<Supporting Information>

Construction of Polyoxometalate-based Inorganic-organic Compounds Using Silver(I) Double-Helicates as Secondary Building Blocks

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Figure S8. XPS for Mo(VI) in compound **2**.

Figure S9. The emission spectra of compound **1** (red, λ_{ex} = 220 nm), ligand L^1 (blue, λ_{ex} = 220 nm) and $[Ag_2L^1_2](NO_3)_2$ (black, λ_{ex} = 220 nm) in solid state at room temperature.

Figure S10. The emission spectra of compound **2** (red, λ_{ex} = 220 nm), ligand L^2 (blue, λ_{ex} = 220 nm) and $[Ag_2L^2_2](NO_3)_2$ (black, λ_{ex} = 220 nm) in solid state at room temperature.

Figure S11. (a) The X-ray powder diffraction (XPD) pattern of the bulk samples (a) and that calculated from the single-crystal diffraction data of **1** (b).

Experimental Section

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. The elemental analyses of C, H and N were performed on a Perkin-Elmer 2400 II elemental analyzer. Elemental analyses (P, Mo, and Ag) were determined by a Leaman inductively coupled plasma (ICP) spectrometer. IR spectra were recorded in KBr pellets with a Nicolet 170 SXFT-IR spectrophotometer in the 4000 ~ 400 cm^{-1} region. The luminescent spectra were performed on a Hitachi F-7000 fluorescence spectrophotometer. The luminescent spectra were performed on a Hitachi F-7000 fluorescence spectrophotometer. XPS analyses were performed on a PHI5000 VersaProbe spectrometer with an Al Kα ($h\nu$ = 1486.7 eV) achromatic X-ray source. N2 adsorption was measured on an ASAP 2020 gas-adsorption apparatus at liquid-nitrogen (77 K) temperature. The crystalline phase of **1** was identified by powder X-ray diffraction (XRD) using a Philips X'Pert Pro Super diffractometer with graphite monochromatized Cu Kα radiation (λ= 1.541 78 A;).

***Synthesis of* 1:** A solution of the L^1 (0.036 g, 0.1 mmol) and $AgNO_3$ (0.057 g, 0.4 mmol) in CH_3OH (6 mL) was slowly layered onto a solution of $H_3PMoO_{40}\cdot xH_2O$ (0.18 g) in DMF (4mL). The solutions were left in darkness at room temperature for two weeks to give brown block crystals in 46% yields (based on $H_3PMoO_{40}\cdot xH_2O$). Anal. Calcd for $C_{303}H_{257}Ag_{12}Mo_{48}N_{53}O_{168}P_4$: C, 27.26; H, 1.94; N, 5.56; P, 0.93; Mo, 34.49; Ag, 9.69%. Found: C, 27.17; H, 1.86; N, 5.63; P, 0.89; Mo, 34.42; Ag, 9.75%. IR (KBr): υ(Mo-Oc) (808 cm^{-1}), υ(Mo-Ob) (877 cm^{-1}), υ(Mo-O_d) (955 cm^{-1}), υ(C=N) (1061 cm^{-1}).

***Synthesis of* 2:** A solution of $H_3PMoO_{40}\cdot xH_2O$ (0.18 g) in CH_3OH (6 mL) was slowly layered onto a solution of the L^2 (0.024 g, 0.1 mmol) and $AgNO_3$ (0.057 g, 0.4 mmol) in DMF (4mL). The solutions were left in darkness at room temperature for one week to give yellow block crystals in 58% yields (based on $H_3PMoO_{40}\cdot xH_2O$). Anal. Calcd for $C_{56}H_{63}Ag_4Mo_{12}N_{16}O_{44}P$: C, 20.52; H, 1.94; N, 6.84; P, 0.94; Mo, 35.12; Ag, 13.16%. Found: C, 20.59; H, 1.89; N, 6.75; P, 0.90; Mo, 35.17; Ag, 13.23%. IR (KBr): υ(Mo-Oc) (805 cm^{-1}), υ(Mo-Ob) (875 cm^{-1}), υ(Mo-O_d) (954 cm^{-1}), υ(C=N) (1060 cm^{-1}).

Table S1. Summary of data collections and structure refinements for compounds **1** and **2**

Compound	1	2
Chemical formula	$C_{303}H_{257}Ag_{12}Mo_{48}N_{53}O_{168}P_4$	$C_{56}H_{63}Ag_4Mo_{12}N_{16}O_{44}P$
Formula weight	13352.06	3277.90
Crystal system	Triclinic	Triclinic
Space group	*P*1	*P*1
T/K	273(2)	273(2)
λ/Å	0.71073	0.71073
a /Å	14.990(1)	11.382 (1)
b /Å	18.055(1)	15.464(2)
c /Å	45.102(2)	15.891(2)
α /º	97.67(1)	112.08(1)
β /º	91.76(1)	105.53(1)
γ /º	100.22(1)	104.10(1)
V /Å^3	11887.2(11)	2304.1(4)
Z	1	1
Dc /g cm^{-3}	1.865	2.357
μ /mm^{-1}	1.791	2.512
F(000)	6430	1563
Measured refls.	139381	20876
Independent refls.	41744	8072
No. of parameters	2741	633
GOF	1.070	1.038
R indices [$I > 2\sigma(I)$]: *R*1, *wR*2	0.0869, 0.1721	0.0604, 0.1471
R indices (all data): *R*1, *wR*2	0.2034, 0.1975	0.1088, 0.1646

