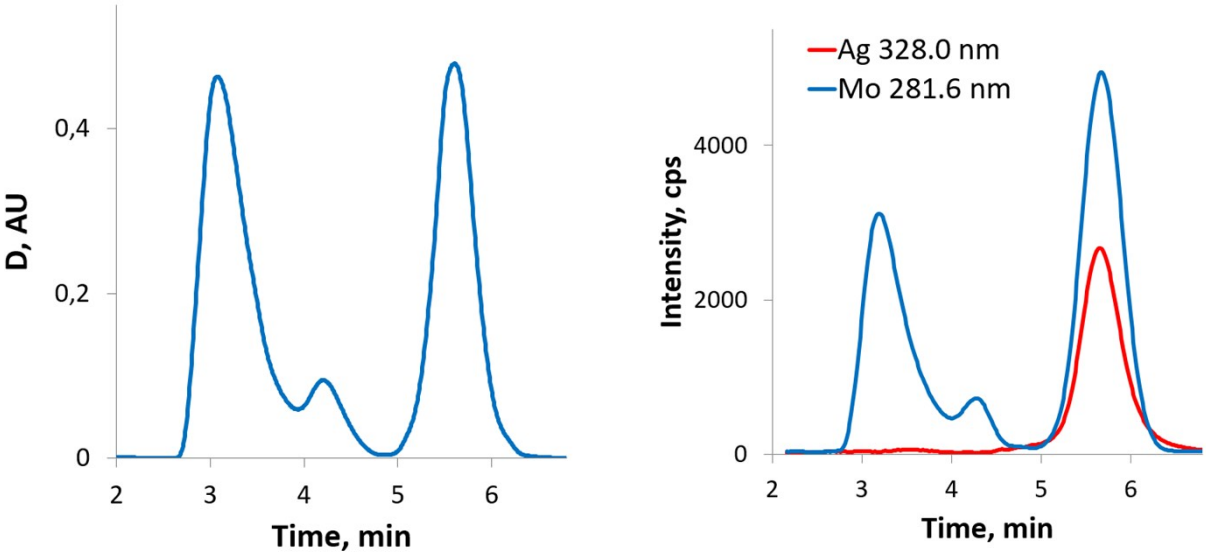

Fig. S13. HPLC-UV (left) and HPLC-ICP-AES (right) chromatograms for 2.

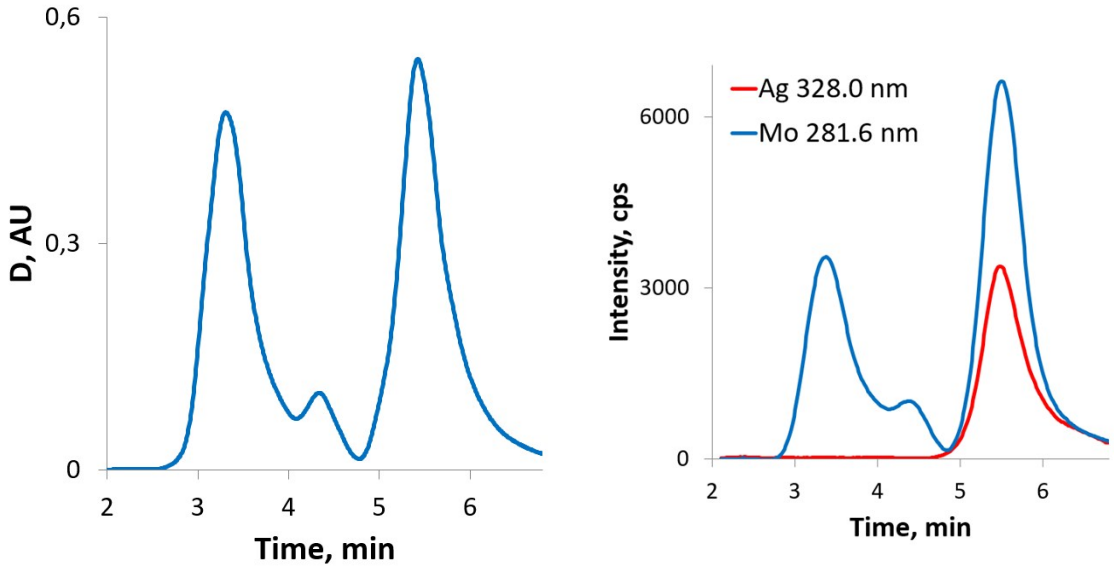

Fig. S14. HPLC-UV (left) and HPLC-ICP-AES (right) chromatograms for 3.

