Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Three molybdophosphates based on Strandberg-type anions and Zn(II)-H_2biim/H_2O subunits: syntheses, structures and catalytic properties

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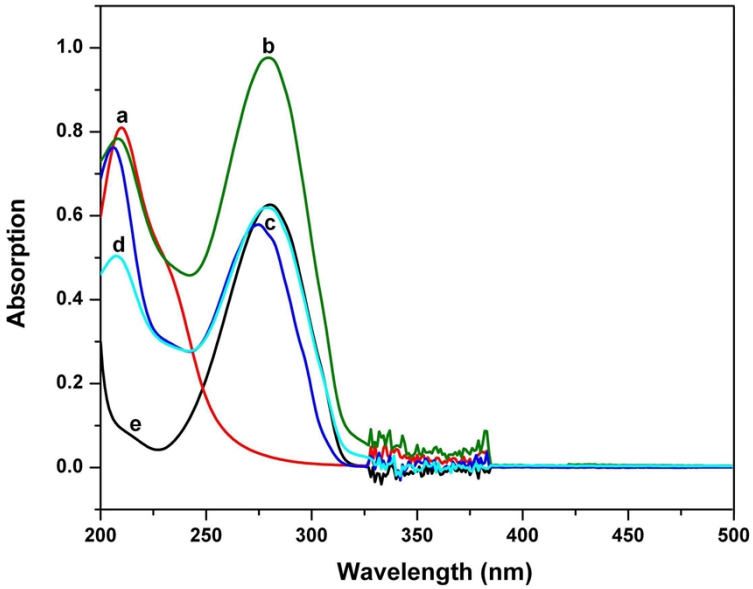

Fig. S1 Comparison of UV-visible spectra for the parent $\{P_2Mo_5\}$, $ZnSO_4$, H_2biim and **1-3** (5×10^{-5} mol L^{-1}) at pH = 6-7 aqueous solutions. In the synthetic process of **1-3**, the pH controlling is very important. When the crystal products **1-3** redissolved in aqueous solution (pH = 6-7), the skeleton of $\{P_2Mo_5\}$ may be transformed to that of $\{P_4Mo_6\}$ according the UV spectra analysis and the literatures[1-3]

As shown in Fig. S1, the UV spectra of the parent $\{P_2Mo_5\}$, and **1-3** in water (a-d), display the strong bands at 209, 208, 206 and 207 nm should be assigned to the characteristic band of $\{P_4Mo_6\}$, respectively.[1-3] While a weak shoulder band at about 234 nm (in curve a) is attributed to the characteristic of $\{P_2Mo_5\}$. For the UV spectra of **1-3** in water (b-d), compared to that of the parent $\{P_2Mo_5\}$ in pH = 4 aqueous solution (Fig. 4), the characteristic band in the range of 220-250 nm disappear, which show that these compounds have been converted to $\{P_4Mo_6\}$. In addition, in the UV region, a strong band at 282 nm (a) in the range of 250-320 nm corresponds to π-π charge transfer transitions of H_2biim. The UV spectra of **1-3** reveal a broad band at 240-330 nm are 280, 274, and 278 nm, respectively, which are attributed to the absorption behaviors of H_2biim. The observed slight shift as compared to that of the parent $\{P_2Mo_5\}$ may be due to the introduction of Zn(II). To sum up, the above phenomenon also indicates that $\{P_2Mo_5\}$ and $\{P_4Mo_6\}$ can be mutually transformed.

References:

1 J. Y. Niu, J. C. Ma, J. W. Zhao, P. T. Ma, J. P. Wang, *Inorg. Chem. Commun*., 2011, **14**, 474-477.

2 J. P. Wang, J. W. Zhao, P. T. Ma, J. C. Ma, L. P. Yang, Y. Bai, M. X. Li and J. Y. Niu, *Chem. Commun*., 2009, 2362-2364.

3 K. Yu, B. B. Zhou, Y. Yu, Z. H. Su, H. Y. Wang, C. M. Wang, and C. X. Wang, *Dalton Trans.*, 2012, **41**, 10014-10020.

