Supporting Information

Syntheses, crystal structures and properties of inorganic-organic hybrids constructed from Keggin-type polyoxometalates and silver coordination compounds†

Wei-Li Zhou,[a] Jun Liang,[a] Chao Qin,*[a] Kui-Zhan Shao,[a] Fang-Ming Wang*[b] and Zhong-Min Su*[a]

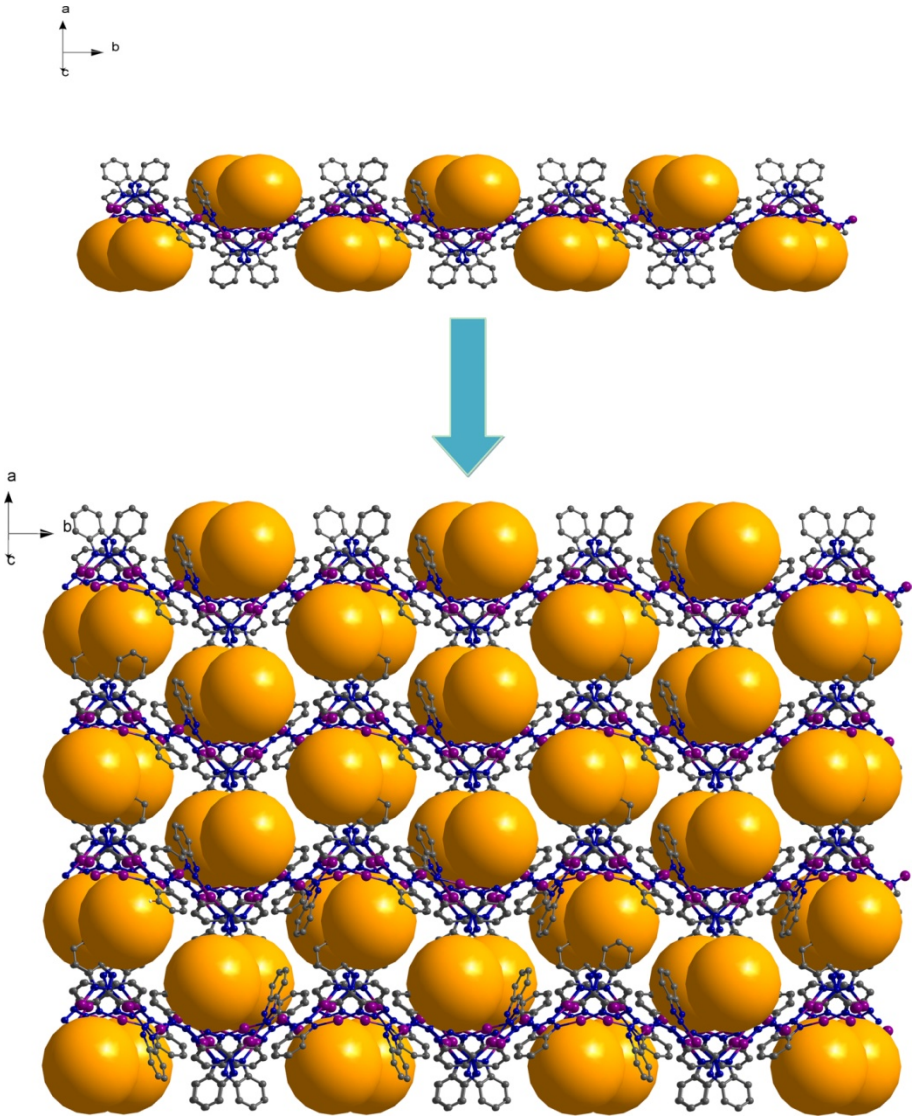

Fig. S1 Ball and stick view of the supramolecular structure of compound **1** (orange ball, PMo_{12} polyoxoanion).

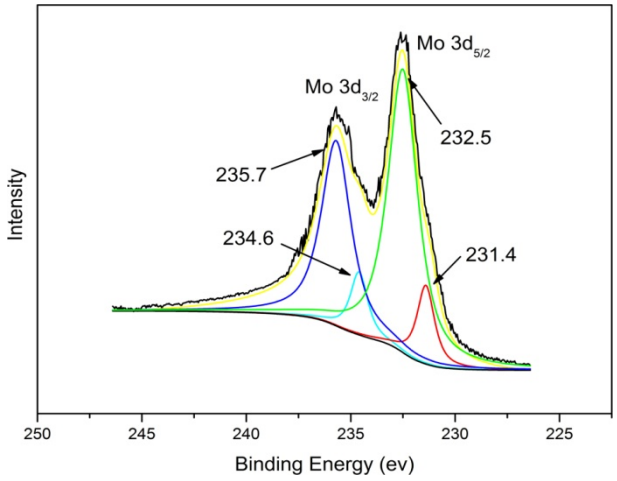

Fig. S2 The XPS spectrum of compound **2**.

The XPS spectra give two overlapped peaks in **2**, at 234.6 and 231.4 eV are attributed to Mo^{5+} ions, and the peaks at 232.5 and 235.7 eV are ascribed to Mo^{6+} ions, respectively.

