Supporting Information

Two POM-based compounds containing Zn-capped Keggin anions as decent heterogeneous catalysts for sulfur oxidation and cycloaddition of CO_2 reactions

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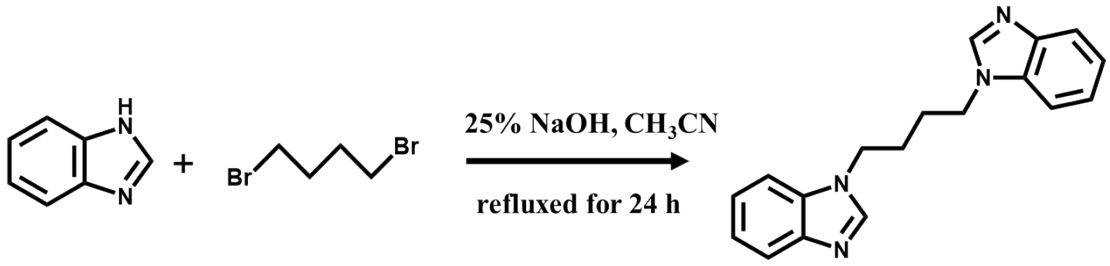
Content

Section 1. Experiment

Synthesis

Synthesis of bbbm (bbbm=1,1-(1,4-butanediyl) bis-1H-benzimidazole)[1].

A mixture of 8 mL NaOH (25%) aqueous solution, benzimidazole (1.18 g, 10 mmol) and CH_3CN (30 ml) was added into a round-bottomed flask and stirred with magnetic force for 4 h under N_2. Then, one portion of dibromo alkane (4 mmol) was dripped slowly into the reaction system and refluxed for 24 h at room temperature. After completion of the reaction, adding water to the reaction solution to make the product precipitate. Finally, white solid was obtained after washing the above precipitate with CH_3CN.



Scheme S1. Synthetic Strategy of the bbbm ligand.

Crystal Structure

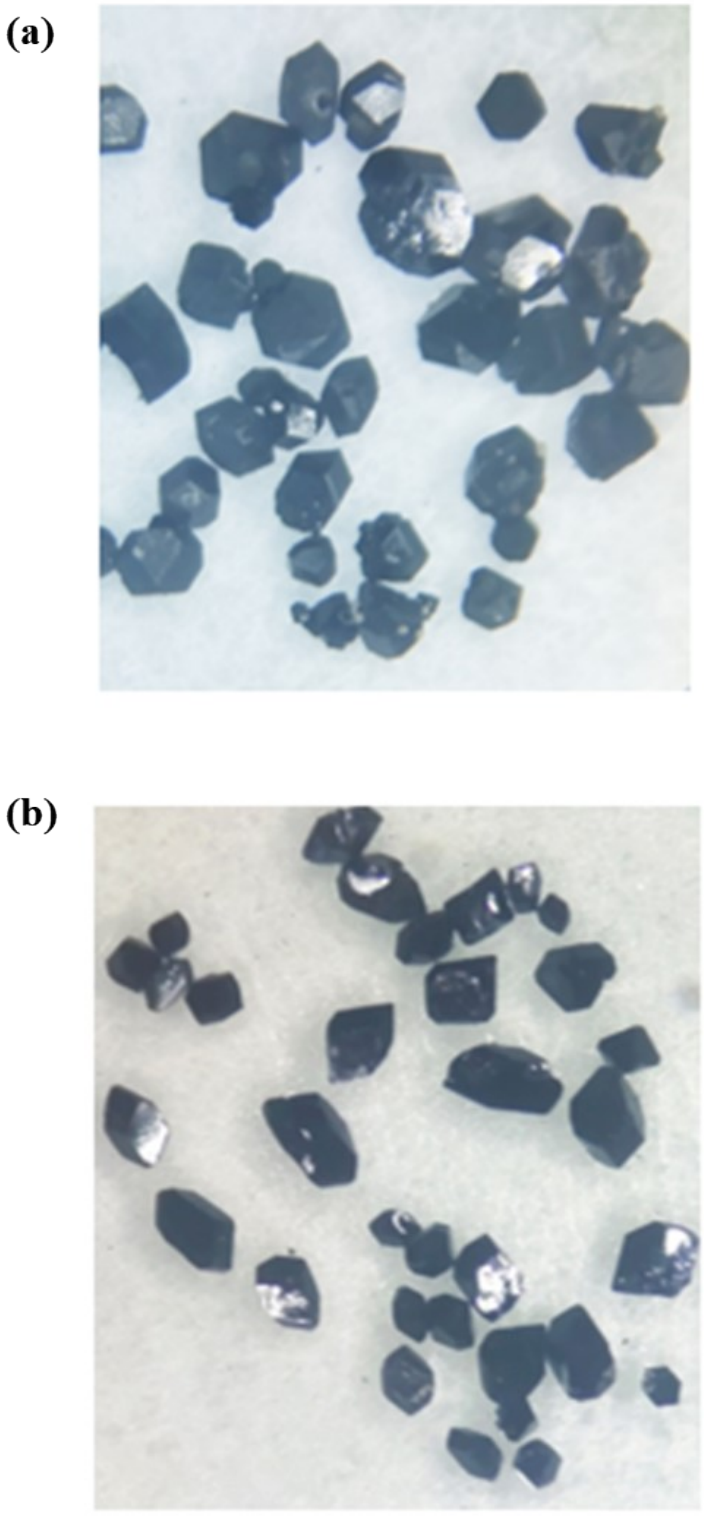


Fig. S1 The crystal images of compounds **1** (a) and **2** (b) under optical microscope.