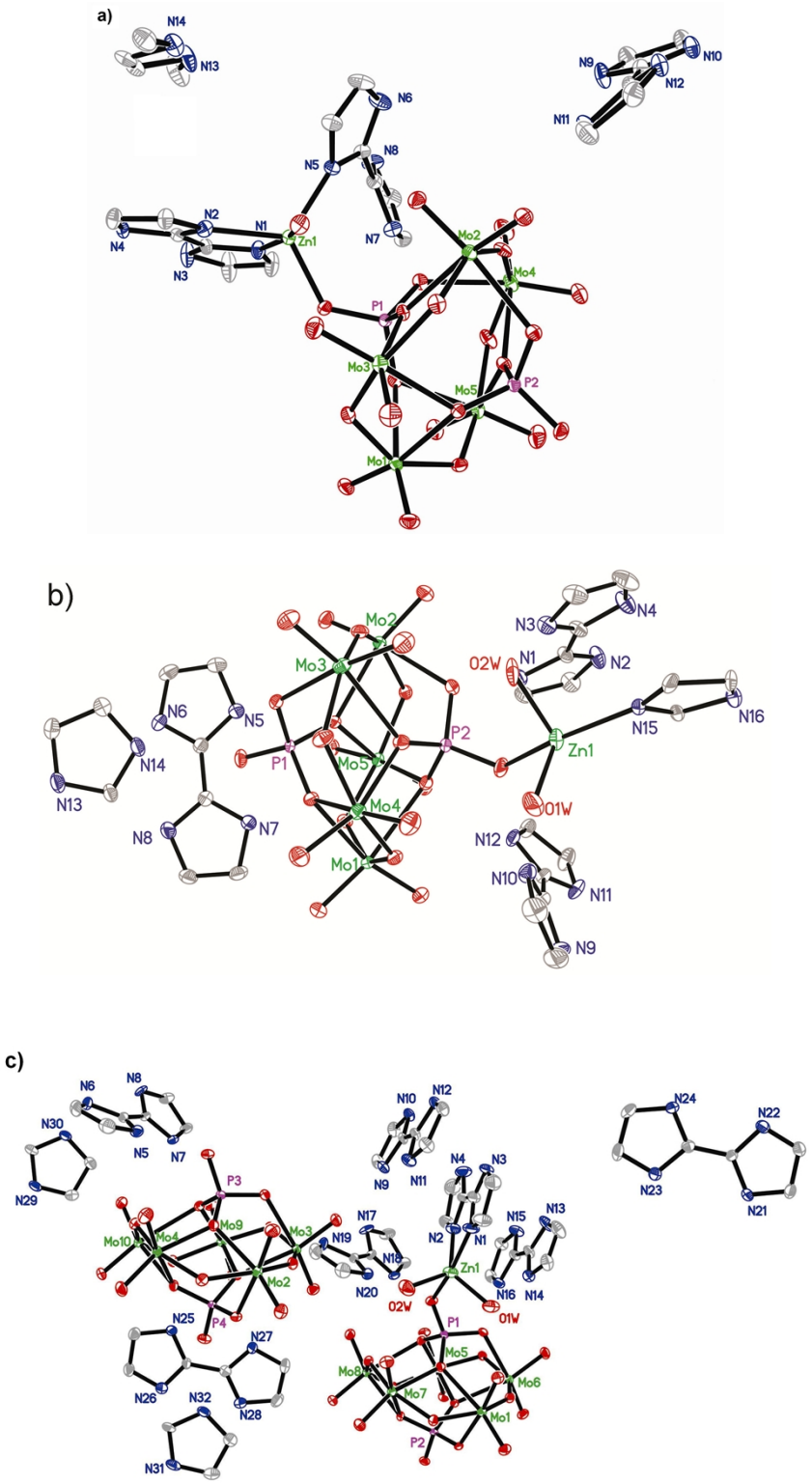

Fig. S2 ORTEP view of the asymmetric unit of the centrosymmetric polyanions **1-3** (a-c) with atom labeling (40% probability displacement ellipsoids; Hydrogen atoms and free water molecules have been omitted for clarity)

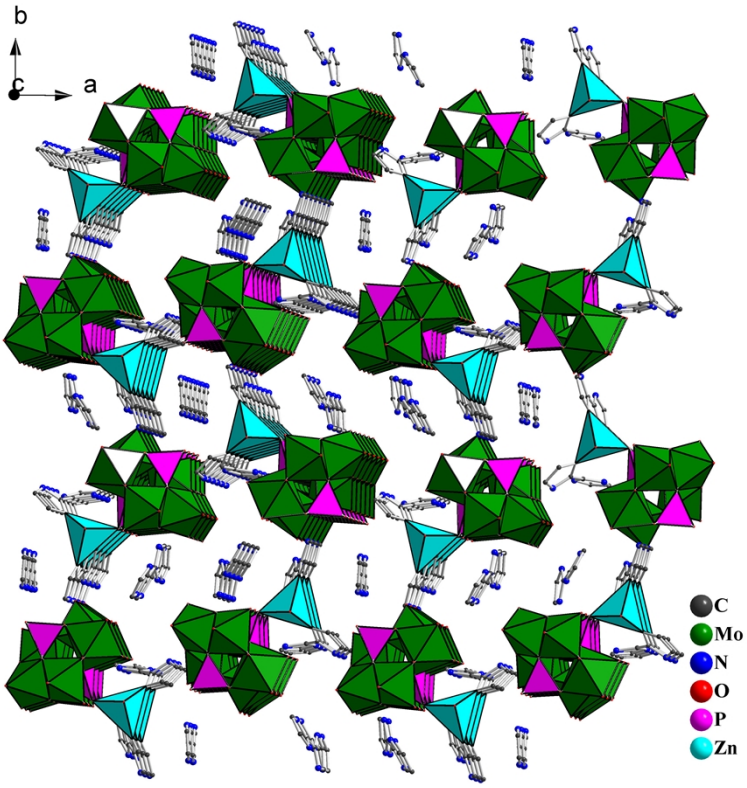

Fig. S3 Polyhedral and ball-and-stick view of the 3D supramolecular framework of **1** (The isolated H_2O molecules and hydrogen atoms have been omitted for clarity)

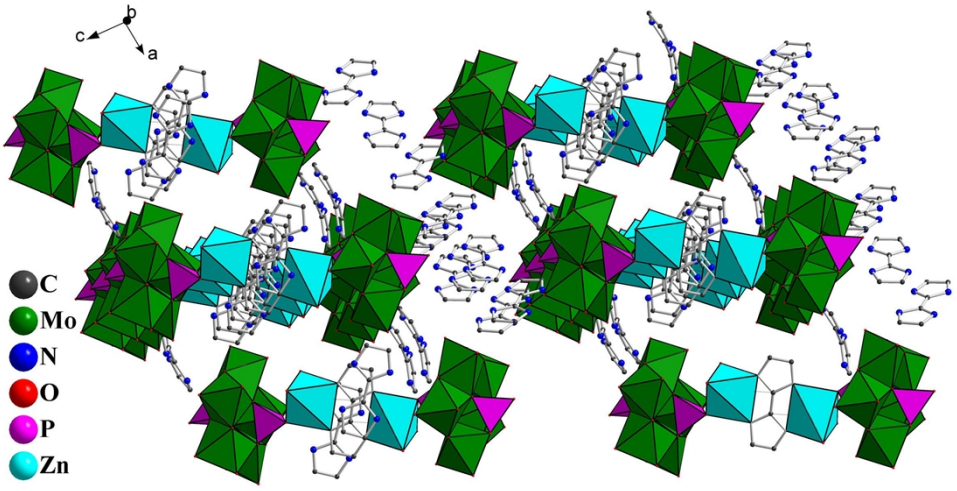

Fig. S4 The packing view of the infinite 3D network for **2** (The isolated H_2O molecules and hydrogen atoms have been omitted for clarity)

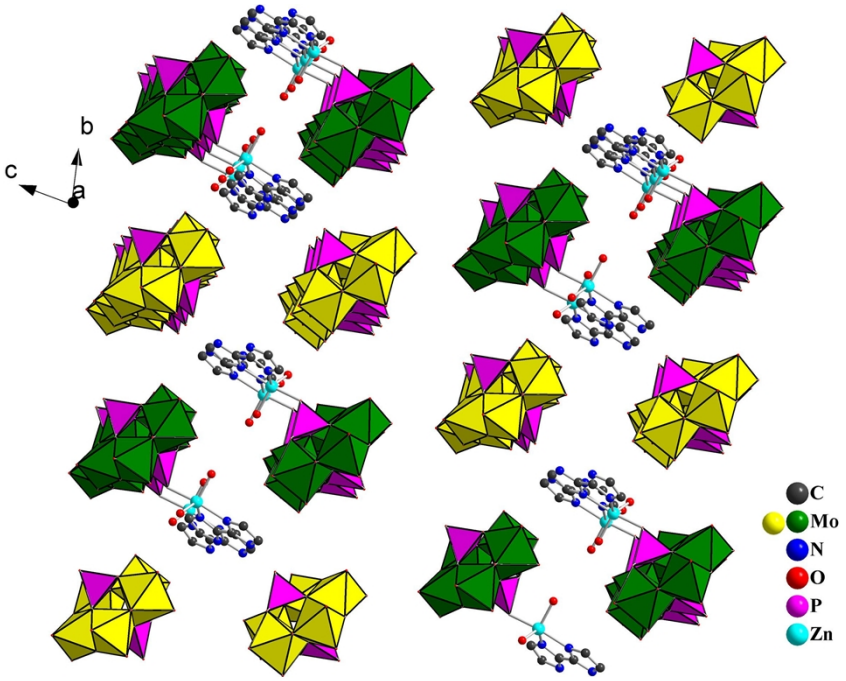

Fig. S5 The packing view of polyoxoanions in **3** (The green part: Zn-{P_2Mo_5}; the yellow part: {P_2Mo_5}, all the free ligands, hydrogen atoms and H_2O molecules have been omitted for clarity)