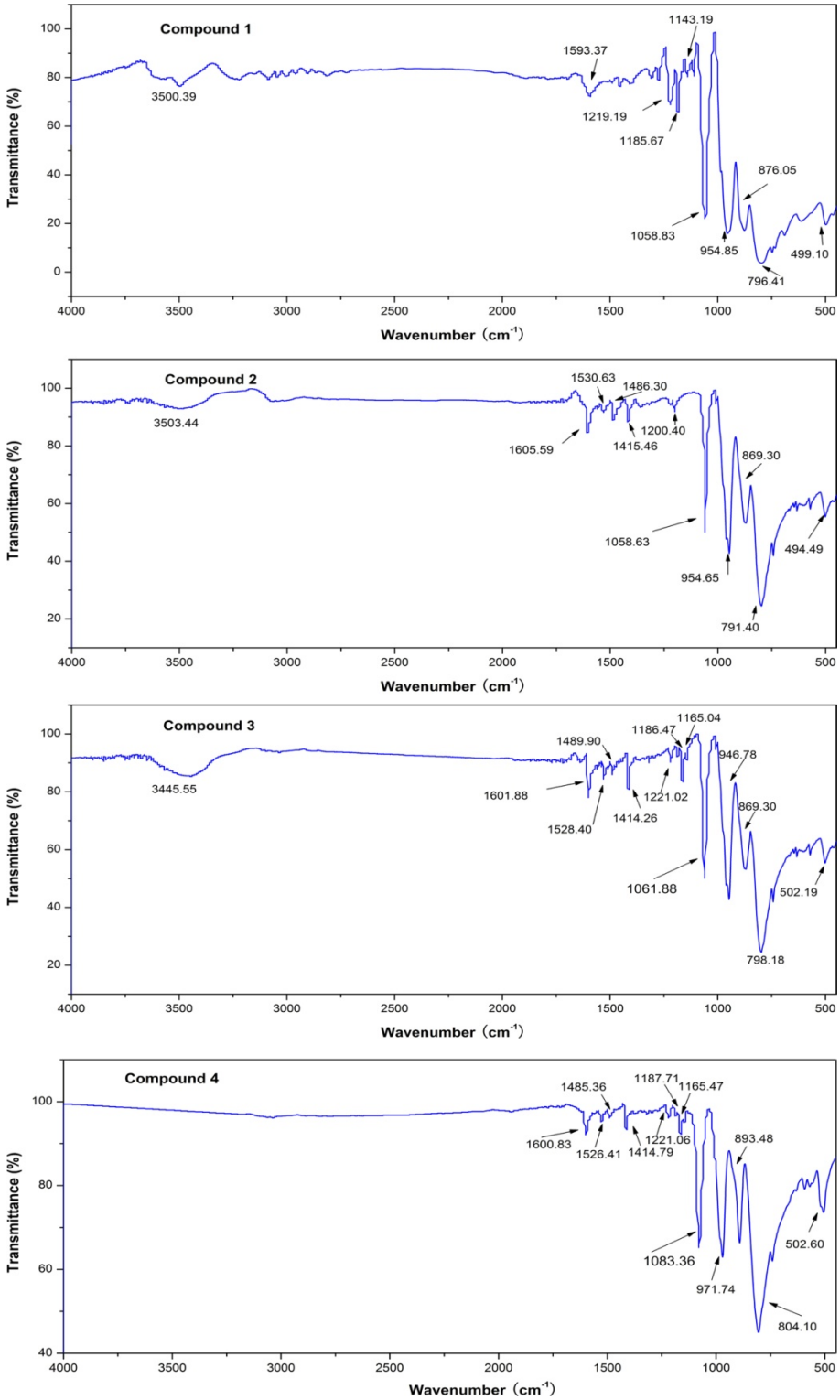

Fig.S3 The IR spectra of compounds **1**–**4**.

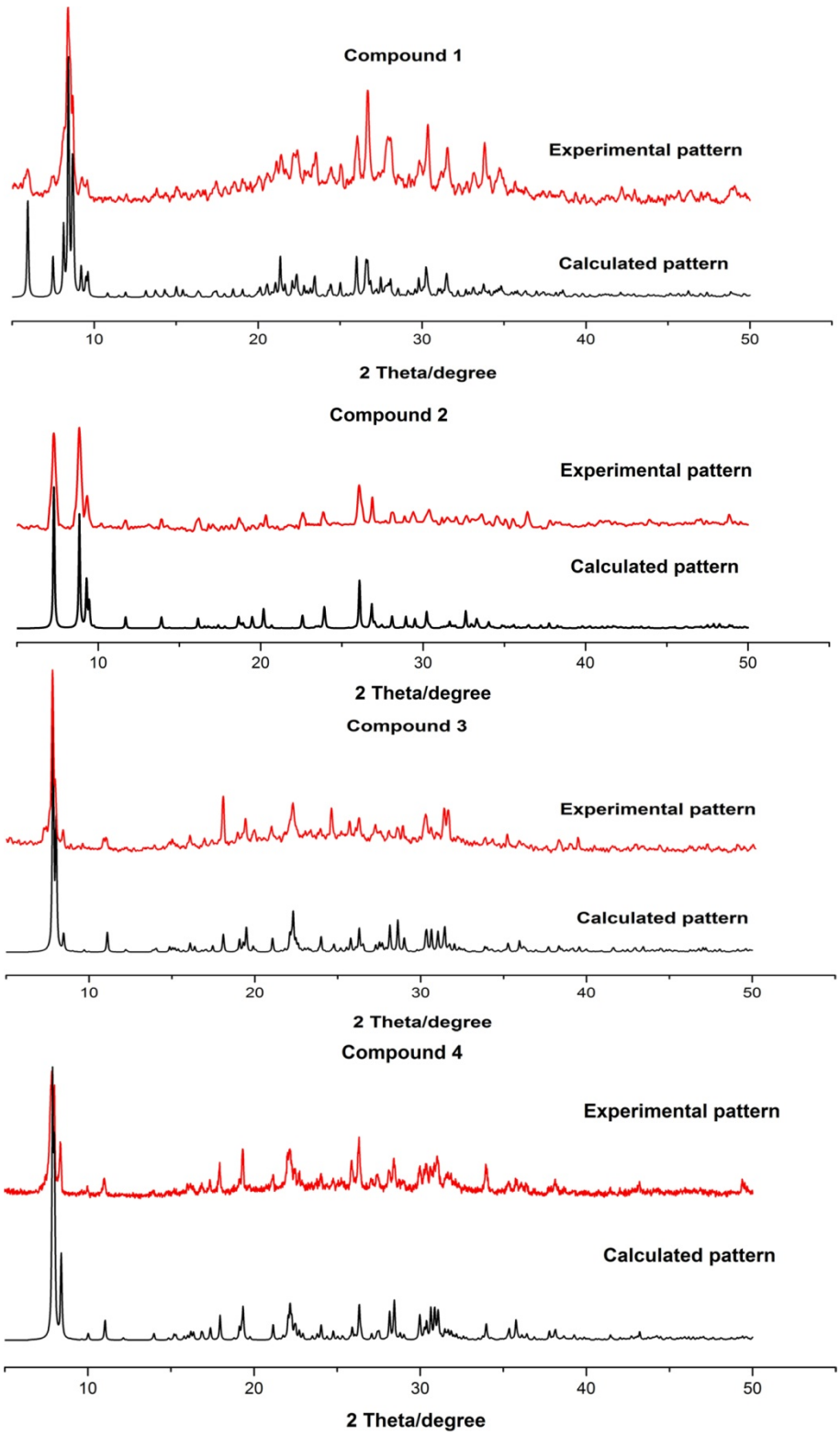

Fig. S4 The PXRD patterns of compounds **1**–**4**.

