Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary information

Three new Strandberg-type phenylphosphomolybdate supports for immobilizing horseradish peroxidase and their catalytic oxidation performances

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1. Crystal structures of TM-$(PhP)_2Mo_5$ (TM = Co, Cu, Ni)

2. Selected bond lengths and angles of TM-$(PhP)_2Mo_5$ (TM = Co, Cu, Ni)

3. Characterizations

4. Catalytic activity tests

5. Enzyme Immobilization

1. Crystal structures of TM-$(PhP)_2Mo_5$ (TM = Co, Cu, Ni)

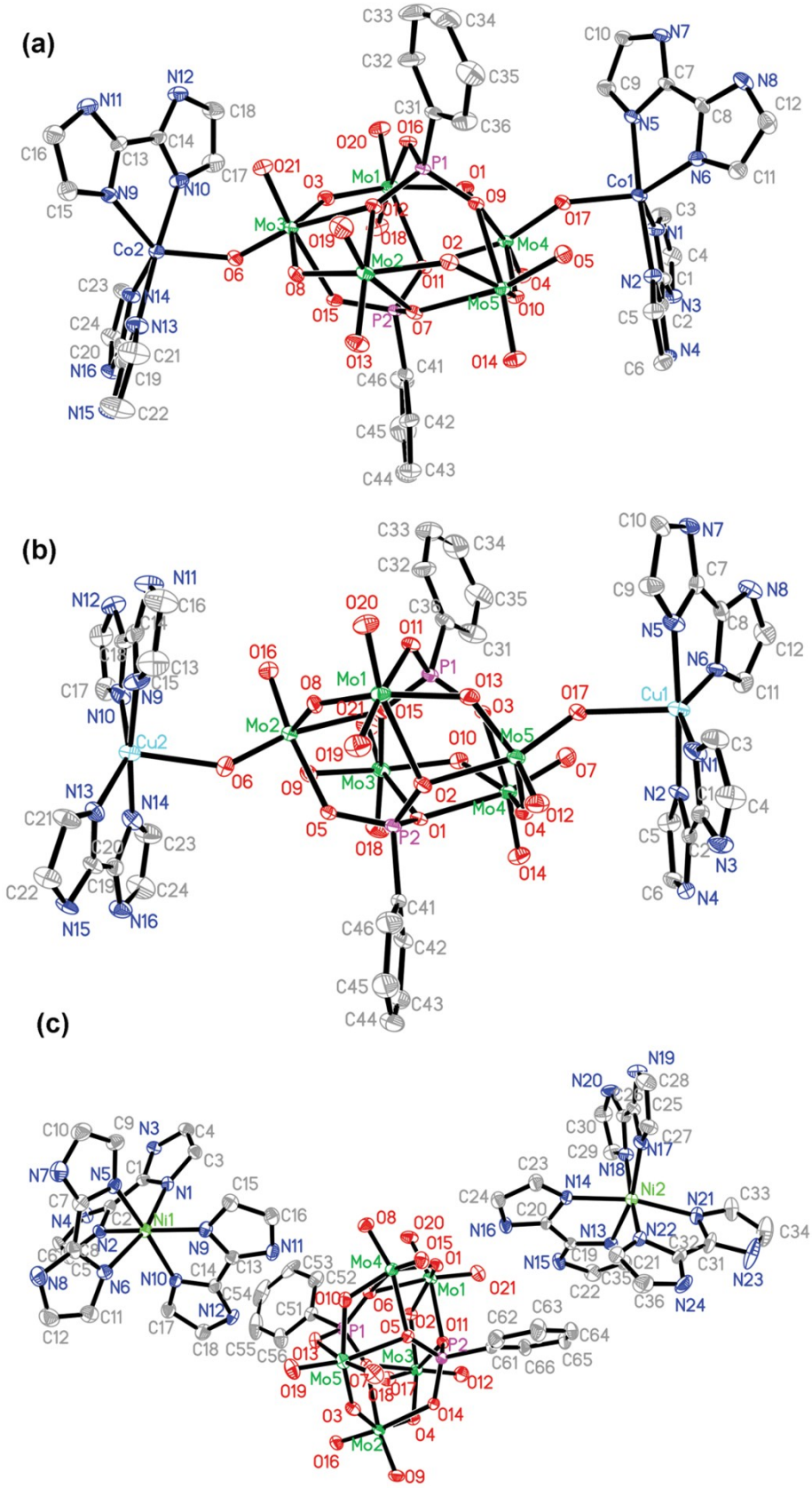

Fig. S1 ORTEP views of the asymmetric units of **TM-$(PhP)_2Mo_5$** (TM = Co(a), Cu(b), Ni(c)) with atom labeling (30% probability displacement ellipsoids; hydrogen atoms and free water molecules have been omitted for clarity)

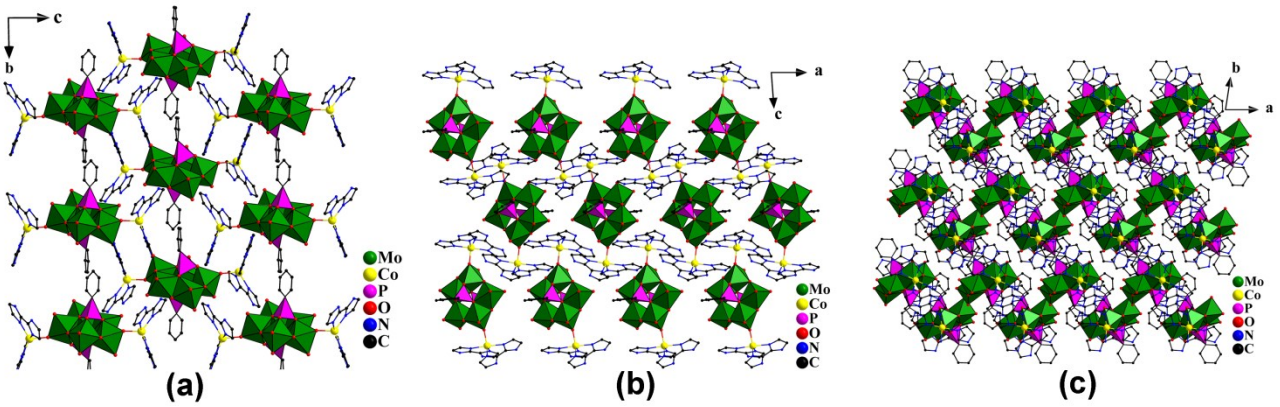

Fig. S2 Polyhedral and ball-and-stick representation of a 3-D structure of **Co-(PhP)$_2$Mo$_5$** packing arrangement along *a*(a), *b* (b), and *c*(c) axes, respectively (hydrogen atoms and free water molecules have been omitted for clarity)

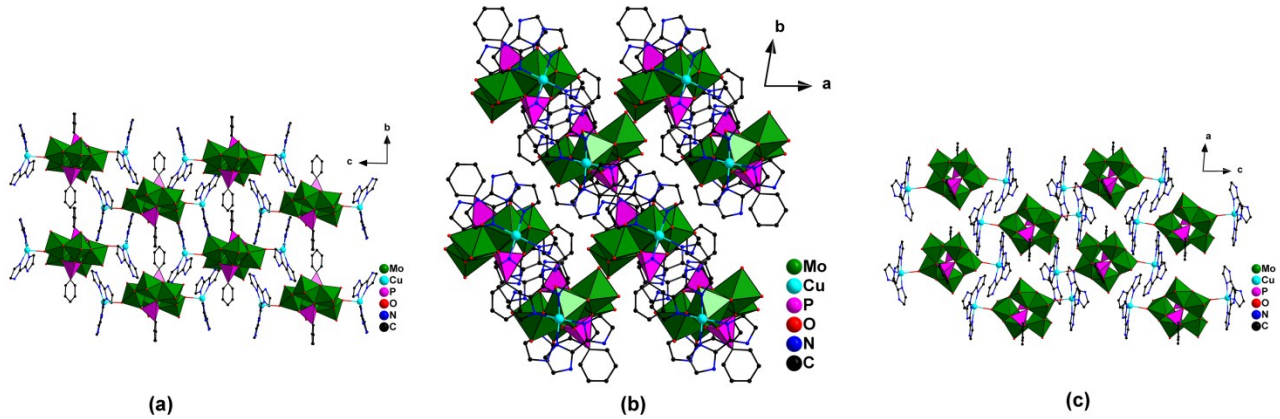

Fig. S3 Polyhedral and ball-and-stick representation of a 3-D structure of **Cu-(PhP)$_2$Mo$_5$** packing arrangement along *a*(a), *b* (b), and *c*(c) axes, respectively (hydrogen atoms and free water molecules have been omitted for clarity)

