Supporting Information

Two Strandberg-type organophosphomolybdates: synthesis, crystal structure and catalytic properties

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1. Crystal structures

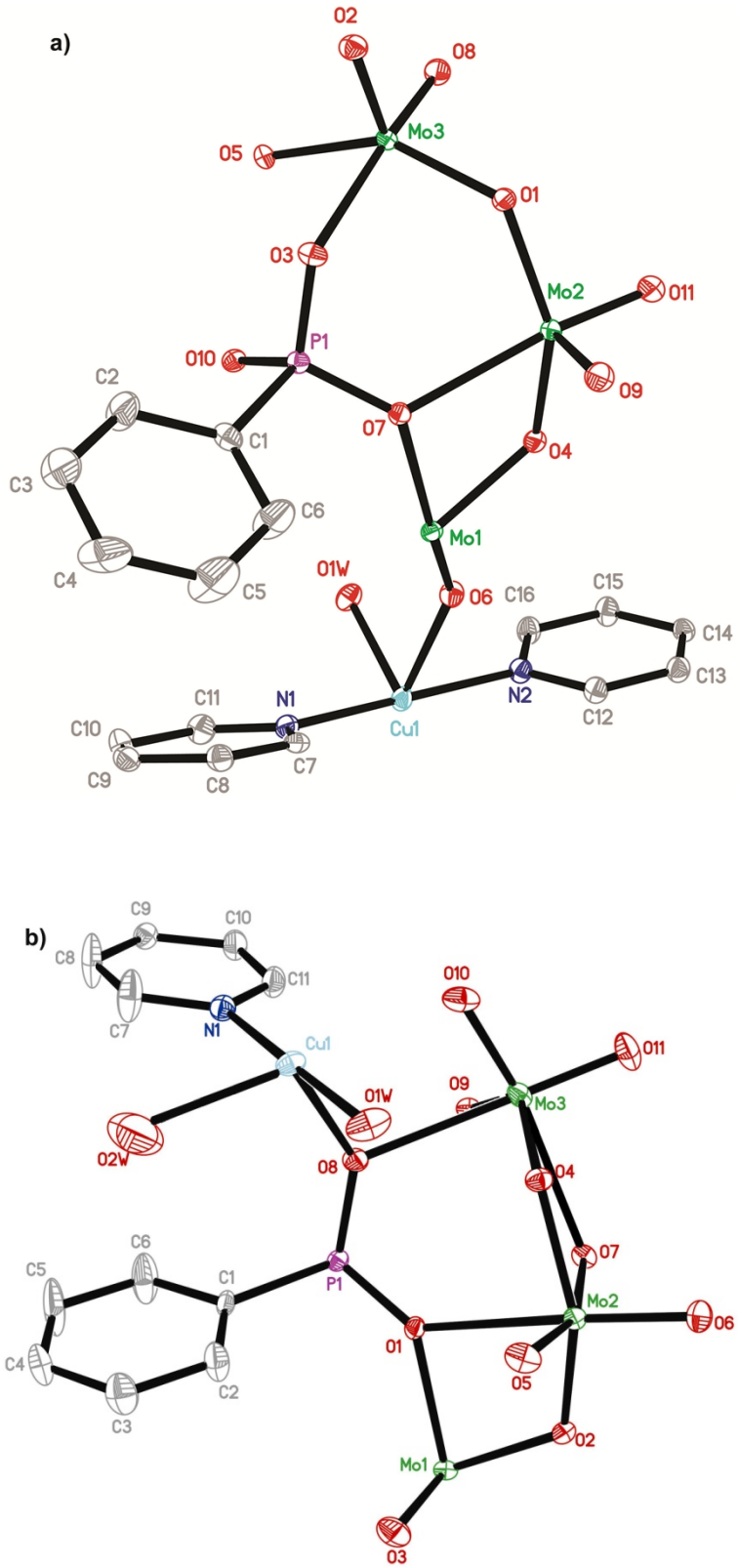


Fig. S1 ORTEP view of the asymmetric units of **1** and **2** (a and b) with atom labeling (30% probability displacement ellipsoids; Hydrogen atoms and free water molecules have been omitted for clarity)

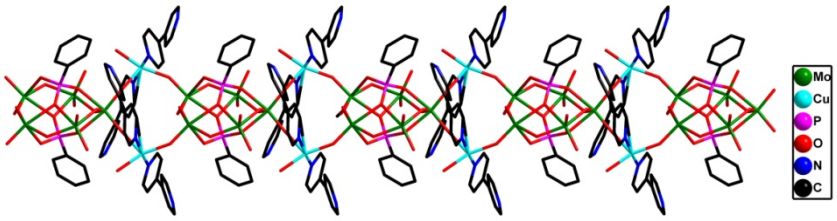


Fig. S2 Wire representation of the coordination type of polyanion **1** to Cu^{2+} ions in a 1-D chain structure (The hydrogen atoms have been omitted for clarity)