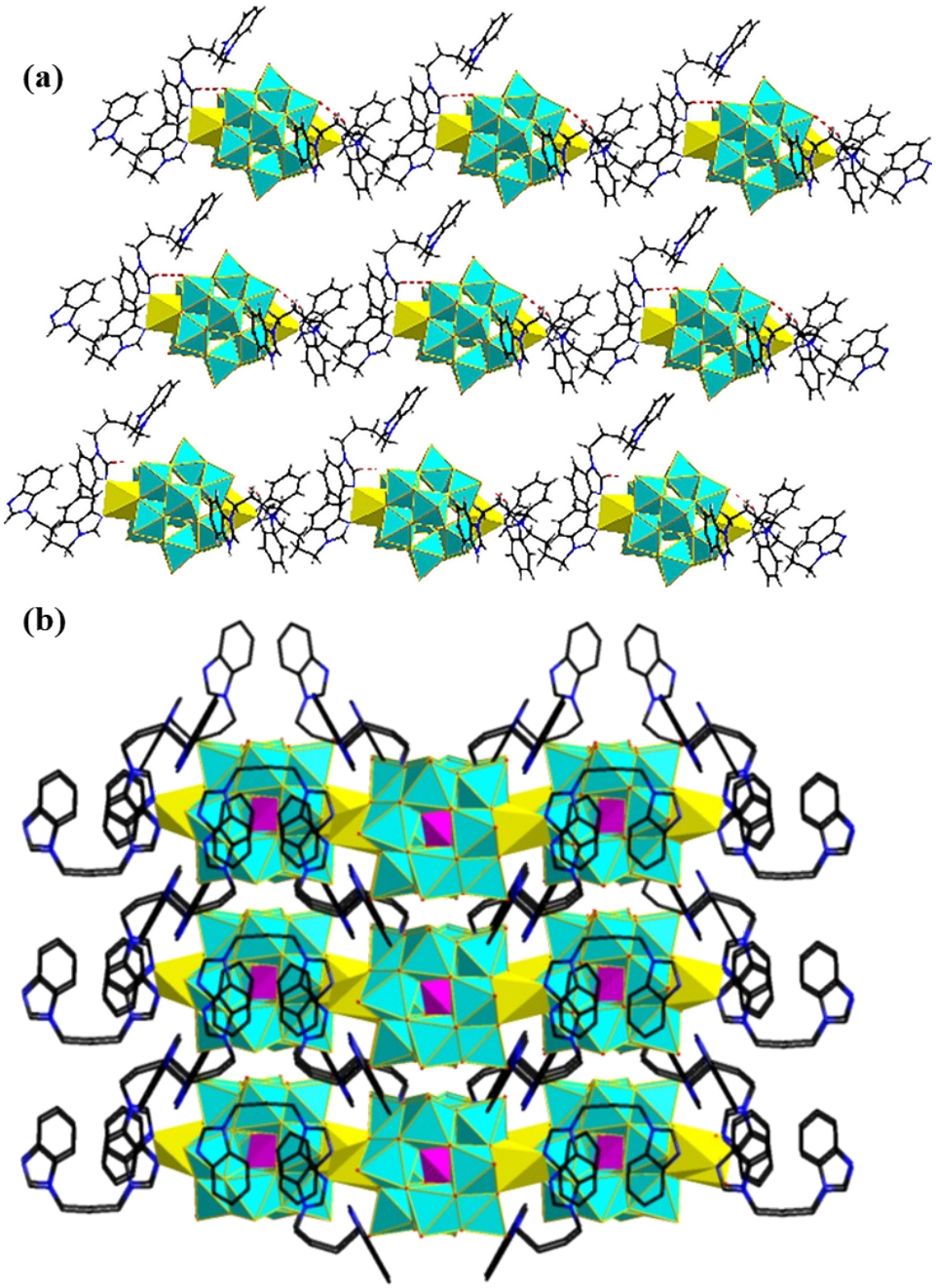


Fig. S2 2D (a) and 3D (b) supramolecular architecture of **1**.

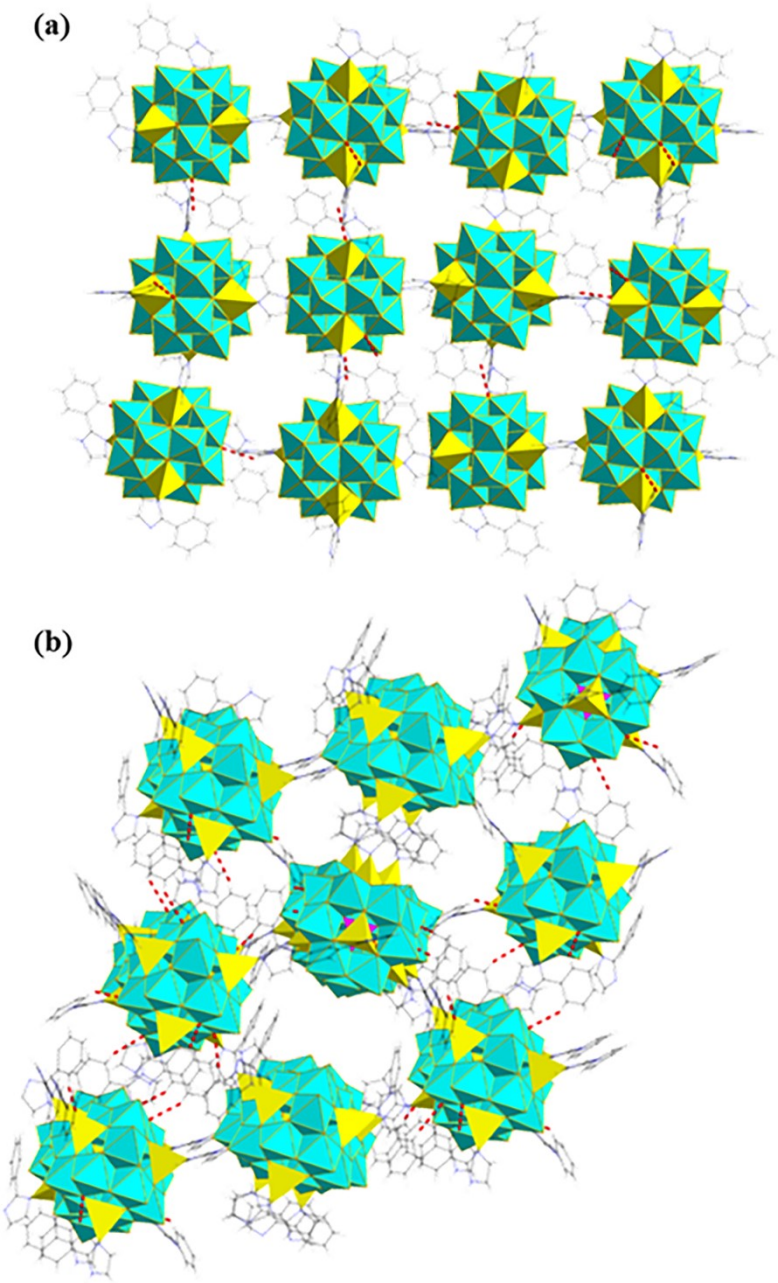


Fig. S3 2D (a) and 3D (b) supramolecular architecture of **2**.

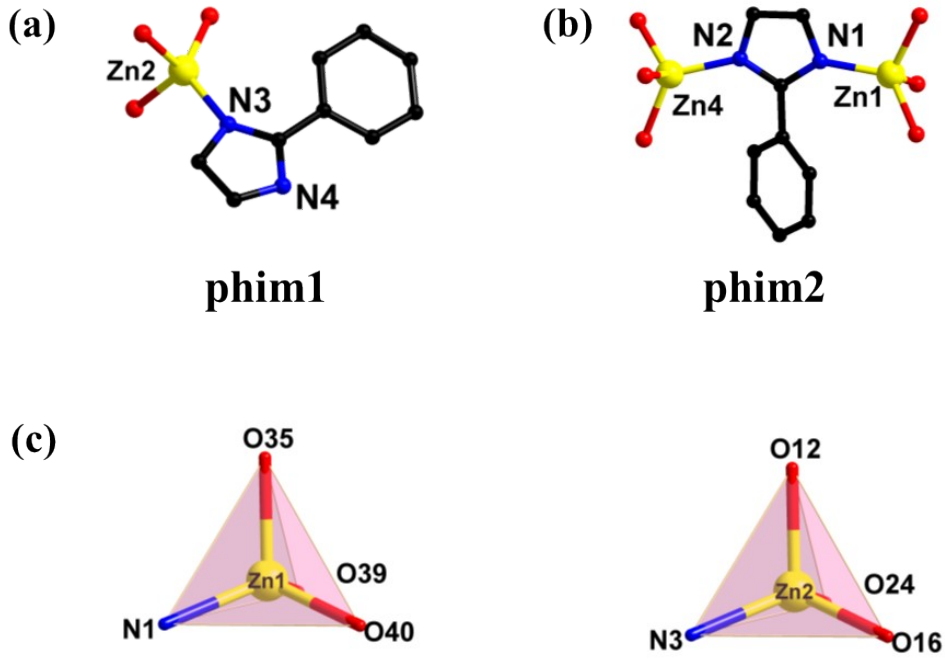


Fig. S4 (a), (b) Ball-and-stick of the two different ligands connected to Zn in **2**. (c) Polyhedral view of coordination environment of Zn1 and Zn2. Hydrogen atoms and guest molecules have been omitted for clarity.

Section 2. Characterizations

PXRD.