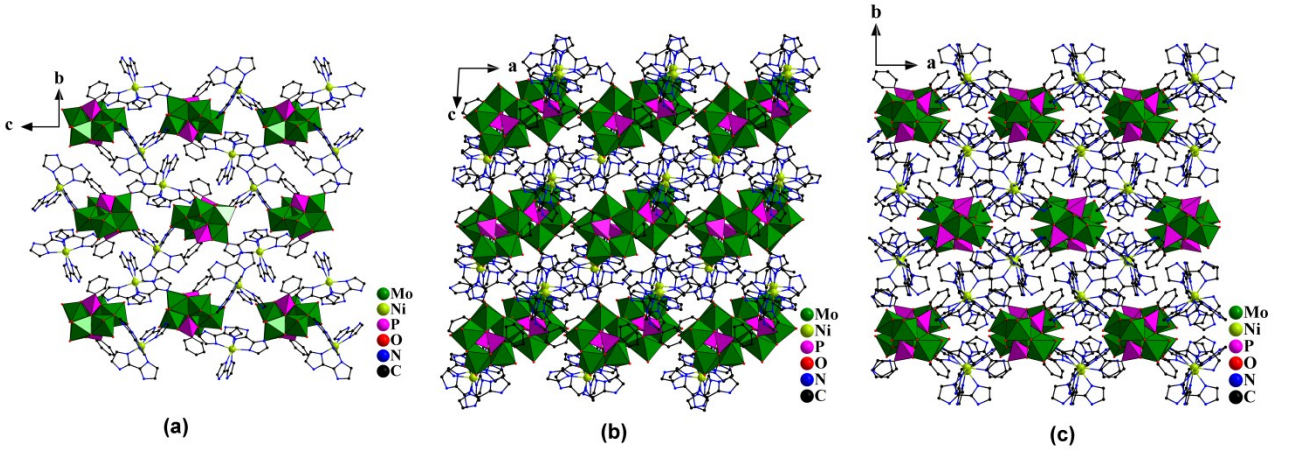

Fig. S4 Polyhedral and ball-and-stick representation of a 3-D structure of **Ni-(PhP)$_2$Mo$_5$** packing arrangement along *a*(a), *b* (b), and *c*(c) axes, respectively (hydrogen atoms and free water molecules have been omitted for clarity)

2. Selected bond lengths and angles of TM-(PhP)$_2$Mo$_5$ (TM = Co, Cu, Ni)

Table S1 Selected bond lengths (Å) and angles (°) for **Co-$(PhP)_2Mo_5$**

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Mo1–O20	1.678(3)	Mo3–O15	2.222(3)	Co1–N6	2.040(4)
Mo1–O18	1.689(3)	Mo3–O12	2.328(3)	Co1–N5	2.122(3)
Mo1–O9	1.938(3)	Mo4–O4	1.678(3)	Co1–N2	2.128(4)
Mo1–O3	1.940(3)	Mo4–O17	1.751(3)	Co2–O6	1.987(3)
Mo1–O16	2.238(3)	Mo4–O9	1.896(3)	Co2–N14	2.031(4)
Mo1–O11	2.438(3)	Mo4–O10	1.906(3)	Co2–N9	2.034(4)
Mo2–O19	1.687(3)	Mo4–O11	2.173(3)	Co2–N13	2.112(4)
Mo2–O13	1.691(3)	Mo4–O1	2.462(3)	Co2–N10	2.141(4)
Mo2–O2	1.926(3)	Mo5–O5	1.691(3)	P1–O16	1.501(3)
Mo2–O8	1.961(3)	Mo5–O14	1.708(3)	P1–O1	1.533(3)
Mo2–O12	2.225(3)	Mo5–O2	1.887(3)	P1–O12	1.538(3)
Mo2–O7	2.397(3)	Mo5–O10	1.953(3)	P1–C31	1.786(4)
Mo3–O21	1.712(3)	Mo5–O7	2.291(3)	P2–O15	1.511(3)
Mo3–O6	1.730(3)	Mo5–O1	2.352(3)	P2–O7	1.526(3)
Mo3–O3	1.856(3)	Co1–O17	1.983(3)	P2–O11	1.533(3)
Mo3–O8	1.899(3)	Co1–N1	2.040(4)	P2–C41	1.781(4)
Bond	**Angle (°)**	**Bond**	**Angle (°)**	**Bond**	**Angle (°)**
O18–Mo1–O16	170.22(13)	O4–Mo4–O1	169.35(12)	N13–Co2–N10	177.38(16)
O9–Mo1–O11	67.79(10)	O9–Mo4–O11	74.62(11)	N9–Co2–N10	79.59(14)
O3–Mo1–O16	77.10(11)	O10–Mo4–O1	71.99(10)	N14–Co2–N13	80.26(14)
O19–Mo2–O7	164.37(13)	O14–Mo5–O1	167.50(12)	O16–P1–O1	111.36(16)
O2–Mo2–O7	70.11(10)	O2–Mo5–O7	73.24(11)	O12–P1–C31	108.17(18)
O2–Mo2–O12	84.02(11)	O10–Mo5–O1	73.87(10)	O16–P1–C31	107.62(18)
O21–Mo3–O15	173.57(13)	N5–Co1–N2	175.43(14)	O15–P2–O7	111.07(16)
O8–Mo3–O12	70.23(11)	N6–Co1–N5	79.96(14)	O7–P2–C41	107.95(19)
O6–Mo3–O8	98.89(14)	N1–Co1–N2	79.41(14)	O11–P2–C41	111.72(19)

Table S2 Partial bond lengths (Å) and angles (°) for **Cu-$(PhP)_2Mo_5$**

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Mo1–O20	1.685(6)	Mo3–O15	2.217(6)	Cu1–N5	1.993(8)
Mo1–O19	1.699(7)	Mo3–O1	2.401(6)	Cu1–N1	2.007(8)
Mo1–O8	1.945(6)	Mo4–O7	1.699(7)	Cu1–N6	2.035(8)
Mo1–O13	1.951(7)	Mo4–O14	1.712(6)	Cu2–O6	2.251(7)
Mo1–O11	2.257(6)	Mo4–O10	1.894(6)	Cu2–N14	1.991(9)
Mo1–O2	2.462(6)	Mo4–O4	1.953(6)	Cu2–N10	1.994(8)
Mo2–O16	1.718(7)	Mo4–O1	2.311(6)	Cu2–N9	2.013(9)
Mo2–O6	1.723(7)	Mo4–O3	2.335(6)	Cu2–N13	2.020(8)
Mo2–O8	1.886(6)	Mo5–O12	1.688(7)	P1–O11	1.511(6)
Mo2–O9	1.913(6)	Mo5–O17	1.736(6)	P1–O3	1.537(6)
Mo2–O5	2.199(6)	Mo5–O13	1.913(6)	P1–O15	1.549(6)
Mo2–O15	2.357(6)	Mo5–O4	1.928(6)	P1–C31	1.815(9)
Mo3–O21	1.686(7)	Mo5–O2	2.198(6)	P2–O5	1.519(3)

Mo3–O18	1.697(6)	Mo5–O3	2.457(6)	P2–O1	1.542(6)
Mo3–O10	1.942(7)	Cu1–O17	2.265(7)	P2–O2	1.544(6)
Mo3–O9	1.972(7)	Cu1–N2	1.988(8)	P2–C41	1.780(9)
Bond	**Angle (°)**	**Bond**	**Angle (°)**	**Bond**	**Angle (°)**
O19–Mo1–O11	170.0(3)	O14–Mo4–O3	167.6(3)	N14–Cu2–N9	173.6(4)
O13–Mo1–O11	76.8(2)	O4–Mo4–O3	74.5(2)	N14–Cu2–N13	82.4(3)
O13–Mo1–O2	67.9(2)	O10–Mo4–O1	72.7(2)	N10–Cu2–N9	81.7(3)
O16–Mo2–O5	173.0(3)	O12–Mo5–O3	169.2(3)	O11–P1–O3	111.3(4)
O9–Mo2–O5	77.9(3)	O13–Mo5–O2	74.5(2)	O15–P1–C31	108.1(4)
O9–Mo2–O15	69.5(2)	O4–Mo5–O3	72.0(2)	O11–P1–C31	107.2(4)
O21–Mo3–O1	164.7(3)	N2–Cu1–N5	177.2(4)	O1–P2–O2	111.8(4)
O9–Mo3–O15	71.7(2)	N5–Cu1–N6	82.2(3)	O1–P2–C41	108.1(4)
O10–Mo3–O1	69.9(2)	N2–Cu1–N1	81.9(3)	O5–P2–C41	105.7(4)

