A "Directed Precursor Self-Assembly" Strategy for Facile Synthesis of Heteropoly Blues: Crystal Structures, Formation Mechanism and Electrons Distribution

Supporting Information

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Contents:

S1. ***Stability Study***

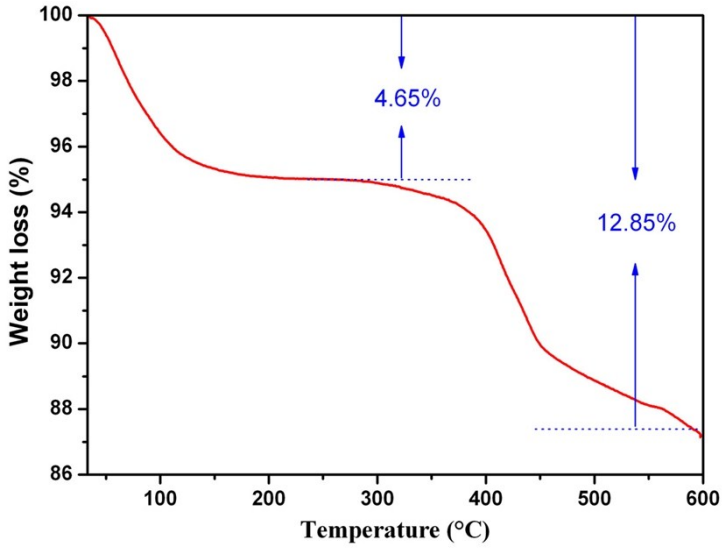


Fig. S1-a. TGA plot of Compound **1**.

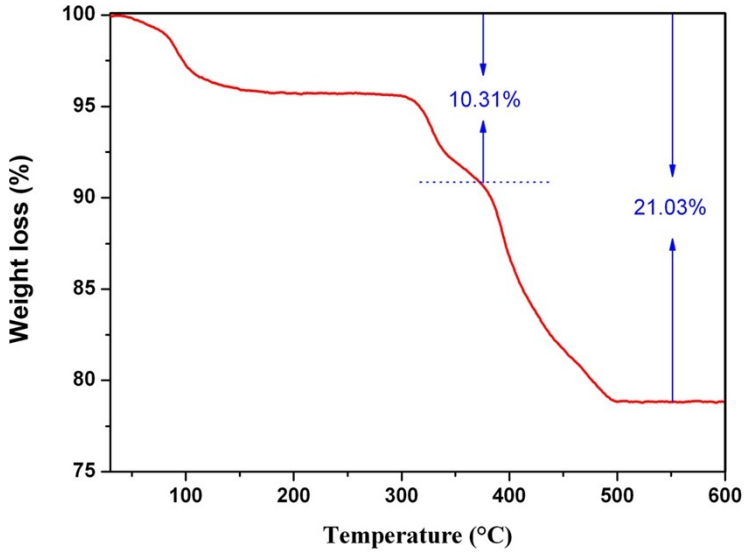


Fig. S1-b. TGA plot of Compound **2**.

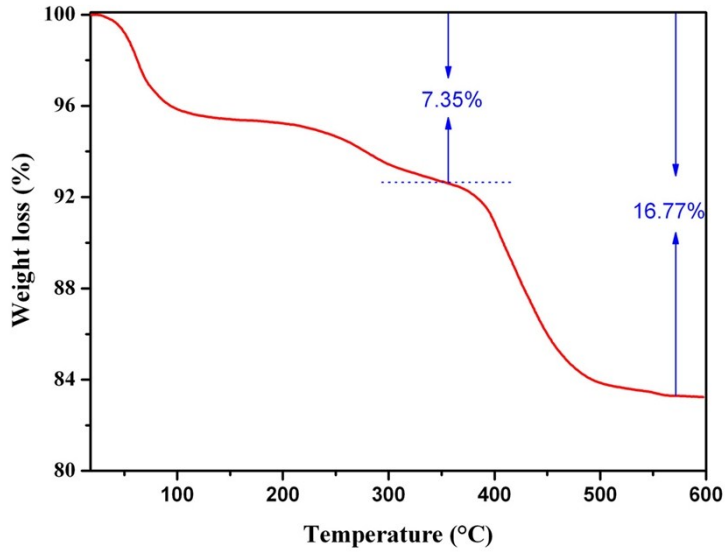


Fig. S1-c. TGA plot of Compound **3**.

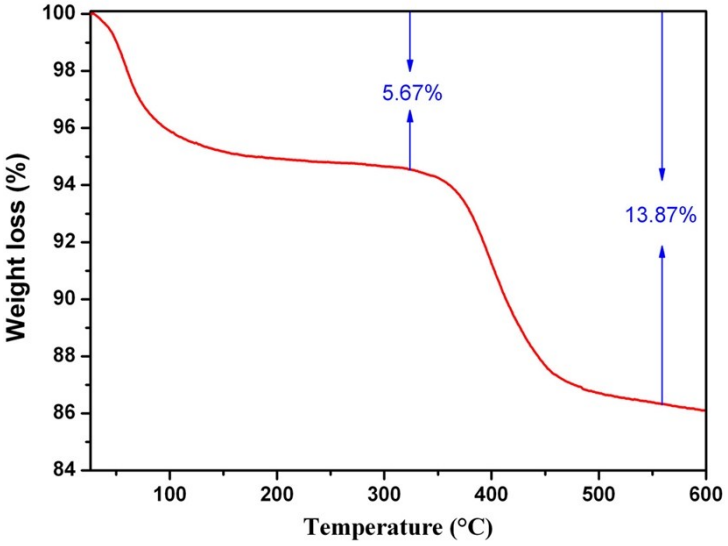


Fig. S1-d. TGA plot of Compound **4**.

UV/Vis spectra stability studies of 1-4.

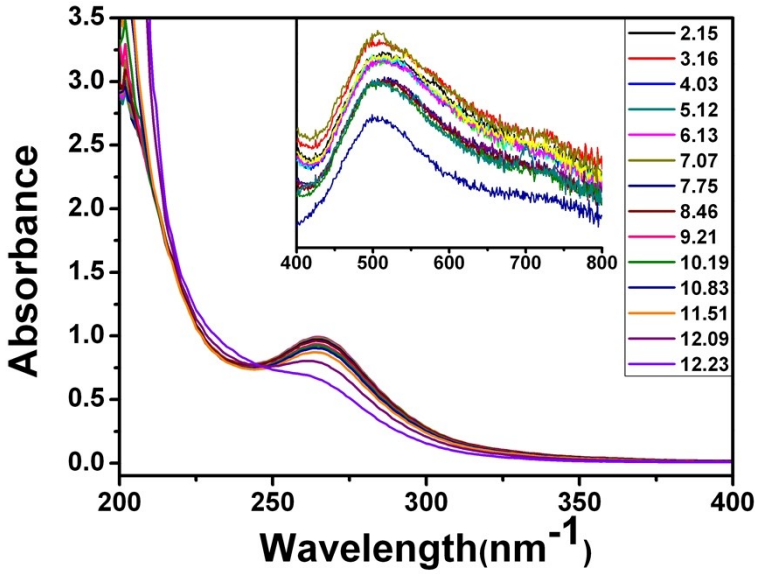


Fig. S1-e. UV/Vis spectra of **1** in aqueous solution at different pH.

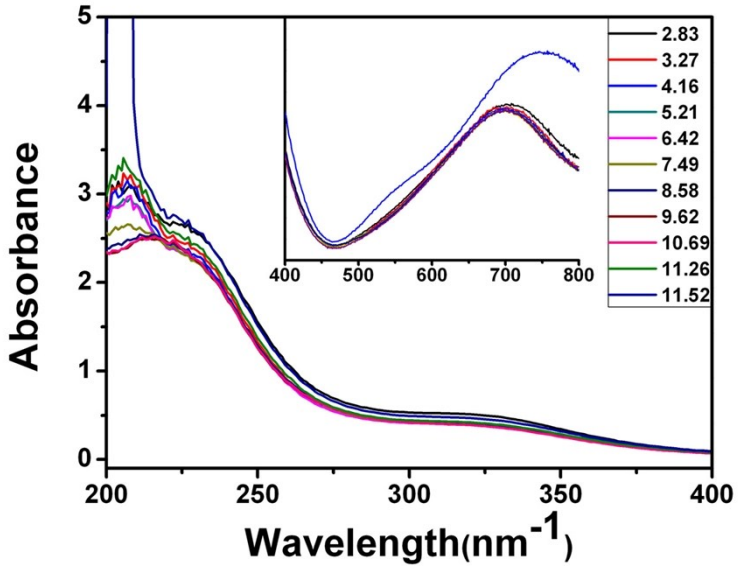


Fig. S1-f. UV/Vis spectra of **2** in aqueous solution at different pH.

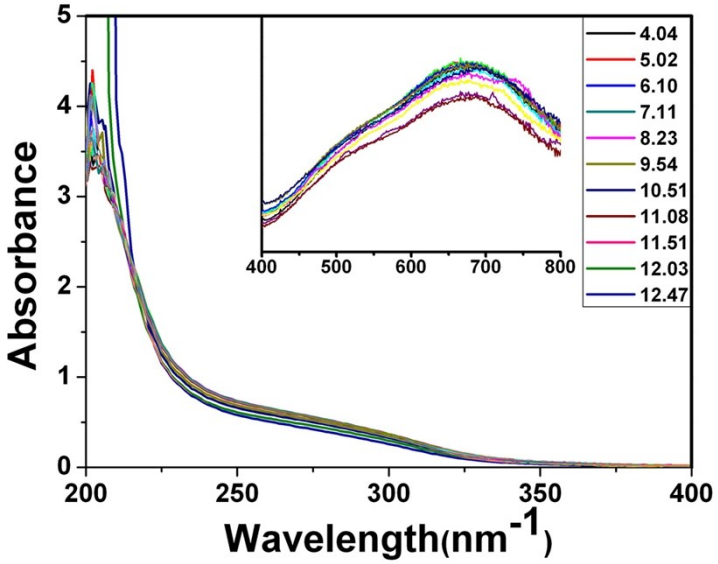


Fig. S1-g. UV/Vis spectra of **3** in aqueous solution at different pH.