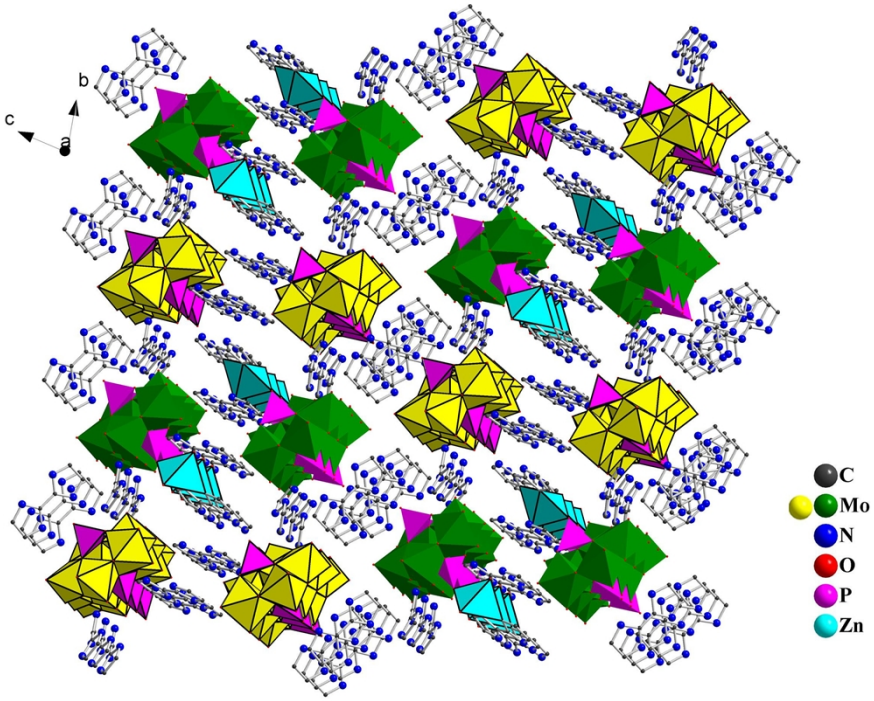

Fig. S6 The packing view of **3** (The green part: Zn-{P_2Mo_5}; the yellow part: {P_2Mo_5}, free H_2O molecules, and hydrogen atoms have been omitted for clarity)

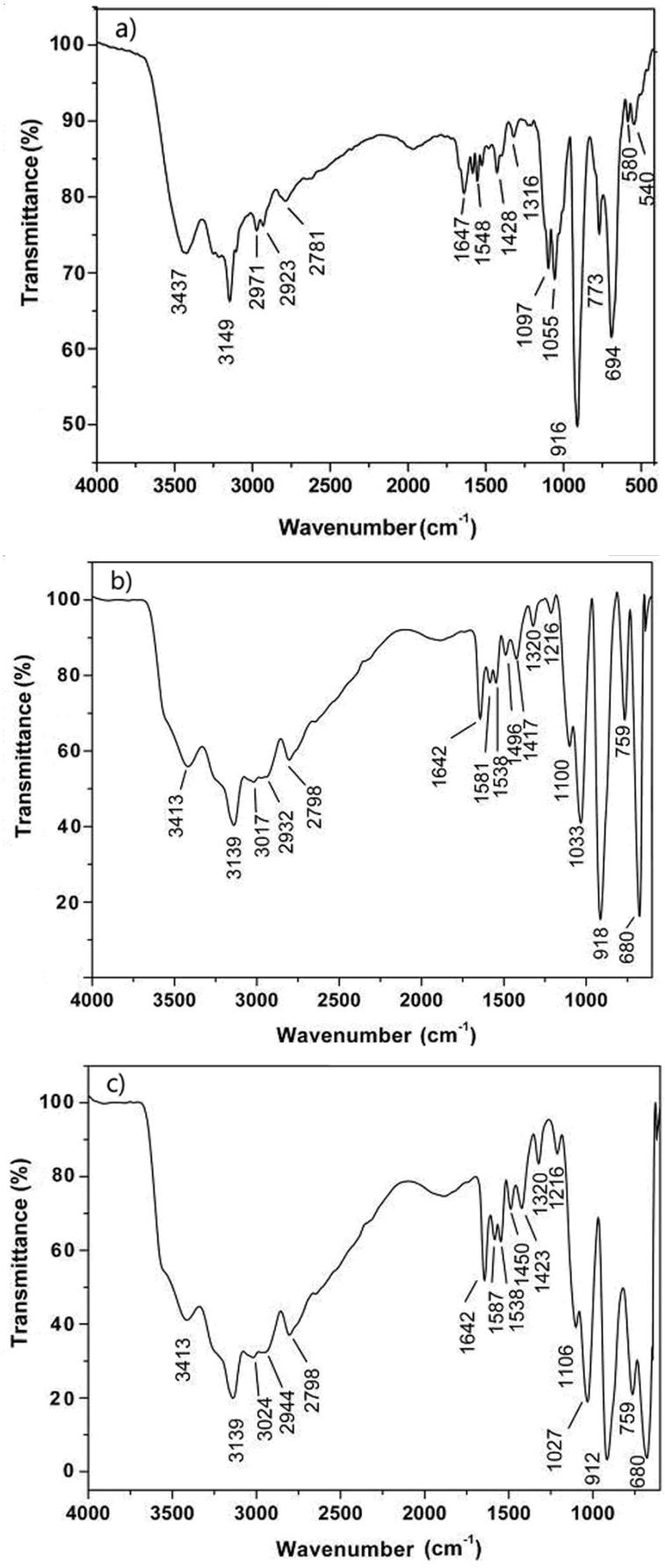

Fig. S7 IR spectra of crystals **1- 3** (a-c)