Table S3 Hydrogen bonds (Å, °) for **Co-$(PhP)_2Mo_5$**

D–H···A	**d(D–H)**	**d(H···A)**	**d(D···A)**	**<(DHA) (°)**
N3–H3A...O14#1	0.86	1.90	2.753(5)	169.9
N4–H4A...O10#1	0.86	2.09	2.933(4)	167.3
N7–H7A...O1#2	0.86	2.22	2.986(5)	149.0
N7–H7A...O17#2	0.86	2.35	2.980(5)	130.3
N8–H8A...O9#2	0.86	2.30	3.109(5)	155.9
N8–H8A...O16#2	0.86	2.36	2.920(5)	123.3
N11–H11A...O21#3	0.86	2.21	2.964(5)	146.8
N12–H12A...O21#3	0.86	1.97	2.768(5)	153.6
N12–H12A...O1W#3	0.86	2.63	3.225(9)	127.2
N15–H15A...O15#4	0.86	2.02	2.764(5)	143.5
N15–H15A...O6#4	0.86	2.49	3.151(5)	134.7
N16–H16A...O8#4	0.86	2.30	3.104(5)	155.5
N16–H16A...O15#4	0.86	2.32	2.991(5)	135.4

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

Table S4 Hydrogen bonds (Å, °) for **Cu-$(PhP)_2Mo_5$**

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA) (°)
N3–H3A...O14#1	0.86	1.88	2.737(10)	172.8
N4–H4A...O4#1	0.86	2.06	2.908(10)	169.2
N7–H7A...O17#2	0.86	2.19	2.922(10)	143.2
N7–H7A...O3#2	0.86	2.37	3.028(10)	133.5
N8–H8A...O13#2	0.86	2.21	3.039(11)	161.1
N8–H8A...O11#2	0.86	2.48	2.952(11)	115.1
N11–H11A...O16#3	0.86	1.94	2.733(11)	153.2
N11–H11A...O1W#3	0.86	2.64	3.190(17)	122.5
N12–H12A...O16#3	0.86	2.29	3.014(12)	141.9
N15–H15A...O6#4	0.86	3.07	3.740(10)	136.8
N15–H15A...O9#4	0.86	2.19	3.013(10)	158.9
N16–H16A...O5#4	0.86	2.19	2.822(11)	130.6
N16–H16A...O6#4	0.86	2.42	3.188(11)	149.0
N16–H16A...O2W#4	0.86	2.57	3.04(2)	115.4

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

Table S5 Partial bond lengths (Å) and angles (°) for **Ni-$(PhP)_2Mo_5$**

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Mo1–O20	1.696(4)	Mo3–O11	2.311(4)	Ni1–N1	2.105(5)
Mo1–O21	1.700(4)	Mo4–O8	1.690(4)	Ni1– N 6	2.134(5)
Mo1–O2	1.913(4)	Mo4–O15	1.706(4)	Ni2–N22	2.075(5)
Mo1–O1	1.917(4)	Mo4–O10	1.932(4)	Ni2–N14	2.077(5)
Mo1–O11	2.329(4)	Mo4–O1	1.943(4)	Ni2–N18	2.105(5)
Mo1–O6	2.339(4)	Mo4–O5	2.217(4)	Ni2–N17	2.108(5)
Mo2–O9	1.702(4)	Mo4–O6	2.363(4)	Ni2–N21	2.123(5)
Mo2–O16	1.723(4)	Mo5–O19	1.689(4)	Ni2–N13	2.136(5)
Mo2–O3	1.897(4)	Mo5–O18	1.710(4)	P1–O13	1.520(4)
Mo2–O4	1.924(4)	Mo5–O3	1.922(4)	P1– O6	1.539(4)
Mo2–O14	2.242(4)	Mo5–O10	1.938(4)	P1–O7	1.541(4)
Mo2–O7	2.389(4)	Mo5–O13	2.278(4)	P1–C51	1.787(6)
Mo3–O12	1.687(4)	Mo5–O5	2.384(4)	P2–O14	1.514(4)
Mo3–O17	1.715(4)	Ni1– N5	2.081(5)	P2– O11	1.529(4)
Mo3–O4	1.900(4)	Ni1–N10	2.092(5)	P2–O5	1.531(4)
Mo3–O2	1.951(4)	Ni1–N2	2.097(5)	P2–C61	1.787(6)
Mo3–O7	2.249(4)	Ni1–N9	2.101(5)		
Bond	**Angle (°)**	**Bond**	**Angle (°)**	**Bond**	**Angle (°)**
O21–Mo1–O6	165.68(18)	O15–Mo4–O6	163.75(17)	N22– Ni2–N18	171.5(2)
O1–Mo1–O6	72.14(14)	O5–Mo4–O6	72.72(13)	N14– Ni2–N13	79.1(2)
O2–Mo1–O11	71.34(15)	O1–Mo4–O6	71.17(14)	N18– Ni2–N17	78.9(2)

O9–Mo2–O7	169.29(18)	O18–Mo5–O13	169.15(18)	O13–P1–O6	111.8(2)
O4–Mo2–O14	77.69(15)	O10–Mo5–O13	75.80(15)	O6–P1–C51	108.0(3)
O4–Mo2–O7	69.56(15)	O10–Mo5–O5	69.95(15)	O13–P1–C51	107.7(3)
O17–Mo3–O11	162.18(18)	N1–Ni1–N6	164.2(2)	O11–P2–O5	111.5(2)
O7–Mo3–O11	73.13(13)	N10– Ni1–N9	79.1(2)	O5–P2–C61	109.7(3)
O2–Mo3–O11	71.14(14)	N5– Ni1–N6	78.8(2)	O11–P2–C61	106.5(3)

Table S6 Table S.2 Hydrogen bonds (Å, °) for **Ni-$(PhP)_2Mo_5$**

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA) (°)
N3–H3A...O17#1	0.86	2.01	2.821(7)	155.8
N4–H4A...O2#1	0.86	1.88	2.734(6)	171.0
N7–H7A...O18#2	0.86	1.89	2.696(7)	154.9
N8–H8A...O1W	0.86	2.16	2.876(8)	140.9
N11–H11A...O10	0.86	1.91	2.744(7)	162.7
N12–H12A...O13	0.86	1.96	2.812(6)	170.7
N15–H15A...O21	0.86	2.05	2.913(7)	175.8
N16–H16A...O1	0.86	1.96	2.788(6)	161.2
N19–H19A...O16#3	0.86	2.22	2.939(7)	141.5
N20–H20A...O16#3	0.86	2.06	2.841(7)	150.7
N23–H23A...O9#4	0.86	2.33	2.964(8)	130.9
N24–H24A...O14#4	0.86	1.92	2.762(7)	165.0