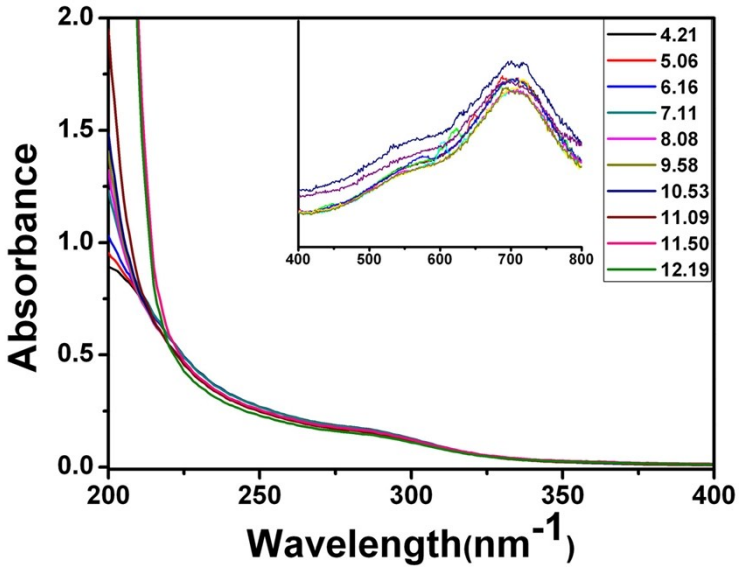


Fig. S1-h. UV/Vis spectra of **4** in aqueous solution at different pH.

S2. ***XPS***

(1) A. Patterson, T.; C. Carver, J.; E. Leyden, D.; M. Hercules, D. *J. Phys. Chem.* **1976**, *80*, 1700–1708.

(2) Wagner, C. D.; Riggs, W. M.; Davis, L. E.; Moulder, J. F.; Muilen-berg, G. E.; *Handbook of X-Ray Photoelectron Spectroscopy,* Perkin-Elmer, Eden Prairie, Minnesota,1979.

(3) Salvatl Jr, L.; Makovsky, E. L.; Stencel, J. M.; Brown, F. R.; Hercules, D. M. *J. Phys. Chem.* **1981**, *85*, 3700-3707.

(4) Ng, K. T.; Hercules, D. M. *J. Phys. Chem.* **1976**, *80*, 2094-2102.

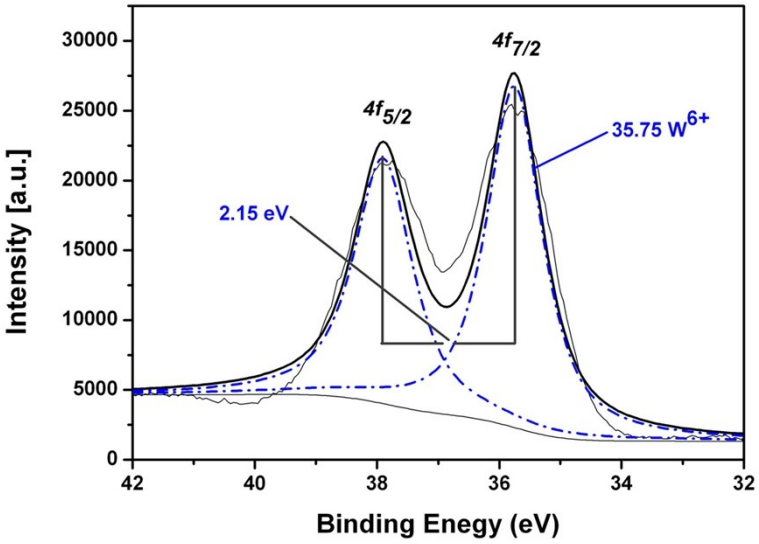


Fig. S2-a. The XPS of W in compound **1**.

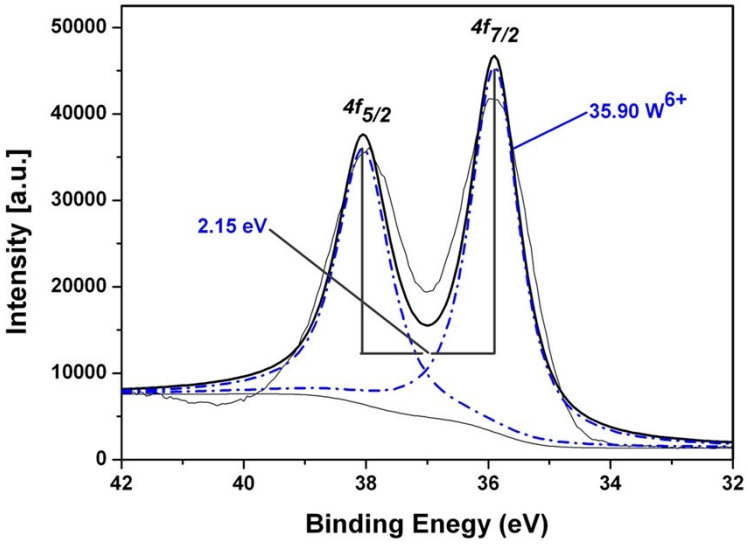


Fig. S2-b. The XPS of W in compound **3**.

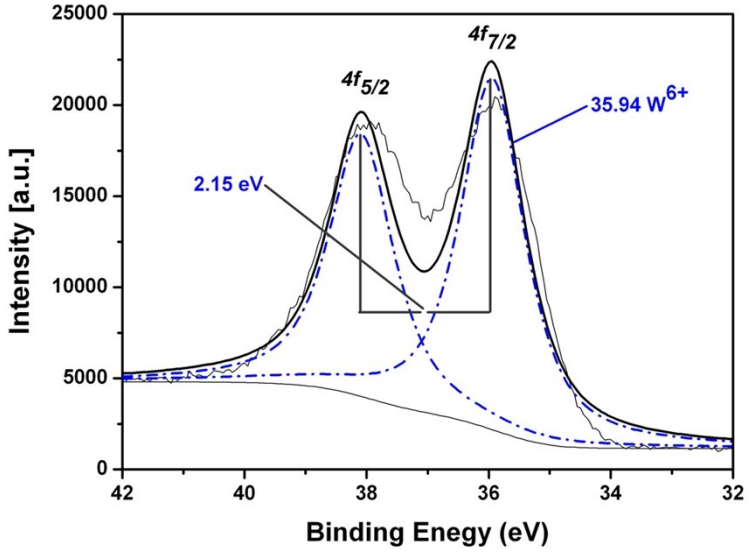


Fig. S2-c. The XPS of W in compound **4**.

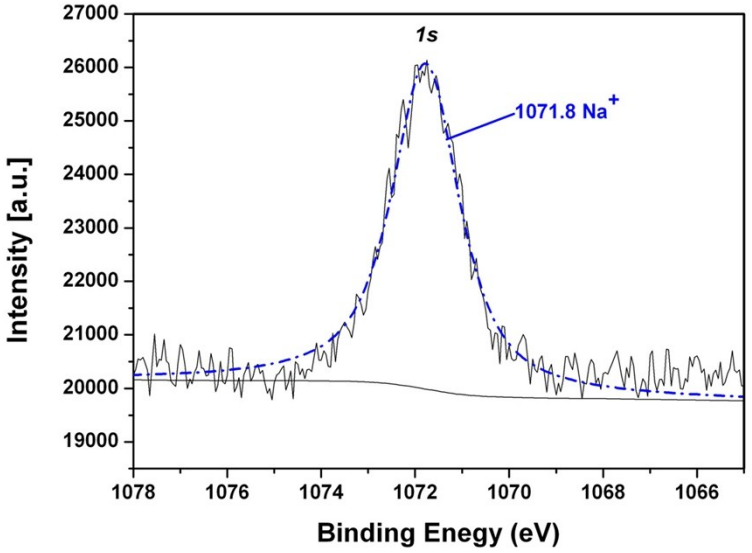


Fig. S2-d. The XPS of Na in compound **4**.

S3. Redox Titrations

Redox Titrations: The cerimetric titration was carried out using a oxidant (0.002 M solution of Ce^{IV} in 0.5 M of sulphuric acid) which added drop wise in a solution of $\mathbf{GeW_{10}Mo^{V}_{2}}$ (0.002 M, 5 ml). After addition of 10 mL oxidant, the color of the solution turned from deep blue to colorless along with a characteristic potential jump showed the presence of two single-electrons (see Table 2) which (formally) corresponds to two Mo^{V} centres (theoretical value for two e^- reduced species 10 mL). Using the same method as the above, we can determine the number of Mo^{V} in $\mathbf{GeMo^{VI}_{10}Mo^{V}_{2}}$ and $\mathbf{P_2W_{16}Mo^{V}_{2}}$ are two (theoretical value for two e^- reduced species 10 mL). However, the result of $\mathbf{P_2W_{12}Mo^{VI}_{2}Mo^{V}_{4}}$ was different with our hypothesis: the titration result showed that there should be four single-electrons in $\mathbf{P_2W_{12}Mo^{VI}_{2}Mo^{V}_{4}}$ (We thought that the number of Mo^{V} in $\mathbf{P_2W_{12}Mo^{VI}_{2}Mo^{V}_{4}}$ should be six). The final result (four Mo^{V} atoms) was confirmed by a combination of structural studies, chemical analysis, redox titration, and solution UV- VIS spectroscopy).