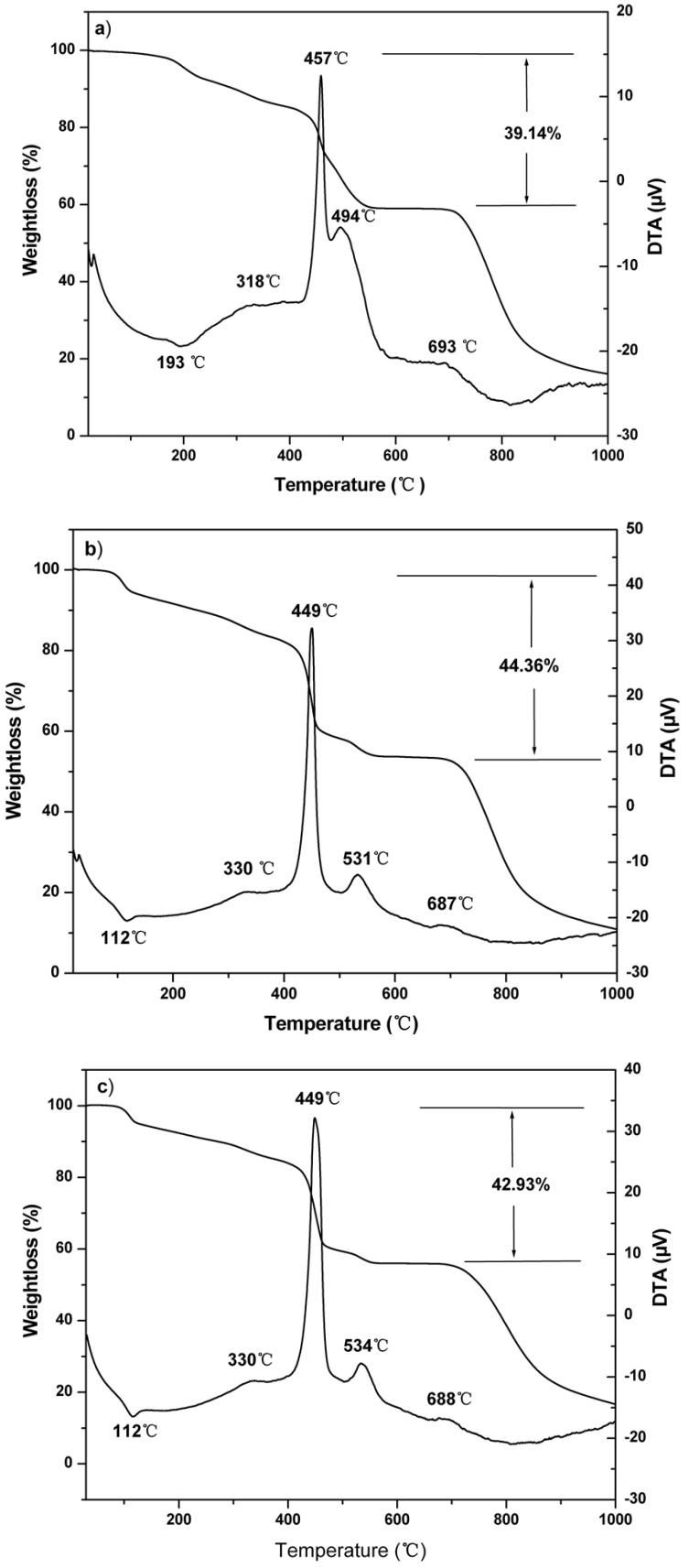

Fig. S8 The TG-DTA curves of **1-3** (a-c)

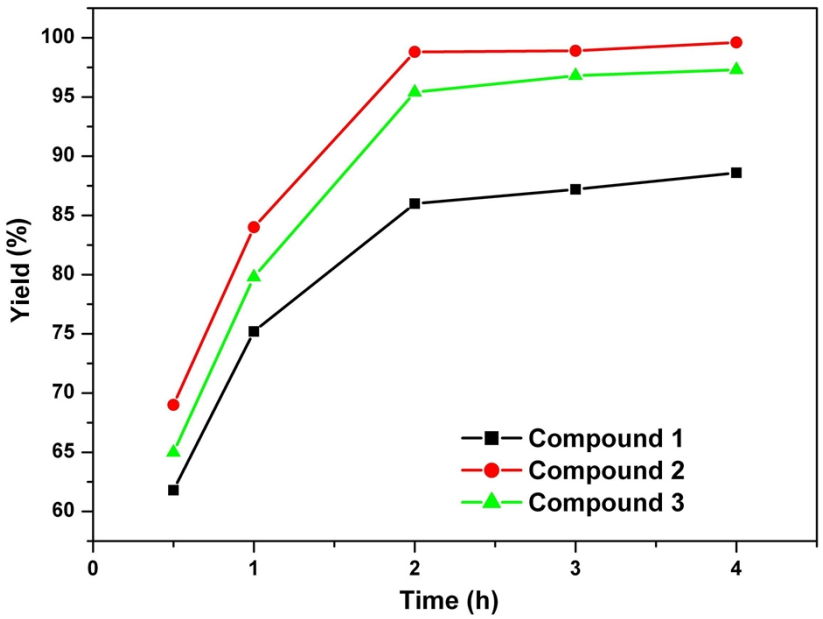

Fig. S9 Effect of reaction time on cyclohexanone ethylene ketal yield: cyclohexanone/glycol molar ratio, 1:1.4; catalyst (of Mo)/cyclohexanone molar ratio, 1:300; reaction temperature, 95-100 °C; water-carring agent, cyclohexane (10 mL)

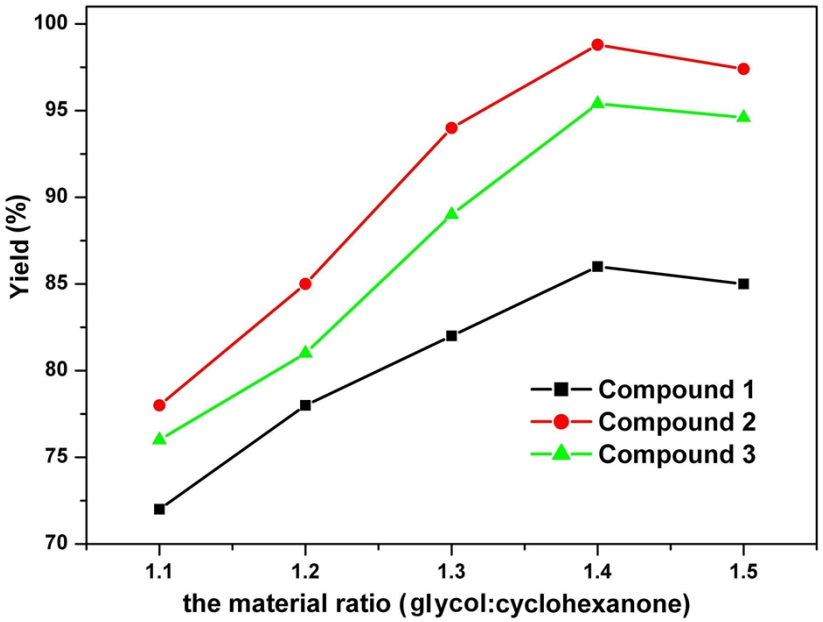

Fig. S10 Effect of the material ratio on cyclohexanone ethylene ketal yield: catalyst (of Mo)/cyclohexanone molar ratio, 1:300; reaction temperature, 95-100 °C; reaction time, 2 h. water-carring agent, cyclohexane (10 mL)