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

3. Characterizations

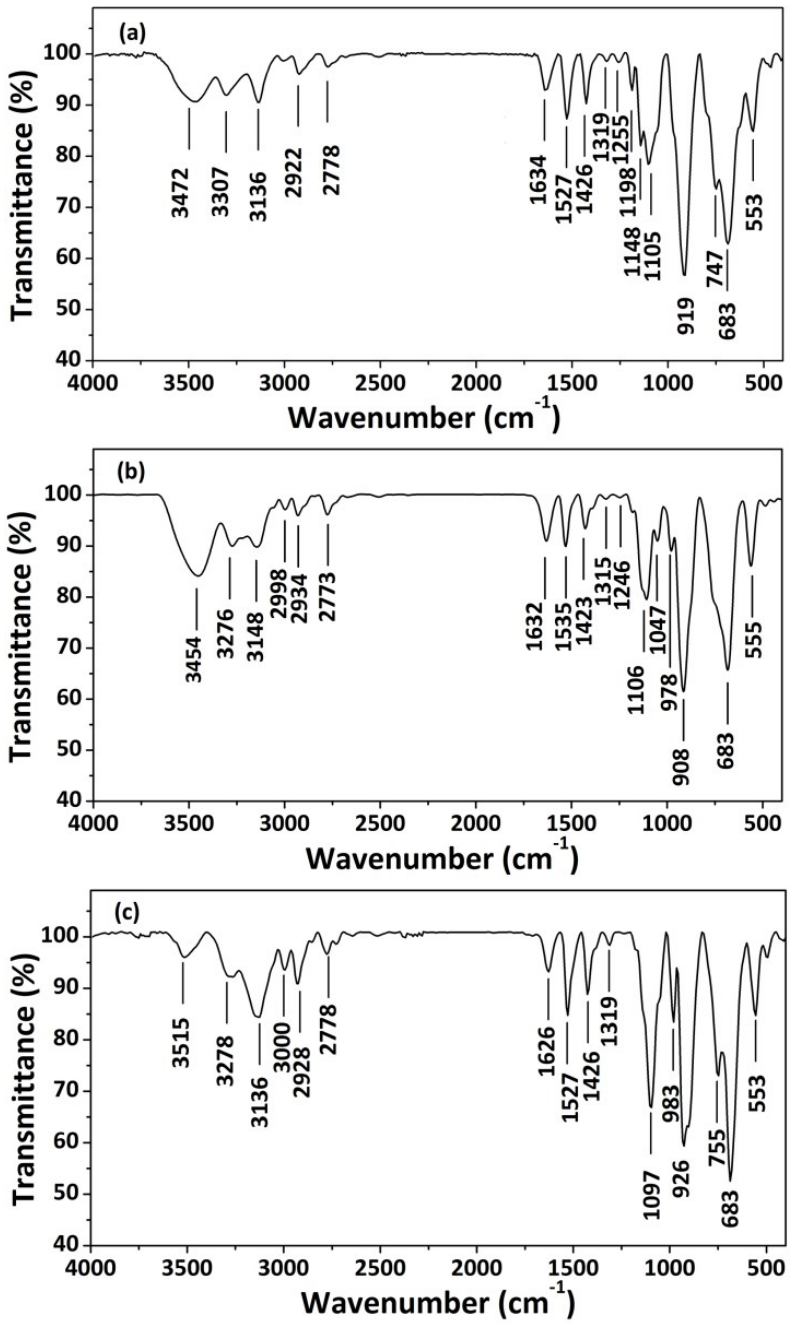

Fig. S5 IR spectra of **TM-(PhP)$_2$Mo$_5$** (TM = Co (a), Cu (b), Ni(c))

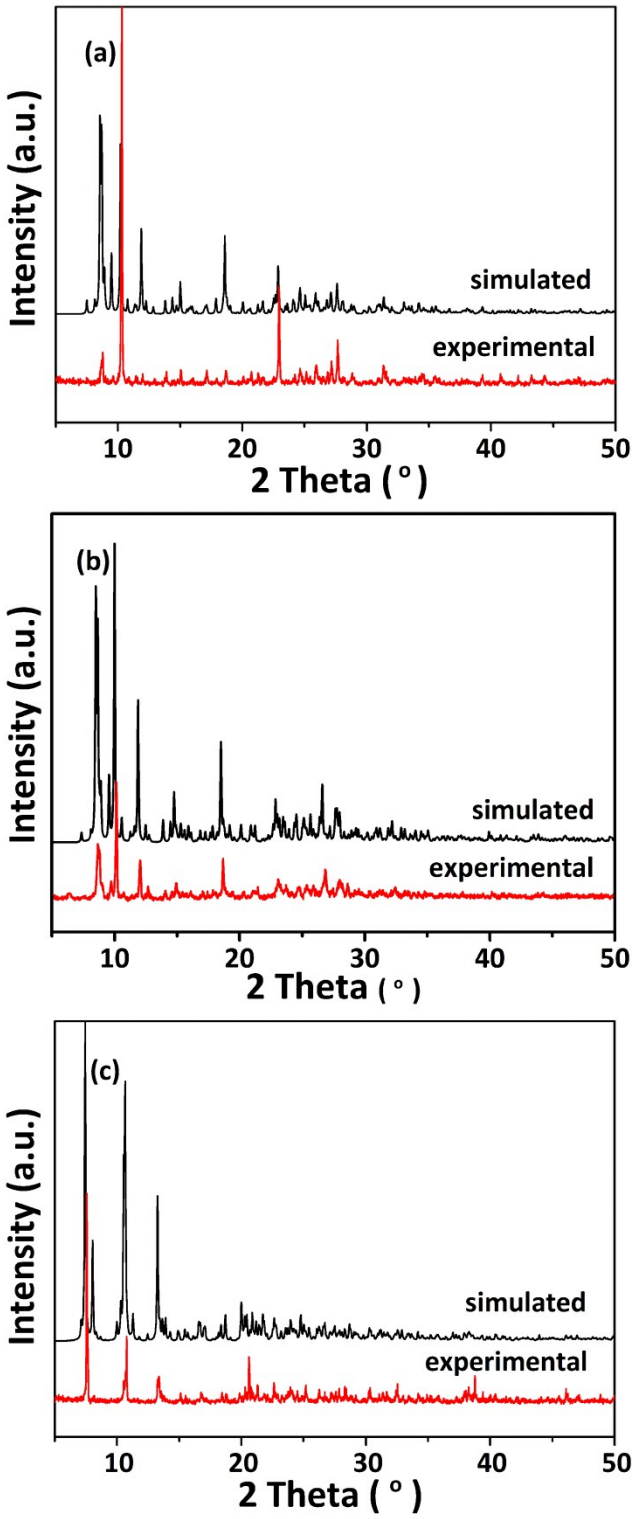

Fig. S6 The simulated and experimental XRPD patterns of **TM-$(PhP)_2Mo_5$** (TM = Co (a), Cu (b), Ni(c))