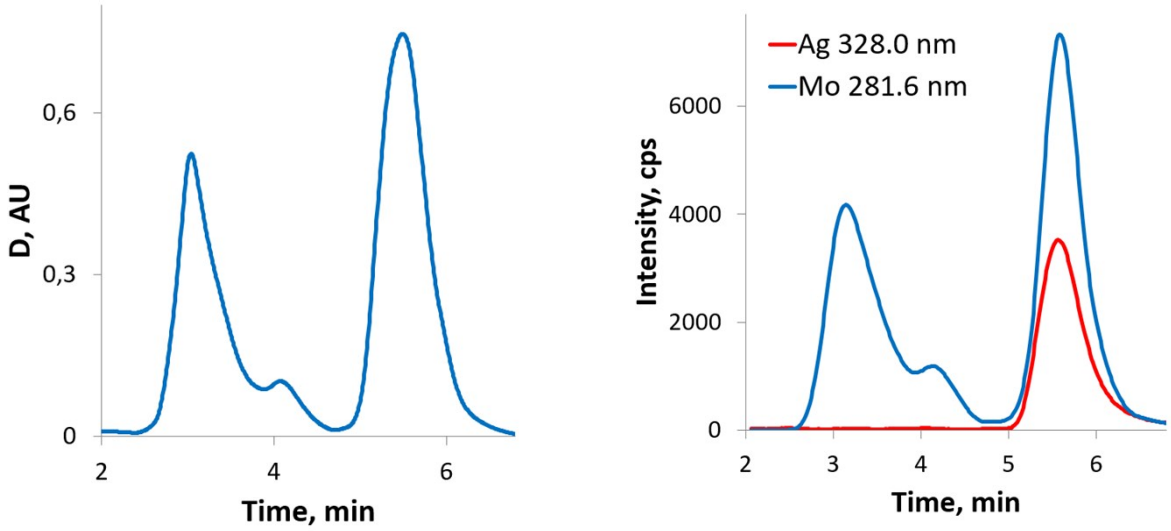

Fig. S15. HPLC-UV (left) and HPLC-ICP-AES (right) chromatograms for 4.