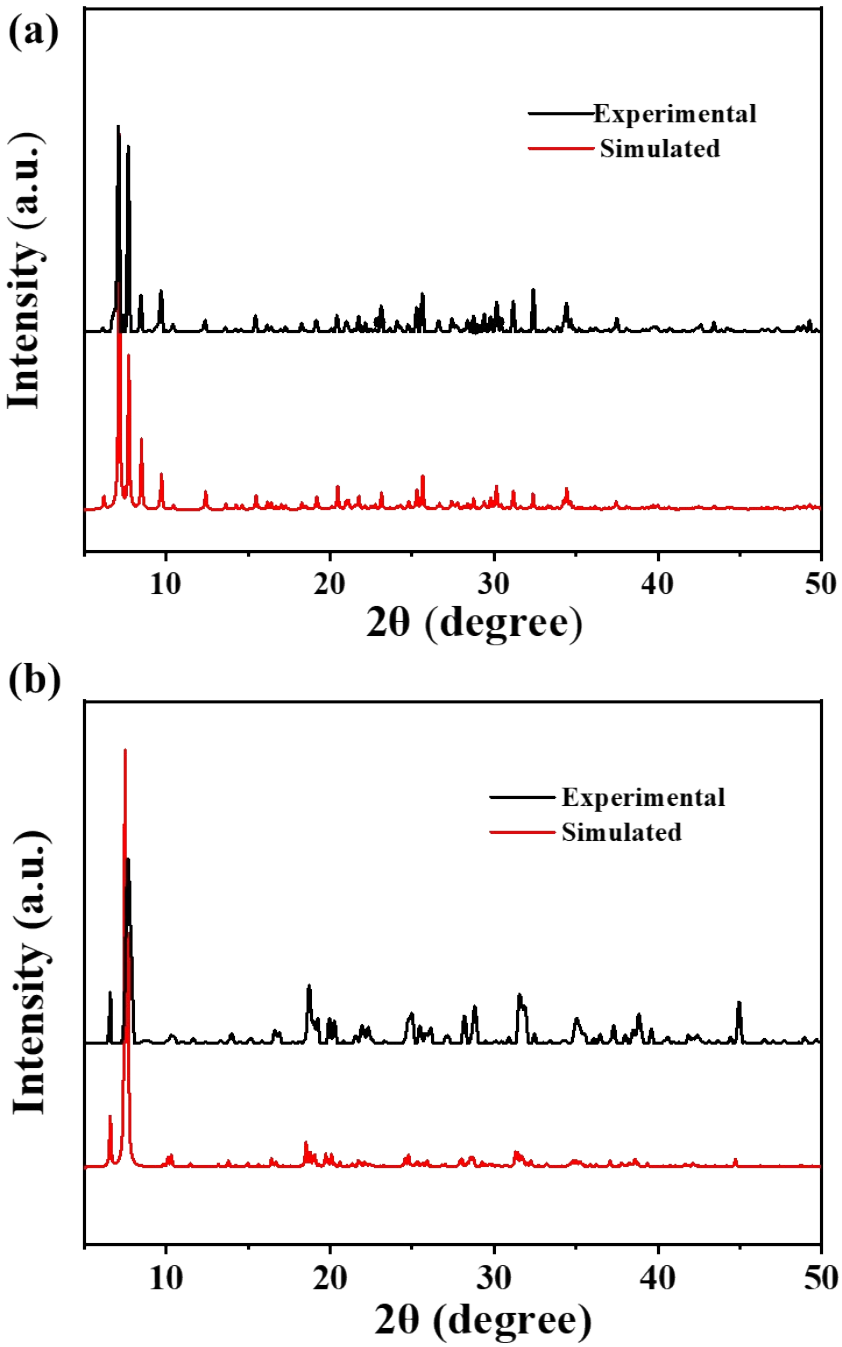


Fig. S5 The simulated (red) and experimental (black) power X-ray diffraction patterns of compounds **1** (a) and **2** (b).

IR

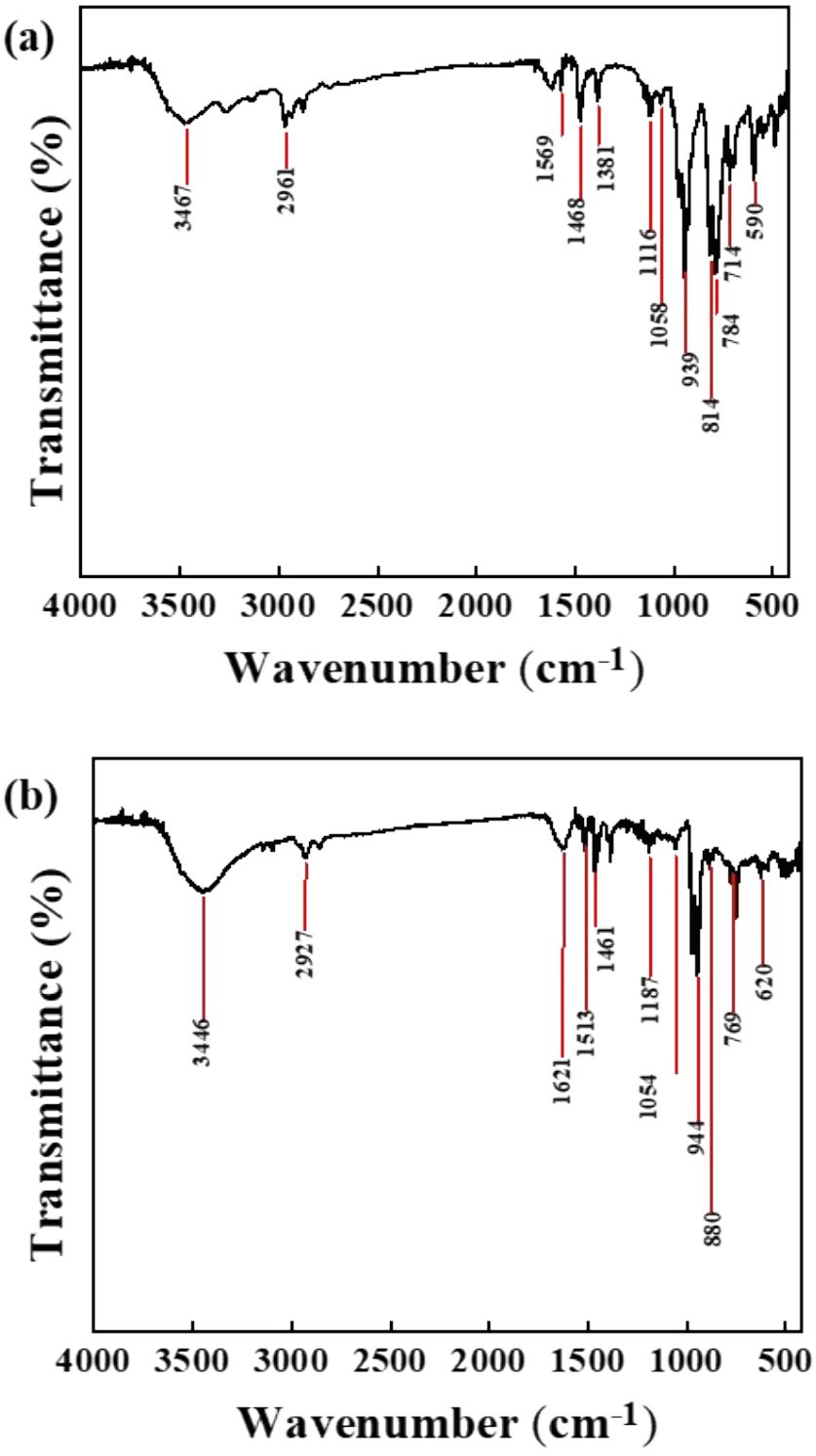


Fig. S6 FT-IR spectra of compounds **1** (a) and **2** (b).