Table S1. The number of $\mathbf{Mo^{V}}$ determined by XPS and redox titration in compounds **1-4**.

	number of Mo	number of Mo^{V} (determined by XPS)	number of Mo^{V} (determine by Redox titration)
1	2	2	2
2	12	2	2
3	2	2	2
4	6	4	4

UV-vis spectra

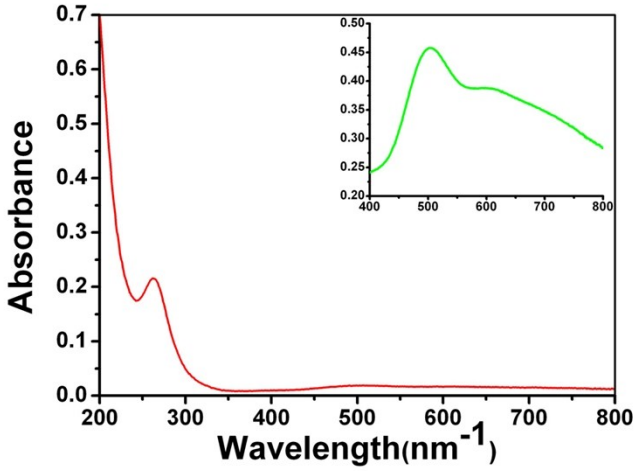


Fig. S3-a. UV-vis spectra of compound **1** in water solution within the range of 200-800 nm.

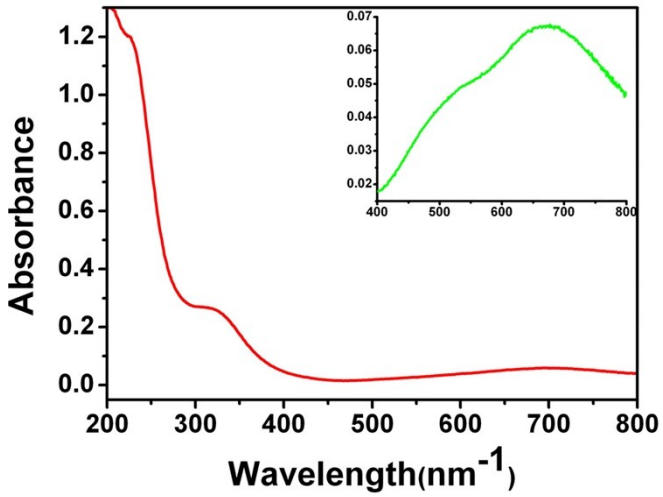


Fig. S3-b. UV-vis spectra of compound **2** in water solution within the range of 200-800 nm.

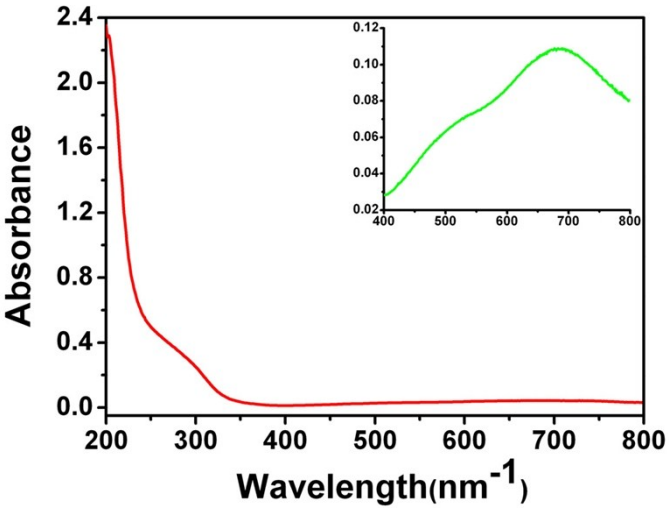


Fig. S3-c. UV-vis spectra of compound **3** in water solution within the range of 200-800 nm.

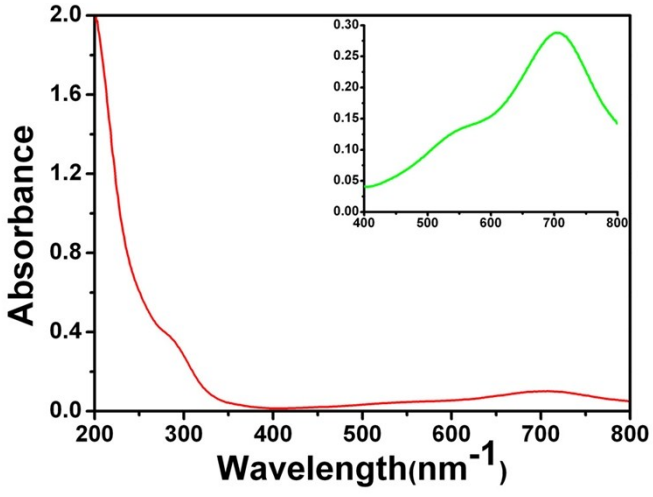


Fig. S3-d. UV-vis spectra of compound **4** in water solution within the range of 200-800 nm.

S4. ***ESI-MS Spectra Analyses***

Electrospray mass spectra (ESI- MS) were performed with a MICROTOF Ⅱ FOCUS ESI-TOF bench-top LC/MS system during the reaction. For compound **1**, the mixture was stirred for 10 min at room temperature then the first 100 μL aliquot for MS testing was removed. ESI- MS spectra of compounds **3** and **4** were obtained following the procedure described for **1**. The m/z values refer to the highest peak of the ion clusters. All experiments were performed in negative mode by direct infusion with a syringe pump. Standard experimental conditions were as follows: sample concentration 10^{-4} mol·L; mobile phase (H_2O/CH_3OH, 1:1 for **1** and **4;** H_2O/CH_3CN, 1:1 for **3**) flow rate 8 L min^{-1}; nebulizing gas N_2: 40 units flow rate; mass range 50-1500 m/z for **1**, 50-1000 m/z for **3** and **4**; capillary/V 4500 V; collision energy -10 eV; collision cell RF 500vpp; transfer time 120 μs, prepulse storage time 10 μs; summation 5000; time of acquisition 2 min; active focus off; capillary temperature 100℃.

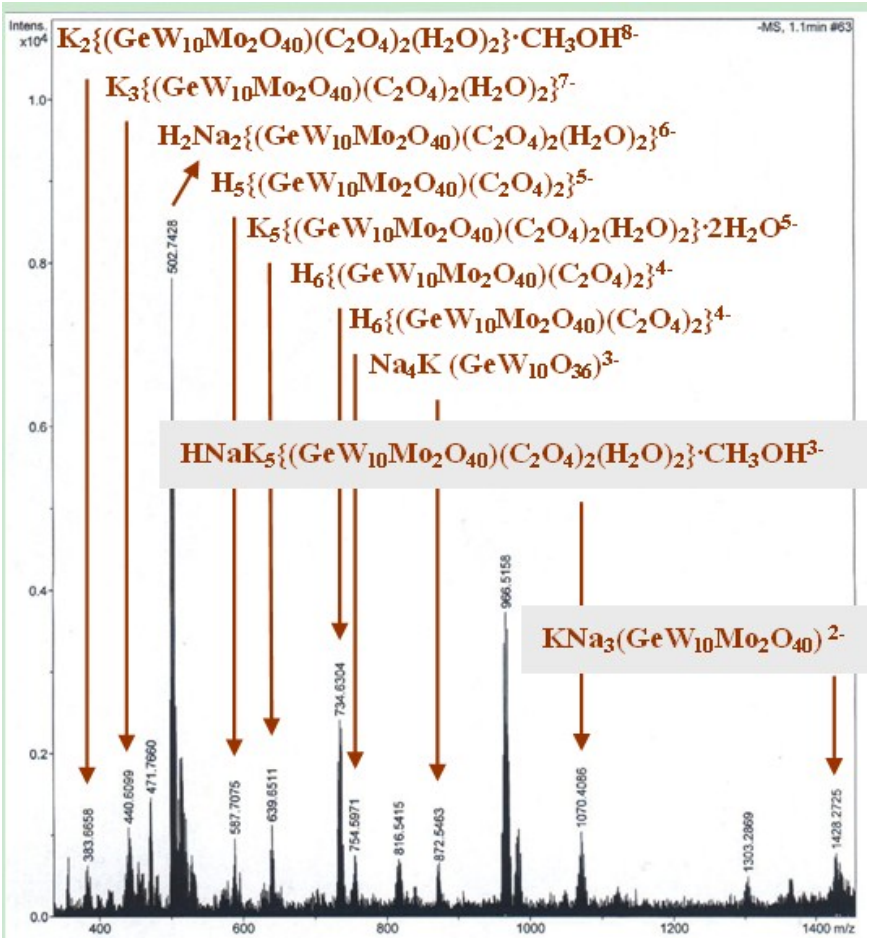


Fig. S4-a. The negative ion mode ESI-MS spectrum of compound **1** in methanol

Table S2-a. Detailed assignment of mass spectral data for compound **1**.