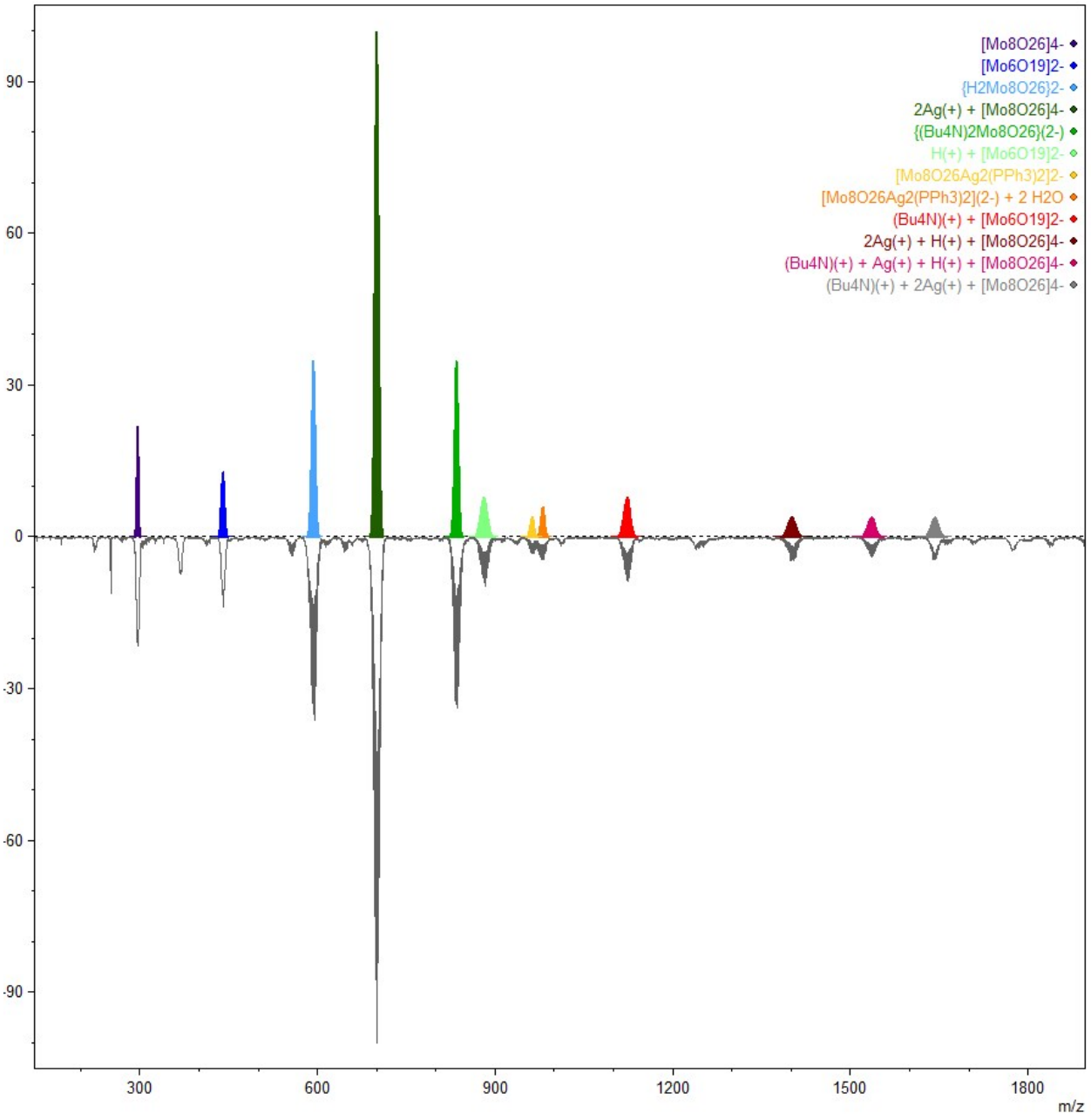

Fig. S16. Full ESI-MS spectrum of 1 in CH_3CN. Experimental peaks have negative intensities, calculated data have positive intensity.

Table S11. Peak assignment for the spectrum of 1 in CH_3CN.

assignment	exp	calc
$[Mo_8O_{26}]^{4-}$	296.0	295.9
$[Mo_6O_{19}]^{2-}$	439.9	439.8
$2H^+ + [Mo_8O_{26}]^{4-}$	592.6	592.7
$2Ag^+ + [Mo_8O_{26}]^{4-}$	699.6	699.6
$(Bu_4N)^+ + [Mo_8O_{26}]^{4-}$	834.3	834.2
$H^+ + [Mo_6O_{19}]^{2-}$	880.7	880.6
$[Mo_8O_{26}Ag_2(PPh_3)_2]^{2-}$	961.9	961.8
$[Mo_8O_{26}Ag_2(PPh_3)_2]^{2-} + 2H_2O$	979.7	979.9
$(Bu_4N)^+ + [Mo_6O_{19}]^{2-}$	1122.0	1122.0
$2Ag^+ + H^+ + [Mo_8O_{26}]^{4-}$	1400.2	1400.2
$(Bu_4N)^+ + Ag^+ + H^+ + [Mo_8O_{26}]^{4-}$	1534.9	1534.8
$(Bu_4N)^+ + 2Ag^+ + [Mo_8O_{26}]^{4-}$	1641.7	1641.6

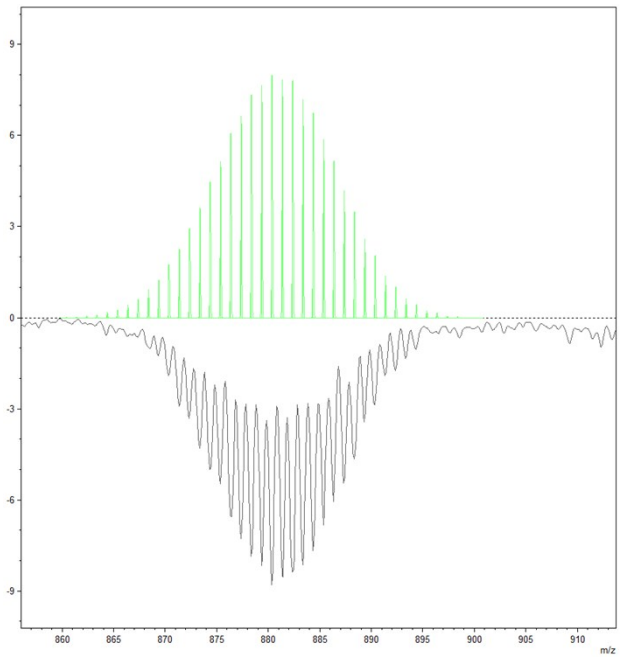

Fig. S17. Comparison of calculated (positive intensity) and observed (negative intensity) isotopic patterns for $\{H^+ + [Mo_6O_{19}]^{2-}\}$ peak.