TGA

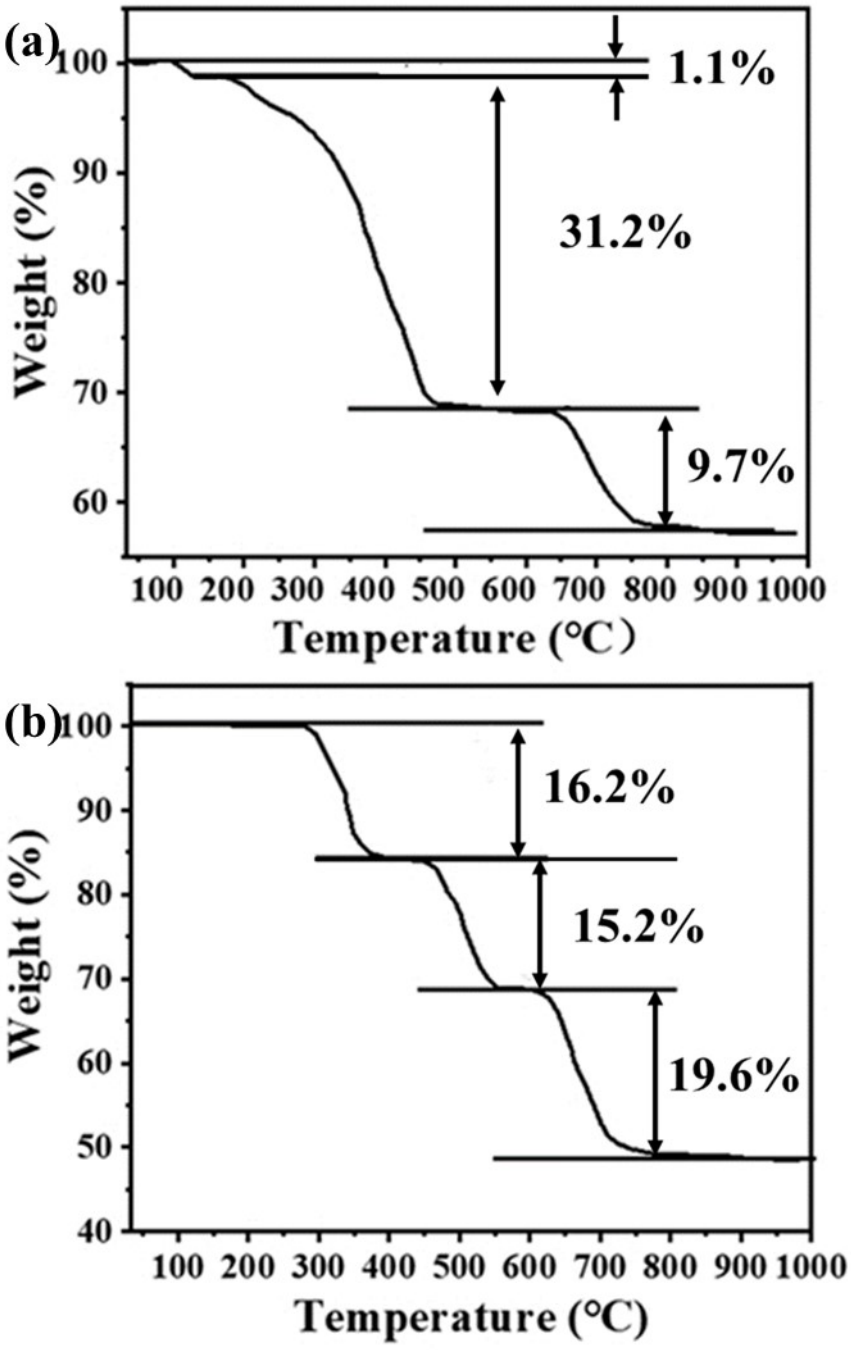


Fig. S7 The TG curve of compound **1**, **2**.

XPS

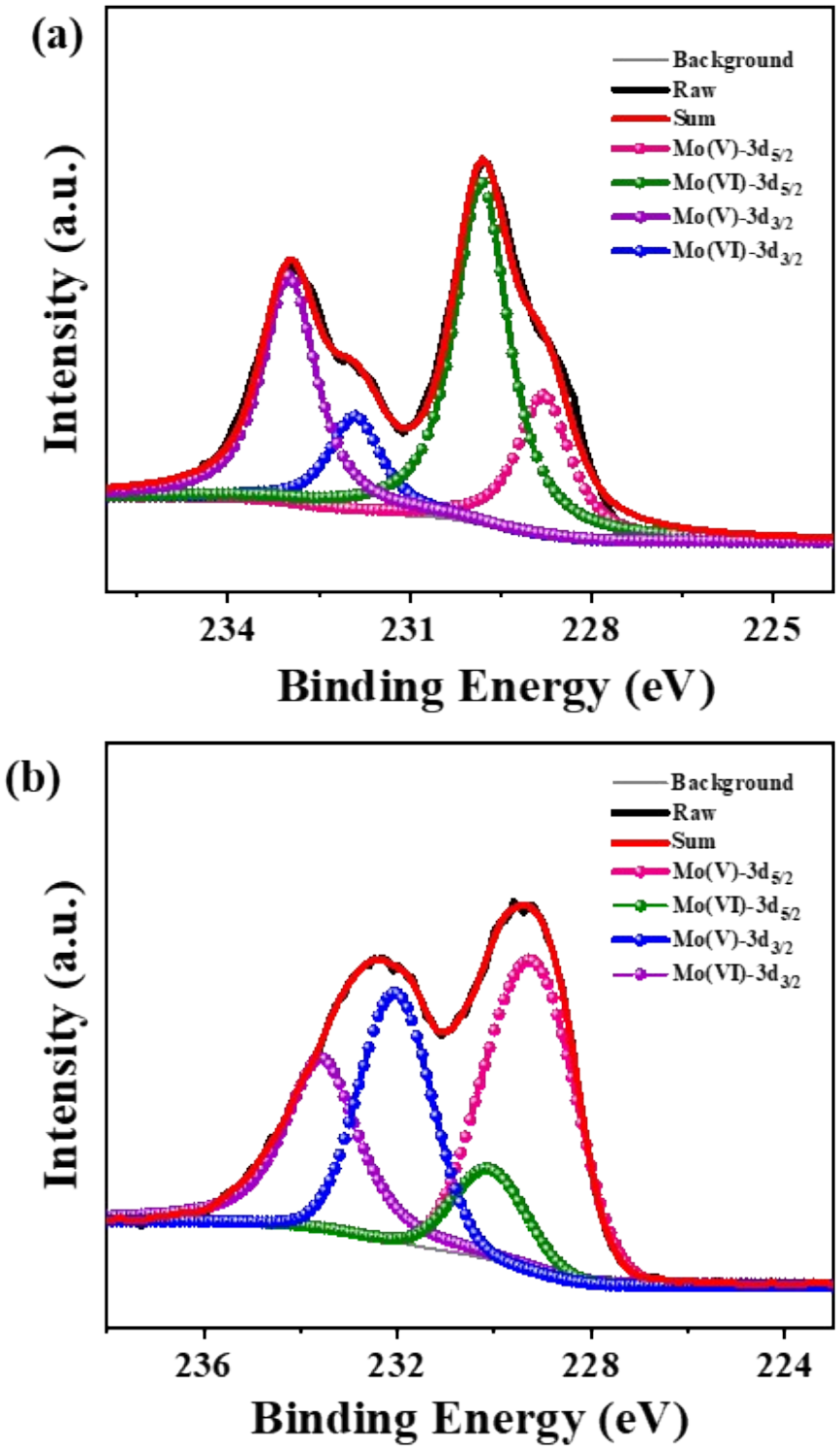


Fig. S8 X-ray photoelectron spectrum of Mo in **1** and **2**.

Section 3. Sulfur Oxidation

Catalytic Procedures

The substrate (1 mmol), tert-Butyl hydroperoxide (TBHP) as oxidant, catalyst (0.01 mmol) and dichloromethane (5 mL) were added into 50 mL three-necked flask equipped with a magnetic stirring rotor and reflux condenser. The mixture was then reacted for 30 min in a water bath at 55 °C under stirring with dodecane as internal standard. After each cycle, the catalyst was collected by centrifugation, and washed by dichloromethane as solvent for five times and then placed in a vacuum drying oven at 80 °C to dry. After the treatment, the next reaction was carried out. In addition, we provided the GC spectrum of five cycles, from which we could calculate that the conversion rate of methyl phenyl sulfide remained at a very high level (99%) after five cycles of reaction. The value of conversion was calculated by gas chromatography analysis.

$$\text{Conversion} = \frac{n2}{n1} \times 100\%$$

Note: *n*1= amount of substrate added, *n*2= amount of product formed.