No.	Ion	m/z Calculated	m/z Observed
1	$K_2\{(GeW_{10}Mo_2O_{40})(C_2O_4)_2(H_2O)_2\}\cdot CH_3OH^{8-}$	383.8715	383.6658
2	$K_3\{(GeW_{10}Mo_2O_{40})(C_2O_4)_2(H_2O)_2\}^{7-}$	439.7014	440.6099
3	$H_2Na_2\{(GeW_{10}Mo_2O_{40})(C_2O_4)_2(H_2O)_2\}^{6-}$	501.5053	502.7428
4	$H_5\{(GeW_{10}Mo_2O_{40})(C_2O_4)_2\}^{5-}$	586.0073	587.7075
5	$K_5\{(GeW_{10}Mo_2O_{40})(C_2O_4)_2(H_2O)_2\}\cdot 2H_2O^{5-}$	638.3716	639.6511
6	$H_6\{(GeW_{10}Mo_2O_{40})(C_2O_4)_2\}^{4-}$	732.7611	734.6304
7	$H_5Na\{(GeW_{10}Mo_2O_{40})(C_2O_4)_2\}^{4-}$	755.2684	754.5971
8	$Na_4K\ (GeW_{10}O_{36})^{3-}$	873.3901	872.5463
9	$NaK_4\ (GeW_{11}O_{39})^{3-}$	966.6759	966.5158
10	$HNaK_5\{(GeW_{10}Mo_2O_{40})(C_2O_4)_2(H_2O)_2\}\cdot CH_3OH^{3-}$	1070.6202	1070.4086
11	$Na_5H(GeW_{10}O_{36})^{2-}$	1302.6021	1303.2869
12	$KNa_3(GeW_{10}Mo_2O_{40})^{2-}$	1428.4855	1428.2825
13	$Na\{Mo_2O_4(C_2O_4)_2(H_2O)_2\}\cdot H_2O^{-}$	512.7713	512.6414

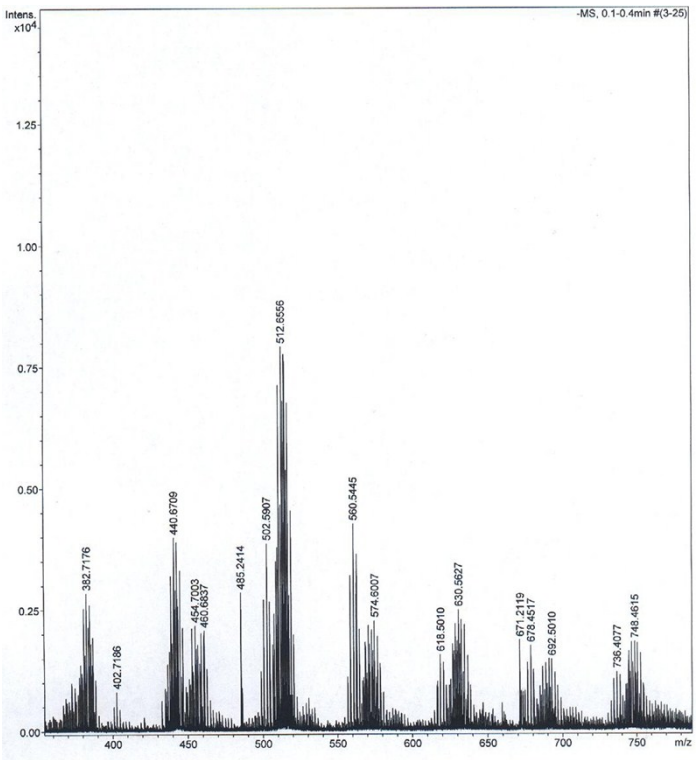


Fig. S4-a. The negative ion mode ESI-MS spectrum of compound **3** in acetonitrile.

Table S2-b. Detailed assignment of mass spectral data for compound **3**.

No.	Ion	m/z Calculated	m/z Observed
1	$Na\{(P_2W_{16}Mo_2O_{62})(C_2O_4)_2(H_2O)_2\}^{11-}$	402.5117	402.7186
2	$H_2\{(P_2W_{16}Mo_2O_{62})(C_2O_4)_2(H_2O)_2\}^{10-}$	440.6654	440.709
3	$K_2\{(P_2W_{16}Mo_2O_{62})(C_2O_4)_2H_2O\}\cdot 2CH_3CN^{10-}$	454.6608	454.7003
4	$H_3\{(P_2W_{16}Mo_2O_{62})(C_2O_4)_2\}^{9-}$	485.7379	485.2414
5	$K_3\{(P_2W_{16}Mo_2O_{62})(C_2O_4)_2(H_2O)_2\}^{9-}$	502.3922	502.5907
6	$H_2K_2\{(P_2W_{16}Mo_2O_{62})(C_2O_4)_2(H_2O)_2\}^{8-}$	560.5727	560.5445
7	$K_4\{(P_2W_{16}Mo_2O_{62})(C_2O_4)_2(H_2O)_2\}\cdot CH_3CN^{8-}$	575.1900	574.6007
8	$Na_2H\{(P_2W_{16}Mo_2O_{62})(C_2O_4)_2\}^{7-}$	618.2321	618.5010
9	$H_4Na\{(P_2W_{16}Mo_2O_{62})(C_2O_4)_2\cdot H_2O\}^{7-}$	630.5213	630.5627
10	$H_6\{(P_2W_{16}Mo_2O_{62})(C_2O_4)_2\}^{6-}$	735.9485	736.4077
11	$H3Na_2K\{(P_2W_{16}Mo_2O_{62})(C_2O_4)_2(H_2O)_2\}^{6-}$	748.7675	748.4615
12	$Na\{Mo_2O_4(C_2O_4)_2(H_2O)_2\}\cdot H_2O^{-}$	512.7713	512.6556

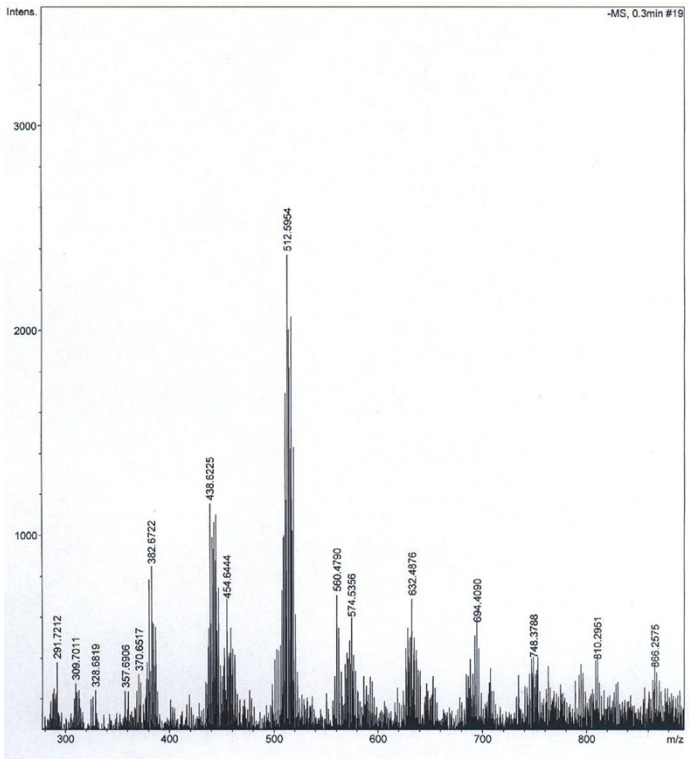


Fig. S4-b. The negative ion mode ESI-MS spectrum of compound **4** in methanol.

Table S2-c. Detailed assignment of mass spectral data for compound **4**.

No.	Ion	m/z Calculated	m/z Observed
1	$Na_3K_3\{(P_2W_{12}\ Mo_2^{VI}Mo^{V}_4O_{62})(C_2O_4)_6(H_2O)_6\}^{16-}$	291.8924	291.7212
2	$Na_7\{(P_2W_{12}\ Mo_2^{VI}Mo^{V}_4O_{62})(C_2O_4)_6(H_2O)_6\}^{15-}$	309.6897	309.7011
3	$Na_5H_3\{(P_2W_{12}\ Mo_2^{VI}Mo^{V}_4O_{62})(C_2O_4)_6(H_2O)_6\}^{14-}$	328.7421	328.6819
4	$Na_7H_2\{(P_2W_{12}\ Mo_2^{VI}Mo^{V}_4O_{62})(C_2O_4)_6(H_2O)_6\}^{13-}$	357.4893	357.6906
5	$NaK_8\{(P_2W_{12}\ Mo_2^{VI}Mo^{V}_4O_{62})(C_2O_4)_6(H_2O)_6\}^{13-}$	370.7013	370.6517
6	$NaHK_7\{(P_2W_{12}\ Mo_2^{VI}Mo^{V}_4O_{62})(C_2O_4)_6(H_2O)_6\}^{12-}$	382.6991	382.6722
7	$Na_3K_7H\{(P_2W_{12}\ Mo_2^{VI}Mo^{V}_4O_{62})(C_2O_4)_6(H_2O)_6\}^{11-}$	438.8309	438.6225
8	$NaKH_{10}\{(P_2W_{12}\ Mo_2^{VI}Mo^{V}_4O_{62})(C_2O_4)_6(H_2O)_6\}^{10-}$	454.7379	454.6444
9	$Na\{Mo_2O_4(C_2O_4)_2(H_2O)_2\}\cdot H_2O^{-}$	512.7713	512.5954
10	$H_{14}\{(P_2W_{12}\ Mo_2^{VI}Mo^{V}_4O_{62})(C_2O_4)_6(H_2O)_5\}^{8-}$	560.0645	560.4790
11	$NaH_{11}K_2\{(P_2W_{12}Mo_2^{VI}Mo^{V}_4O_{62})(C_2O_4)_6(H_2O)_6\}^{8-}$	574.5526	574.5356
12	$H_{15}\{(P_2W_{12}\ Mo_2^{VI}Mo^{V}_4O_{62})(C_2O_4)_6(H_2O)_2\}^{7-}$	632.4989	632.4876
13	$Na_{13}K_2\{(P_2W_{12}\ Mo_2^{VI}Mo^{V}_4O_{62})(C_2O_4)_6(H_2O)_6\}^{7-}$	694.4588	694.4090
14	$Na_2H_{14}\{(P_2W_{12}\ Mo_2^{VI}Mo^{V}_4O_{62})(C_2O_4)_6(H_2O)_3\}^{6-}$	748.4123	748.3788
15	$Na_{13}K_2H\{(P_2W_{12}Mo_2^{VI}Mo^{V}_4O_{62})(C_2O_4)_6(H_2O)_6\}^{6-}$	810.3699	810.2951

S5. <u>Electron paramagnetic resonance (ESR) spectra</u>

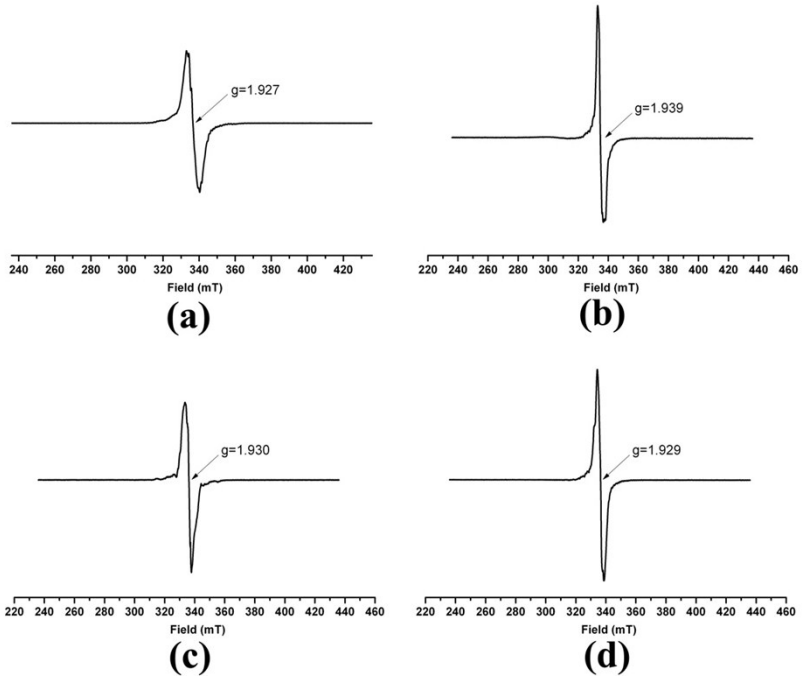


Fig. S5. The ESR spectra for powdered samples of **1**-**4**.