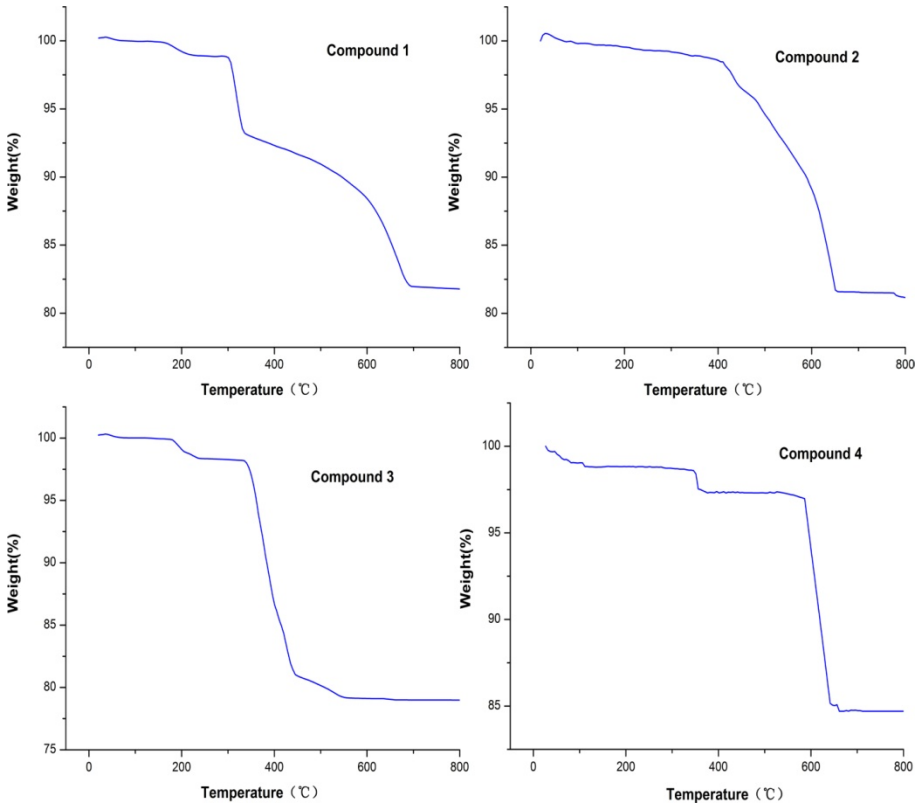

Fig. S5 The TG curves of compounds **1**–**4**.

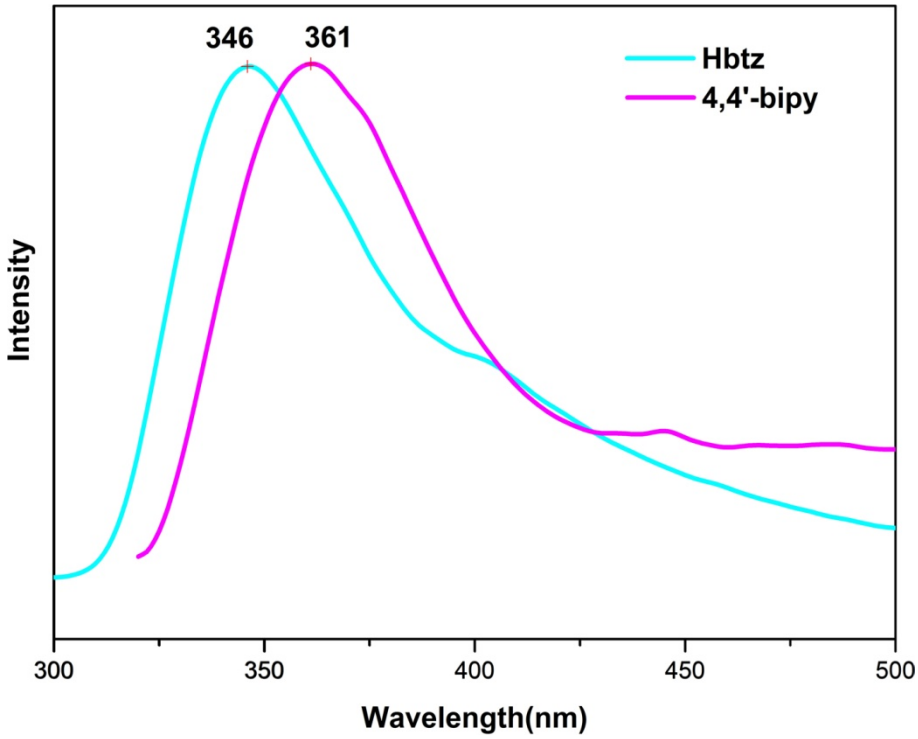

Fig. S6 The emission spectra of free ligands (blue: Hbtz, pink: 4,4′-bpy).