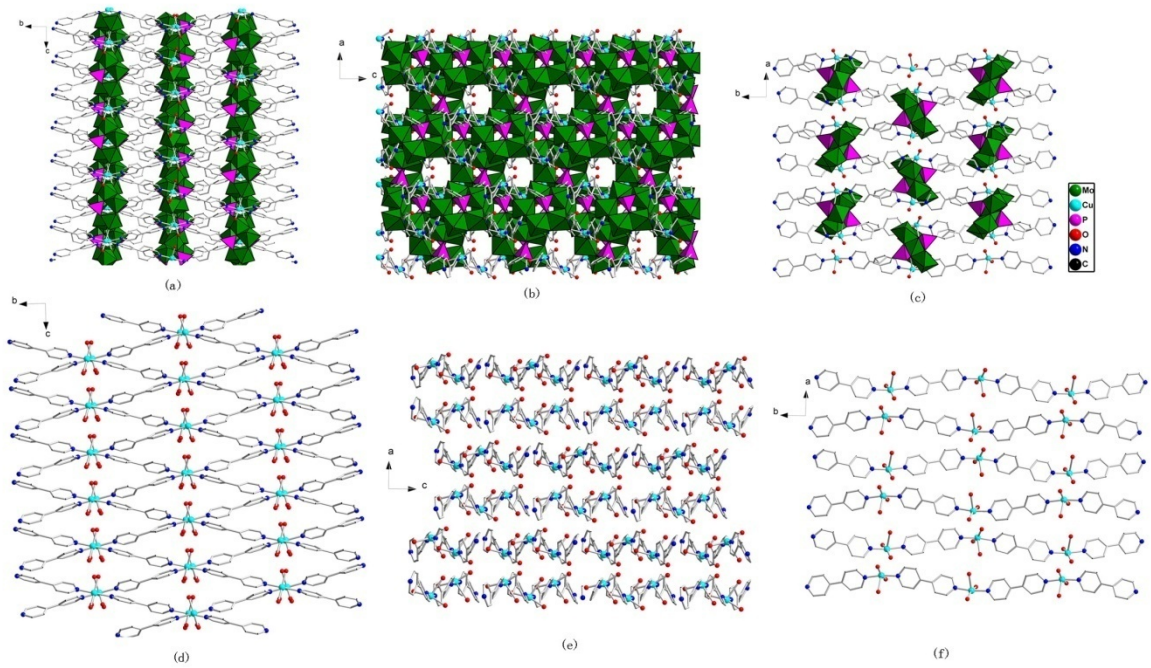


Fig. S3 Polyhedral and Ball-and-stick representation of the arrange of **1** (a/b/c), and the connective types of Cu^{2+} ions and 4,4'-bipyridyl ligands (d/e/f) in **1** along *a*, *b* and *c* axis, respectively (The polyanions and hydrogen atoms have been omitted for clarity)

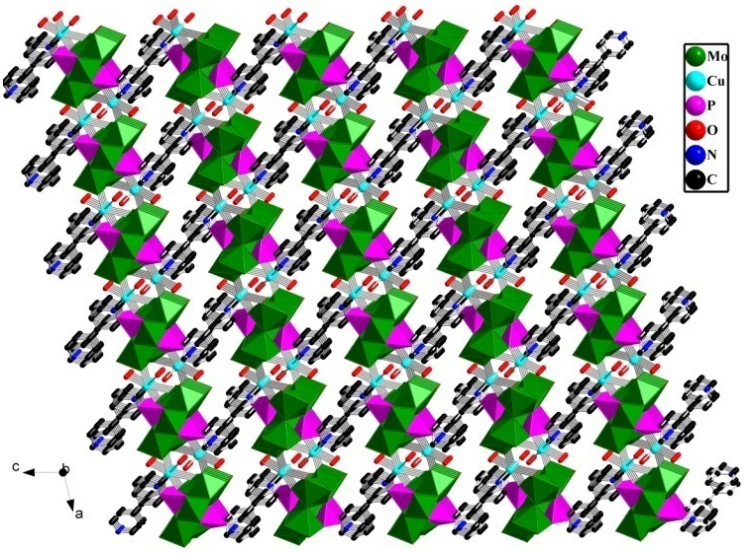


Fig. S4 Polyhedral and ball-and-stick representation of the 3-D structure of **2** (The hydrogen atoms have been omitted for clarity)

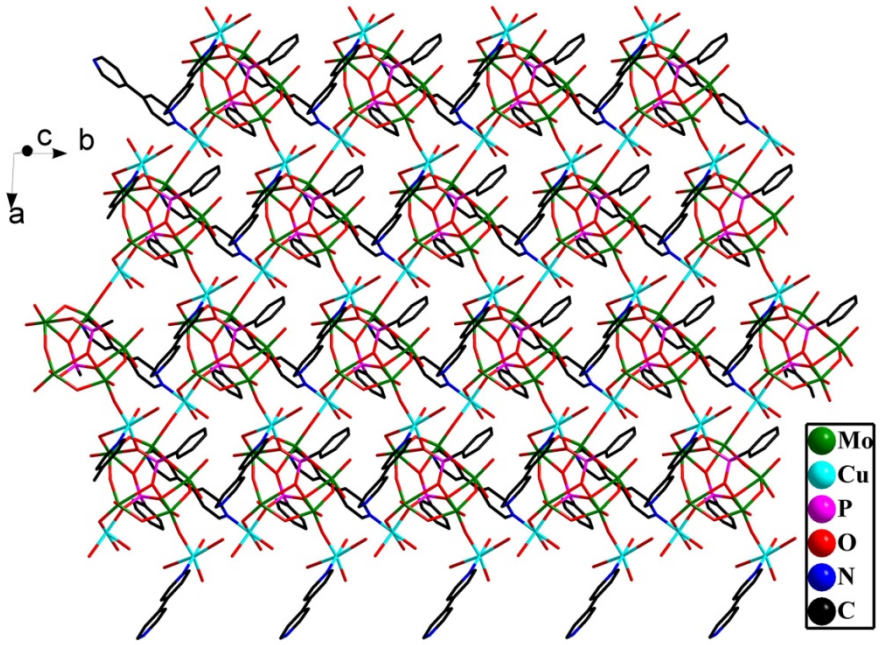


Fig. S5 Wire representation of the coordination type of polyanion **2** to Cu^{2+} ions (The hydrogen atoms have been omitted for clarity)