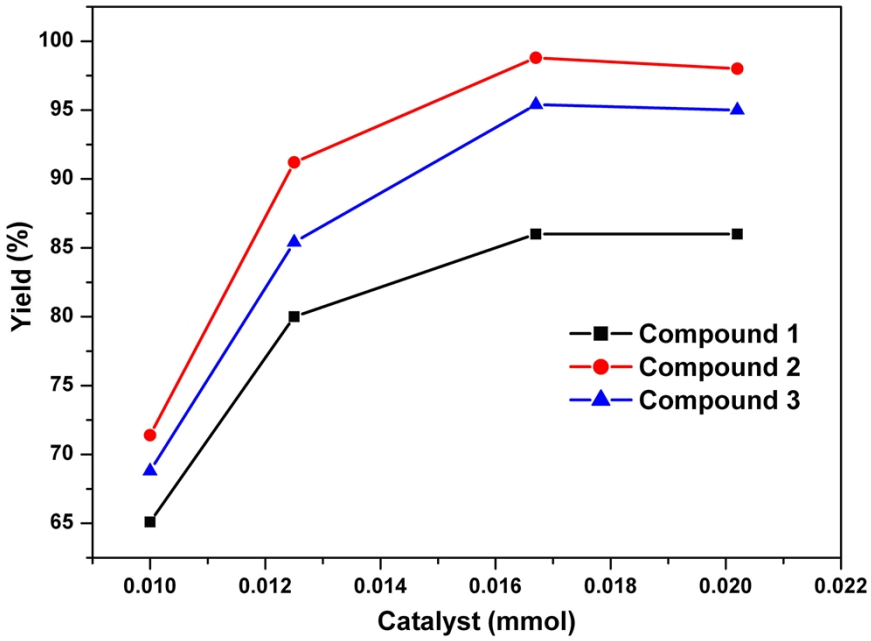

Fig. S11 Effect of the amount of **1/2/3** on cyclohexanone ethylene ketal yield: cyclohexanone/glycol molar ratio, 1:1.4; reaction temperature, 95-100 °C; reaction time, 2 h; water-carring agent, cyclohexane (10 mL).

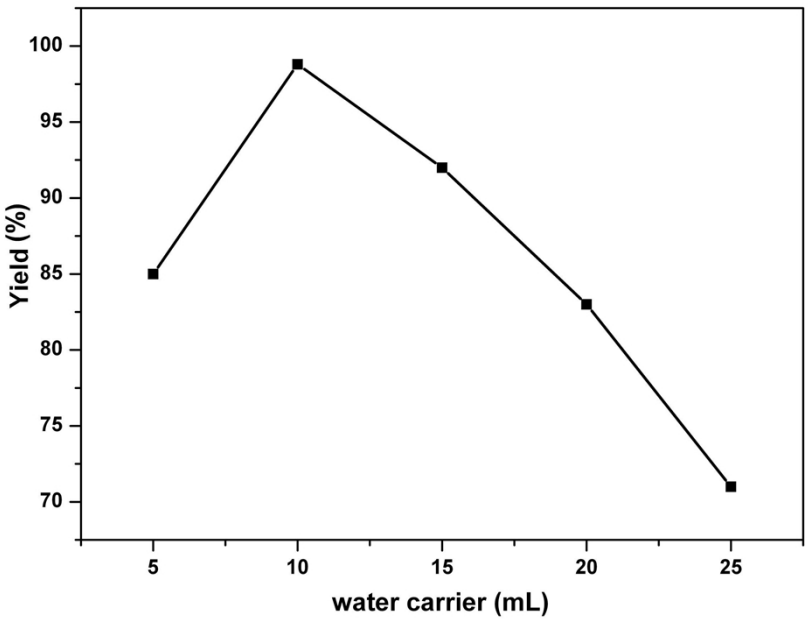

Fig. S12 Effect of the amount of water-carring agent on cyclohexanone ethylene ketal yield: cyclohexanone/ glycol molar ratio, 1:1.4; catalyst (compound **2**, of Mo)/cyclohexanone molar ratio, 1:300; reaction time, 2 h