Table S2. Selected bond lengths (Å) for compound **1**

bond	length	bond	length
P(1)–O(37)	1.533(7)	P(1)–O(38)	1.515(8)
P(1)–O(39)	1.526(8)	P(1)–O(40)	1.531(8)
P(1)–O(37')	1.592(16)	P(1)–O(38')	1.599(16)
P(1)–O(39')	1.599(16)	P(1)–O(40')	1.596(16)
Mo(1)–O(1)	1.647(9)	Mo(1)–O(13)	1.863(11)
Mo(1)–O(14)	1.803(11)	Mo(1)–O(15)	1.961(11)
Mo(1)–O(16)	2.011(10)	Mo(1)–O(37)	2.408(10)
Mo(1)–O(38')	2.55(3)	Mo(2)–O(2)	1.654(10)
Mo(2)–O(15)	1.839(9)	Mo(2)–O(17)	2.041(11)
Mo(2)–O(18)	1.975(9)	Mo(2)–O(19)	1.844(9)
Mo(2)–O(38)	2.451(10)	Mo(2)–O(38')	2.33(3)
Mo(3)–O(3)	1.654(9)	Mo(3)–O(16)	1.851(10)
Mo(3)–O(20)	1.817(10)	Mo(3)–O(21)	2.020(10)
Mo(3)–O(22)	1.968(9)	Mo(3)–O(37)	2.487(10)
Mo(3)–O(40')	2.49(2)	Mo(4)–O(4)	1.671(9)
Mo(4)–O(19)	2.002(10)	Mo(4)–O(20)	1.997(9)
Mo(4)–O(23)	1.792(10)	Mo(4)–O(24)	1.827(8)
Mo(4)–O(38)	2.458(10)	Mo(4)–O(40')	2.40(2)
Mo(5)–O(5)	1.669(9)	Mo(5)–O(18)	1.872(10)
Mo(5)–O(24)	2.006(9)	Mo(5)–O(25)	1.825(10)
Mo(5)–O(27)	1.972(10)	Mo(5)–O(38)	2.505(10)
Mo(5)–O(39')	2.36(2)	Mo(6)–O(6)	1.670(9)
Mo(6)–O(22)	1.807(9)	Mo(6)–O(23)	1.989(10)
Mo(6)–O(26)	1.868(10)	Mo(6)–O(28)	1.984(9)
Mo(6)–O(39)	2.431(10)	Mo(6)–O(40')	2.50(3)
Mo(7)–O(7)	1.659(8)	Mo(7)–O(27)	1.810(10)
Mo(7)–O(28)	1.836(9)	Mo(7)–O(29)	1.974(9)
Mo(7)–O(30)	1.983(9)	Mo(7)–O(39)	2.454(10)
Mo(7)–O(39')	2.48(3)	Mo(8)–O(8)	1.665(9)
Mo(8)–O(26)	1.973(10)	Mo(8)–O(29)	1.845(9)
Mo(8)–O(31)	1.839(9)	Mo(8)–O(32)	1.976(8)
Mo(8)–O(39)	2.453(10)	Mo(8)–O(37')	2.47(3)
Mo(9)–O(9)	1.676(9)	Mo(9)–O(25)	1.968(10)
Mo(9)–O(30)	1.807(9)	Mo(9)–O(33)	1.818(9)

Mo(9)–O(35)	2.007(11)	Mo(9)–O(40)	2.481(10)
Mo(9)–O(39')	2.52(3)	Mo(10)–O(10)	1.657(10)
Mo(10)–O(31)	1.967(9)	Mo(10)–O(33)	1.984(9)
Mo(10)–O(34)	1.812(9)	Mo(10)–O(36)	1.806(10)
Mo(10)–O(40)	2.413(10)	Mo(10)–O(37')	2.44(3)
Mo(11)–O(11)	1.665(9)	Mo(11)–O(13)	1.956(10)
Mo(11)–O(21)	1.837(10)	Mo(11)–O(32)	1.815(9)
Mo(11)–O(34)	1.999(9)	Mo(11)–O(37)	2.463(9)
Mo(11)–O(37')	2.48(3)	Mo(12)–O(12)	1.659(9)
Mo(12)–O(14)	1.989(10)	Mo(12)–O(17)	1.767(11)
Mo(12)–O(35)	1.825(10)	Mo(12)–O(36)	2.012(10)
Mo(12)–O(40)	2.473(11)	Mo(12)–O(38')	2.51(3)
P(2)–O(59)	1.517(11)	P(2)–O(60)	1.502(10)
P(2)–O(61)	1.506(11)	P(2)–O(62)	1.492(10)
Mo(13)–O(41)	1.680(13)	Mo(13)–O(47)	1.861(11)
Mo(13)–O(48)	1.936(12)	Mo(13)–O(49)	1.961(12)
Mo(1)–O(53A)	1.847(11)	Mo(13)–O(61A)	2.443(19)
Mo(13)–O(62A)	2.466(17)	Mo(14)–O(42)	1.661(11)
Mo(14)–O(49)	1.834(14)	Mo(14)–O(50)	1.877(13)
Mo(14)–O(51)	1.855(10)	Mo(14)–O(58A)	1.937(12)
Mo(14)–O(59)	2.492(16)	Mo(15)–O(43)	1.656(12)
Mo(15)–O(50)	1.891(12)	Mo(15)–O(52)	1.862(11)
Mo(15)–O(53)	1.930(11)	Mo(15)–O(54)	1.941(10)
Mo(15)–O(59)	2.446(16)	Mo(15)–O(62)	2.600(16)
Mo(16)–O(44)	1.645(10)	Mo(16)–O(51)	1.929(11)
Mo(16)–O(54)	1.829(11)	Mo(16)–O(55)	1.961(13)
Mo(16)–O(56)	1.854(11)	Mo(16)–O(59)	2.461(15)
Mo(16)–O(60)	2.547(16)	Mo(17)–O(45)	1.650(10)
Mo(17)–O(47A)	1.911(12)	Mo(17)–O(56)	1.918(11)
Mo(17)–O(57)	1.883(13)	Mo(17)–O(58)	1.856(11)
Mo(17)–O(60)	2.490(16)	Mo(17)–O(61)	2.417(16)
Mo(18)–O(46)	1.658(10)	Mo(18)–O(48)	1.858(12)
Mo(18)–O(52A)	1.924(11)	Mo(18)–O(55)	1.842(12)
Mo(18)–O(57)	1.918(12)	Mo(18)–O(60)	2.417(16)
Mo(18)–O(62A)	2.414(14)	P(3)–O(83)	1.484(9)
P(3)–O(84)	1.502(10)	P(3)–O(81)	1.527(10)
P(3)–O(82)	1.529(10)	Mo(19)–O(63)	1.670(10)