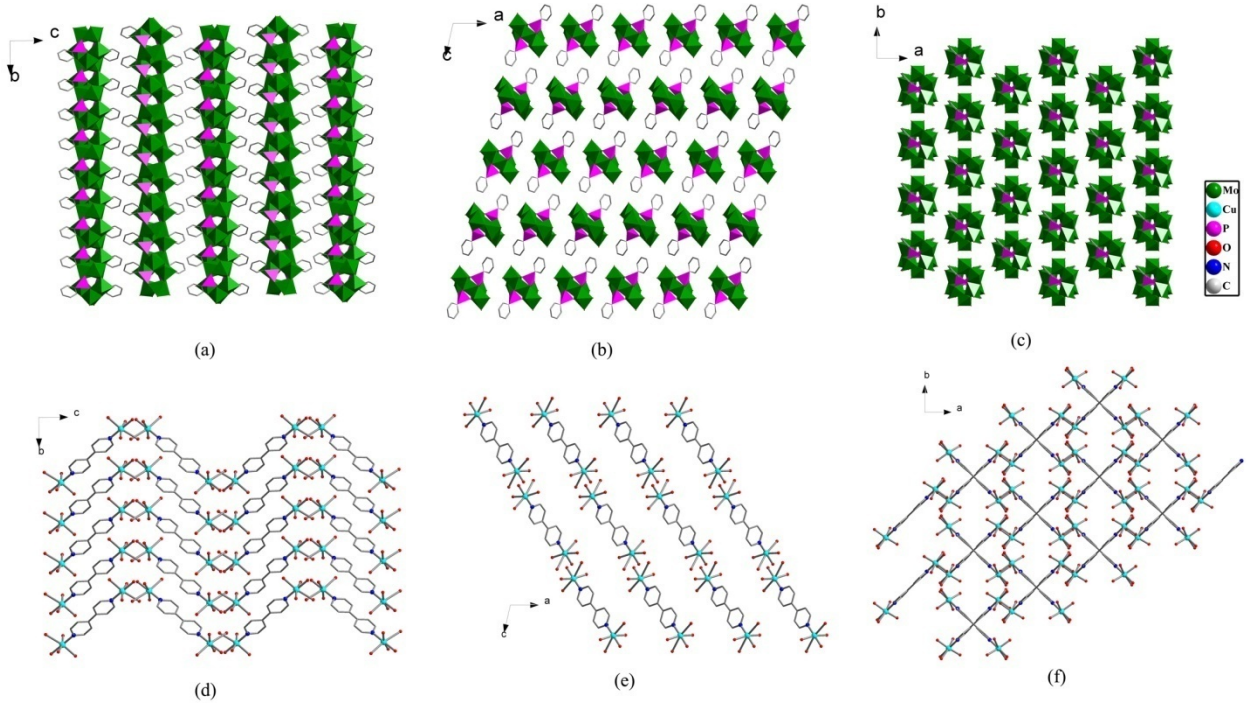


Fig. S6 Polyhedral and Ball-and-stick representation of the arrange of polyanions (a/b/c), and the connective type of Cu^{2+} ions and 4,4'-bipyridyl ligands (d/e/f) in **2** along *a*, *b* and *c* axis, respectively (The polyanions and hydrogen atoms have been omitted for clarity)