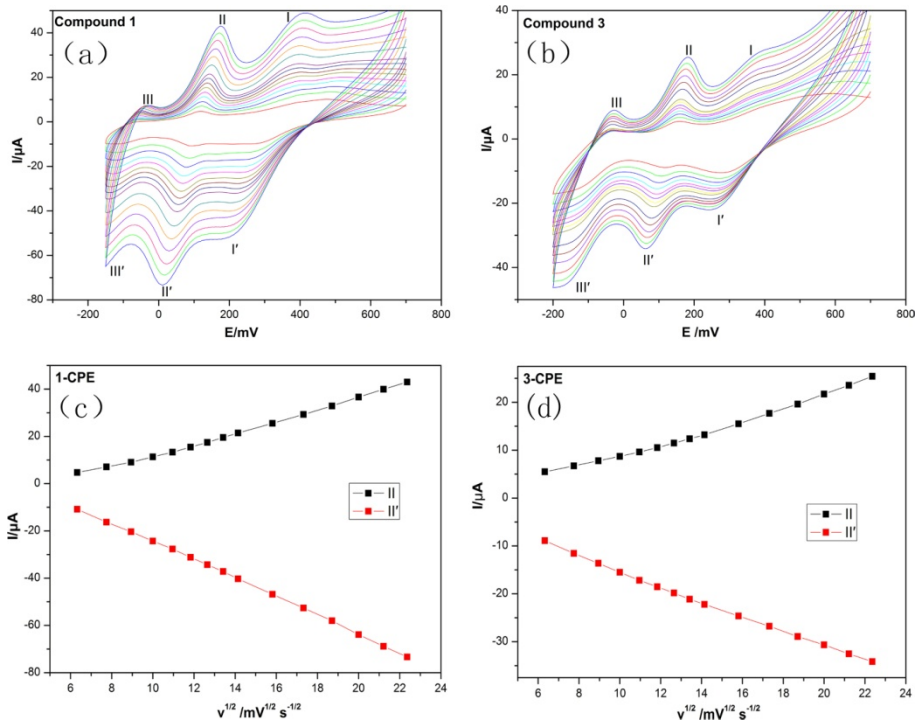

Fig. S7 The cyclic voltammograms of the **1-** (a) and **3-**CPEs (b) in 0.1M H_2SO_4 + 0.5M Na_2SO_4 aqueous solution at different scan rates (from inner to outer: 40, 60, 80, 100, 120, 140, 160, 180, 200, 250, 300, 350, 400, 450 and 500 mV·s^{-1}, respectively). The dependence of anodic peak (II) and cathodic peak (II') currents of **1-** (c) and **3-**CPEs (d) on square root of the scan rate.

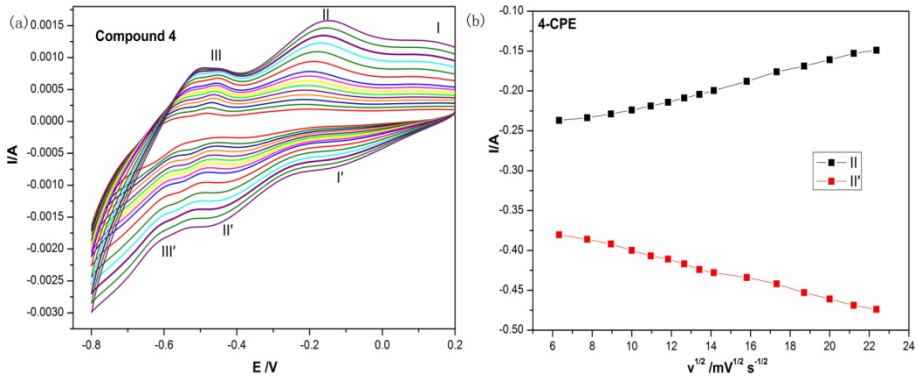

Fig. S8 The cyclic voltammograms of the **4-**CPE (a) in 1M H_2SO_4 aqueous solution at different scan rates (from inner to outer: 40, 60, 80, 100, 120, 140, 160, 180, 200, 250, 300, 350, 400, 450 and 500 mV·s^{-1}, respectively). The dependence of anodic peak (II) and cathodic peak (II') currents of **4**–CPE (b) on square root of the scan rate.

The cyclic voltammograms of **4-**CPE are presented in the potential range of +200 to −800 mV (Fig. S8a). There exist three reversible redox peaks I–I′, II–II′, and III–III′ with the mean peak potentials $E_{1/2} = (E_{pa} + E_{pc})/2$ at −15 (I–I′), −320 (II–II′) and −510 (III–III′) mV (scan rate: 40 mV s^{-1}), respectively, in which I–I′ and II–II′ correspond to two consecutive one-electron processes of W centers, while III–III′ corresponds to a two-electron process of PW_{12}. Furthermore, when the scan rate was varied from 40 to 500 mV s^{-1}, the peak potentials changed gradually: the cathodic peak potentials shift toward the negative direction and the corresponding anodic peak potentials to the positive direction with increasing scan rates. These chemically reversible processes are diffusion-controlled, as revealed by the peak current dependence on the square root of the scan

rate from 40 to 500 mV s^{-1} (Fig. S8b).

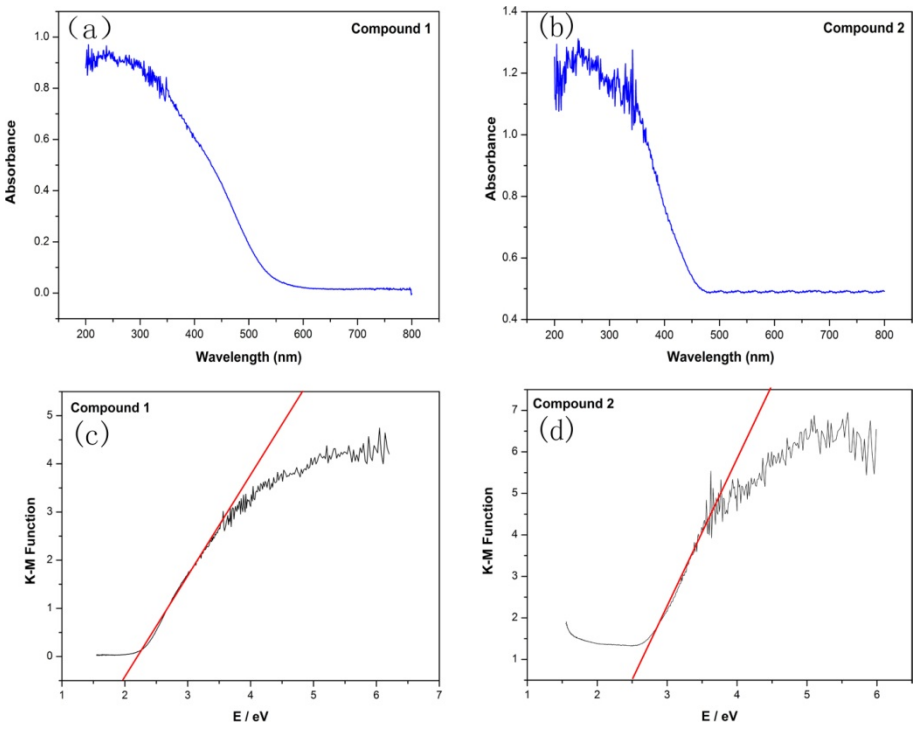

Fig. S9 The diffuse reflectance UV-vis absorption spectra of compound **1** (a) and **2** (b). The diffuse reflectance UV-vis-NIR spectra of K-M function vs. energy (eV) of compound **1** (c) and **2** (d).