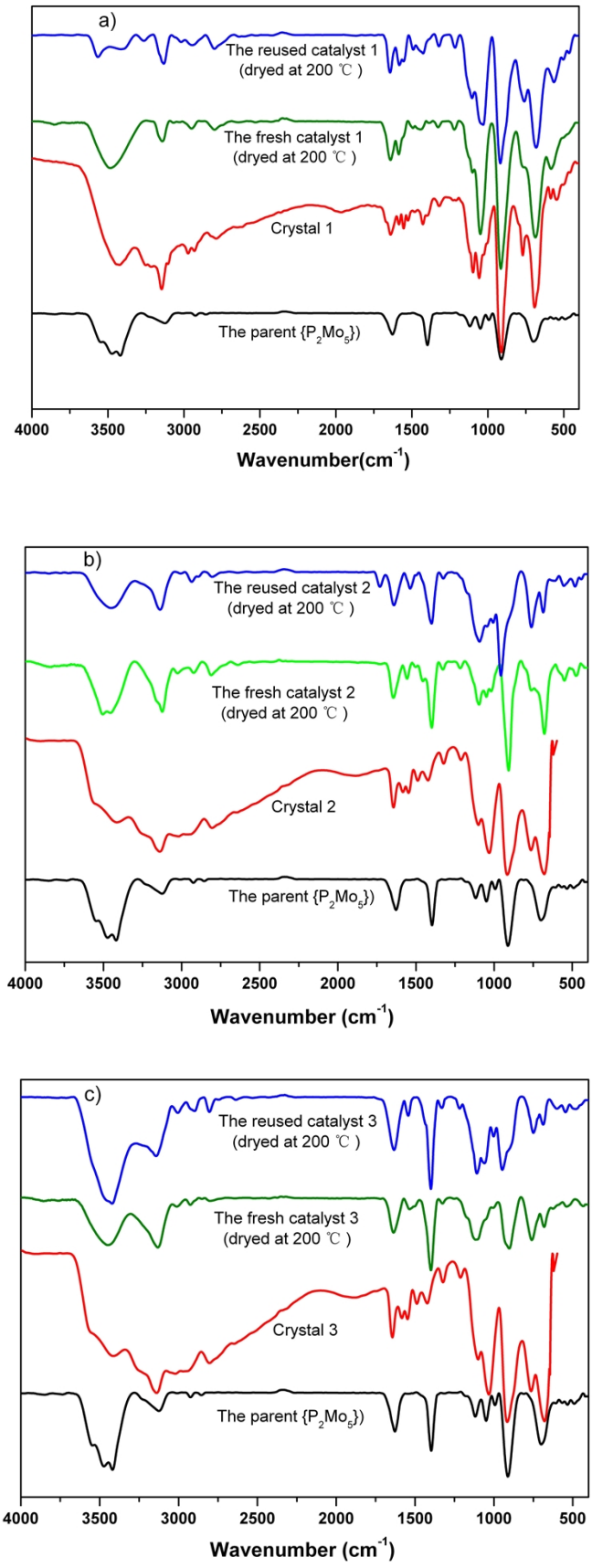

Fig. S13 Comparisons of IR spectra of the parent $\{P_2Mo_5\}$, the crystal, and the fresh and the used catalysts **1**/**2**/**3 (**a/b/c**)**.

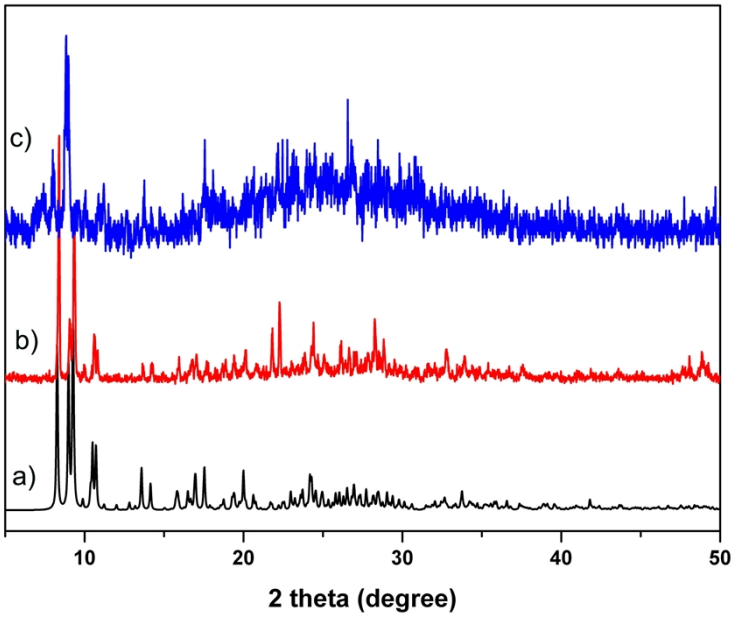

Fig. S14 The simulated (a) and experimental powder X-ray diffraction patterns for the fresh (b) and the used (c) catalyst **2**

Table S1 Selected bond lengths and angles for compound **1**

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Mo1–O10	1.707(4)	Mo3–O3	1.956(4)	Zn1–O8	1.932(3)
Mo1–O14	1.715(4)	Mo3–O15	2.220(4)	Zn1–N5	2.029(5)
Mo1–O5	1.880(4)	Mo3–O16	2.361(4)	Zn1–N2	2.062(5)
Mo1-O3	1.924(4)	Mo4–O22	1.693(5)	Zn1–N1	2.206(5)
Mo1–O16	2.330(4)	Mo4–O20	1.708(4)	Zn1–O1W	2.251(3)
Mo1–O18	2.395(4)	Mo4–O4	1.934(4)	P1–O8	1.514(4)
Mo2–O17	1.714(4)	Mo4–O9	1.947(4)	P1–O7	1.528(4)
Mo2–O12	1.722(4)	Mo4–O7	2.243(4)	P1–O18	1.553(4)
Mo2–O4	1.884(4)	Mo4–O23	2.303(4)	P1–O15	1.553(4)
Mo2–O1	1.902(4)	Mo5–O6	1.700(4)	P2–O2	1.520(4)
Mo2–O15	2.313(4)	Mo5–O21	1.712(4)	P2–O16	1.544(4)
Mo2–O2	2.360(4)	Mo5–O9	1.895(4)	P2–O13	1.542(4)
Mo3–O11	1.698(4)	Mo5–O5	1.959(4)	P2–O23	1.546(4)
Mo3–O19	1.720(4)	Mo5–O23	2.203(4)		
Mo3–O1	1.931(4)	Mo5–O18	2.450(4)		
Bond	Angle (º)	Bond	Angle (º)	Bond	Angle (º)
O10–Mo1–O14	104.22(19)	O11–Mo3–O15	157.35(18)	N1–Zn1–O1W	166.07(15)
O3–Mo1–O16	73.49(15)	O22–Mo4–O4	102.6(2)	N5–Zn1–N2	117.06(19)
O16–Mo1–O18	82.80(12)	O9–Mo4–O23	70.46(15)	O8–P1–O7	111.2(2)
O12–Mo2–O4	100.06(19)	O7–Mo4–O23	83.48(13)	O8–P1–O18	107.9(2)
O1–Mo2–O15	69.93(16)	O6–Mo5–O5	96.5(2)	O8–P1–O15	111.2(2)
O15–Mo2–O2	86.86(12)	O6–Mo5–O23	99.12(19)	O2–P2–O13	111.0(2)
O19–Mo3–O1	100.02(19)	O9–Mo5–O18	88.81(15)	O13–P2–O16	108.9(2)
O19–Mo3–O3	95.98(19)	O8–Zn1–N5	121.13(17)	O16–P2–O23	109.9(2)