2. Characterizations

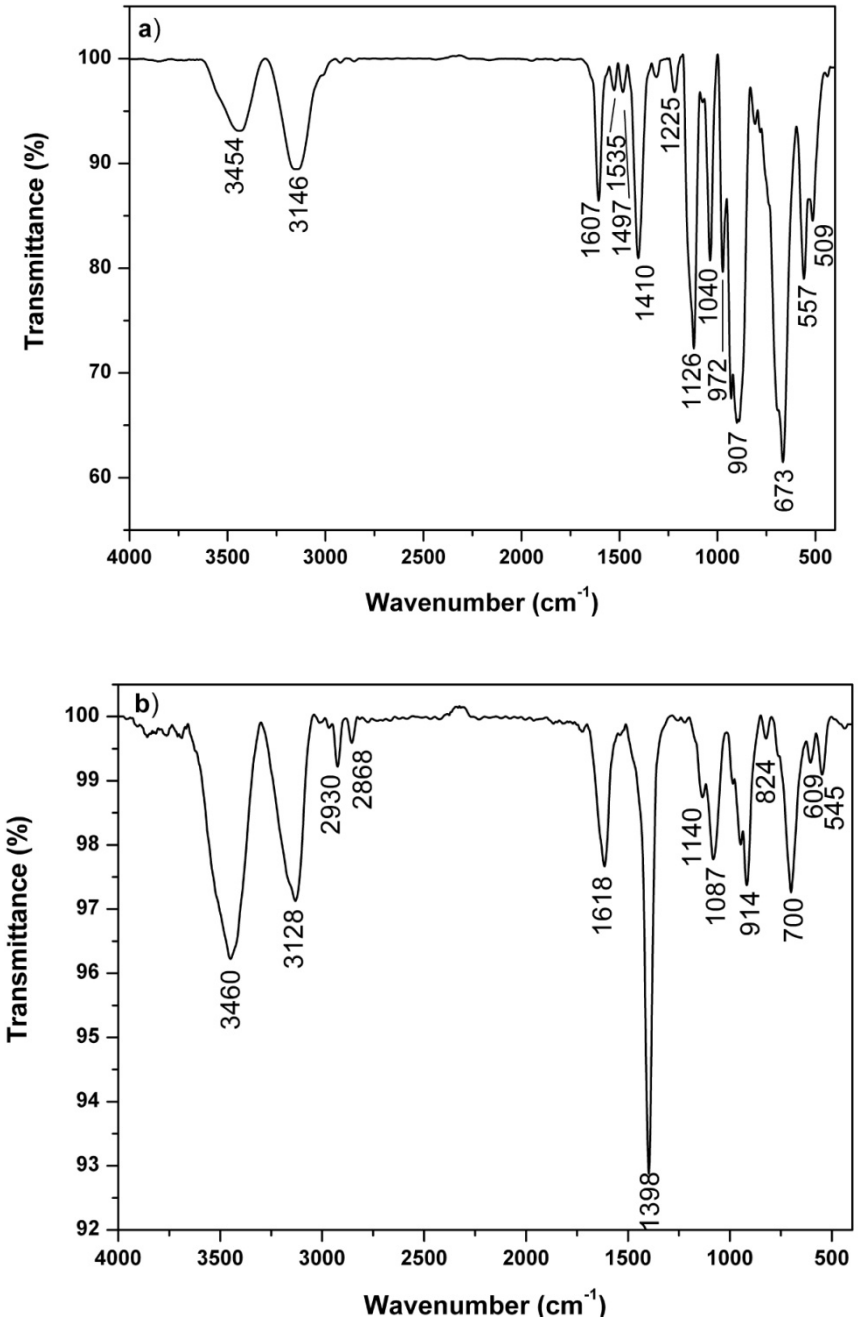
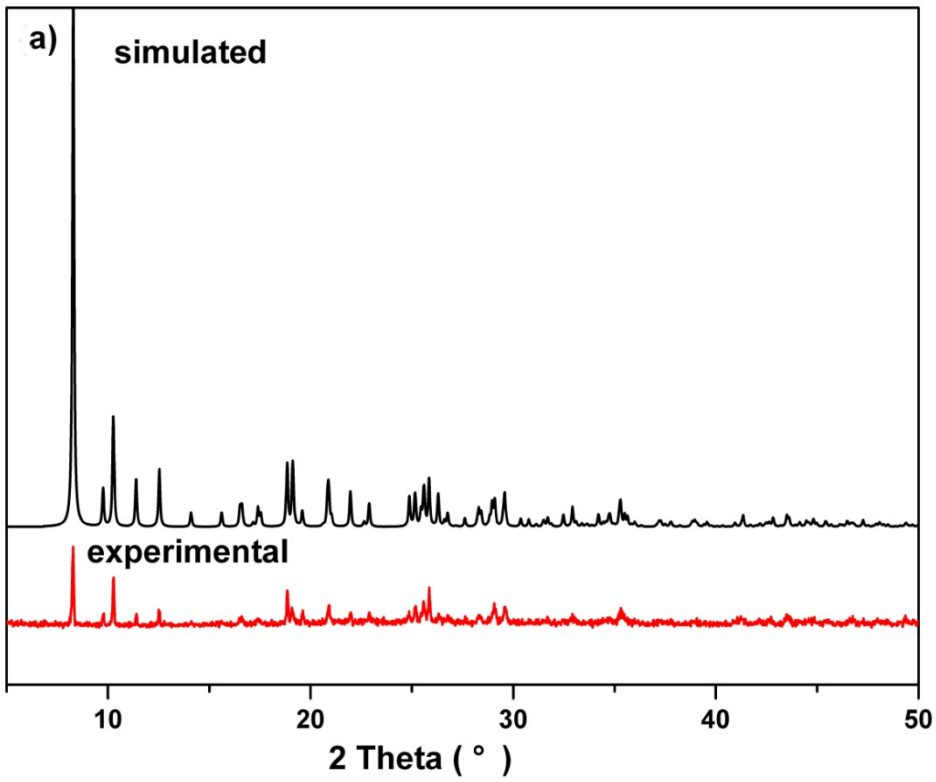


Fig. S7 IR spectra of **1** and **2** (a and b).