Coordination sites of PMo_{12}	Coordination number and modes of silver ions	Coordination number and modes of ligands	PMo_{12}-based frameworks

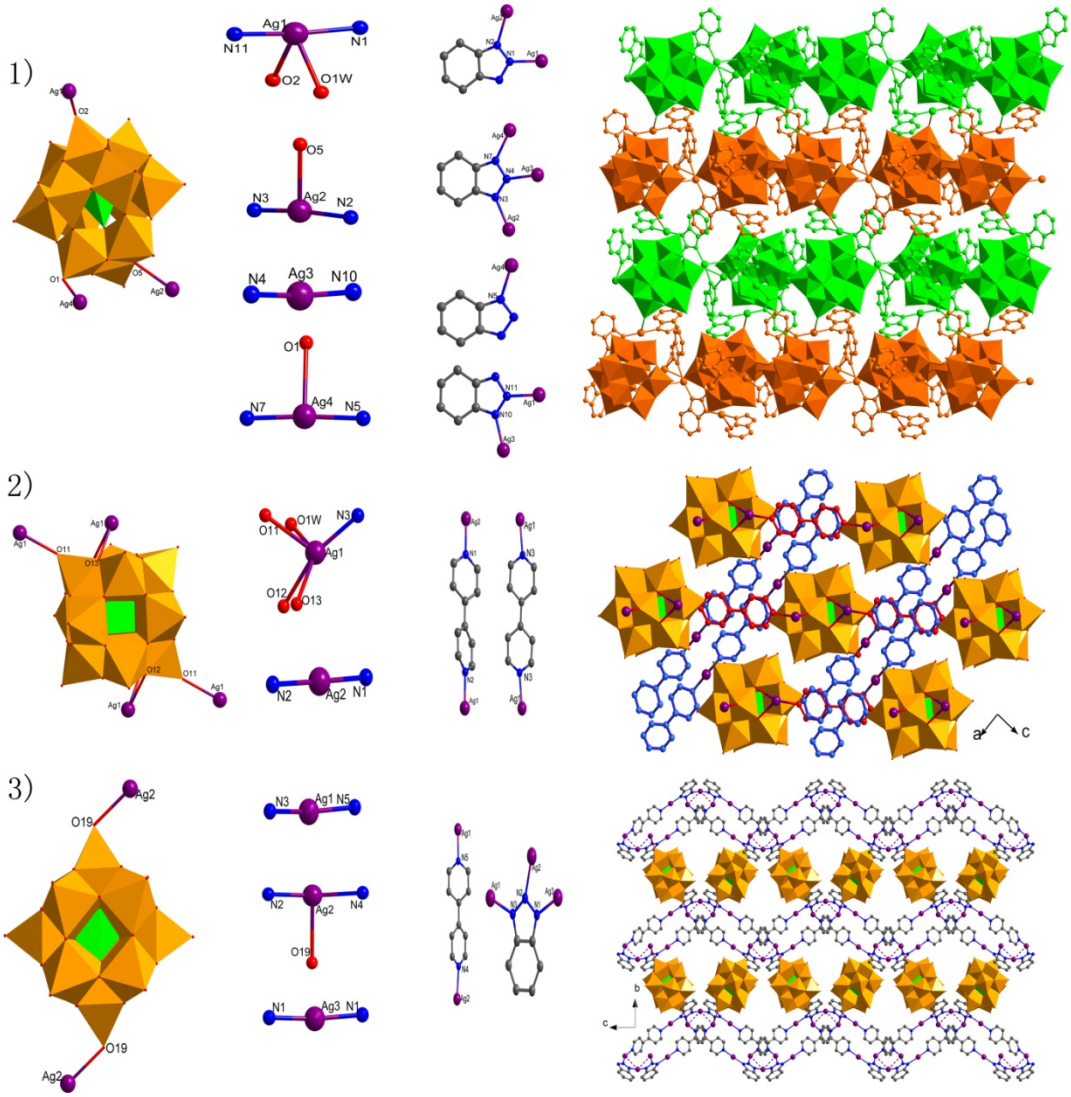

Fig. S10 The coordination numbers and modes of PMo_{12}, Ag^{I} ions, organic ligands (btz and 4,4′-bpy) and the frameworks of compounds **1**–**3**.

Table S1 Bond valence sum calculations of Mo, Ag and P for **1.**

Bonds	Bond length (Å)	BVS*
Mo(1)-O(40)	1.665(4)	1.923
Mo(1)-O(17)	1.830(3)	1.231
Mo(1)-O(11)	1.841(4)	1.195
Mo(1)-O(39)	1.994(3)	0.790
Mo(1)-O(16)	2.027(4)	0.723
Mo(1)-O(14)	2.448(3)	0.232
	$V_{Mo(1)}$ = **6.095**	
Mo(2)-O(35)	1.674(4)	1.877
Mo(2)-O(21)	1.836(4)	1.212
Mo(2)-O(36)	1.853(4)	1.157
Mo(2)-O(17)	1.983(4)	0.814
Mo(2)-O(20)	1.999(4)	0.780
Mo(2)-O(19)	2.455(3)	0.227
	$V_{Mo(2)}$ = **6.067**	
Mo(3)-O(2)	1.691(4)	1.793
Mo(3)-O(16)	1.801(4)	1.332
Mo(3)-O(22)	1.848(4)	1.173
Mo(3)-O(21)	1.980(4)	0.821
Mo(3)-O(28)	2.013(4)	0.751
Mo(3)-O(18)	2.424(3)	0.247
	$V_{Mo(3)}$ = **6.117**	
Mo(4)-O(30)	1.680(4)	1.847
Mo(4)-O(29)	1.836(4)	1.212
Mo(4)-O(28)	1.846(4)	1.179
Mo(4)-O(26)	1.990(3)	0.799
Mo(4)-O(27)	1.999(3)	0.780
Mo(4)-O(18)	2.430(3)	0.243
	$V_{Mo(4)}$ = **6.060**	
Mo(5)-O(38)	1.689(3)	1.803
Mo(5)-O(33)	1.827(3)	1.241
Mo(5)-O(27)	1.836(4)	1.212
Mo(5)-O(15)	1.983(4)	0.814
Mo(5)-O(22)	1.988(4)	0.803
Mo(5)-O(18)	2.436(3)	0.239
	$V_{Mo(5)}$ = **6.113**	
Mo(6)-O(1)	1.681(4)	1.842
Mo(6)-O(23)	1.814(4)	1.286
Mo(6)-O(6)	1.844(4)	1.186
Mo(6)-O(33)	2.008(3)	0.761
Mo(6)-O(24)	2.020(4)	0.737
Mo(6)-O(12)	2.415(3)	0.253