Mo(19)–O(69)	1.884(12)	Mo(19)–O(70)	1.921(12)
Mo(19)–O(71)	1.877(11)	Mo(19)–O(75B)	1.908(11)
Mo(19)–O(82B)	2.422(16)	Mo(19)–O(84)	2.565(15)
Mo(20)–O(64)	1.650(10)	Mo(20)–O(70)	1.878(11)
Mo(20)–O(72)	1.906(11)	Mo(20)–O(77)	1.921(10)
Mo(20)–O(80)	1.869(9)	Mo(20)–O(83)	2.383(15)
Mo(20)–O(84)	2.376(13)	Mo(21)–O(65)	1.664(10)
Mo(21)–O(71)	1.906(11)	Mo(21)–O(72)	1.893(11)
Mo(21)–O(73)	1.897(11)	Mo(21)–O(79B)	1.921(11)
Mo(21)–O(81)	2.476(15)	Mo(21)–O(84)	2.521(14)
Mo(22)–O(66)	1.664(9)	Mo(22)–O(73)	1.890(11)
Mo(22)–O(74)	1.892(13)	Mo(22)–O(75)	1.882(11)
Mo(22)–O(76)	1.944(12)	Mo(22)–O(81)	2.587(15)
Mo(22)–O(82)	2.587(16)	Mo(23)–O(67)	1.667(11)
Mo(23)–O(69B)	1.886(10)	Mo(23)–O(76)	1.868(10)
Mo(23)–O(77)	1.878(10)	Mo(23)–O(78)	1.914(10)
Mo(23)–O(82)	2.396(14)	Mo(23)–O(83)	2.543(15)
Mo(24)–O(68)	1.675(9)	Mo(24)–O(74B)	1.914(11)
Mo(24)–O(78)	1.869(10)	Mo(24)–O(79)	1.835(11)
Mo(24)–O(80)	1.907(10)	Mo(24)–O(81B)	2.372(14)
Mo(24)–O(83)	2.598(15)	Ag(1)–N(1)	2.232(15)
Ag(1)–N(2)	2.539(16)	Ag(1)–N(5)	2.240(14)
Ag(1)–N(6)	2.409(14)	Ag(2)–N(3)	2.506(15)
Ag(2)–N(4)	2.236(12)	Ag(2)–N(7)	2.475(13)
Ag(2)–N(8)	2.233(12)	Ag(3)–N(9)	2.160(11)
Ag(3)–N(10)	2.543(12)	Ag(3)–N(15)	2.422(12)
Ag(3)–N(16)	2.232(13)	Ag(4)–N(11)	2.478(11)
Ag(4)–N(12)	2.251(11)	Ag(4)–N(13)	2.167(12)
Ag(4)–N(14)	2.575(12)	Ag(5)–N(19)	2.397(11)
Ag(5)–N(20)	2.251(12)	Ag(5)–N(21)	2.202(13)
Ag(5)–N(22)	2.544(12)	Ag(6)–N(17)	2.229(10)
Ag(6)–N(18)	2.469(11)	Ag(6)–N(23)	2.481(11)
Ag(6)–N(24)	2.238(11)		

Symmetry codes: A, – 2 – *x*, – *y*, – *z*; B, – *x*, – *y*, 1 – *z*;

Table S3. Selected bond angles (°) for compound **1**

bond angle	degree	bond angle	degree
N(1)–Ag(1)–N(5)	163.5(6)	N(1)–Ag(1)–N(6)	125.1(4)
N(5)–Ag(1)–N(6)	70.1(5)	N(1)–Ag(1)–N(2)	68.8(6)
N(5)–Ag(1)–N(2)	108.2(5)	N(6)–Ag(1)–N(2)	89.4(5)
N(8)–Ag(2)–N(4)	163.8(5)	N(8)–Ag(2)–N(7)	70.4(4)
N(4)–Ag(2)–N(7)	120.1(4)	N(8)–Ag(2)–N(3)	123.0(4)
N(4)–Ag(2)–N(3)	71.5(5)	N(7)–Ag(2)–N(3)	89.1(5)
N(9)–Ag(3)–N(16)	152.1(5)	N(9)–Ag(3)–N(15)	135.7(5)
N(16)–Ag(3)–N(15)	71.3(5)	N(9)–Ag(3)–N(10)	69.7(4)
N(16)–Ag(3)–N(10)	108.4(4)	N(15)–Ag(3)–N(10)	92.2(4)
N(13)–Ag(4)–N(12)	160.3(4)	N(13)–Ag(4)–N(11)	129.0(4)
N(12)–Ag(4)–N(11)	70.3(4)	N(13)–Ag(4)–N(14)	71.3(4)
N(12)–Ag(4)–N(14)	108.9(4)	N(11)–Ag(4)–N(14)	89.8(4)
N(21)–Ag(5)–N(20)	161.8(5)	N(21)–Ag(5)–N(19)	127.9(4)
N(20)–Ag(5)–N(19)	70.1(4)	N(21)–Ag(5)–N(22)	68.6(5)
N(20)–Ag(5)–N(22)	112.1(4)	N(19)–Ag(5)–N(22)	91.7(4)
N(17)–Ag(6)–N(24)	166.9(4)	N(17)–Ag(6)–N(18)	69.3(4)
N(24)–Ag(6)–N(18)	120.7(4)	N(17)–Ag(6)–N(23)	120.3(4)
N(24)–Ag(6)–N(23)	70.4(4)	N(18)–Ag(6)–N(23)	88.1(4)