S6. IR spectra

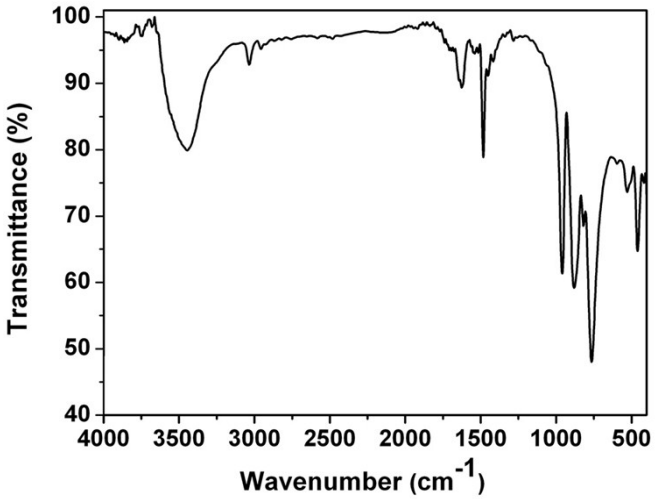


Fig. S6-a. IR spectrum of compound **1**.

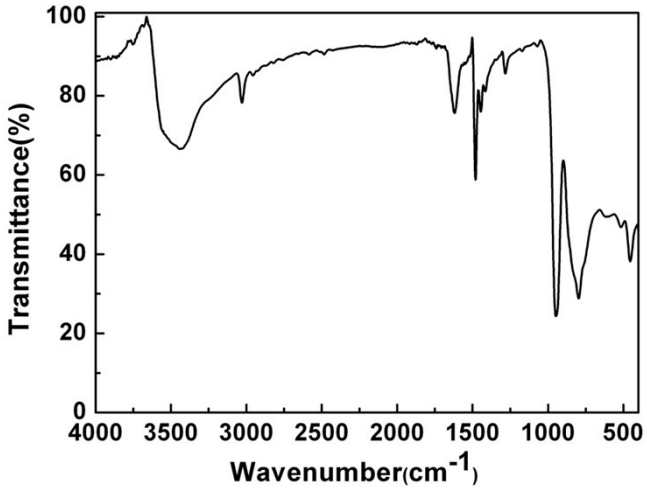


Fig. S6-b. IR spectrum of compound **2**.

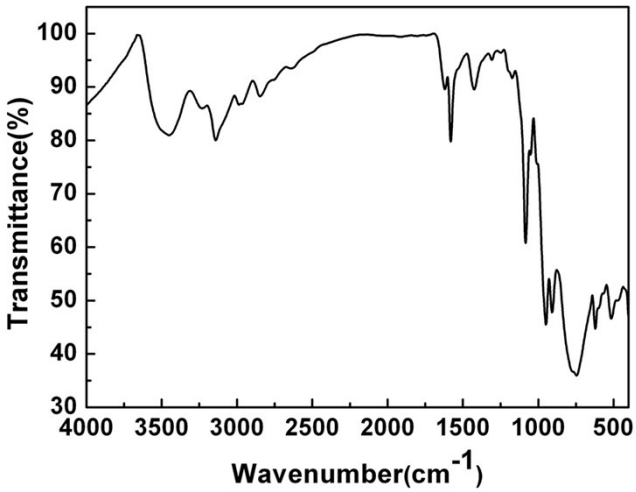


Fig. S6-c. IR spectrum of compound **3**.

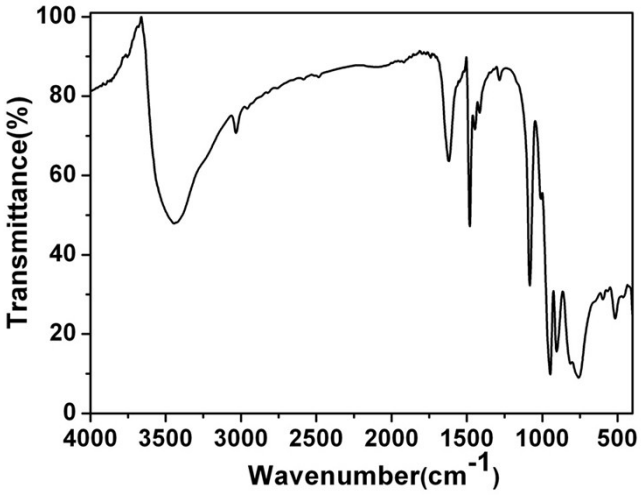


Fig. S6-d. IR spectrum of compound **4**.

S7. X-ray powder diffraction

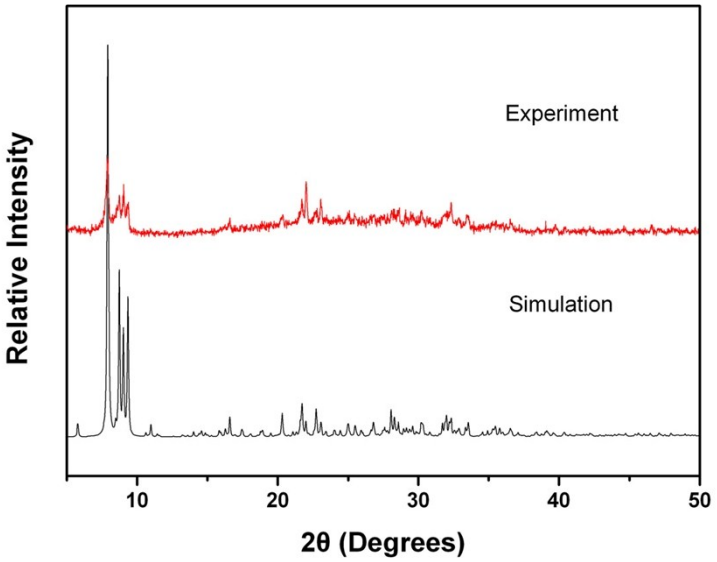


Fig. S7-a. XRD patterns of compound **1**.

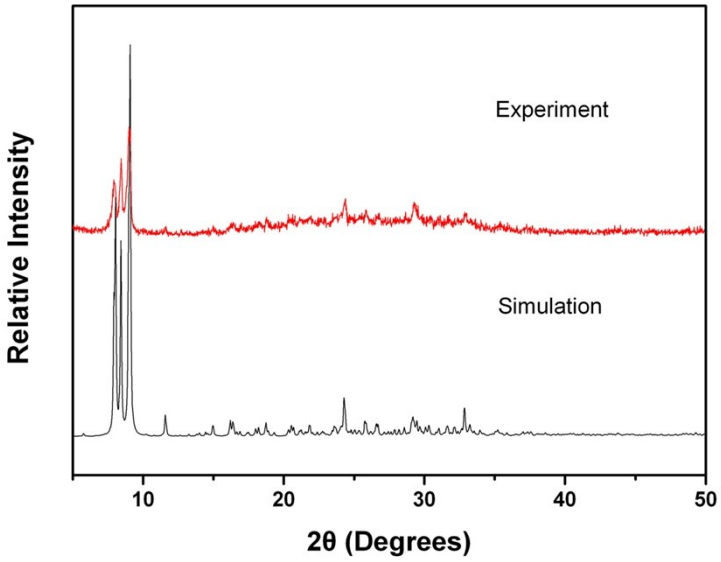


Fig. S7-b. XRD patterns of compound **2**.

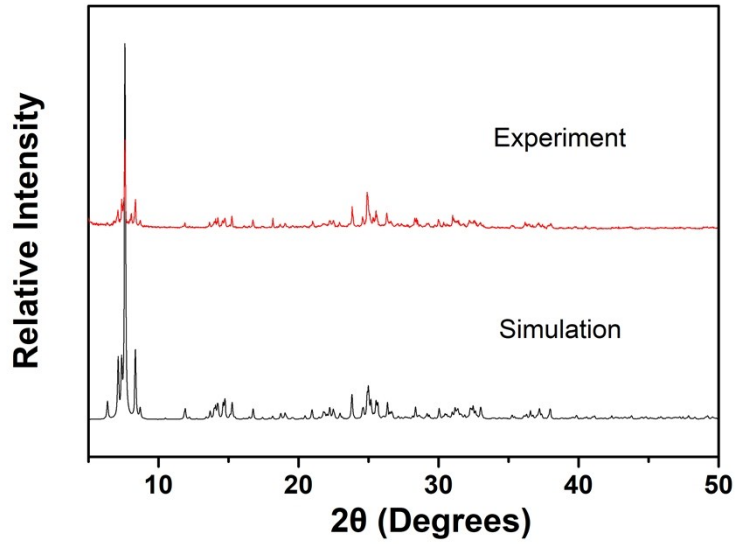


Fig. S7-c. XRD patterns of compound **3**.