	$V_{Mo(6)}$ = **6.065**	
Mo(7)-O(3)	1.676(4)	1.867
Mo(7-O(4)	1.832(3)	1.225
Mo(7)-O(5)	1.857(4)	1.145
Mo(7)-O(7)	1.986(4)	0.808
Mo(7)-O(6)	1.996(4)	0.786
Mo(7)-O(12)	2.471(3)	0.218
	$V_{Mo(7)}$ = **6.048**	
Mo(8)-O(34)	1.689(4)	1.803
Mo(8)-O(26)	1.831(3)	1.228
Mo(8)-O(24)	1.836(3)	1.212
Mo(8)-O(25)	2.005(3)	0.767
Mo(8)-O(5)	2.004(4)	0.769
Mo(8)-O(12)	2.409(3)	0.257
	$V_{Mo(8)}$ = **6.036**	
Mo(9)-O(13)	1.680(4)	1.847
Mo(9)-O(15)	1.827(4)	1.241
Mo(9)-O(39)	1.835(4)	1.215
Mo(9)-O(23)	2.008(4)	0.761
Mo(9)-O(10)	2.017(3)	0.743
Mo(9)-O(14)	2.416(3)	0.253
	$V_{Mo(9)}$ = **6.060**	
Mo(10)-O(8)	1.677(4)	1.862
Mo(10)-O(7)	1.833(4)	1.221
Mo(10)-O(10)	1.837(3)	1.208
Mo(10)-O(9)	1.989(4)	0.801
Mo(10)-O(11)	2.005(4)	0.767
Mo(10)-O(14)	2.458(3)	0.226
	$V_{Mo(10)}$ = **6.086**	
Mo(11)-O(37)	1.673(4)	1.882
Mo(11)-O(9)	1.826(4)	1.245
Mo(11)-O(20)	1.843(4)	1.189
Mo(11)-O(4)	1.997(3)	0.784
Mo(11)-O(32)	2.022(4)	0.733
Mo(11)-O(19)	2.436(3)	0.239
	$V_{Mo(11)}$ = **6.072**	
Mo(12)-O(31)	1.691(4)	1.793
Mo(12)-O(32)	1.824(4)	1.251
Mo(12)-O(25)	1.835(3)	1.215
Mo(12)-O(36)	1.977(3)	0.828
Mo(12)-O(29)	2.004(4)	0.769
Mo(12)-O(19)	2.404(3)	0.261
	$V_{Mo(12)}$ = **6.117**	
Ag(1)-N(11)	2.208(5)	0.380

Ag(1)-N(1)	2.226(5)	0.362
Ag(1)-O(2)	2.583(4)	0.122
Ag(1)-O(1W)	2.449(5)	0.175
	$V_{Ag(1)}$ = **1.039**	
Ag(2)-N(3)	2.155(4)	0.439
Ag(2)-N(2)	2.203(5)	0.385
Ag(2)-O(5)	2.623(5)	0.110
	$V_{Ag(2)}$ = **0.934**	
Ag(3)-N(4)	2.100(5)	0.509
Ag(3)-N(10)	2.110(5)	0.495
	$V_{Ag(3)}$ = **1.004**	
Ag(4)-N(7)	2.108(5)	0.498
Ag(4)-N(5)	2.132(5)	0.467
Ag(4)-O(1)	2.672(6)	0.096
	$V_{Ag(4)}$ = **1.061**	
P(1)-O(12)	1.527(3)	1.231
P(1)-O(18)	1.533(3)	1.212
P(1)-O(14)	1.531(4)	1.218
P(1)-O(19)	1.533(3)	1.212
	$V_{P(1)}$ = **4.873**	
$V_{O(1)}$ = **1.938**	$V_{O(2)}$ = **1.915**	$V_{O(3)}$ = **1.867**
$V_{O(4)}$ = **2.009**	$V_{O(5)}$ = **2.024**	$V_{O(6)}$ = **1.972**
$V_{O(7)}$ = **2.029**	$V_{O(8)}$ = **1.862**	$V_{O(9)}$ = **2.046**
$V_{O(10)}$ = **1.951**	$V_{O(11)}$ = **1.962**	$V_{O(12)}$ = **1.959**
$V_{O(13)}$ = **1.847**	$V_{O(14)}$ = **1.929**	$V_{O(15)}$ = **2.055**
$V_{O(16)}$ = **2.055**	$V_{O(17)}$ = **2.072**	$V_{O(18)}$ = **1.941**
$V_{O(19)}$ = **1.939**	$V_{O(20)}$ = **1.969**	$V_{O(21)}$ = **2.033**
$V_{O(22)}$ = **1.976**	$V_{O(23)}$ = **2.047**	$V_{O(24)}$ = **1.949**
$V_{O(25)}$ = **1.982**	$V_{O(26)}$ = **2.027**	$V_{O(27)}$ = **1.992**
$V_{O(28)}$ = **1.930**	$V_{O(29)}$ = **1.981**	$V_{O(30)}$ = **1.847**
$V_{O(31)}$ = **1.793**	$V_{O(32)}$ = **1.984**	$V_{O(33)}$ = **2.002**
$V_{O(34)}$ = **1.803**	$V_{O(35)}$ = **1.877**	$V_{O(36)}$ = **1.985**
$V_{O(37)}$ = **1.882**	$V_{O(38)}$ = **1.803**	$V_{O(39)}$ = **2.005**
$V_{O(40)}$=**1.923**		

Table S2 Bond valence sum calculations of Mo, Ag and P for **2.**

Bonds	Bond length (Å)	BVS*
Mo(1)-O(15)	1.649(5)	2.008
Mo(1)-O(16)	1.921(5)	0.963
Mo(1)-O(18)	1.866(5)	1.117
Mo(1)-O(19)	2.449(11)	0.231
Mo(1)-O(1)	1.880(6)	1.076
Mo(1)-O(22)	2.486(9)	0.209