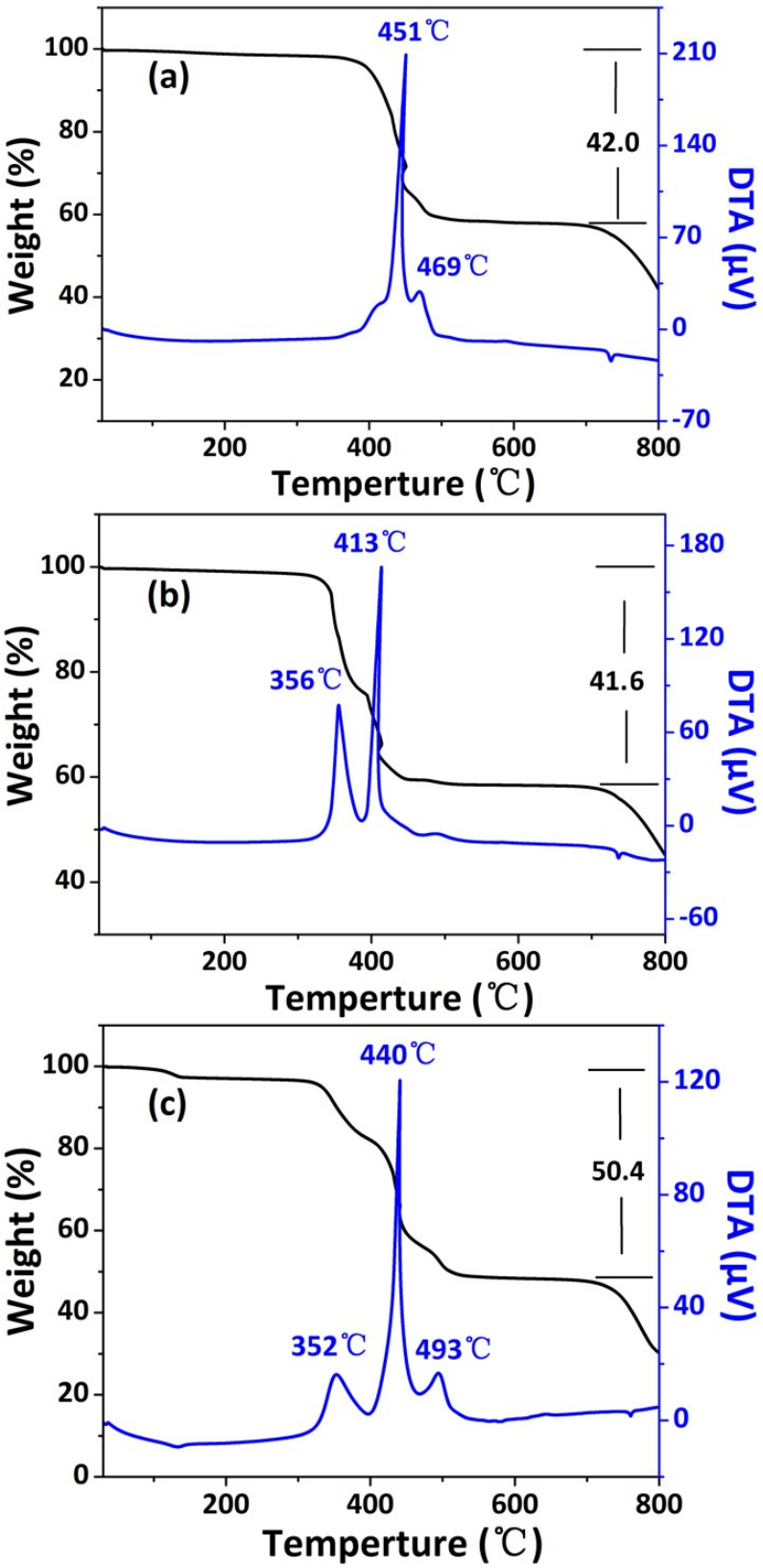

Fig. S7 The TG–DTA curves of **TM-(PhP)$_2$Mo$_5$** (TM = Co (a), Cu (b), Ni(c))

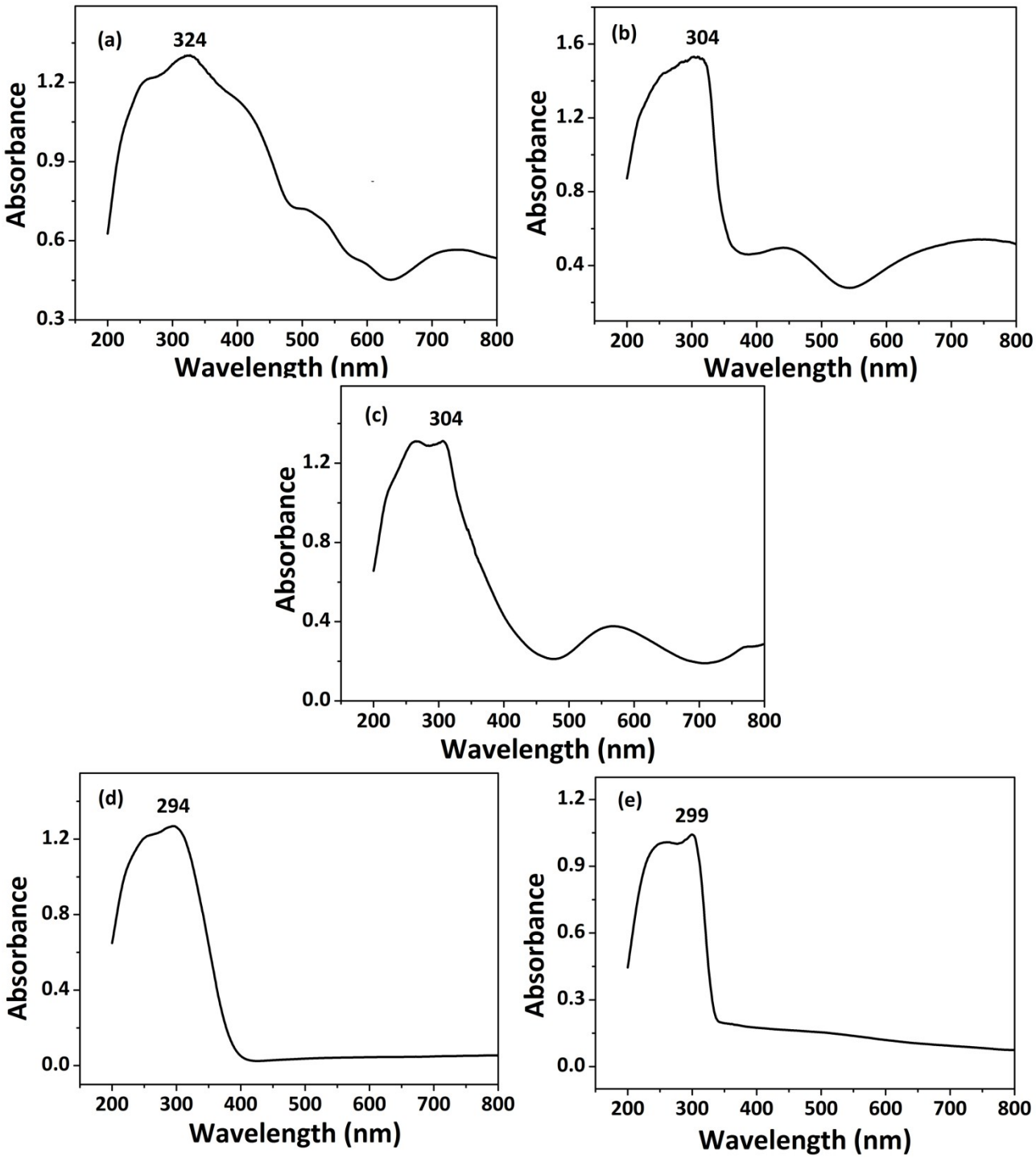

Fig. S8 Solid UV–vis absorption spectra of **TM-$(PhP)_2Mo_5$** (TM = Co (a), Cu (b), Ni(c)), **$(PhP)_2Mo_5$** (d), and H_2biim (e) at room temperature

4. Catalytic activity tests

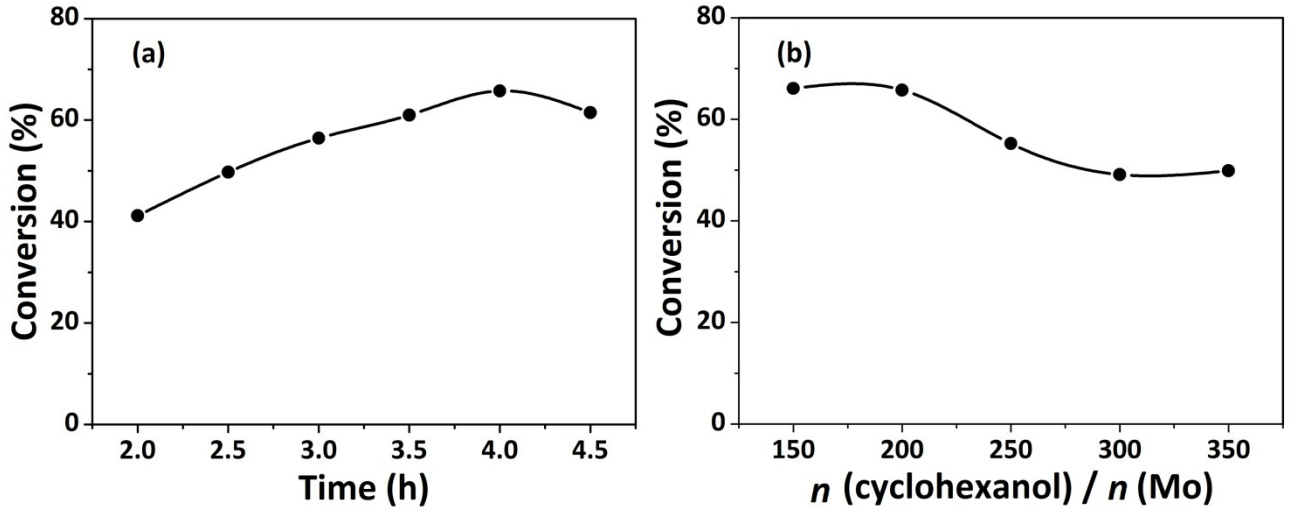

Fig. S9 Effect of the reaction time (a) and the amount of catalyst (b) on cyclohexanol conversion. Cyclohexanol to H_2O_2 molar ratio, 1:2.2; catalyst (**Co-$(PhP)_2Mo_5$**, based on Mo) to cyclohexanol molar ratio, 1:200; reflux temperature, 85–86 °C; acetonitrile, 10 mL