Table S2 Selected bond lengths and angles for compound **2**

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Mo1–O11	1.699(2)	Mo3–O10	1.949(2)	Zn1–O2W	1.998(4)
Mo1–O12	1.708(2)	Mo3–O7	2.240(2)	Zn1–O1W	2.055(6)
Mo1–O4	1.901(2)	Mo3–O8	2.3944(17)	Zn1–O18	2.126(2)
Mo1–O14	1.923(2)	Mo4–O21	1.703(3)	Zn1–N15	2.221(7)
Mo1–O6	2.3319 (17)	Mo4–O22	1.722(3)	Zn1–N16A	2.008(5)
Mo1–O3	2.461(2)	Mo4–O9	1.9224(19)	P1–O13	1.516(2)
Mo2–O19	1.707(2)	Mo4–O4	1.9255(18)	P1–O7	1.5320(18)
Mo2–O20	1.712(2)	Mo4–O8	2.207(2)	P1–O6	1.538(2)
Mo2–O10	1.873(2)	Mo4–O6	2.370(2)	P1–O1	1.551(2)
Mo2–O2	1.9482(17)	Mo5–O16	1.710(2)	P2–O18	1.523(3)
Mo2–O1	2.2925(19)	Mo5–O15	1.724(2)	P2–O5	1.531(2)
Mo2–O5	2.349(2)	Mo5–O2	1.8967(19)	P2–O8	1.545(2)
Mo3–O17	1.696(2)	Mo5–O14	1.919(2)	P2–O3	1.549(2)
Mo3–O23	1.707(3)	Mo5–O1	2.2039(17)		
Mo3–O9	1.910(2)	Mo5–O3	2.341(2)		
Bond	Angle (º)	Bond	Angle (º)	Bond	Angle (º)
O11–Mo1–O3	169.97(9)	O17–Mo3–O10	101.62(11)	O1W–Zn1–N16A	126. 4(2)
O12–Mo1–O14	100.80(10)	O21–Mo4–O22	104.08(13)	N15–Zn1–O18	161.97(16)
O4–Mo1–O6	73.20(8)	O9–Mo4–O4	152.13(10)	O13–P1–O1	109.98(13)
O19–Mo2–O20	102.84(12)	O8–Mo4–O6	72.73(8)	O7–P1–O6	109.18(12)
O2–Mo2–O1	70.52(7)	O15–Mo5–O3	165.23(9)	O7–P1–O1	106.22(11)
O10–Mo2–O5	79.47(8)	O14–Mo5–O1	81.96(7)	O8–P2–O3	110.85(12)
O23–Mo3–O7	170.31(9)	O16–Mo5–O2	98.68(10)	O5–P2–O8	106.65(11)
O9–Mo3–O8	68.75(8)	O2W–Zn1–N15	91.5(2)	O18–P2–O3	108.40(11)

Table S3 Selected bond lengths and angles for compound **3**

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Mo1–O7	1.696(4)	Mo5–O9	1.914(4)	Mo10–O22	1.700(4)
Mo1–O12	1.714(4)	Mo5–O31	2.202(4)	Mo10–O29	1.705(4)
Mo1–O4	1.915(4)	Mo5–O28	2.338(4)	Mo10–O8	1.897(4)
Mo1–O5	1.945(4)	Mo6–O43	1.705(4)	Mo10–O30	1.918(4)
Mo1–O6	2.216(3)	Mo6–O35	1.715(4)	Mo10–O46	2.318(4)
Mo1–O40	2.384(4)	Mo6–O5	1.878(4)	Mo10–O33	2.474(4)
Mo2–O2	1.696(4)	Mo6–O15	1.950(4)	Zn1–O1W	2.004(5)
Mo2–O23	1.709(4)	Mo6–O31	2.301(3)	Zn1–O2W	2.014(5)
Mo2–O11	1.914(4)	Mo6–O13	2.349(4)	Zn1–N2	2.063(6)
Mo2–O3	1.948(4)	Mo7–O19	1.708(4)	Zn1–O10	2.094(4)
Mo2–O36	2.275(4)	Mo7–O16	1.716(4)	Zn1–N1	2.177(6)
Mo2–O34	2.407(4)	Mo7–O4	1.925(4)	P1–O10	1.517(4)
Mo3–O41	1.704(4)	Mo7–O32	1.926(4)	P1–O13	1.533(4)
Mo3–O17	1.719(4)	Mo7–O40	2.203(4)	P1–O28	1.553(4)
Mo3–O3	1.875(4)	Mo7–O38	2.354(4)	P1–O40	1.554(4)
Mo3–O1	1.953(4)	Mo8–O24	1.690(4)	P2–O39	1.512(4)
Mo3–O42	2.290(3)	Mo8–O20	1.701(4)	P2–O6	1.538(4)
Mo3–O26	2.335(4)	Mo8–O32	1.906(4)	P2–O38	1.541(4)
Mo4–O45	1.693(4)	Mo8–O9	1.920(4)	P2–O31	1.554(3)
Mo4–O37	1.723(4)	Mo8–O38	2.345(4)	P3–O27	1.521(4)
Mo4–O11	1.920(4)	Mo8–O28	2.447(4)	P3–O26	1.536(4)
Mo4–O8	1.937(4)	Mo9–O14	1.717(4)	P3–O34	1.545(4)
Mo4–O34	2.220(4)	Mo9–O21	1.722(4)	P3–O33	1.546(4)
Mo4–O46	2.379(4)	Mo9–O1	1.898(4)	P4–O44	1.518(4)
Mo5–O18	1.719(4)	Mo9–O30	1.920 (4)	P4–O36	1.531(4)
Mo5–O25	1.724(4)	Mo9–O42	2.209(4)	P4–O46	1.539(4)
Mo5–O15	1.896(4)	Mo9–O33	2.335(4)	P4–O42	1.553(4)
Bond	Angle (º)	Bond	Angle (º)	Bond	Angle (º)
O4–Mo1–O5	145.69(16)	O43–Mo6–O5	102.45(18)	O2W–Zn1–O10	92.1(2)
O7–Mo1–O12	102.4(2)	O43–Mo6–O13	173.14(17)	N2–Zn1–N1	78.0(2)
O12–Mo1–O40	85.05(16)	O35–Mo6–O13	82.84(17)	O1W–Zn1–O2W	103.9(2)
O2–Mo2–O23	102.9(2)	O19–Mo7–O16	104.1(2)	O10–P1–O13	111.5(2)
O3–Mo2–O36	77.09(15)	O4–Mo7–O32	152.86(16)	O10–P1–O40	109.3(2)
O23–Mo2–O36	170.52(18)	O4–Mo7–O40	73.09(14)	O28–P1–O40	110.7(2)
O41–Mo3–O3	103.06(19)	O24–Mo8–O20	104.55(19)	O39–P2–O6	110.5(2)
O17–Mo3–O1	98.37(18)	O20–Mo8–O9	101.16(18)	O38–P2–O31	109.8(2)
O17–Mo3–O26	83.93(17)	O24–Mo8–O28	169.53(16)	O6–P2–O38	109.2(2)
O45–Mo4–O11	101.1(2)	O14–Mo9–O21	104.1(2)	O27–P3–O26	109.8(2)
O37–Mo4–O8	100.84(19)	O1–Mo9–O30	152.22(16)	O27–P3–O33	109.0(2)
O37–Mo4–O46	86.01(18)	O21–Mo9–O33	165.53(16)	O34–P3–O33	111.2(2)
O18–Mo5–O25	104.28(19)	O22–Mo10–O8	104.1(2)	O44–P4–O36	111.2(2)
O25–Mo5–O9	94.87(17)	O8–Mo10–O30	143.43 (16)	O44–P4–O42	109.5(2)
O15–Mo5–O31	73.51(14)	O8–Mo10–O33	80.39(15)	O36–P4–O42	106.4(2)