	$V_{Mo(1)}$ = **5.604**	
Mo(2)-O(14)	1.644(6)	2.036
Mo(2)-O(3)	1.865(6)	1.120
Mo(2)-O(11)	1.865(7)	1.120
Mo(2)-O(18)	1.921(7)	0.963
Mo(2)-O(17)	1.943(6)	0.907
Mo(2)-O(19)	2.484(9)	0.210
	$V_{Mo(2)}$ = **6.356**	
Mo(3)-O(12)	1.643(5)	2.041
Mo(3)-O(2)	1.841(6)	1.195
Mo(3)-O(13)	1.898(7)	1.025
Mo(3)-O(4)	1.906(6)	1.003
Mo(3)-O(3)	1.937(6)	0.922
Mo(3)-O(22)	2.462(9)	0.223
	$V_{Mo(3)}$ = **6.409**	
Mo(4)-O(5)	1.665(5)	1.923
Mo(4)-O(17)	1.840(6)	1.199
Mo(4)-O(4)	1.886(6)	1.058
Mo(4)-O(7)	1.890(6)	1.047
Mo(4)-O(6)	1.890(6)	0.853
Mo(4)-O(20)	2.405(9)	0.260
	$V_{Mo(4)}$ = **6.340**	
Mo(5)-O(8)	1.640(6)	2.058
Mo(5)-O(7)	1.888(6)	1.053
Mo(5)-O(1)	1.894(6)	1.036
Mo(5)-O(10)	1.903(5)	1.011
Mo(5)-O(13)	1.910(7)	0.992
Mo(5)-O(22)	2.439(9)	0.237
	$V_{Mo(5)}$ = **6.386**	
Mo(6)-O(9)	1.655(5)	1.976
Mo(6)-O(6)	1.835(6)	1.215
Mo(6)-O(16)	1.852(6)	1.160
Mo(6)-O(10)	1.927(5)	0.947
Mo(6)-O(11)	1.975(7)	0.832
Mo(6)-O(19)	2.432(9)	0.242
	$V_{Mo(6)}$ = **6.373**	
Ag(1)-N(3)	2.218(8)	0.370
Ag(1)-O(11)	2.445(6)	0.177
Ag(1)-O(9)	2.552(5)	0.133
Ag(1)-O(10)	2.562(6)	0.129
Ag(1)-O(1W)	2.489(8)	0.157
	$V_{Ag(1)}$ = **0.966**	
Ag(2)-N(1)	2.162(6)	0.430
Ag(2)-N(2)	2.169(6)	0.422

	$V_{Ag(2)}$ = 0.853	
P(1)-O(21)	1.492(9)	1.354
P(1)-O(20)	1.540(9)	1.189
P(1)-O(22)	1.542(9)	1.182
P(1)-O(19)	1.566(9)	1.108
	$V_{P(1)}$ = 4.833	
$V_{O(1)}$ = 2.112	**$V_{O(2)}$ = 2.090**	**$V_{O(3)}$ = 2.042**
$V_{O(4)}$ = 2.061	**$V_{O(5)}$ = 1.923**	**$V_{O(6)}$ = 2.068**
$V_{O(7)}$ = 2.100	**$V_{O(8)}$ = 2.058**	**$V_{O(9)}$ = 2.109**
$V_{O(10)}$ = 2.087	**$V_{O(11)}$ = 2.129**	**$V_{O(12)}$ = 2.041**
$V_{O(13)}$ = 2.017	**$V_{O(14)}$ = 2.036**	**$V_{O(15)}$ = 2.008**
$V_{O(16)}$ = 2.123	**$V_{O(17)}$ = 2.106**	**$V_{O(18)}$ = 2.080**
$V_{O(19)}$ = 1.791	**$V_{O(20)}$ = 1.859**	**$V_{O(21)}$ = 1.968**
$V_{O(22)}$ = 1.851		

Table S3 Bond valence sum calculations of Mo, Ag and P for **3.**

Bonds	Bond length (Å)	BVS*
Mo(1)-O(19)	1.660(8)	1.949
Mo(1)-O(21)	1.800(9)	1.335
Mo(1)-O(11)	1.815(9)	1.282
Mo(1)-O(20)	1.962(8)	0.862
Mo(1)-O(4)	2.390(12)	0.271
Mo(1)-O(5)	2.165(4)	0.498
	$V_{Mo(1)}$ = 6.198	
Mo(2)-O(15)	1.626(8)	2.137
Mo(2)-O(10)	1.810(9)	1.300
Mo(2)-O(20)	1.813(8)	1.289
Mo(2)-O(16)	1.989(8)	0.801
Mo(2)-O(14)	2.004(8)	0.769
Mo(2)-O(1)	2.382(12)	0.277
	$V_{Mo(2)}$ = 6.574	
Mo(3)-O(18)	1.651(7)	1.997
Mo(3)-O(16)	1.809(10)	1.303
Mo(3)-O(17)	1.879(10)	1.079
Mo(3)-O(9)	1.921(9)	0.963
Mo(3)-O(21)	2.001(10)	0.776
Mo(3)-O(4)	2.485(12)	0.210
	$V_{Mo(3)}$ = 6.327	
Mo(4)-O(8)	1.658(8)	1.960
Mo(4)-O(7)	1.832(9)	1.225
Mo(4)-O(9)	1.857(8)	1.145
Mo(4)-O(6)	1.938(8)	0.920
Mo(4)-O(10)	1.948(9)	0.895