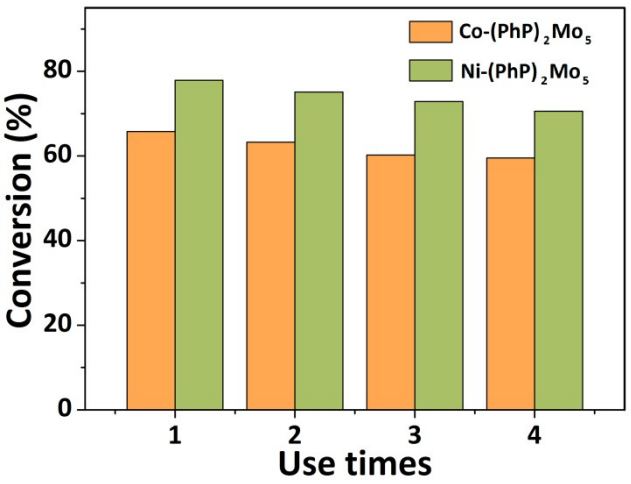

Fig. S10 The catalytic activity of **Co-$(PhP)_2Mo_5$** and **Ni-$(PhP)_2Mo_5$** used after four runs (the reaction time, 4 h; the molar ratio of catalyst to cyclohexanol, 1 : 200; cyclohexanol to H_2O_2, 1 : 2.2; acetonitrile, 10 mL ; reflux temperature, 85 – 86 °C)

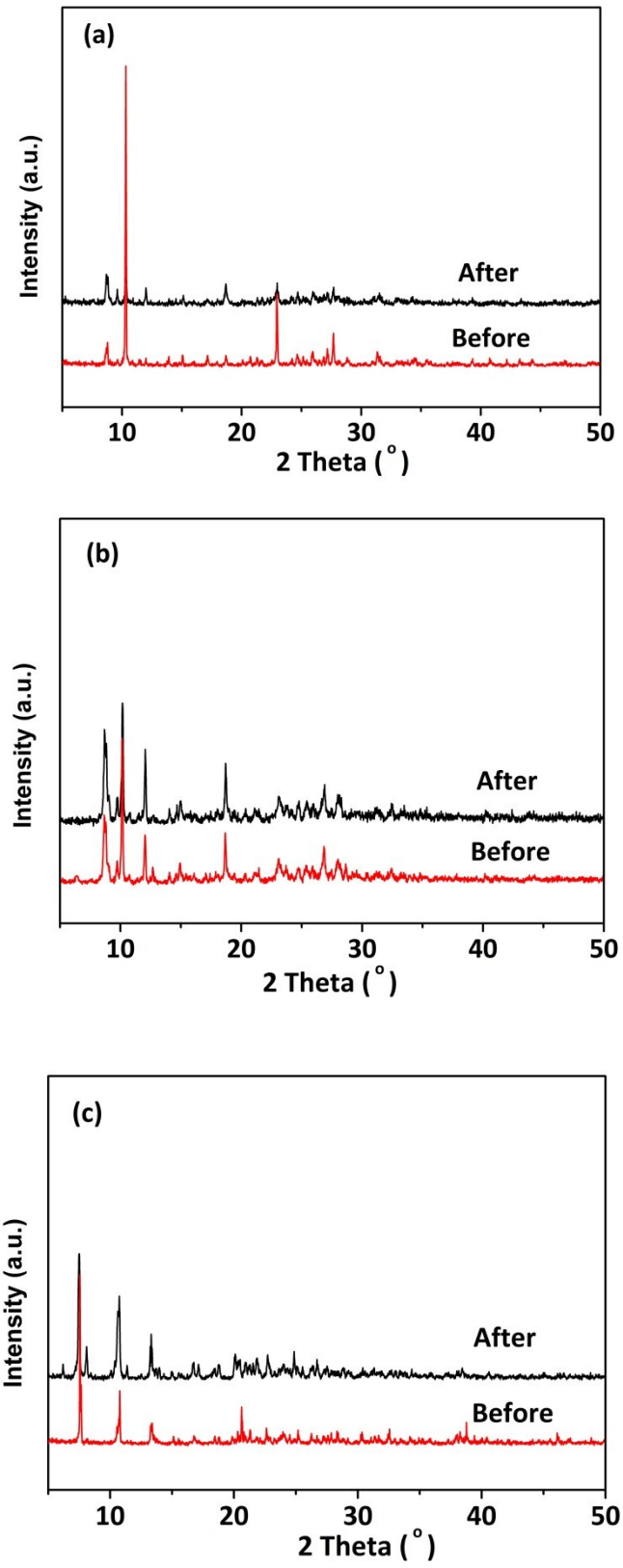

Fig. S11 XRPD spectra of **TM-$(PhP)_2Mo_5$** (TM = Co (a), Cu (b), Ni(c)) before and after the catalytic reaction

5. Enzyme Immobilization

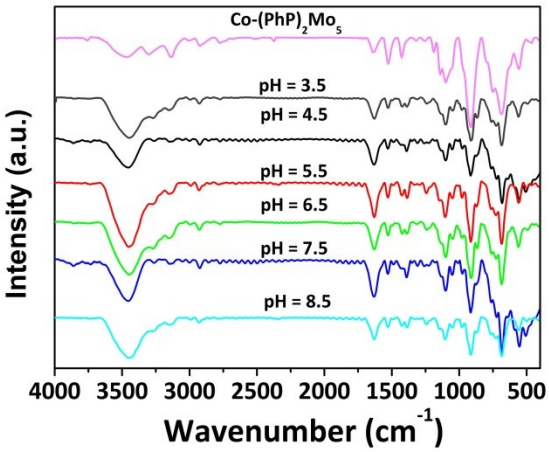

Fig. S12 IR spectra of **Co-$(PhP)_2Mo_5$** before (crystalline sample) and after (solid powders) soaking in a PBS at pH 3.5 – 8.5, respectively

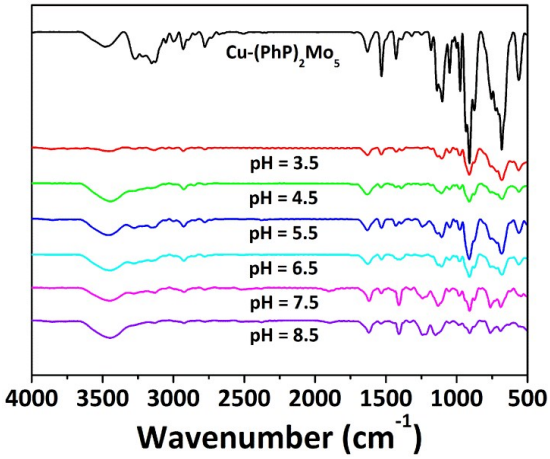

Fig. S13 IR spectra of **Cu-$(PhP)_2Mo_5$** before (crystalline sample) and after (solid powders) soaking in a PBS at pH 3.5 – 8.5, respectively

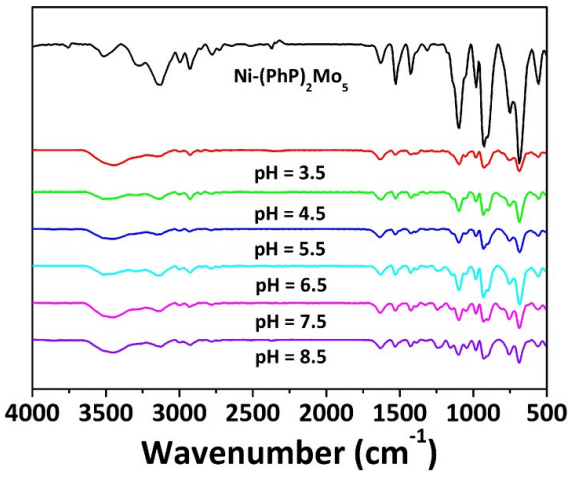

Fig. S14 IR spectra of **Ni-$(PhP)_2Mo_5$** before (crystalline sample) and after (solid powders) soaking in a PBS at pH 3.5 – 8.5, respectively