Chemical Stability

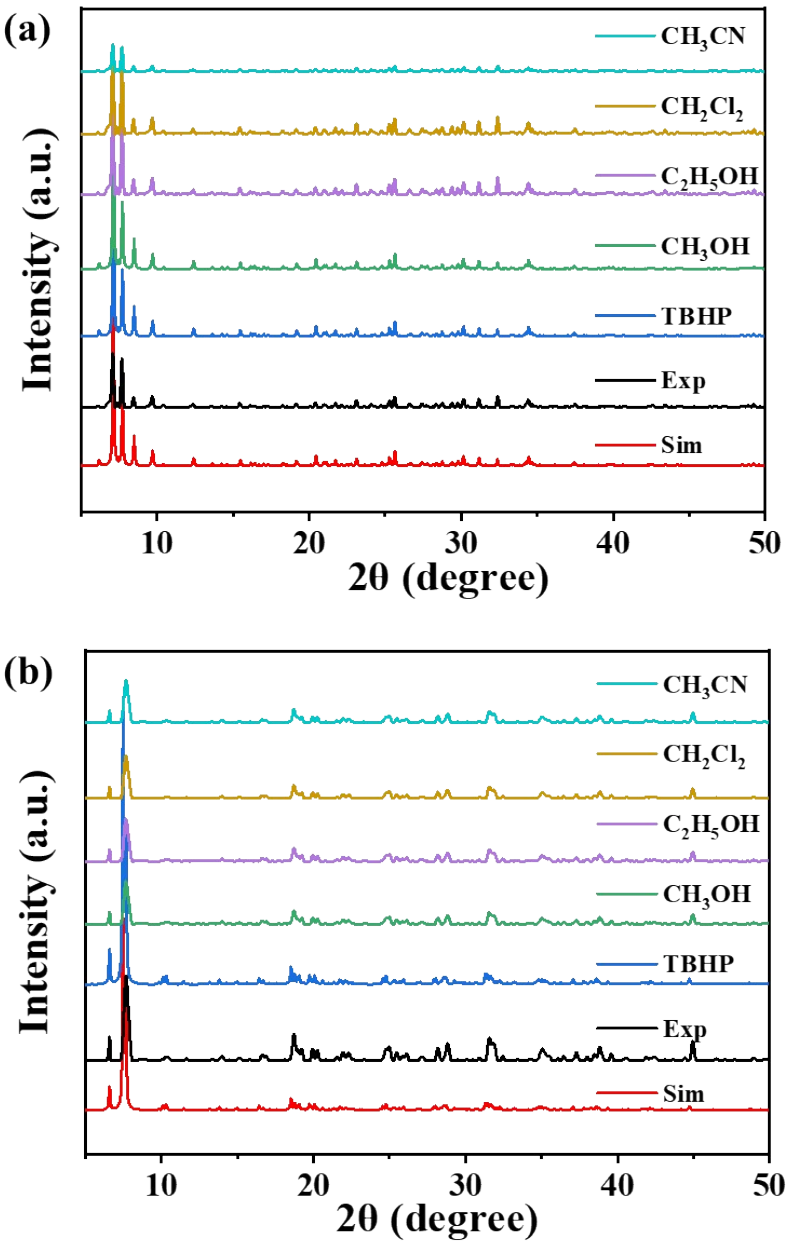
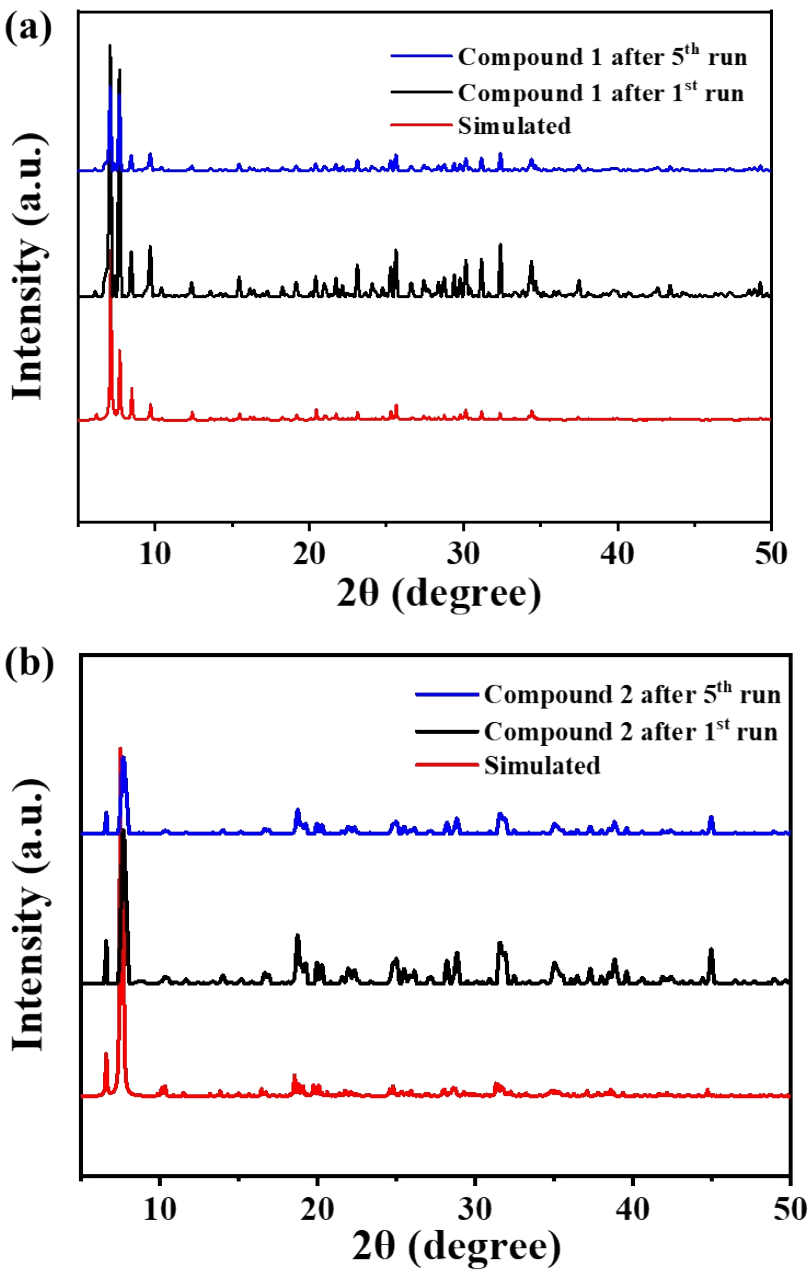


Fig. S9 X-ray diffraction patterns of compounds **1**, **2** in different solution.