Mo(4)-O(1)	2.385(11)	0.275
	$V_{Mo(4)}$ = 6.419	
Mo(5)-O(22)	1.640(6)	1.992
Mo(5)-O(6)	1.888(6)	1.205
Mo(5)-O(17)	1.894(6)	0.874
Mo(5)-O(13)	1.903(5)	0.806
Mo(5)-O(4)	1.910(7)	0.287
Mo(5)-O(5)	1.995(3)	0.788
	$V_{Mo(5)}$ = 5.951	
Mo(6)-O(12)	1.653(7)	1.987
Mo(6)-O(14)	1.816(8)	1.279
Mo(6)-O(13)	1.818(7)	1.272
Mo(6)-O(7)	1.973(8)	0.837
Mo(6)-O(11)	1.978(8)	0.825
Mo(6)-O(3)	2.415(12)	0.253
	$V_{Mo(6)}$ = 6.453	
Ag(1)-N(3)	2.185(9)	0.404
Ag(1)-N(5)	2.213(9)	0.375
	$V_{Ag(1)}$ = 0.779	
Ag(2)-N(2)	2.176(8)	0.414
Ag(2)-N(4)	2.196(9)	0.393
Ag(2)-O(19)	2.639(6)	0.105
	$V_{Ag(2)}$ = 0.912	
Ag(3)-N(1)	2.084(8)	0.531
Ag(3)-N(1)	2.084(8)	0.531
	$V_{Ag(3)}$ = 1.063	
P(1)-O(2)	1.444(11)	1.541
P(1)-O(3)	1.458(12)	1.484
P(1)-O(1)	1.596(12)	1.022
P(1)-O(4)	1.636(11)	0.917
	$V_{P(1)}$ = 4.964	
$V_{O(1)}$ = 1.574	**$V_{O(2)}$ = 1.782**	**$V_{O(3)}$ = 1.737**
$V_{O(4)}$ = 1.685	**$V_{O(5)}$ = 1.935**	**$V_{O(6}$ = 2.125**
$V_{O(7)}$ = 2.062	**$V_{O(8)}$ = 1.960**	**$V_{O(9)}$ = 2.108**
$V_{O(10)}$ = 2.195	**$V_{O(11)}$ = 2.107**	**$V_{O(12)}$ = 1.987**
$V_{O(13)}$ = 2.078	**$V_{O(14)}$ = 2.048**	**$V_{O(15)}$ = 2.137**
$V_{O(16)}$ = 2.104	**$V_{O(17)}$ = 1.953**	**$V_{O(18)}$ = 1.997**
$V_{O(19)}$ = 1.949	**$V_{O(20)}$ = 2.151**	**$V_{O(21)}$ = 2.111**
$V_{O(22)}$ = 1.992		

Table S4 Bond valence sum calculations of Mo, Ag and P for **4.**

Bonds	Bond length (Å)	BVS*
W(1)-O(5)	1.668(12)	1.960

W(1)-O(6)	1.867(14)	1.145
W(1)-O(9)	1.879(15)	1.108
W(1)-O(7)	1.918(17)	0.997
W(1)-O(8)	1.926(14)	0.976
W(1)-O(1)	2.43(2)	0.250
	$V_{W(1)}$ = **6.436**	
W(2)-O(11)	1.695(15)	1.822
W(2)-O(12)	1.874(15)	1.123
W(2)-O(19)	1.88(2)	1.105
W(2)-O(9)	1.910(17)	1.019
W(2)-O(10)	1.945(18)	0.927
W(2)-O(2)	2.39(2)	0.278
	$V_{W(2)}$ = **6.574**	
W(3)-O(13)	1.662(14)	1.992
W(3)-O(8)	1.863(16)	1.157
W(3)-O(12)	1.891(15)	1.073
W(3)-O(17)	1.897(18)	1.056
W(3)-O(3)	2.40(2)	0.271
W(3)-O(14)	2.011(8)	0.776
	$V_{W(3)}$ = **6.325**	
W(4)-O(21)	1.689(14)	1.852
W(4)-O(15)	1.85(2)	1.199
W(4)-O(10)	1.86(2)	1.167
W(4)-O(20)	1.90(2)	1.047
W(4)-O(2)	2.46(2)	0.230
W(4)-O(14)	2.045(4)	0.708
	$V_{W(4)}$ = **6.202**	
W(5)-O(22)	1.699(15)	1.803
W(5)-O(7)	1.865(18)	1.151
W(5)-O(20)	1.88(2)	1.105
W(5)-O(18)	1.897(18)	1.056
W(5)-O(19)	1.92(2)	0.992
W(5)-O(2)	2.36(2)	0.302
	$V_{W(5)}$ = **6.408**	
W(6)-O(17)	1.855(19)	1.182
W(6)-O(18)	1.870(18)	1.135
W(6)-O(6)	1.928(17)	0.971
W(6)-O(15)	1.941(19)	0.937
W(6)-O(3)	2.39(2)	0.278
W(6)-O(16)	1.855(4)	1.182
	$V_{W(6)}$ = **5.686**	
Ag(1)-N(3)	2.169(17)	0.422
Ag(1)-N(5)	2.214(16)	0.374
	$V_{Ag(1)}$ = **0.796**	

Ag(2)-N(2)	2.154(16)	0.440
Ag(2)-N(4)	2.177(17)	0.413
Ag(2)-O(22)	2.624(7)	0.109
	$V_{Ag(2)}$ = 0.962	
Ag(3)-N(1)	2.059(15)	0.568
Ag(3)-N(1)	2.059(15)	0.568
	$V_{Ag(3)}$ = 1.137	
P(1)-O(1)	1.45(2)	1.516
P(1)-O(4)	1.45(2)	1.516
P(1)-O(3)	1.57(2)	1.096
P(1)-O(2)	1.67(2)	0.837
	$V_{P(1)}$ = 4.966	
$V_{O(1)}$ = 1.766	**$V_{O(2)}$ = 1.647**	**$V_{O(3)}$ = 1.645**
$V_{O(4)}$ = 1.759	**$V_{O(5)}$ = 1.960**	**$V_{O(6}$ = 2.116**
$V_{O(7)}$ = 2.148	**$V_{O(8)}$ = 2.133**	**$V_{O(9)}$ = 2.127**
$V_{O(10)}$ = 2.094	**$V_{O(11)}$ = 1.822**	**$V_{O(12)}$ = 2.196**
$V_{O(13)}$ = 1.992	**$V_{O(14)}$ = 1.879**	**$V_{O(15)}$ = 2.136**
$V_{O(16)}$ = 1.690	**$V_{O(17)}$ = 2.238**	**$V_{O(18)}$ = 2.191**
$V_{O(19)}$ = 2.097	**$V_{O(20)}$ = 2.152**	**$V_{O(21)}$ = 1.852**
$V_{O(22)}$ = 1.912		

* $V_M = \sum_j S_{M-O_j} = \sum_j \exp(\frac{r_0 - r_{M-O_j}}{0.37})$; $r_{Mo\text{-}O}$ =1.907 Å; $r_{W\text{-}O}$ =1.917 Å; $r_{Ag^+\text{-}O}$ = 1.805 Å; $r_{Ag^+\text{-}N}$ = 1.85 Å; $r_{P^{5+}\text{-}O}$ = 1.604 Å.