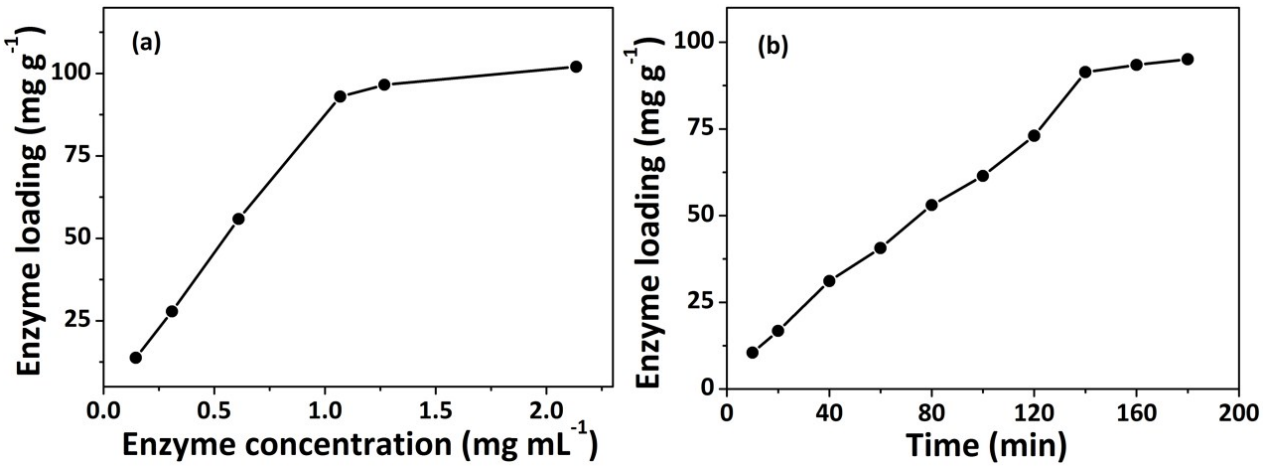

Fig. S15 The influence of concentration of HRP solution after HRP full adsorption (a) and immobilized time (1.1 mg mL^{-1} HRP in 0.1 mol L^{-1} PBS) (b) on enzyme loading for **Co-$(PhP)_2Mo_5$** at pH 5.5

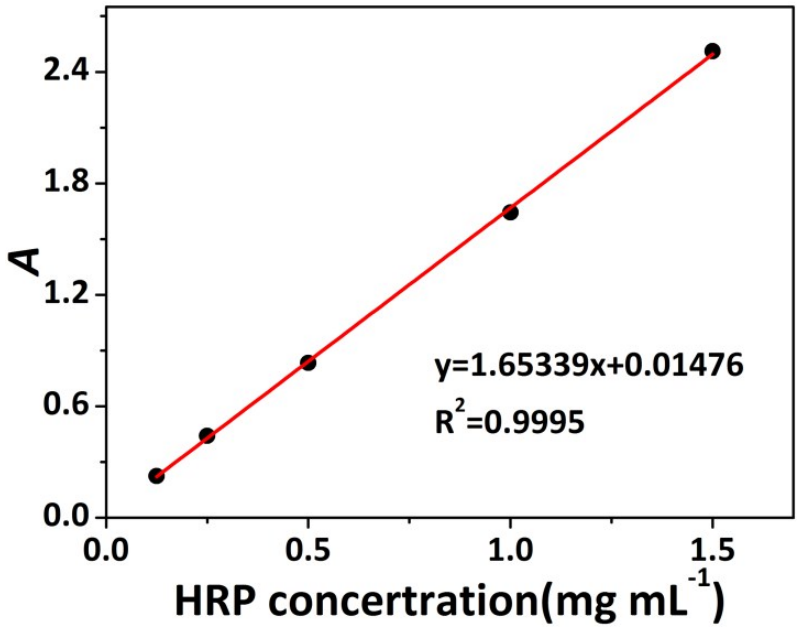

Fig. S16 The standard curve of HRP

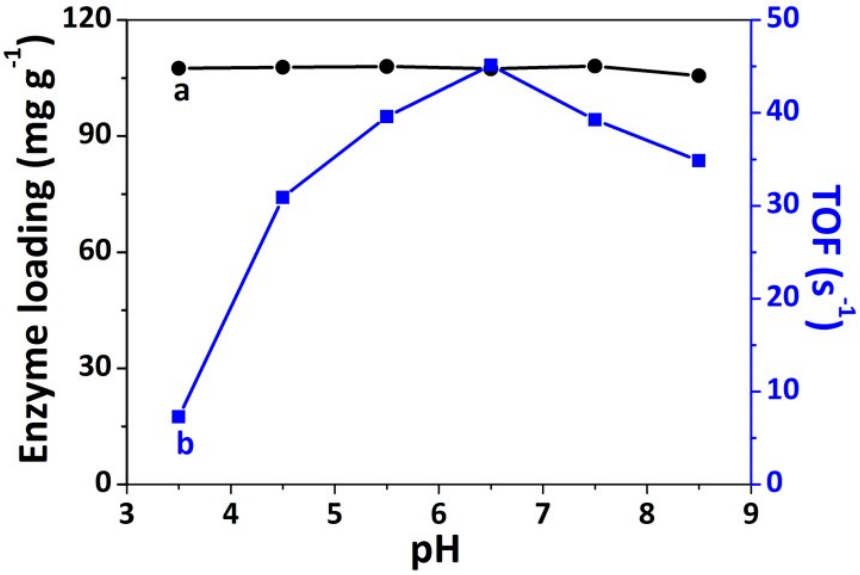

Fig. S17 Enzyme loading (a) and immobilized enzyme activity (b) for **Cu-(PhP)$_2$Mo$_5$** at different pH values (HRP solution: 1.1 mg mL $^{-1}$, **Cu-(PhP)$_2$Mo$_5$**: 5 mg, immobilization time: 240 min, in PBS)

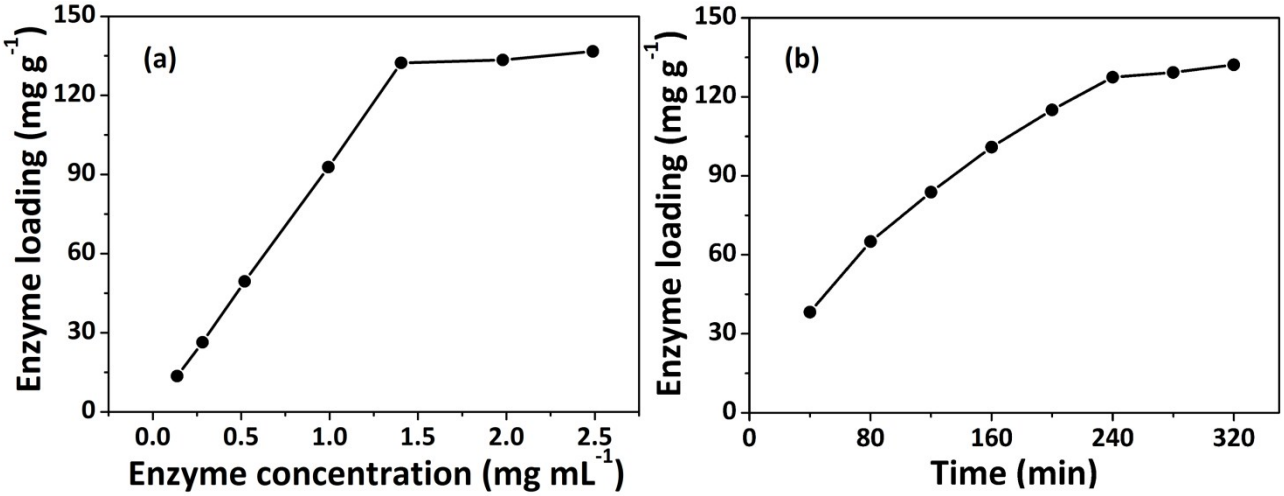

Fig. S18 The influence of the concentration of HRP solution after HRP full adsorption (a) and immobilized time at 1.4 mg mL^{-1} HRP in 0.1 mol L^{-1} PBS (b) on the enzyme loading for **Cu-(PhP)$_2$Mo$_5$** at pH 6.5