Table S4. Hydrogen bond parameters (Å, °) of compound **1**

D–H···A	D(D–H)	d(H···A)	d(D···A)	∠(DHA)	Symmetry transformation for A
C(1)–H(1A)···O(52)	0.93	2.51	3.20(2)	131	
C(9)–H(9A)···O(44)	0.93	2.53	3.29(3)	139	$1 + x, y, z$
C(113)–H(11D)···O(88)	0.93	2.51	3.41(3)	163	
C(118)–H(11H)···O(1)	0.93	2.39	3.30(2)	163	$1 + x, y, z$
C(119)–H(11I)···O(66)	0.93	2.60	3.22(2)	125	$1 - x, 1 - y, 1 - z$
C(12)–H(12A)···N(3)	0.93	2.41	2.80(3)	105	
C(132)–H(13C)···N(23)	0.93	2.50	2.88(2)	105	
C(138)–H(13G)···O(3)	0.93	2.54	3.44(3)	162	$1 + x, y, z$
C(146)–H(14F)···O(85)	0.96	2.03	2.51(5)	108	
C(149)–H(14M)···O(86)	0.96	2.27	2.70(5)	107	
C(150)–H(15C)···O(65)	0.96	2.45	3.40(3)	169	
C(23)–H(23A)···O(11)	0.93	2.51	3.33(2)	148	
C(26)–H(26A)···O(44)	0.93	2.50	3.07(3)	119	
C(27)–H(27A)···O(7)	0.93	2.35	3.24(3)	161	$-1 + x, y, z$
C(39)–H(39A)···N(6)	0.93	2.42	2.85(2)	108	
C(59)–H(59A)···O(24)	0.93	2.45	3.255(19)	145	
C(59)–H(59A)···O(27)	0.93	2.46	3.24(2)	142	
C(60)–H(60A)···O(7)	0.93	2.56	3.45(2)	160	
C(60)–H(60A)···N(11)	0.93	2.47	2.89(2)	108	
C(65)–H(65A)···O(48)	0.93	2.43	3.31(4)	158	$1 + x, y, z$
C(83)–H(83A)···O(15)	0.93	2.51	3.42(2)	164	$x, -1 + y, z$
C(84)–H(84A)···O(1)	0.93	2.23	2.965(18)	135	$x, -1 + y, z$
C(84)–H(84A)···N(15)	0.93	2.50	2.90(2)	106	
C(87)–H(87A)···O(63)	0.93	2.25	3.11(2)	153	
C(99)–H(99A)···O(75)	0.93	2.36	3.18(2)	148	$-x, 1 - y, 1 - z$

Table S5. Selected bond lengths (Å) for compound **2**

bond	length	bond	length
P(1)–O(19)	1.513(11)	P(1)–O(20)	1.527(11)
P(1)–O(21)	1.516(11)	P(1)–O(22)	1.589(11)
Mo(1)–O(1)	1.637(7)	Mo(1)–O(8)	1.827(8)
Mo(1)–O(10)	1.852(8)	Mo(1)–O(7)	1.933(8)
Mo(1)–O(9)	1.934(8)	Mo(1)–O(21A)	2.458(12)
Mo(1)–O(20)	2.467(11)	Mo(2)–O(2)	1.654(7)
Mo(2)–O(12)	1.839(8)	Mo(2)–O(11)	1.859(9)
Mo(2)–O(10)	1.934(9)	Mo(2)–O(18A)	1.950(9)
Mo(2)–O(22A)	2.439(11)	Mo(2)–O(21A)	2.495(12)
Mo(3)–O(3)	1.642(7)	Mo(3)–O(13)	1.858(7)
Mo(3)–O(9)	1.865(8)	Mo(3)–O(12)	1.924(8)
Mo(3)–O(15)	1.938(8)	Mo(3)–O(21A)	2.466(12)
Mo(3)–O(19)	2.474(11)	Mo(4)–O(4)	1.663(7)
Mo(4)–O(14)	1.843(9)	Mo(4)–O(7A)	1.845(8)
Mo(4)–O(11)	1.919(8)	Mo(4)–O(16)	1.949(8)
Mo(4)–O(22A)	2.423(11)	Mo(4)–O(20A)	2.470(12)
Mo(5)–O(5)	1.648(7)	Mo(5)–O(16)	1.825(8)
Mo(5)–O(15)	1.849(8)	Mo(5)–O(8A)	1.941(8)
Mo(5)–O(17)	1.944(7)	Mo(5)–O(20A)	2.452(12)
Mo(5)–O(19)	2.472(11)	Mo(6)–O(6)	1.654(7)
Mo(6)–O(18)	1.844(8)	Mo(6)–O(17)	1.865(7)
Mo(6)–O(13)	1.920(8)	Mo(6)–O(14A)	1.936(8)
Mo(6)–O(22)	2.418(12)	Mo(6)–O(19)	2.485(12)
Ag(1)–N(1)	2.251(8)	Ag(1)–N(7)	2.454(10)
Ag(1)–N(2)	2.432(8)	Ag(1)–N(8)	2.254(10)
Ag(1)–O(4)	2.687(8)	Ag(2)–N(3)	2.413(8)
Ag(2)–N(4)	2.252(8)	Ag(2)–N(5)	2.220(10)
Ag(2)–N(6)	2.517(10)		

Symmetry code: A, 2 – *x*, 3 – *y*, 3 – *z*.

Table S6. Selected bond angles (°) for compound **2**

bond angle	degree	bond angle	degree
O(19)–P(1)–O(21)	110.1(7)	O(19)–P(1)–O(20)	111.0(6)
O(21)–P(1)–O(20)	110.1(6)	O(19A)–P(1)–O(22)	109.2(6)
O(21A)–P(1)–O(22)	108.0(6)	O(20A)–P(1)–O(22)	108.3(6)
N(1)–Ag(1)–N(8)	153.9(4)	N(1)–Ag(1)–N(2)	70.7(3)
N(8)–Ag(1)–N(2)	130.3(3)	N(1)–Ag(1)–N(7)	130.8(3)
N(8)–Ag(1)–N(7)	70.2(4)	N(2)–Ag(1)–N(7)	91.0(3)
N(5)–Ag(2)–N(4)	160.4(3)	N(5)–Ag(2)–N(3)	123.4(3)
N(4)–Ag(2)–N(3)	70.0(3)	N(5)–Ag(2)–N(6)	69.7(4)
N(4)–Ag(2)–N(6)	127.6(3)	N(3)–Ag(2)–N(6)	90.8(3)

Table S7. Hydrogen bond parameters (Å, °) of compound **2**

D–H···A	D(D–H)	d(H···A)	d(D···A)	∠(DHA)	Symmetry transformation for A
C(7)–H(7A)···N(3)	0.96	2.31	2.752(17)	107	
C(9)–H(9A)···N(2)	0.96	2.30	2.748(17)	107	
C(15)–H(15A)···O(17)	0.93	2.60	3.380(19)	142	$-1+x, -1+y, -1+z$
C(16)–H(16A)···O(2)	0.93	2.56	3.44(2)	157	$1-x, 2-y, 2-z$
C(18)–H(18A)···O(6)	0.93	2.44	3.268(19)	148	$2-x, 3-y, 3-z$
C(21)–H(21A)···N(7)	0.96	2.34	2.740(19)	104	
C(23)–H(23A)···N(6)	0.96	2.34	2.77(2)	107	
C(25)–H(25A)···O(13)	0.93	2.53	3.39(2)	154	$1-x, 3-y, 3-z$
C(26)–H(26A)···O(7)	0.93	2.38	3.30(2)	173	$1-x, 3-y, 3-z$
C(28)–H(28A)···O(4)	0.93	2.50	3.061(15)	119	$1-x, 3-y, 2-z$