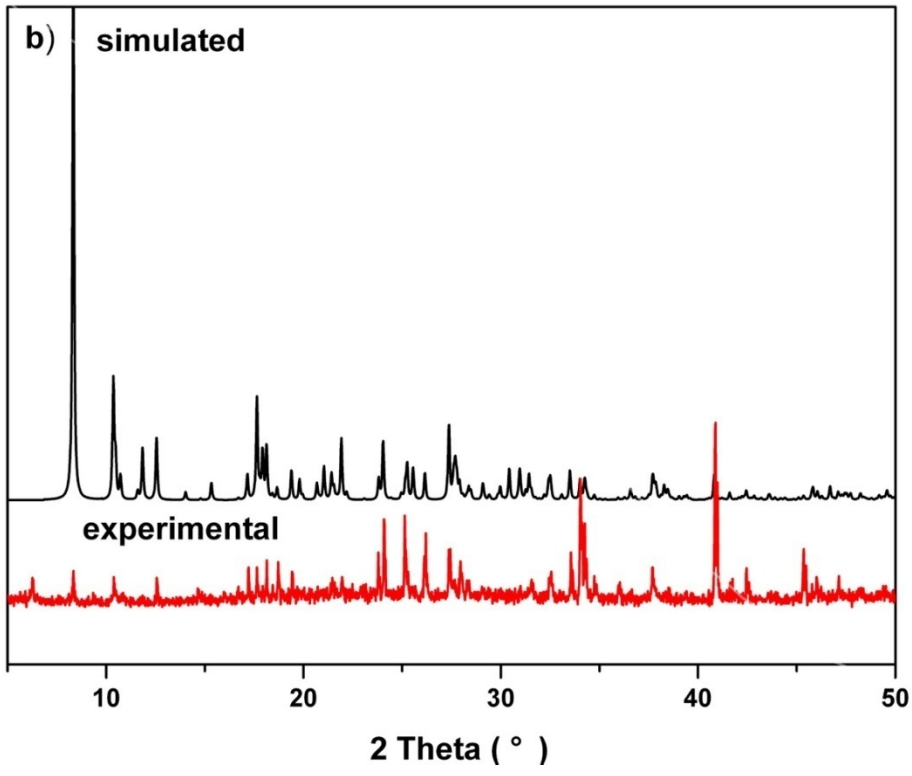


Fig. S8 The simulated and experimental XRPD patterns of **1** and **2** (a and b)

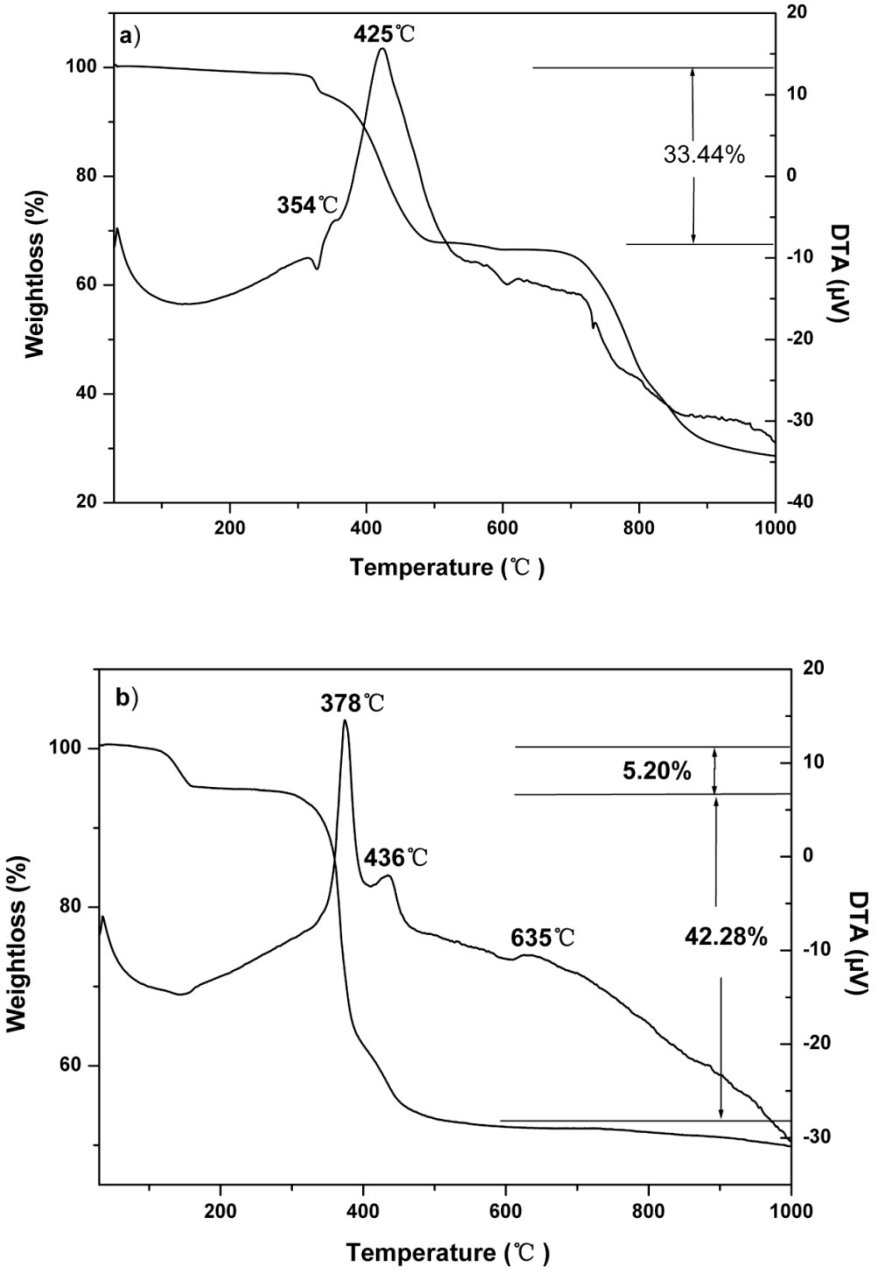


Fig. S9 The TG-DTA curves of **1** and **2** (a and b).