Recyclability Test



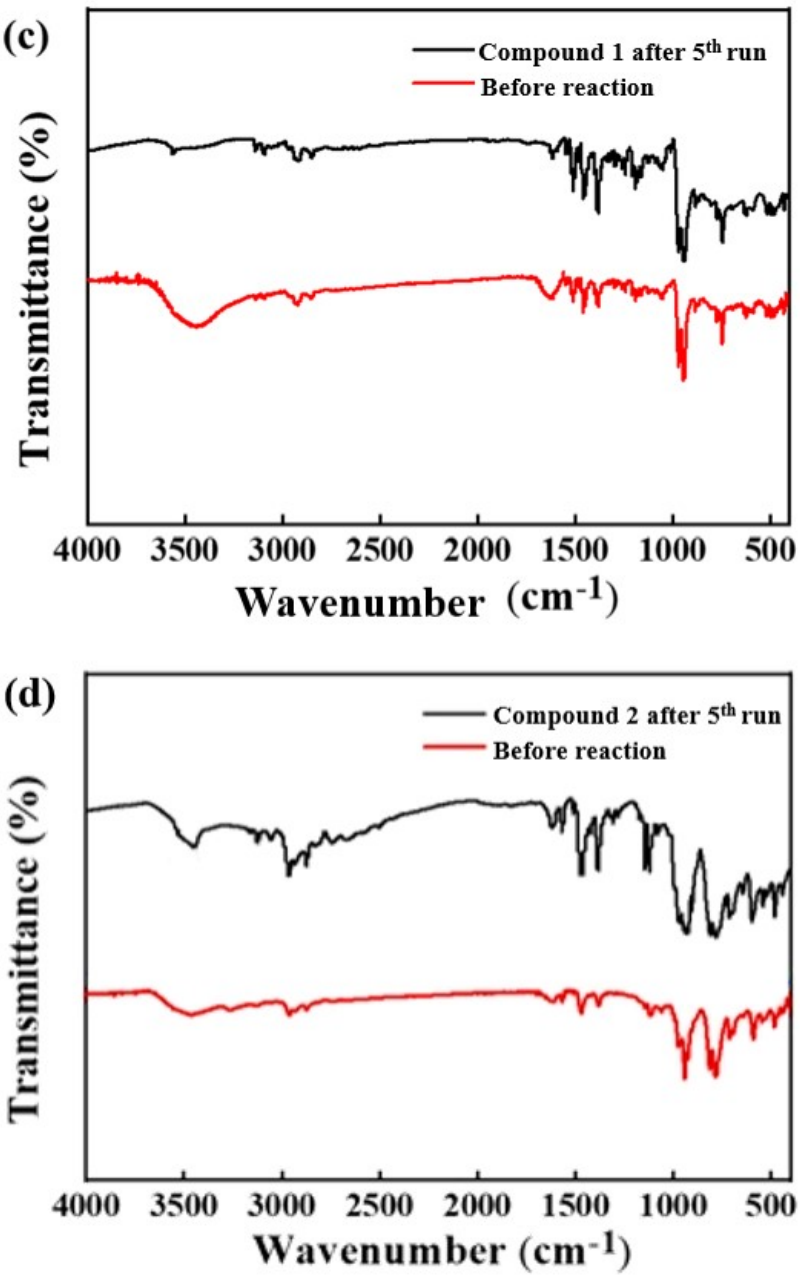


Fig. S10 The PXRD patterns (a) and (b), FT-IR spectra (c) and (d) before reaction and after 5 th cycle with catalyst **1**, **2** for sulfur oxidation.

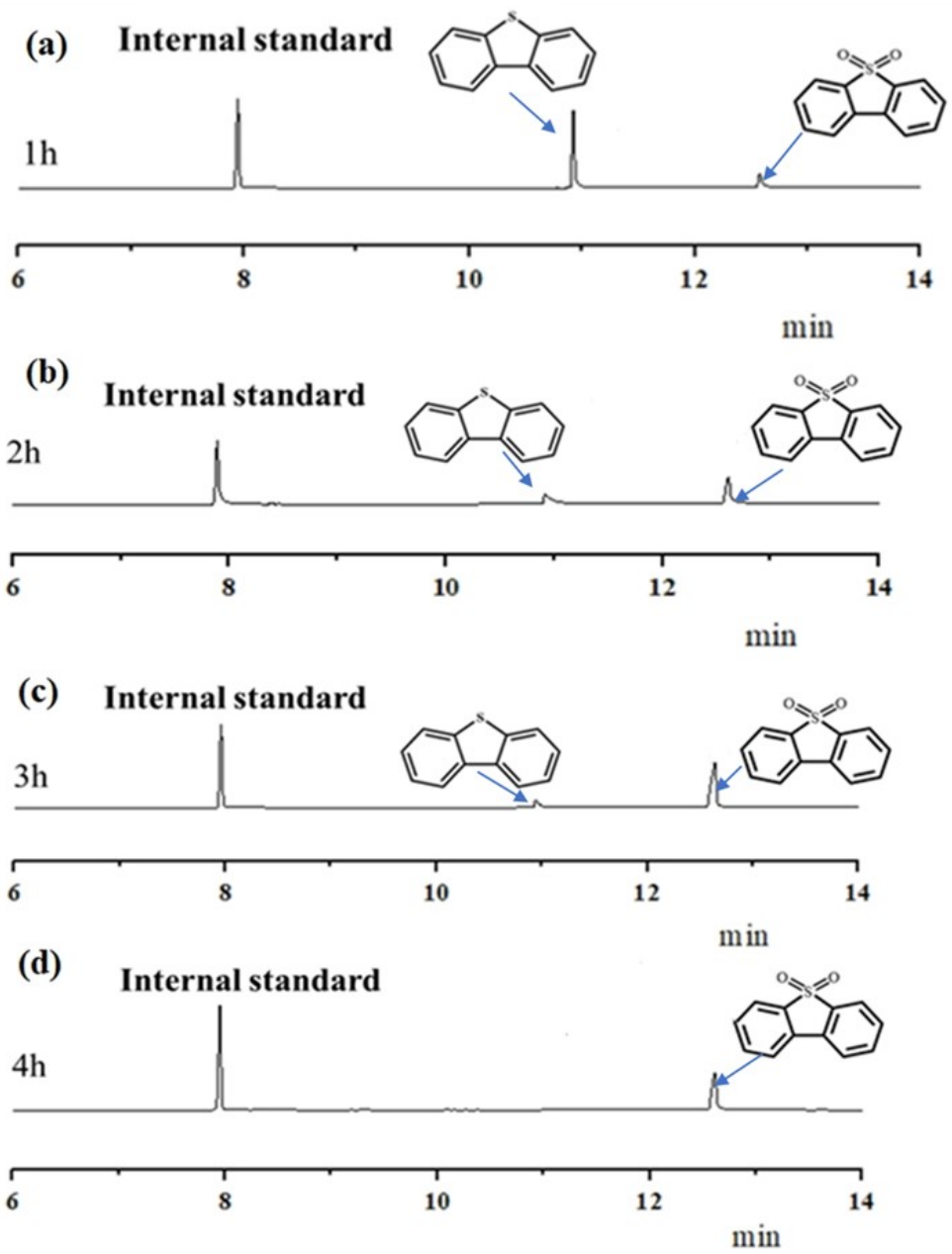


Fig. S11 GC of sulfur oxidation reaction with catalyst **2**, TBHP as oxidant, dodecane as the internal standard and dibenzothiophene for increasing reaction time: (a) 1 h, (b) 2 h, (c) 3 h, (d) 4 h.

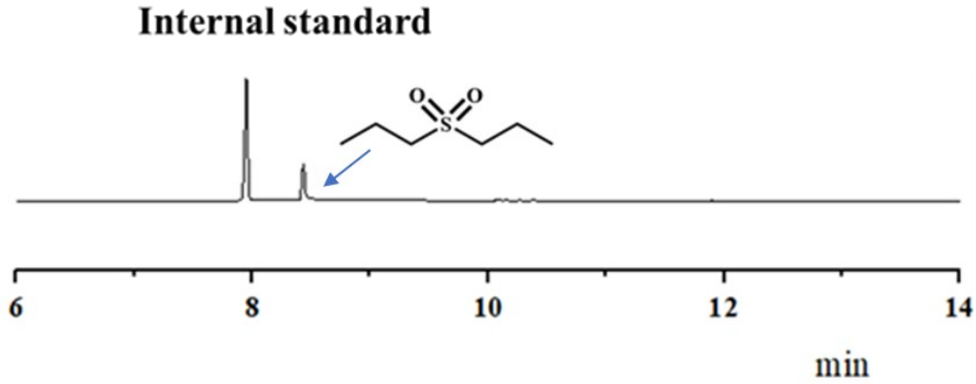


Fig. S12 GC of sulfur oxidation reaction for the catalytic product of the dipropyl sulfide for 30 min, **2** as catalyst, TBHP as oxidant and dodecane as the internal standard.