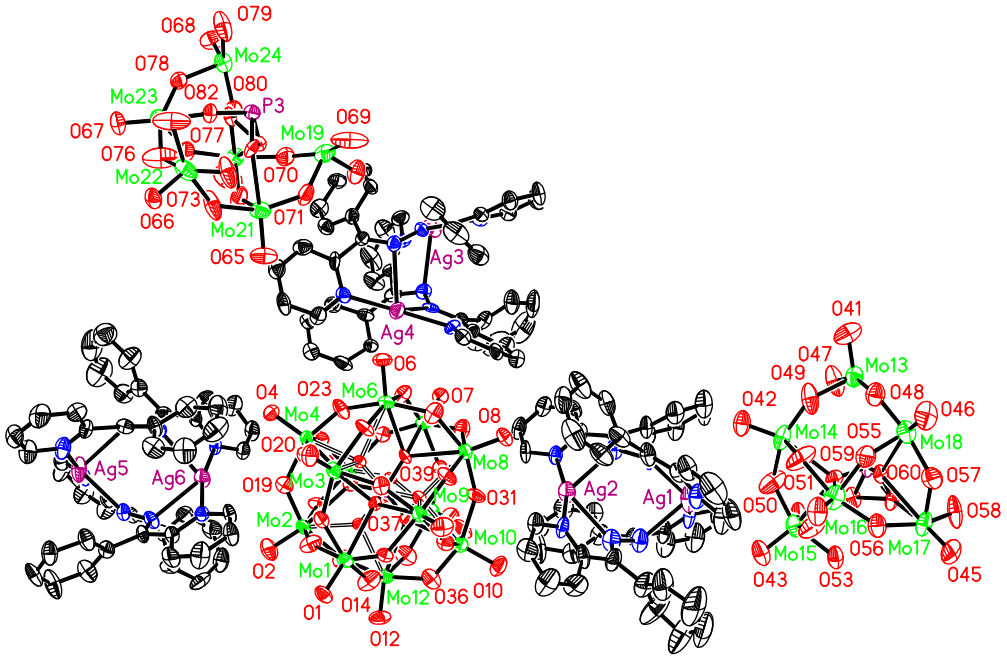


Figure S1 Molecular structure with atomic numbering of the compound **1**. The thermal ellipsoids are drawn at the 30% probability level. All H atoms and solvent molecules are omitted for clarity.

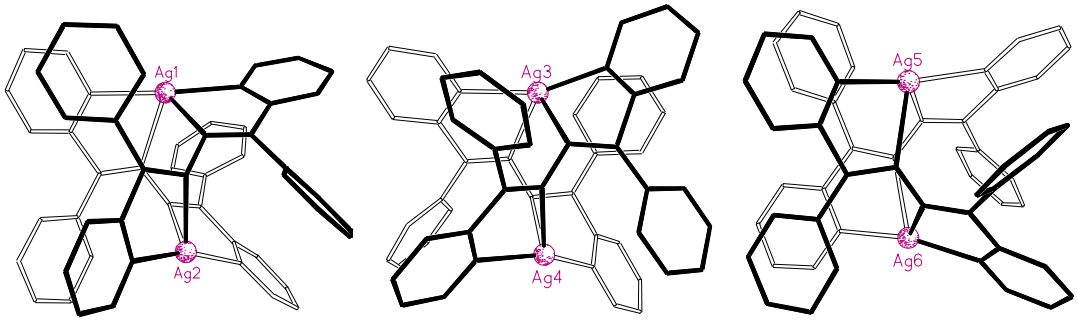


Figure S2. Two P helicates and one M helicate of compound **1**.

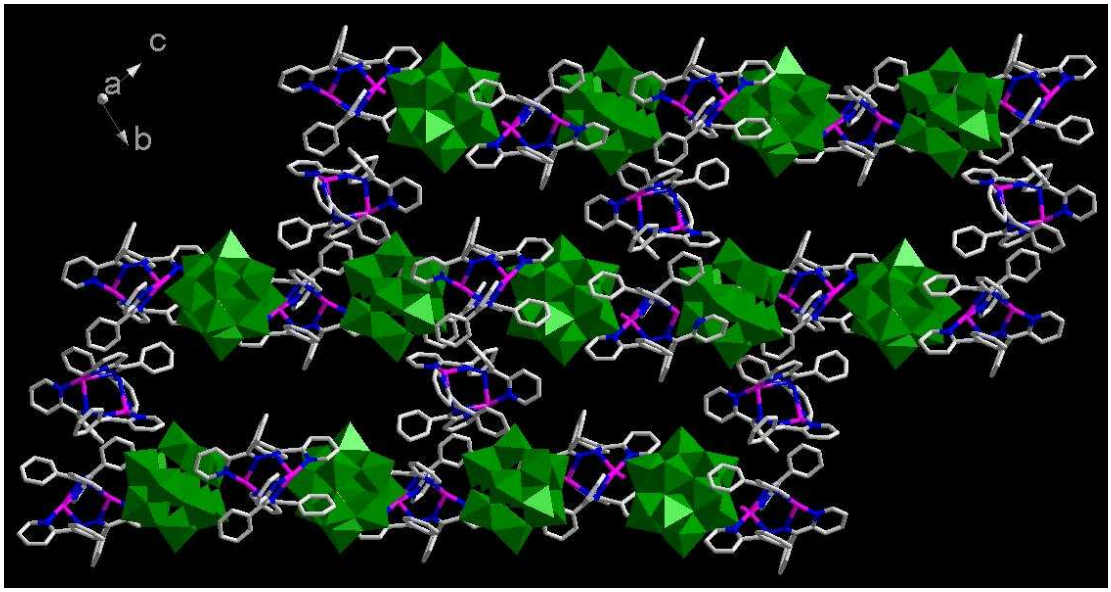


Figure S3. The packing diagram for compound **1**.