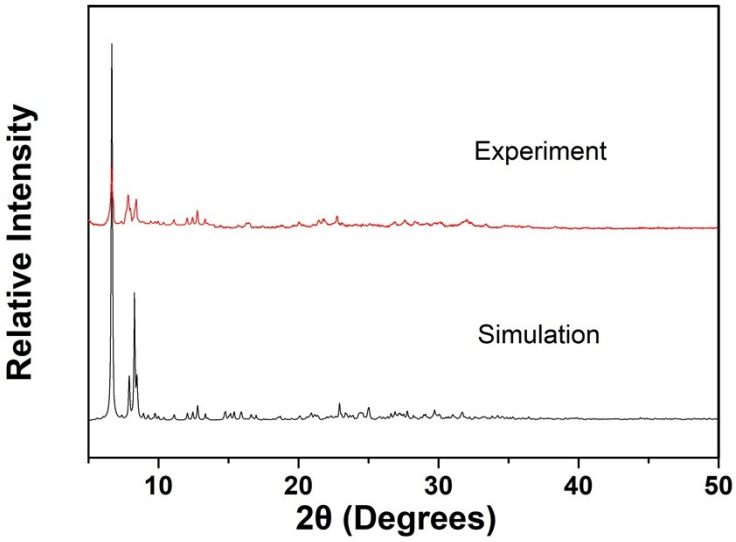


Fig. S7-d. XRD patterns of compound **4**.

S8. Selected Bond Lengths (Å) and Angles (deg) for Compounds 1-4

Selected Bond Lengths (Å) and Angles (deg) for Compounds 1

Ge1-O6	1.707(9)	W3-O40	1.918(10)	W6-O36	1.959(10)	W9-O6	2.311(9)
Ge1-O18	1.713(9)	W3-O11	1.925(10)	W6-O17	2.299(10)	W10-O29	1.696(12)
Ge1-O17	1.714(10)	W3-O18	2.300(9)	W7-O35	1.716(10)	W10-O30	1.914(10)
Ge1-O5	1.716(9)	W4-O1	1.721(10)	W7-O37	1.892(11)	W10-O19	1.918(10)
W1-O10	1.714(10)	W4-O2	1.922(9)	W7-O36	1.924(10)	W10-O9	1.942(10)
W1-O25	1.906(9)	W4-O37	1.928(12)	W7-O16	1.925(10)	W10-O15	1.945(10)
W1-O9	1.916(11)	W4-O3	1.929(11)	W7-O8	1.959(10)	W10-O5	2.314(10)
W1-O26	1.936(10)	W4-O11	1.936(9)	W7-O17	2.304(9)	W11-O28	1.721(12)
W1-O13	1.937(10)	W4-O18	2.307(9)	W8-O27	1.705(12)	W11-O31	1.908(11)
W1-O5	2.297(9)	W5-O24	1.692(10)	W8-O30	1.911(10)	W11-O19	1.914(10)
W2-O12	1.719(10)	W5-O7	1.913(11)	W8-O4	1.911(10)	W11-O4	1.927(10)
W2-O16	1.901(10)	W5-O25	1.932(9)	W8-O3	1.931(10)	W11-O20	1.931(11)
W2-O2	1.905(9)	W5-O31	1.940(11)	W8-O38	1.933(10)	W11-O6	2.309(10)
W2-O15	1.920(11)	W5-O23	1.942(10)	W8-O18	2.308(10)	W12-O32	1.729(10)
W2-O13	1.928(10)	W5-O6	2.299(9)	W9-O39	1.714(10)	W12-O26	1.894(10)
W2-O5	2.295(8)	W6-O14	1.710(11)	W9-O40	1.902(10)	W12-O7	1.912(10)
W3-O34	1.695(10)	W6-O22	1.891(11)	W9-O20	1.910(12)	W12-O33	1.931(11)
W3-O38	1.905(11)	W6-O21	1.924(10)	W9-O22	1.921(12)	W12-O8	1.931(10)
W3-O21	1.906(10)	W6-O33	1.928(11)	W9-O23	1.925(10)	W12-O17	2.289(9)

O18-Ge1-O5	109.7(4)	O28-W11-O6	169.8(5)	W5-O6-W11	93.2(3)	W6-O17-W7	93.8(4)
O17-Ge1-O5	109.1(5)	O32-W12-O7	102.5(5)	Ge1-O6-W9	122.7(5)	Ge1-O18-W3	123.1(5)
O10-W1-O25	101.2(4)	W2-O2-W4	152.8(6)	W5-O6-W9	93.2(3)	Ge1-O18-W4	123.0(5)
O12-W2-O16	99.6(5)	W4-O3-W8	120.5(5)	W11-O6-W9	92.9(3)	W3-O18-W4	93.4(3)
O34-W3-O38	101.0(5)	W8-O4-W11	151.4(5)	W12-O7-W5	153.0(6)	Ge1-O18-W8	122.6(5)
O37-W4-O3	157.7(4)	Ge1-O5-W2	122.9(5)	W12-O8-W7	119.2(5)	W3-O18-W8	93.4(3)
O24-W5-O31	101.8(5)	Ge1-O5- W1	122.9(5)	W1-O9-W10	120.5(5)	W4-O18-W8	93.1(3)
O22-W6-O36	158.1(4)	W2-O5-W1	93.9(3)	W3-O11-W4	120.5(5)	W3-O21-W6	152.6(5)
O35-W7-O16	103.1(5)	Ge1-O5-W10	122.6(5)	W2-O13-W1	120.5(5)	W6-O22-W9	152.8(6)
O27-W8-O38	100.6(6)	W2-O5-W10	93.2(3)	W2-O16-W7	152.1(6)	W9-O23-W5	120.1(5)
O39-W9-O22	104.1(5)	W1- O5-W10	93.2(3)	Ge1-O17-W6	122.2(5)	W1-O25-W5	151.6(6)
O29-W10-O5	169.9(5)	Ge1-O6-W5	123.5(5)	Ge1-O17-W7	122.1(5)	O6-Ge1-O18	109.2(5)

Selected Bond Lengths (Å) and Angles (deg) for Compounds 2

O1-Mo2	1.907(12)	O8-Mo4	1.949(12)	O27-Mo2	1.879(12)	O56-Mo1	1.655(15)
O1-Mo7	1.922(13)	O9 -Ge2	1.728(11)	O28-Mo12	2.301(11)	O57-Mo5	1.712(15)
O2 -Ge2	1.755(14)	O10-Mo6	1.681(13)	O28-Mo8	2.301(11)	O58-Mo7	1.956(12)
O2-Mo7	2.261(12)	O11-Mo11	1.894(12)	O29-Mo6	1.922(12)	O59-Mo1	1.952(16)
O2-Mo11	2.276(13)	O12-Mo12	1.695(13)	O29-Mo5	1.977(13)	O60-Mo3	1.869(13)
O2-Mo2	2.329(13)	O13-Mo12	1.937(12)	O30-Mo4	1.714(13)	O60-Mo10	1.963(13)
O3-Mo5	1.917(11)	O14-Mo11	1.899(12)	O31-Mo11	2.124(13)	O61-Mo10	1.898(15)
O3-Mo16	1.950(11)	O15-Mo7	1.924(12)	O31-Mo2	2.128(11)	O62-Mo10	1.855(14)
O4 -Ge2	1.739(13)	O15-Mo11	1.929(12)	O32-Mo7	1.682(13)	O62-Mo9	1.966(14)
O4-Mo5	2.270(12)	O16-Mo9	1.878(13)	O33-Mo11	1.695(13)	O65 -Ge1	1.736(13)
O4-Mo6	2.292(13)	O18-Mo3	2.012(12)	O37-Mo3	1.938(15)	O65-Mo1	2.284(18)
O4-Mo4	2.316(12)	O19-Mo3	1.691(16)	O38-Mo8	1.687(12)	O66-Mo3	1.859(14)
O5-Mo5	1.858(13)	O22-Mo6	1.864(12)	O39-Mo2	1.704(13)	O70 -Ge1	1.720(16)
O5-Mo7	1.945(13)	O23-Mo6	1.863(10)	O45-Mo10	1.860(13)	O71-Mo8	1.853(14)
O6-Mo2	1.870(11)	O23-Mo8	2.001(10)	O45-Mo1	1.932(15)	O71-Mo4	1.959(13)
O6-Mo4	1.925(11)	O24-Mo12	1.930(12)	O46-Mo10	1.695(14)	O78 -Ge1	1.735(15)
O7-Mo4	1.914(12)	O24-Mo8	1.959(14)	O47-Mo9	1.913(15)	O78-Mo9	2.279(16)
O7-Mo6	1.974(12)	O25-Mo8	1.865(12)	O49-Mo12	1.932(12)	O78-Mo10	2.317(16)
O8-Mo5	1.931(13)	O26-Mo12	1.888(12)	O53-Mo9	1.870(14)	O79-Mo1	1.908(17)