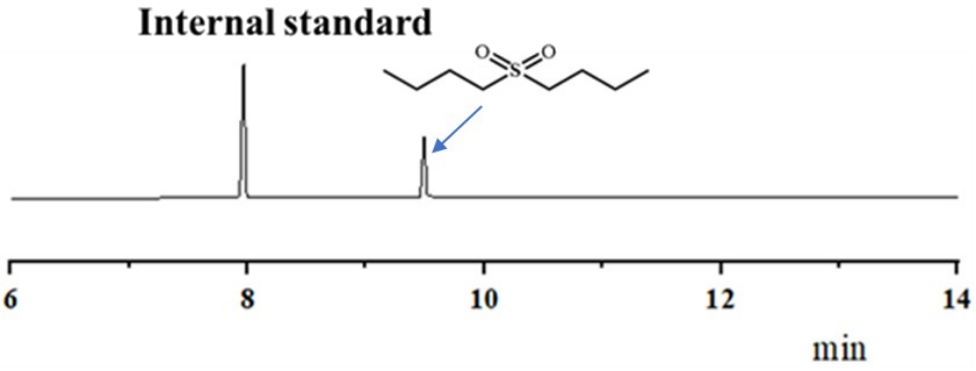


Fig. S13 GC of sulfur oxidation reaction for the catalytic product of the dibutyl sulfide for 30 min, **2** as catalyst, TBHP as oxidant and dodecane as the internal standard.

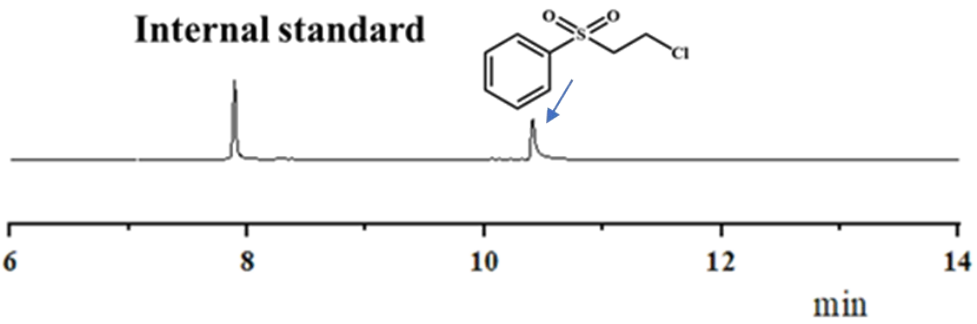


Fig. S14 GC of sulfur oxidation reaction for the catalytic product of the 2-chloroethyl phenyl sulfide for 1h, **2** as catalyst, TBHP as oxidant and dodecane as the internal standard.

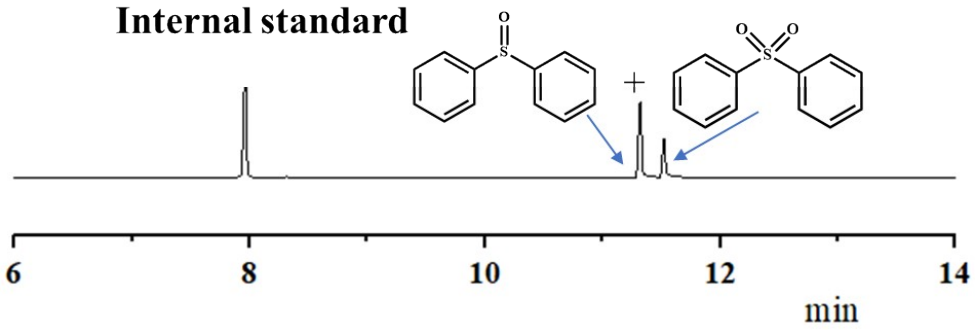


Fig. S15 GC of the sulfur oxidation reaction for the catalytic product of the diphenyl sulfide for 30 min, **2** as catalyst, TBHP as oxidant and dodecane as the internal standard.

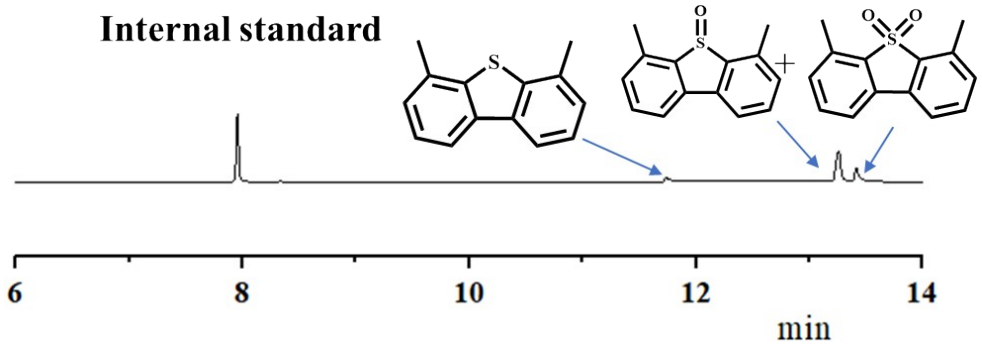


Fig. S16 GC of the sulfur oxidation reaction for the catalytic product of the 4,6-dimethyldibenzothiophene for 4 h, **2** as catalyst, TBHP as oxidant and dodecane as the internal standard.

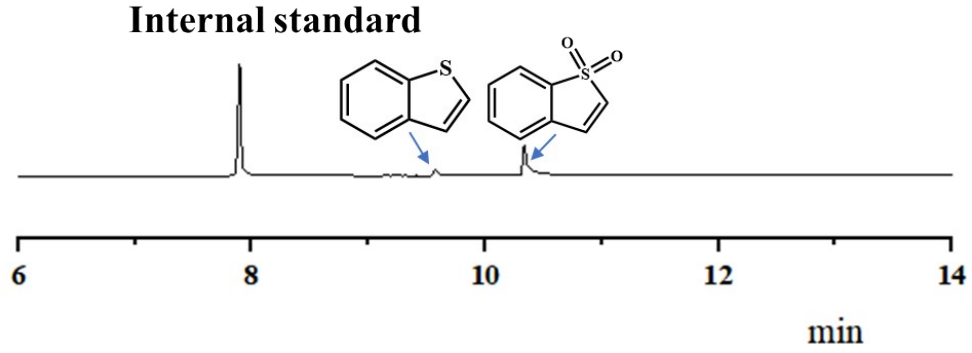


Fig. S17 GC of the sulfur oxidation reaction for the catalytic product of the benzothiophene for 7 h, **2** as catalyst, TBHP as oxidant and dodecane as the internal standard.

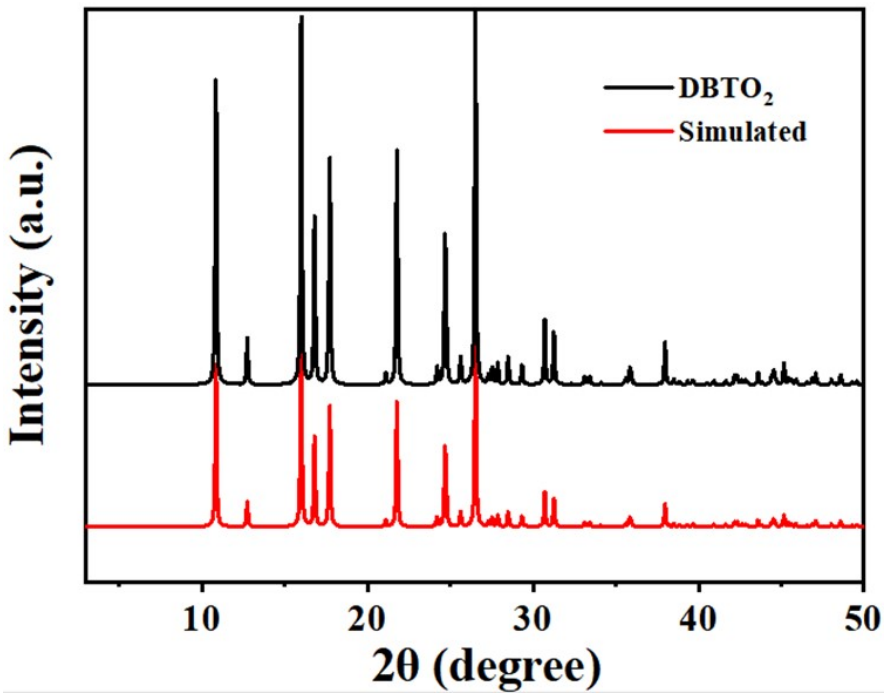


Fig. S18 PXRD pattern of oxidation products of DBT dissolved in $CDCl_3$ at room temperature.