Table S4 Hydrogen bonds for **1**

D–H···A	d(D–H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA) (º)
N3–H3A···O2#2	0.86	2.18	2.954(6)	149.1
N3–H3A...O4#2	0.86	2.52	3.185(7)	134.4
N4–H4A...O2#2	0.86	1.99	2.792(6)	153.7
N6–H6A...O14#3	0.86	2.20	2.958(7)	146.9
N6–H6A...O16#3	0.86	2.32	2.974(6)	132.5
N7–H7A...O7	0.86	1.76	2.592(6)	163.3
N8–H8A...O13#3	0.86	2.09	2.820(7)	141.8
N8–H8A...O5#3	0.86	2.28	2.872(6)	126.3
N9–H9A...O2W	0.86	1.80	2.640(6)	165.2
N10–H10A...O18#4	0.86	1.94	2.793(6)	174.2
N10–H10A...O8#4	0.86	2.56	3.053(6)	117.2
N11–H11A...O12	0.86	1.95	2.741(6)	151.3
N12–H12A...O3#4	0.86	1.95	2.749(6)	154.8
N12–H12A...O10#4	0.86	2.64	3.276(7)	131.6
N13–H13A...O13#5	0.86	2.01	2.808(7)	154.0
N14–H14A...O13#5	0.86	1.75	2.566(7)	158.5

Symmetry transformations used to generate equivalent atoms: #1 -x-1,-y-1,z; #2 -x-1/2, y-1/2, z-1/2; #3 x-1/2, -y-1/2, z-1/2; #4 -x-1/2, y+1/2, z+1/2; #5 x-1/2, -y-1/2, z+1/2

Table S5 Hydrogen bonds for **2**

D-H···A	d(D–H) (Å)	d(H...A) (Å)	d(D...A) (Å)	<(DHA) (º)
N1–H1A...O5	0.86	2.09	2.886(4)	153.7
N1–H1A...O2	0.86	2.31	2.967(3)	133.2
N2–H2A...O4W#1	0.86	2.32	2.972(5)	133.1
N3–H3A...O5	0.86	1.93	2.756(4)	160.1
N4–H4A...O20#3	0.86	1.98	2.745(4)	147.7
N5–H5A...O15	0.86	1.92	2.738(3)	159.0
N6–H6A...O3W#2	0.86	1.94	2.759(4)	158.2
N7–H7A...O15	0.86	2.20	2.993(4)	152.6
N7–H7A...O14	0.86	2.31	2.972(4)	133.5
N8–H8A...O5W#2	0.86	2.16	2.849(4)	136.6
N9–H9A...O5W#4	0.86	1.93	2.693(4)	147.3
N10–H10A...O18	0.86	1.76	2.610(3)	168.2
N11–H11A...O7#4	0.86	1.74	2.594(3)	173.2
N12–H12A...O3	0.86	2.14	3.002(3)	176.5
N13–H13A...O13#2	0.86	2.02	2.810(4)	151.5
N14–H14A...O13	0.86	1.75	2.574(3)	160.3

Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y+1, -z; #2 -x, -y, -z+1; #3 -x+1, -y, -z; #4 x+1, y+1, z

Table S6 Hydrogen bonds for **3**

D–H...A	d(D–H) (Å)	d(H...A) (Å)	d(D...A) (Å)	<(DHA) (º)
N3–H3A...O27#3	0.86	1.91	2.755(7)	167.8
N5–H5A...O27	0.86	1.72	2.568(7)	168.6
N6–H6A...O4W#4	0.86	1.90	2.692(8)	152.2
N7–H7A...O33	0.86	2.10	2.956(6)	177.4
N8–H8A...O6#4	0.86	1.73	2.588(6)	175.1
N9–H9A...O17	0.86	1.95	2.745(6)	153.3
N10–H10A...O26#3	0.86	1.88	2.703(6)	160.3
N12–H12A...O26#3	0.86	2.05	2.850(6)	154.6
N12–H12A...O1#3	0.86	2.36	3.011(6)	133.0
N14–H14A...O13	0.86	2.01	2.817(6)	157.0
N15–H15A...O11W#5	0.86	2.01	2.766(19)	146.5
N15–H15A...O5W#5	0.86	2.48	3.096(8)	128.7
N16–H16A...O13	0.86	2.15	2.938(6)	152.3
N16–H16A...O15	0.86	2.28	2.940(6)	134.1
N17–H17A...O36#5	0.86	1.74	2.598(6)	171.2
N18–H18A...O28	0.86	2.21	3.066 (6)	175.7
N18–H18A...O18	0.86	2.54	2.958(6)	110.8
N19–H19A...O3W	0.86	1.96	2.697(7)	142.3
N19–H19A...O36#5	0.86	2.58	3.248(7)	135.5
N20–H20A...O10	0.86	1.80	2.644(7)	167.5
N21–H21A...O25#6	0.86	2.22	3.012(6)	153.1
N21–H21A...O9#6	0.86	2.31	2.964(6)	133.0
N23–H23A...O25#6	0.86	1.92	2.738(7)	159.4
N24–H24A...O7W#7	0.86	1.93	2.756(7)	159.3
N25–H25A...O21	0.86	2.21	2.991(6)	151.7
N25–H25A...O30	0.86	2.31	2.978(6)	134.9
N27–H27A...O21	0.86	1.91	2.732(7)	159.1
N28–H28A...O6W#8	0.86	1.95	2.763(7)	156.3
N29–H29A...O39#8	0.86	2.00	2.786(6)	152.3
N30–H30A...O39#4	0.86	1.76	2.585(6)	160.1
N31–H31A...O44#2	0.86	2.06	2.839(7)	151.2
N32–H32A...O44	0.86	1.73	2.560(6)	160.5

Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y+2, -z; #2 -x, -y+1, -z; #3 -x+1, -y+1, -z+1; #4 x, y+1, z; #5 x+1, y, z; #6 -x+1, -y, -z+1; #7 x, y, z+1; #8 -x+1, -y+1, -z