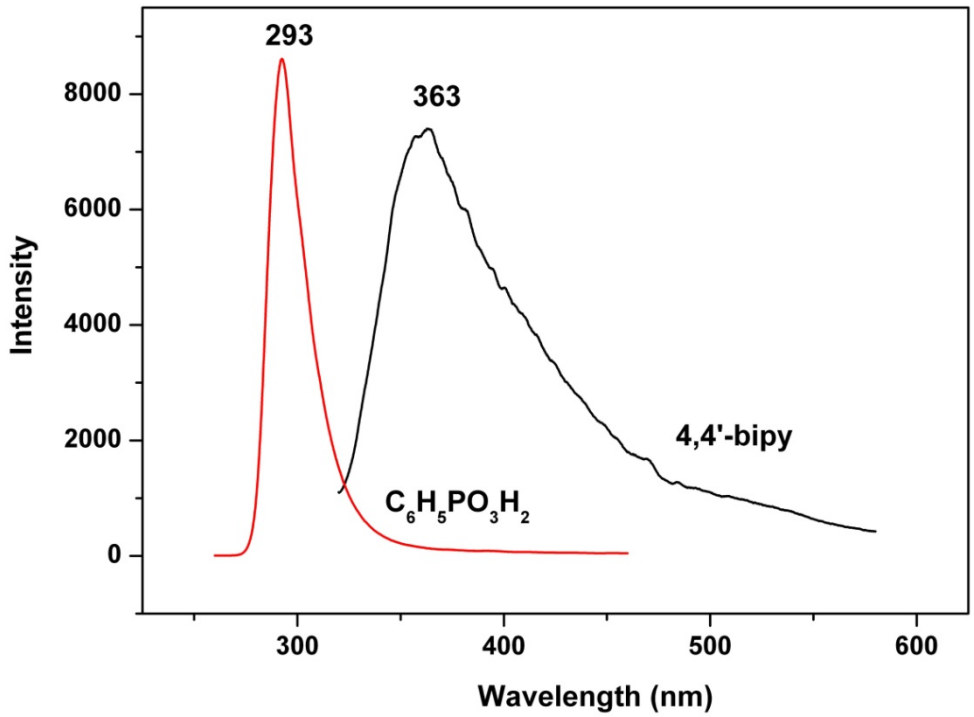
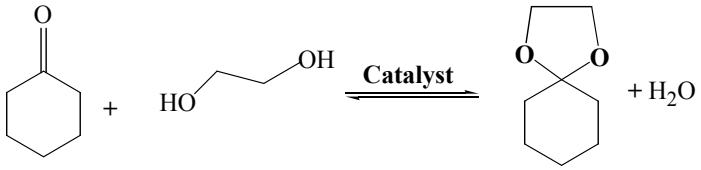


Fig. S10 Emission spectra of 4,4′- bipyridyl and phenylphosphonic acid ($C_6H_5PO_3H_2$)

3. Catalytic activity tests



Scheme S1 Ketalization of cyclohexanone with glycol

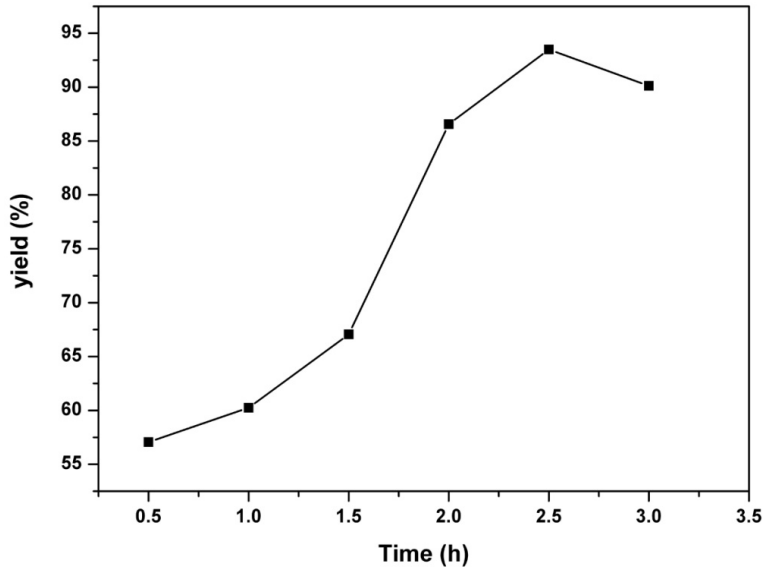


Fig. S11 Effect of reaction time on cyclohexanone ethylene ketal yield: cyclohexanone (0.1 mol)/glycol molar ratio, 1:1.4; catalyst (based on Mo)/cyclohexanone molar ratio, 1:200; reaction temperature, 95-100 °C; water-carring agent, cyclohexane (10 mL)