O70-Ge1-O78	109.5(7)	Mo2-O1-Mo7	121.2(7)	Mo13-O14-Mo11	158.1(7)	Mo12-O28-Mo8	93.3(4)
O70-Ge1-O65	106.4(7)	Mo7-O2-Mo11	94.9(5)	Mo7-O15-Mo11	120.3(6)	Ge2-O28-Mo19	123.1(6)
O56-Mo1-O79	98.6(8)	Mo7-O2-Mo2	93.2(5)	Mo9-O16-Mo1	144.9(8)	Mo12-O28-Mo19	93.8(4)
O39-Mo2-O27	101.9(6)	Mo11-O2-Mo2	98.9(5)	Mo22-O17-Mo17	145.1(9)	Mo8-O28-Mo19	93.3(4)
O19-Mo3-O66	103.2(8)	Ge2-O4-Mo5	122.9(6)	Mo23-O18-Mo3	116.8(6)	Mo6-O29-Mo5	120.1(6)
O30-Mo4-O8	100.6(6)	Ge2-O4-Mo6	120.9(7)	Mo18-O20-Mo13	117.4(6)	Mo11-O31-Mo2	110.8(5)
O57-Mo5-O5	105.0(7)	Mo5-O4-Mo6	95.5(5)	Mo6-O22-Mo18	157.4(7)	Mo18-O34-Mo16	119.5(6)
O29-Mo6-O7	84.0(5)	Ge2-O4-Mo4	124.0(6)	Mo6-O23-Mo8	146.9(6)	Mo3-O37-Mo17	125.8(9)
O32-Mo7-O1	102.1(6)	Mo5-O4-Mo4	93.8(5)	Mo12-O24-Mo8	118.8(7)	Mo21-O41-Mo20	128.8(8)
O38-Mo8-O71	101.5(6)	Mo6-O4-Mo4	91.9(4)	Mo8-O25-Mo19	122.1(6)	Mo21-O43-Mo23	144.4(8)
O35-Mo9-O53	101.0(7)	Mo5-O5-Mo7	155.5(8)	Mo12-O26-Mo19	120.2(6)	Mo10-O45-Mo1	143.3(9)
O46-Mo10-O62	102.1(7)	Mo2-O6-Mo4	157.2(7)	Mo2-O27-Mo19	147.1(7)	Mo9-O47-Mo22	124.3(9)
O33-Mo11-O11	102.1(6)	Mo4-O7-Mo6	116.8(6)	Ge2-O28-Mo12	122.0(6)	Mo18-O49-Mo12	147.1(8)
O12-Mo12-O24	98.9(6)	Mo5-O8-Mo4	119.3(7)	Ge2-O28-Mo8	123.2(5)	Mo16-O50-Mo13	121.3(6)

Selected Bond Lengths (Å) and Angles (deg) for Compounds 3

W1-O42	1.703(16)	W5-O23	1.946(17)	W10-O51	1.922(14)	W15-O29	1.889(18)
W1-O60	1.886(14)	W5-O49	2.374(14)	W10-O31	1.961(16)	W15-O3	1.899(15)
W1-O24	1.898(18)	W6-O38	1.708(16)	W10-O36	2.365(15)	W15-O34	1.926(17)
W1-O62	1.918(16)	W6-O35	1.914(15)	W11-O41	1.717(17)	W15-O30	1.934(15)
W1-O4	1.927(17)	W6-O51	1.916(14)	W11-O10	1.890(17)	W15-O26	2.388(14)
W1-O48	2.343(15)	W6-O27	1.919(17)	W11-O18	1.921(17)	W16-O52	1.711(18)
W2-O39	1.716(18)	W6-O36	2.360(15)	W11-O54	1.929(16)	W16-O31	1.893(15)
W2-O1	1.884(16)	W7-O59	1.721(19)	W11-O9	1.935(15)	W16-O4	1.909(16)
W2-O17	1.908(17)	W7-O27	1.884(17)	W11-O50	2.379(14)	W16-O56	1.910(16)
W2-O58	1.913(15)	W7-O10	1.921(16)	W12-O13	1.733(19)	W16-O55	1.926(16)
W2-O28	1.945(19)	W7-O14	1.932(15)	W12-O25	1.885(15)	W16-O20	2.366(19)
W2-O32	2.324(14)	W7-O25	1.950(16)	W12-O7	1.933(16)	W17-O44	1.698(15)
W3-O46	1.73(2)	W7-O50	2.323(15)	W12-O34	1.936(15)	W17-O23	1.893(17)
W3-O11	1.846(14)	W8-O45	1.698(17)	W12-O2	1.944(15)	W17-O54	1.903(15)
W3-O14	1.888(15)	W8-O16	1.862(17)	W12-O26	2.388(17)	W17-O7	1.925(18)
W3-O17	1.903(17)	W8-O30	1.891(16)	W13-O12	1.690(15)	W17-O3	1.932(15)
W3-O2	1.904(16)	W8-O22	1.908(16)	W13-O8	1.860(15)	W17-O26	2.397(14)
W3-O33	2.347(16)	W8-O11	1.948(15)	W13-O21	1.913(17)	W18-O57	1.729(18)
W4-O15	1.688(14)	W8-O33	2.402(14)	W13-O16	1.914(16)	W18-O19	1.905(18)
W4-O22	1.885(17)	W9-O47	1.735(15)	W13-O29	1.957(18)	W18-O53	1.914(15)
W4-O58	1.903(16)	W9-O21	1.885(17)	W13-O49	2.354(14)	W18-O56	1.920(18)
W4-O61	1.903(16)	W9-O62	1.898(17)	W14-O37	1.742(18)	W18-O5	1.925(14)
W4-O19	1.945(18)	W9-O61	1.898(17)	W14-O28	1.882(18)	W18-O20	2.401(16)
W4-O32	2.380(13)	W9-O53	1.926(16)	W14-O5	1.905(14)	P1-O33	1.511(15)
W5-O43	1.705(16)	W9-O48	2.371(14)	W14-O55	1.909(17)	P1-O49	1.516(16)
W5-O9	1.879(13)	W10-O40	1.715(16)	W14-O35	1.913(15)	P1-O26	1.551(18)
W5-O24	1.907(18)	W10-O18	1.887(17)	W14-O20	2.386(16)	P2-O20	1.560(19)
W5-O8	1.931(14)	W10-O60	1.899(14)	W15-O6	1.691(16)	P2-O32	1.563(16)

O42-W1-O60	102.7(6)	O29-W15-O3	86.3(7)	W3-O2-W12	150.3(9)	P2-O20-W16	125.8(9)
O39-W2-O1	103.0(7)	O52-W16-O56	102.1(8)	W15-O3-W17	123.4(8)	P2-O20-W14	125.3(10)
O46-W3-O11	99.5(7)	O23-W17-O3	88.3(7)	W16-O4-W1	150.7(11)	W16-O20-W14	90.5(6)
O15-W4-O22	98.5(7)	O19-W18-O53	86.7(7)	W14-O5-W18	123.8(7)	P2-O20-W18	123.8(8)
O43-W5-O24	99.0(8)	O33-O1-O49	112.3(9)	W17-O7-W12	122.0(9)	W16-O20-W18	90.9(7)
O38-W6-O35	96.2(7)	O33-O1-O26	106.5(9)	W13-O8-W5	124.4(8)	W14-O20-W18	89.8(6)
O27-W7-O14	87.7(6)	O49-O1-O26	106.2(9)	W5-O9-W11	149.4(9)	W9-O21-W13	163.6(10)
O16-W8-O22	88.2(7)	O33-O1-O50	110.5(8)	W11-O10-W7	123.5(8)	W4-O22-W8	164.9(10)
O21-W9-O62	91.7(7)	O49-O1-O50	113.0(9)	W3-O11-W8	124.0(8)	W17-O23-W5	150.7(8)
O40-W10-O60	101.6(7)	O26-O1-O50	107.8(8)	W3-O14-W7	150.9(8)	W1-O24-W5	162.6(9)
O41-W11-O10	101.3(7)	O36-O2-O48	112.1(8)	W8-O16-W13	153.6(9)	W12-O25-W7	151.8(9)
O13-W12-O25	101.7(7)	O36-O2-O20	105.7(9)	W3-O17-W2	163.3(9)	P1-O26-W15	126.0(7)
O12-W13-O16	104.2(7)	O48-O2-O32	111.8(8)	W10-O18-W11	162.5(9)	P1-O26-W12	125.0(8)
O28-W14-O5	89.1(7)	O20-O2-O32	108.4(9)	W18-O19-W4	149.9(9)	W15-O26-W12	90.2(6)