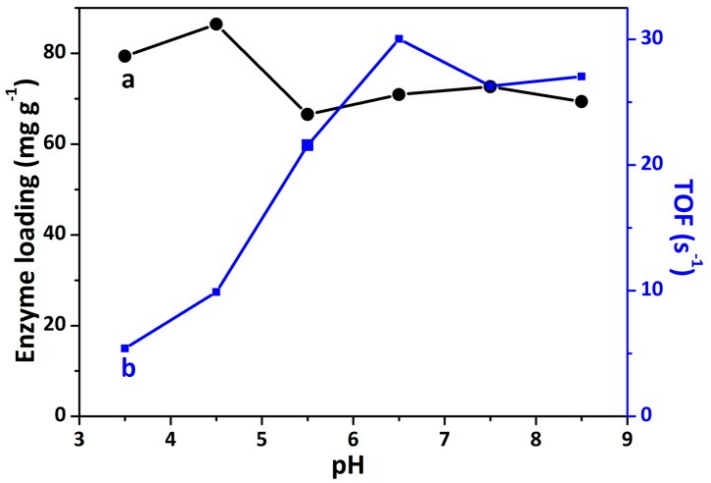

Fig. S19 Enzyme loading (a) and immobilized enzyme activity (b) for **Ni-(PhP)$_2$Mo$_5$** at different pH values (HRP solution: 0.7 mg mL^{-1}, **Ni-(PhP)$_2$Mo$_5$**: 5 mg, immobilization time: 180 min, in PBS)

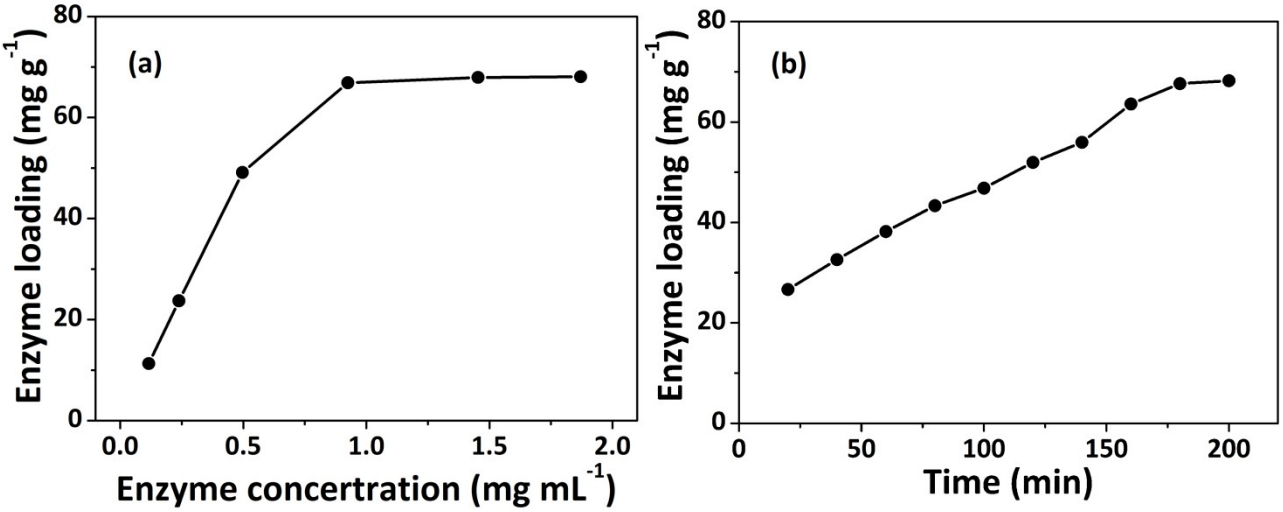

Fig. S20 The influence of the concentration of HRP solution after HRP full adsorption (a) and immobilized time at 1.4 mg mL^{-1} HRP in 0.1 mol L^{-1} PBS (b) on the enzyme loading for **Ni-(PhP)$_2$Mo$_5$** at pH 6.5

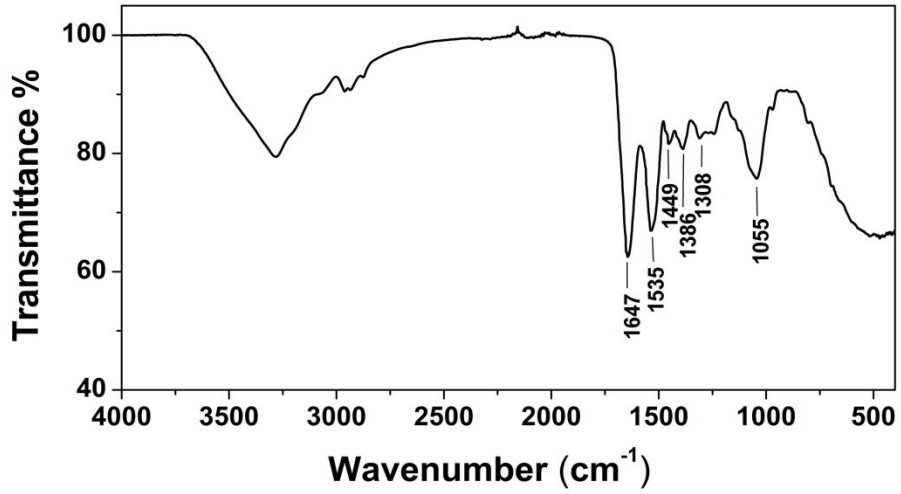

Fig. S21 IR spectrum of free HRP

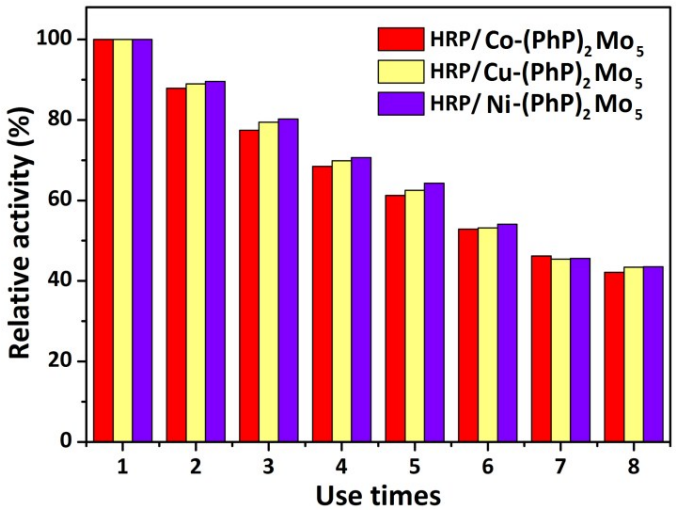

Fig. S22 The activity of HRP/**TM-(PhP)$_2$Mo$_5$** (TM = Co, Cu, Ni) after being used 8 times

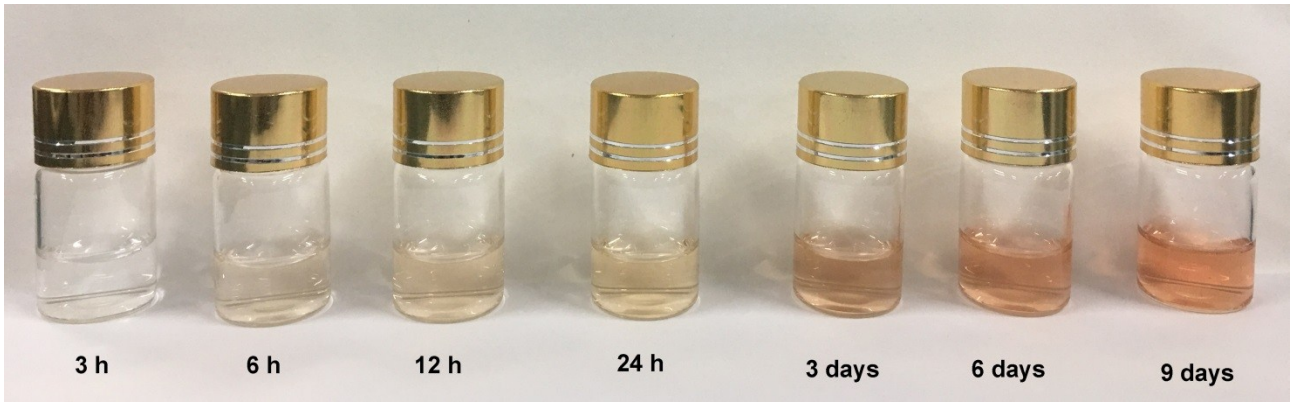

Fig. S23 The color change of the co-oxidation solution of phenol and 4-AAP catalyzed by **Ni-(PhP)$_2$Mo$_5$** taking the place of HRP in the presence of H_2O_2 at 3 – 9 days