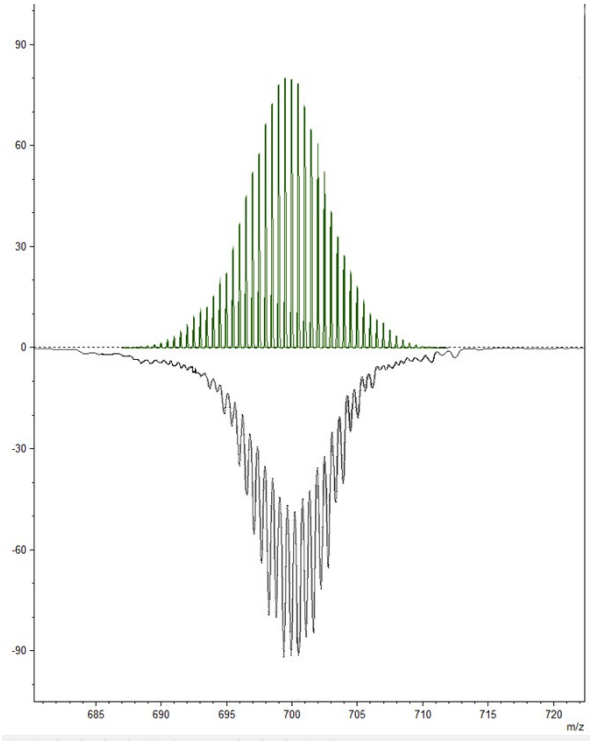

Fig. S18. Comparison of calculated (positive intensity) and observed (negative intensity) isotopic patterns for $\{2Ag^+ + [Mo_8O_{26}]^{4-}\}$ peak.

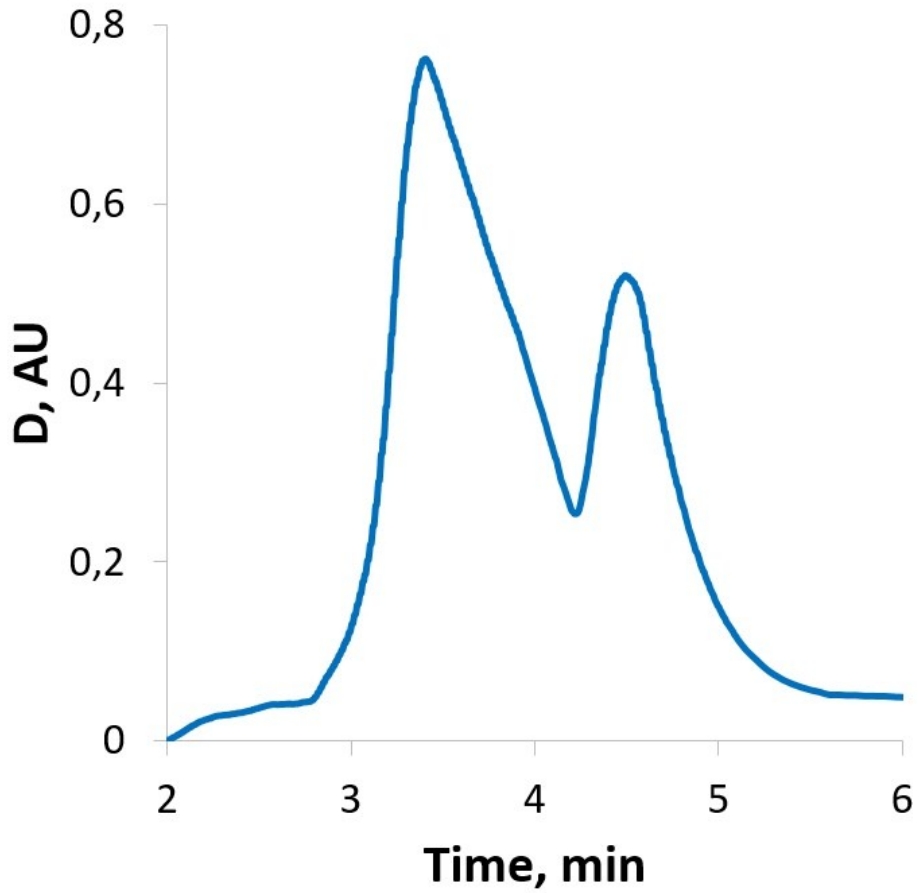

Fig. S19. The HPLC-UV chromatogram of the specially prepared mixture of $(Bu_4N)_4[\beta\text{-}Mo_8O_{26}]$ (the first peak) and $(Bu_4N)_2[Mo_6O_{19}]$ in CH_3CN.