Selected Bond Lengths (Å) and Angles (deg) for Compounds 4

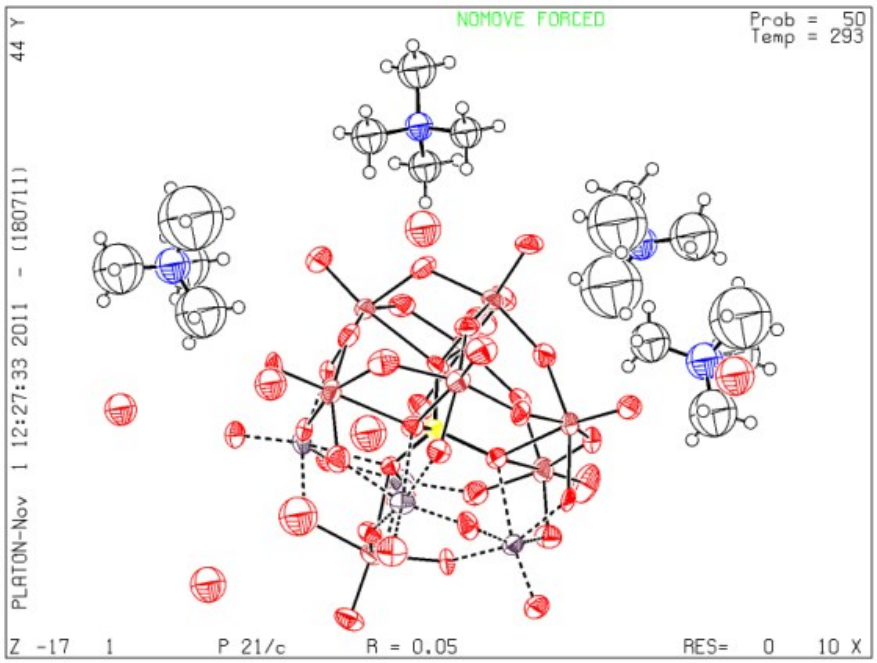
W1-O50	1.709(10)	W7-O60	2.365(11)	W12-O96	1.906(11)	W3-O74	2.380(10)
W1-O38	1.898(9)	W8-O81	1.726(11)	W12-O58	2.367(9)	W16-O63	1.889(9)
W1-O39	1.902(11)	W8-O46	1.893(10)	W13-O11	1.707(11)	W4-O95	1.714(11)
W1-O41	1.907(11)	W8-O12	1.897(10)	W13-O17	1.852(9)	W4-O97	1.883(12)
W1-O8	1.923(9)	W8-O49	1.903(11)	W13-O20	1.887(10)	W4-O25	1.903(11)
W1-O35	2.334(10)	W8-O10	1.964(10)	W13-O65	1.918(10)	W4-O98	1.908(10)
W2-O45	1.699(10)	W8-O75	2.332(11)	W13-O37	1.972(10)	W4-O96	1.939(11)
W2-O38	1.883(9)	W9-O32	1.706(12)	W13-O4	2.339(10)	W4-O77	2.350(9)
W2-O41	1.891(10)	W9-O14	1.877(10)	W10-O57	2.337(11)	W5-O29	1.684(11)
W2-O20	1.937(10)	W9-O90	1.913(11)	W14-O62	1.707(11)	W5-O76	1.874(12)
W2-O31	1.954(10)	W9-O91	1.913(11)	W14-O80	1.864(11)	W5-O98	1.893(10)
W2-O4	2.362(10)	W9-O18	1.968(10)	W11-O77	2.355(10)	W5-O91	1.923(11)
W14-O37	1.891(11)	W9-O73	2.348(11)	W14-O1	1.945(11)	W11-O47	1.695(11)
W3-O56	1.765(11)	W10-O48	1.683(12)	W14-O59	1.962(10)	W11-O46	1.894(10)
W3-O8	1.909(9)	W10-O89	1.872(11)	W14-O74	2.383(10)	W11-O14	1.908(11)
W3-O31	1.911(11)	W10-O90	1.875(10)	W15-O40	1.674(12)	W11-O25	1.931(11)
W3-O59	1.925(11)	W10-O12	1.902(10)	W15-O16	1.883(10)	W11-O78	1.937(11)
W3-O3	1.926(11)	W10-O88	1.930(11)	W15-O39	1.917(11)	W16-O24	1.919(11)
W15-O35	2.358(10)	-W15-O9	1.966(9)	W15-O17	1.936(9)	W16-O80	1.978(10)
W16-O43	2.353(10)	W17-O44	1.732(11)	W17-O68	1.902(11)	W17-O78	1.916(11)
P1-O77	1.520(11)	P1-O58	1.587(10)	P2-O73	1.534(11)	P3-O35	1.533(10)
P1-O28	1.537(11)	P2-O57	1.529(11)	P2-O92	1.589(11)	P3-O4	1.537(11)
P1-O75	1.559(11)	P2-O60	1.530(11)	P3-O43	1.524(10)	P3-O74	1.573(10)
W17-O52	1.933(10)	W18-O2	1.679(12)	W18-O9	1.878(10)	W18-O3	1.966(10)
W17-O58	2.384(10)	W18-O22	1.865(11)	W18-O1	1.903(11)	W18-O74	2.385(11)
O1-Mo14	1.945(11)	O4-W2	2.362(10)	O31-W2	1.954(10)	O41-W2	1.891(10)
O1-W14	1.945(11)	O4-Mo2	2.362(10)	O31-Na1	2.641(14)	O44-Na1	2.482(15)
O4-Mo13	2.339(10)	O20-Na1	2.711(13)	O37-Na1	2.721(13)	O59-Mo14	1.962(10)
O4-W13	2.339(10)	O31-Mo2	1.954(10)	O41-Mo2	1.891(10)	O59-W14	1.962(10)

O50-W1-O38	99.0(5)	O11-W13-O17	98.7(5)	O57-P2-O60	111.3(6)	Mo13-O4-W2	90.9(3)
O45-W2-O38	98.0(5)	O62-W14-O80	102.4(5)	O57-P2-O73	111.0(6)	W13-O4-W2	90.9(3)
O56-W3-O8	102.7(5)	O40-W15-O39	97.9(5)	O60-P2-O73	113.6(6)	P3-O4 Mo2	127.7(6)
O95-W4-O97	102.2(5)	O55-W16-O24	100.7(5)	O57-P2-O92	105.4(6)	Mo13-O4 Mo2	90.9(3)
O29-W5-O98	98.0(5)	O10-W17-O78	86.7(5)	O60-P2-O92	107.9(6)	W3-O8-W1	152.1(6)
O26-W6-O23	100.5(5)	O9-W18-O74	84.8(4)	O73-P2-O92	107.1(6)	W18-O9-W15	148.5(6)
O64-W7-O86	101.3(5)	O77-P1-O28	113.0(6)	W18-O1 Mo14	124.2(5)	W17-O10-W8	150.2(7)
O81-W8-O12	99.7(5)	O77-P1-O75	112.6(6)	W18-O1-W14	124.2(5)	W8-O12-W10	163.5(6)
O32-W9-O14	98.2(5)	O28-P1-O75	110.7(6)	P3-O4-W2	127.7(6)	W6-O13-W7	165.1(7)
O12-W10-O88	163.9(5)	O77-P1-O58	107.4(5)	W3-O3-W18	121.0(5)	W9-O14-W11	162.4(7)
O47-W11-O25	99.9(5)	O28-P1-O58	105.4(6)	P3-O4 Mo13	129.2(5)	W15-O16-W19	152.7(6)
O6-W12-O19	89.7(5)	O75-P1-O58	107.3(6)	P3-O4-W13	129.2(5)	W13-O17-W15	162.9(6)

S9. Thermal ellipsoidal plots for compounds 1-4

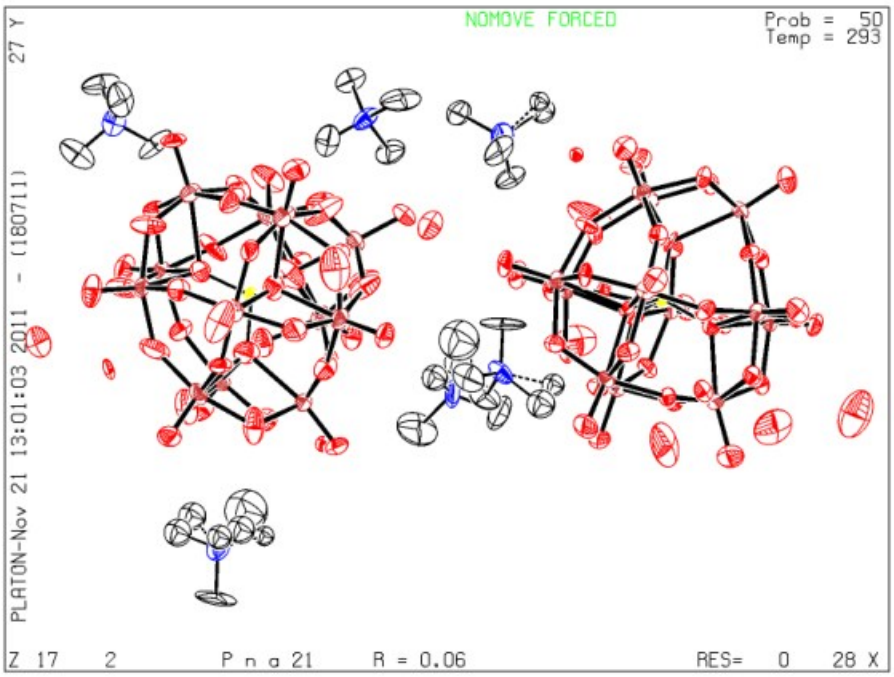
Thermal ellipsoidal plot for compound 1

Datablock 1_ - ellipsoid plot



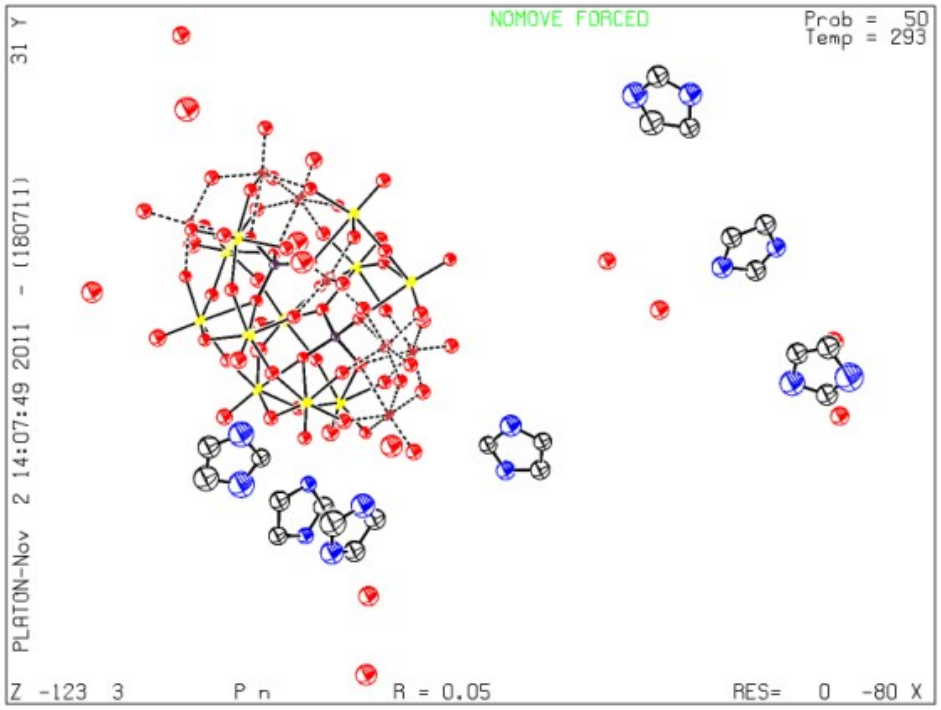
Thermal ellipsoidal plot for compound 2

Datablock 2_ - ellipsoid plot



Thermal ellipsoidal plot for compound 3

Datablock 3_ - ellipsoid plot



Thermal ellipsoidal plot for compound 4

Datablock 4_ - ellipsoid plot