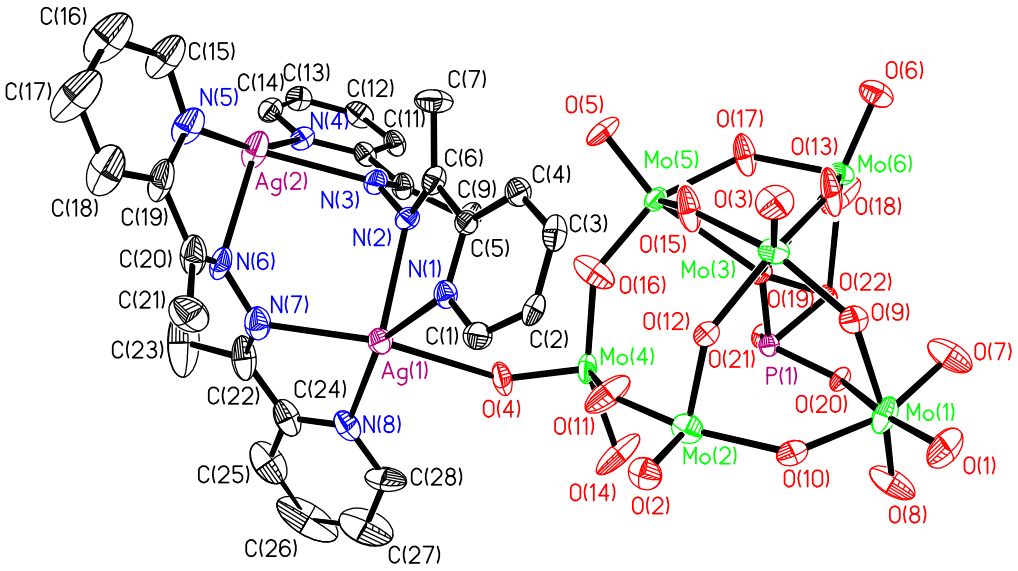


Figure S4 Molecular structure with atomic numbering of the compound **2**. The thermal ellipsoids are drawn at the 30% probability level. All H atoms are omitted for clarity.

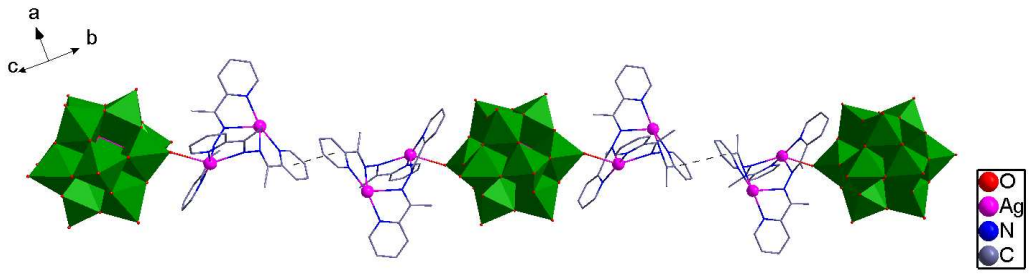


Figure S5. Polyhedral and ball-and-stick representation of **2** showing π···π interactions in dashed lines. Hydrogen atoms and solvent molecules have been omitted for clarity.

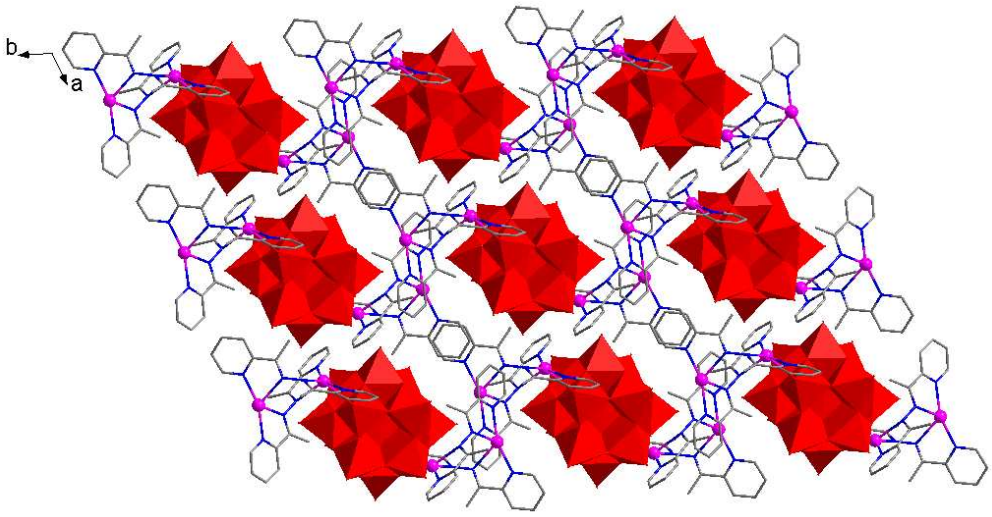


Figure S6. The packing diagram for compound **2**. Hydrogen atoms and solvent molecules have been omitted for clarity.