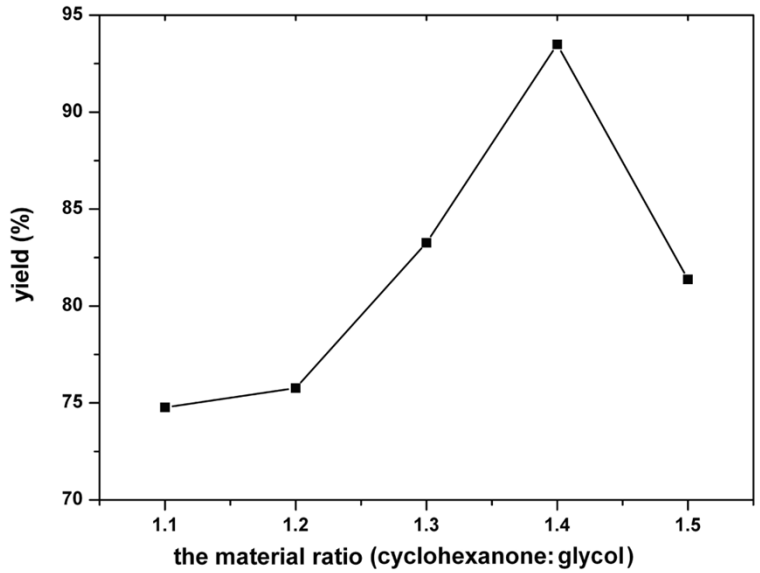


Fig. S12 Effect of the material ratio on cyclohexanone ethylene ketal yield: catalyst (based on Mo)/cyclohexanone (0.1 mol) molar ratio, 1:200; reaction temperature, 95-100 °C; reaction time, 2.5 h. water-carring agent, cyclohexane (10 mL)

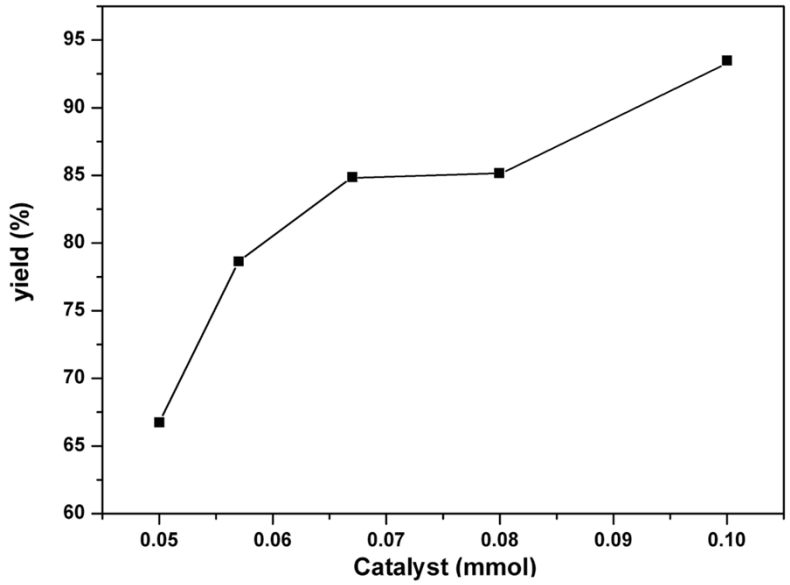


Fig. S13 Effect of the amount of **1** on cyclohexanone ethylene ketal yield: cyclohexanone (0.1 mol)/glycol molar ratio, 1:1.4; reaction temperature, 95-100 °C; reaction time, 2.5 h; water-carring agent, cyclohexane (10 mL)