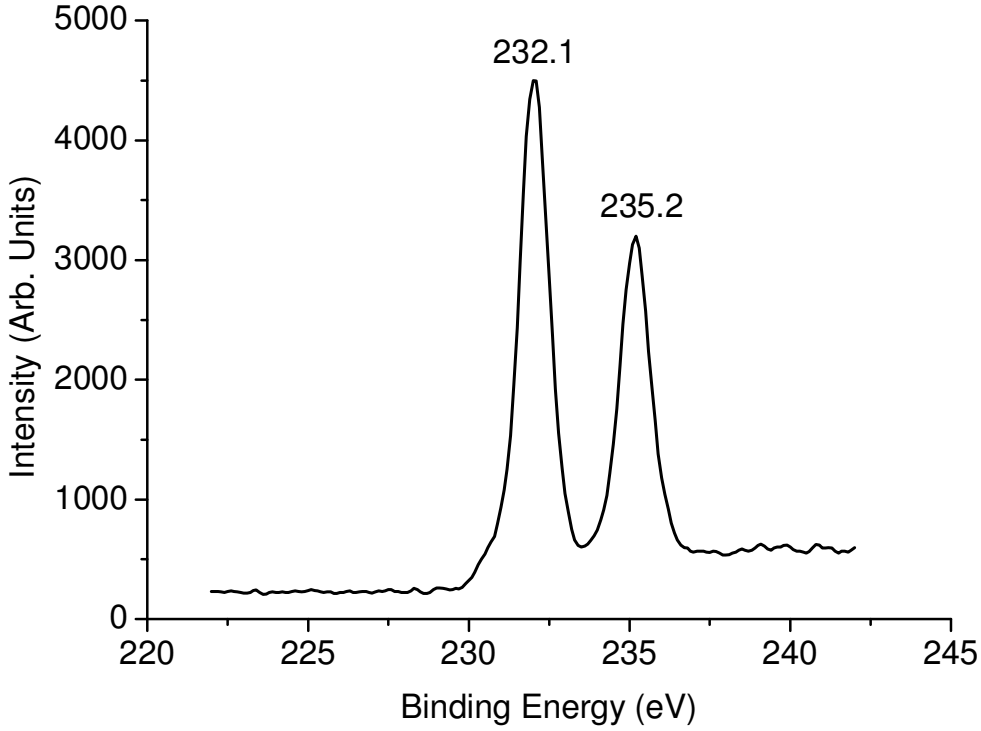


Figure S7. XPS for Mo(VI) in compound **1**.

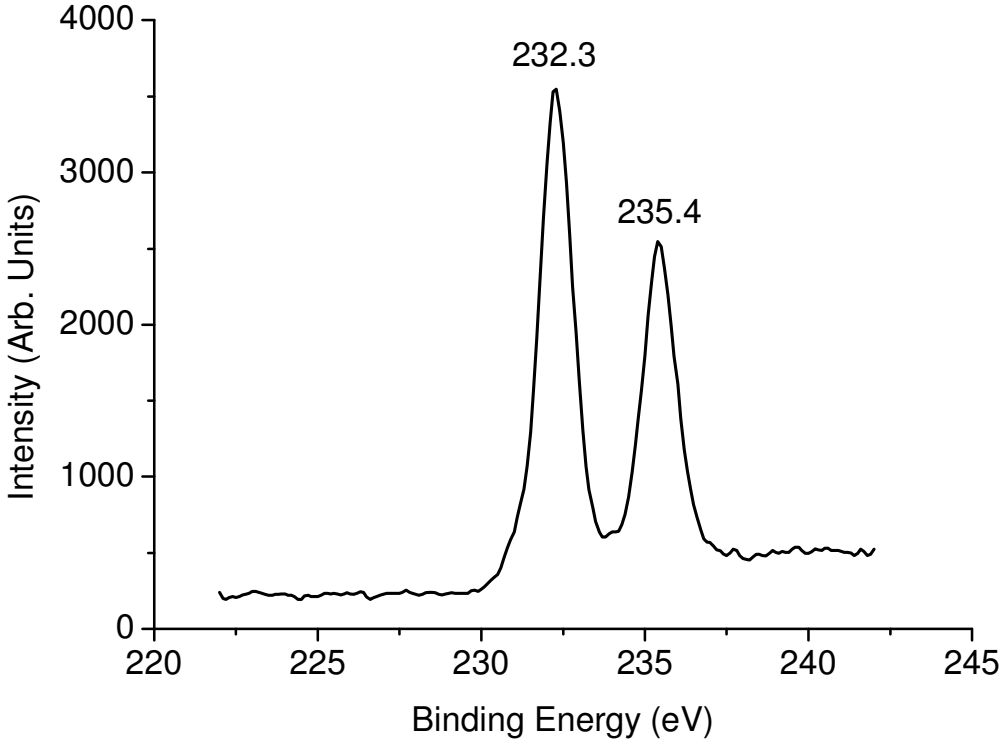


Figure S8. XPS for Mo(VI) in compound **2**.

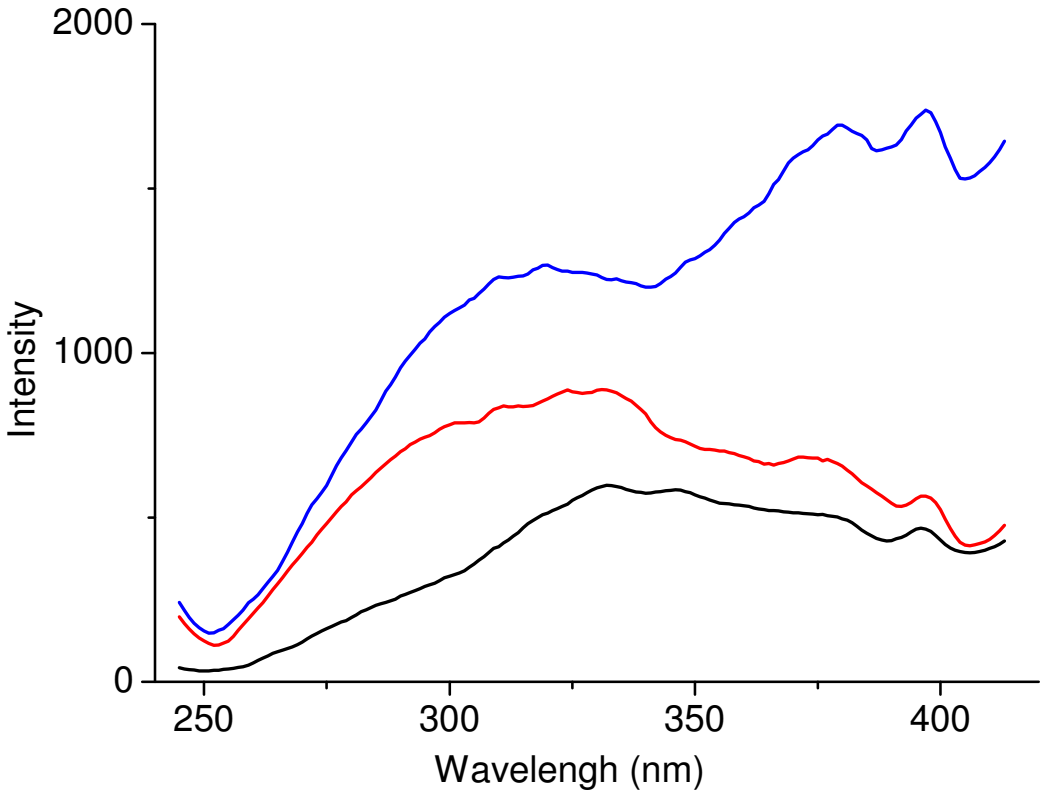


Figure S9. The emission spectra of compound **1** (red, λ_{ex} = 220 nm), ligand L^1 (blue, λ_{ex} = 220 nm) and $[Ag_2L^1_2](NO_3)_2$ (black, λ_{ex} = 220 nm) in solid state at room temperature.