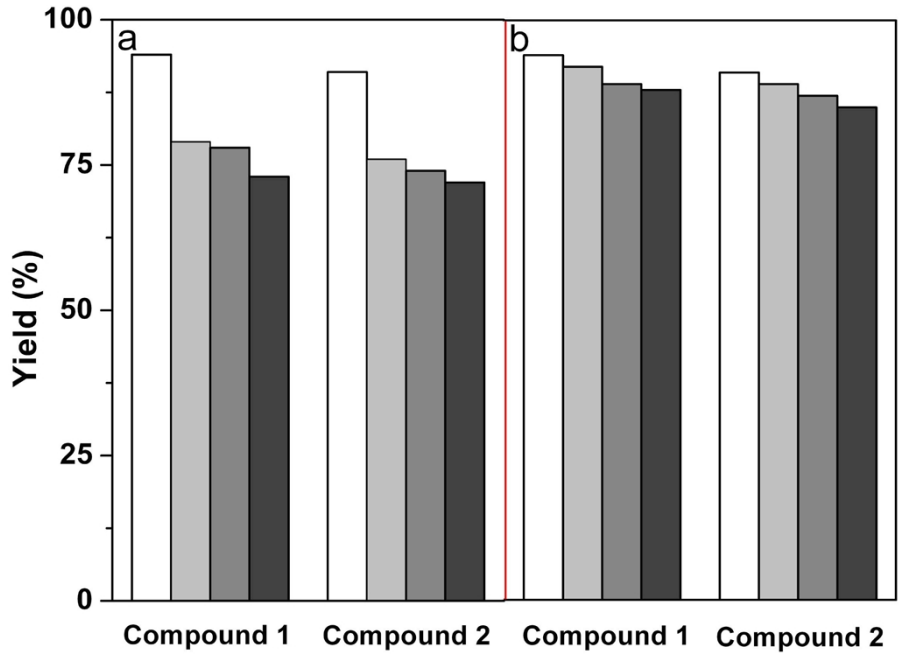


Fig. S14 The catalytic activities of **1** and **2** used four cycles. (a) The catalysts were recovered by simple filtration without any treatment; (b) The recovered catalysts were washed with ethyl ether and water, respectively. The reaction conditions: catalyst (based on Mo)/cyclohexanone (0.1 mol) molar ratio, 1:200; cyclohexanone (0.1 mol)/glycol molar ratio, 1:1.4; reaction temperature, 95-100 °C; reaction time, 2.5 h; water-carring agent, cyclohexane (10 mL)

4. Bond lengths and angles

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

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Mo1–O6	1.718(3)	Mo2–O1	1.996(3)	Cu1–O1W	1.944(3)
Mo1–O6#1	1.718(3)	Mo2–O10#1	2.206(3)	Cu1–O2#2	1.955(3)
Mo1–O4	1.903(2)	Mo2–O7	2.376(2)	Cu1–N1	2.013(3)
Mo1-O4#1	1.903(2)	Mo3–O8	1.686(2)	Cu1–N2	2.015(3)
Mo1–O7	2.296(3)	Mo3–O2	1.741(3)	Cu1–O6	2.381(3)
Mo1–O7#1	2.296(3)	Mo3–O5	1.8964(10)	P1–O3	1.502(3)
Mo2–O11	1.688(3)	Mo3–O1	1.900(3)	P1–O7	1.533(3)
Mo2–O9	1.718(3)	Mo3–O3	2.235(3)	P1–O10	1.560(3)
Mo2–O4	1.908(3)	Mo3–O10#1	2.325(3)	P1–C1	1.787(4)
Bond	Angle (º)	Bond	Angle (º)	Bond	Angle (º)
O6–Mo1–O6#1	102.14 (19)	O4–Mo2–O1	152.90(11)	N1–Cu1–O6	90.03(12)
O6#1–Mo1–O4	101.73(12)	O8–Mo3–O2	102.30(13)	N1–Cu1–N2#2	171.47(14)
O4–Mo1–O4#1	145.36(16)	O8–Mo3–O5	96.37(10)	O3–P1–O7	111.38(15)
O11–Mo2–O9	104.01(14)	O5–Mo3–O1	148.13(14)	O3–P1–O10	109.21(15)
O11–Mo2–O4	95.49(13)	O1W–Cu1–N2#2	91.32(13)	O7–P1–C1	107.96(18)

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

Table S2 Hydrogen bonds for **1**

D–H···A	d(D–H) (Å)	d(H···A) (Å)	d(D···A) (Å)	∠(DHA) (º)
O1W-H1WA...O1#1	0.845(10)	1.769(13)	2.609(4)	173(5)
O1W-H1WB...O9#2	0.842(10)	1.916(16)	2.741(4)	166(5)

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

Table S3 Selected bond lengths and angles for compound **2**

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Mo1–O3	1.702(3)	Mo2–O4	1.946(3)	Cu1–O5#2	1.927(3)
Mo1–O3#1	1.702(3)	Mo2–O7	2.183(3)	Cu1–O8	1.956(3)
Mo1–O2#1	1.938(3)	Mo2–O1	2.379(3)	Cu1– O1W	1.962(3)
Mo1-O2	1.938(3)	Mo3–O11	1.685(3)	Cu1–N1	1.992(4)
Mo1–O1#1	2.278(3)	Mo3–O10	1.708(3)	Cu1– O2W	2.511(3)
Mo1–O1	2.278(3)	Mo3–O9	1.8839(7)	P1–O8	1.528(3)
Mo2–O6	1.677(3)	Mo3–O4	1.885(3)	P1–O1	1.534(3)
Mo2–O5	1.735(3)	Mo3–O8	2.519(3)	P1–O7#1	1.536(3)
Mo2–O2	1.892(3)	Mo3–O7	2.597(3)	P1–C1	1.781(4)
Bond	Angle (º)	Bond	Angle (º)	Bond	Angle (º)
O3–Mo1–O3#1	104.6 (2)	O2–Mo2–O4	149.39(12)	O8–Cu1–N1	93.44(14)
O3–Mo1–O2#1	100.13(14)	O11–Mo3–O10	103.22(17)	O1W–Cu1–N1	178.92(16)
O3–Mo1–O2	98.86(14)	O9–Mo3–O4	134.62(14)	O8–P1–O1	109.68(16)
O6–Mo2–O5	103.82(15)	O10–Mo3–O8	76.38(13)	O8–P1–O7#1	107.15(16)
O5–Mo2–O4	94.18(13)	O8–Cu1–O1W	85.79(13)	O1–P1–C1	107.10(18)

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

Table S4 Hydrogen bonds for **2**

D–H···A	d(D–H) (Å)	d(H···A) (Å)	d(D···A) (Å)	∠(DHA) (º)
O1W-H1WA...O3#1	0.845(10)	1.967(15)	2.800(4)	168(5)
O1W-H1WB...O4	0.843(11)	2.05(2)	2.833(5)	155(5)

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