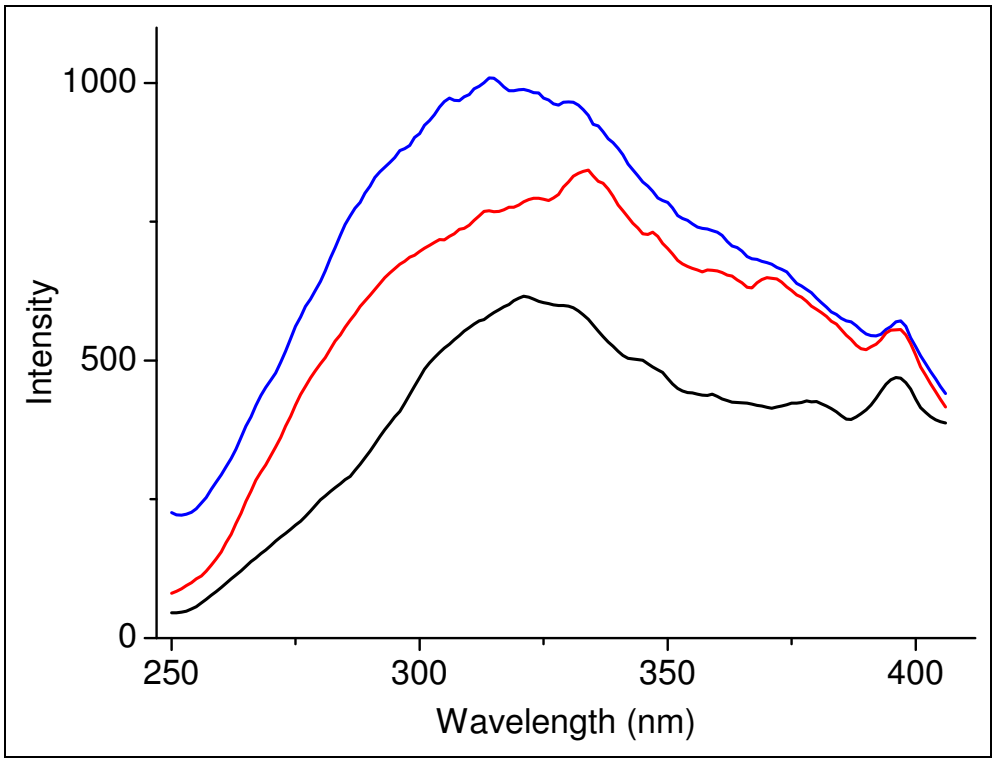
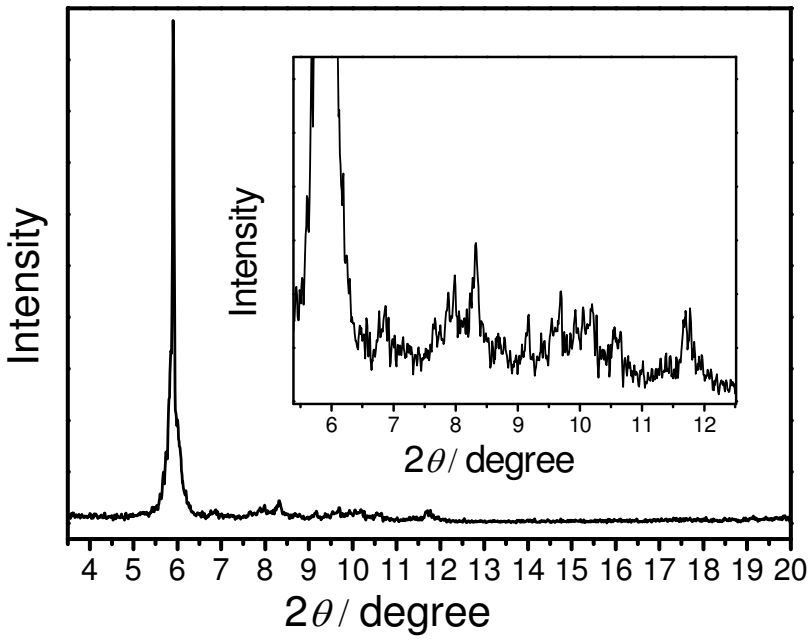
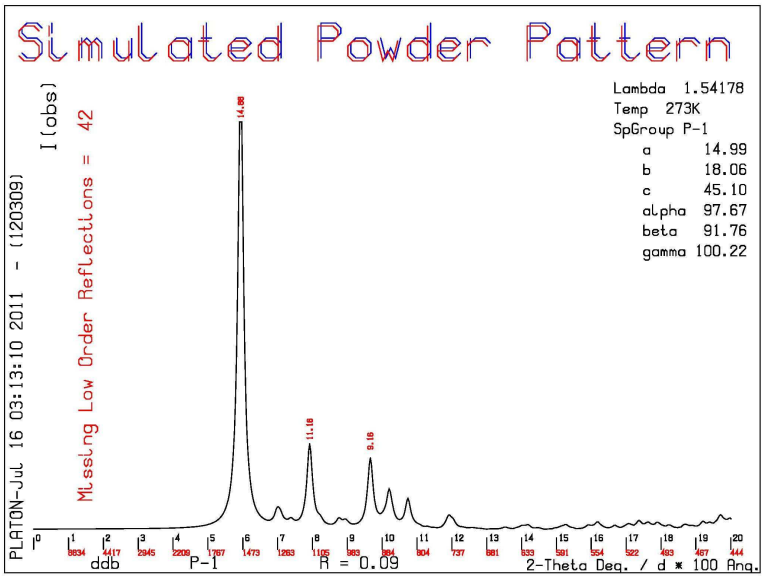


Figure S10. The emission spectra of compound **2** (red, λ_{ex} = 220 nm), ligand L^2 (blue, λ_{ex} = 220 nm) and $[Ag_2L^2_2](NO_3)_2$ (black, λ_{ex} = 220 nm) in solid state at room temperature.



(a)



(b)

Figure S11. (a) The X-ray powder diffraction (XPD) pattern of the bulk samples (a) and that calculated from the single-crystal diffraction data of **1** (b).