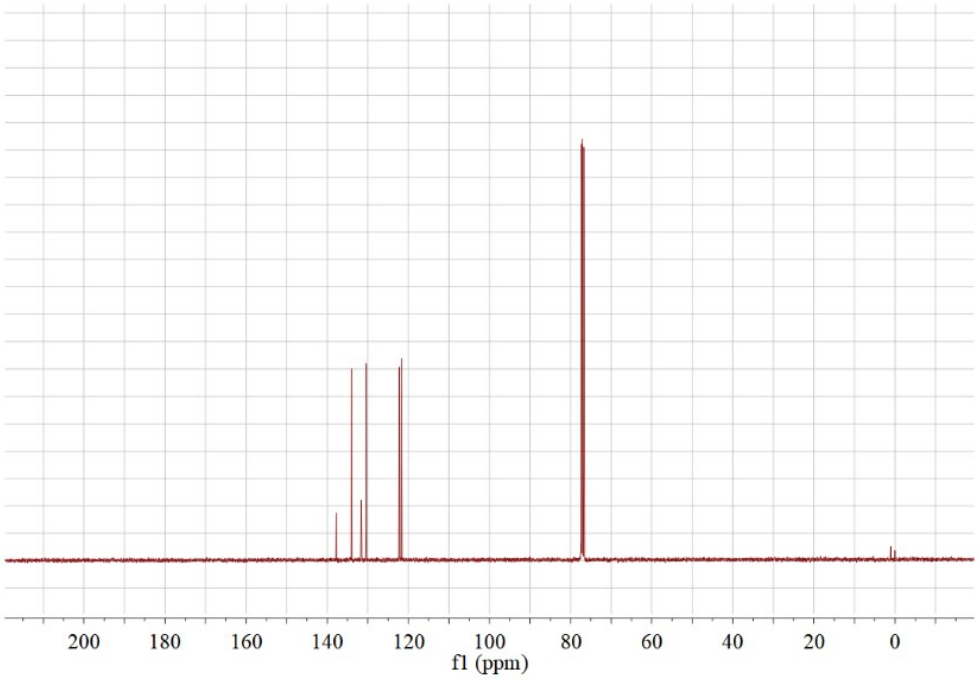


Fig. S19 ^{13}C NMR spectra of oxidation products of DBT dissolved in $CDCl_3$ at room temperature.

Hot Filtration Test of catalyst 1

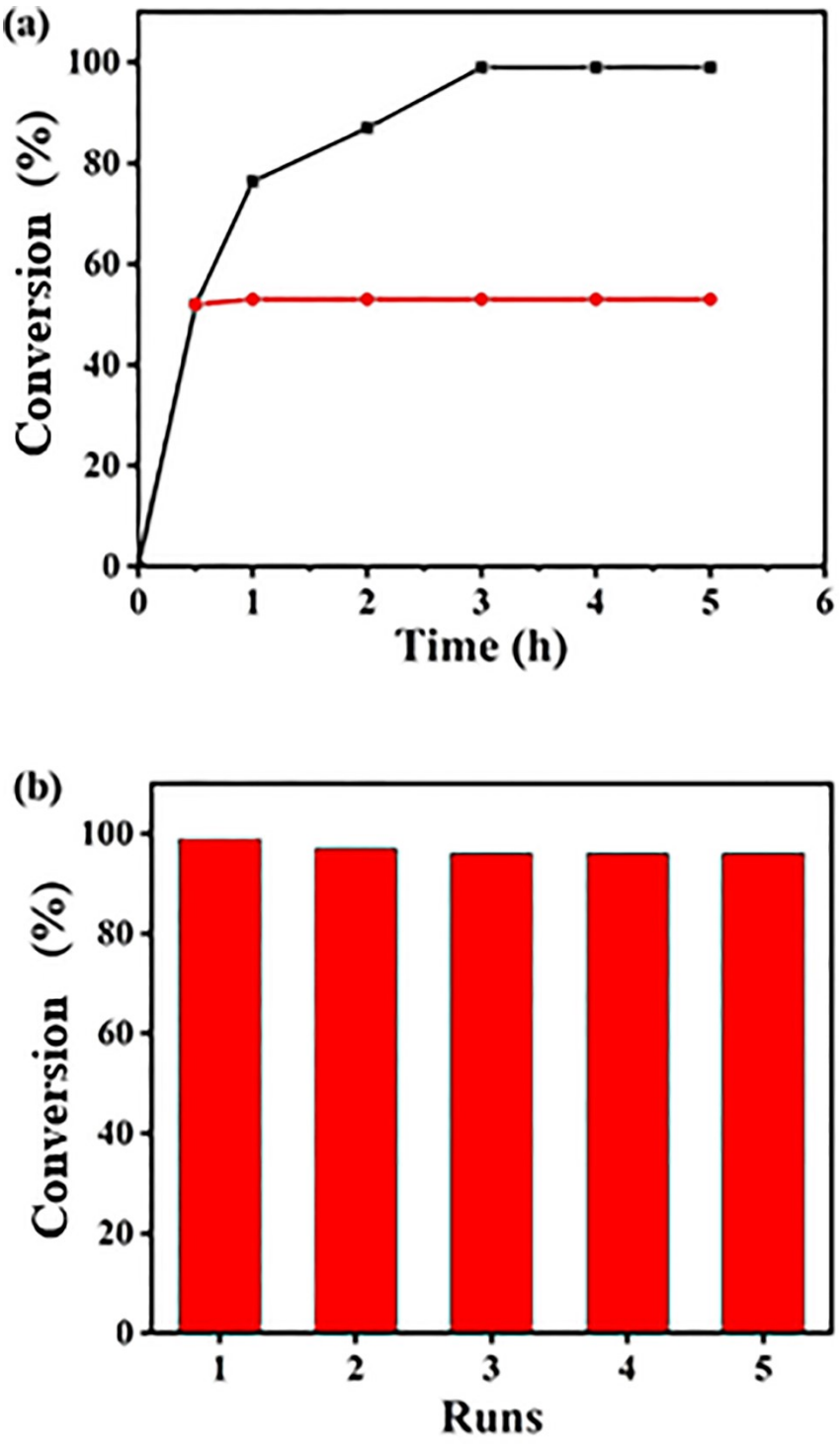


Fig. S20 (a) Catalytic dynamic (black) and hot filtration (red) studies for the oxidation of diphenyl sulfide by **1** at 60 °C. (b) Recycling experiments based on compound **1** for the oxidation of methyl phenyl sulfide.

Section 4. Cycloaddition of CO_2 to Epoxides

Catalytic Procedures

Before catalytic measurements, freshly-prepared samples were soaked in CH_2Cl_2 for solvent exchanging, with CH_2Cl_2 refreshed every 4 h to remove guest molecules in the framework. The catalytic reactions were carried out in 25 mL stainless-steel high-pressure reactor. The activated catalyst 0.03 mmol, together with the epoxide (40 mmol) and cocatalyst of tetra-*n*-tertbutyl ammonium bromide (*n*-Bu_4NBr, 322.4 mg, 1 mmol) were transferred to the reactor immediately. The reactor was pressurized with CO_2 up to 0.5 MPa and stirred at 60 °C for 7 h. When the reaction was completed, the reactor was quickly cooled in ice water. For the catalyst recycling test, the catalyst was isolated by filtration and washed several times with EtOH and CH_2Cl_2 to fully remove the substrates, then dried under vacuum and reused in another catalytic experiment. The yield of product was determined by GC, ^1H NMR spectroscopy.

Recyclability Test of catalyst 2

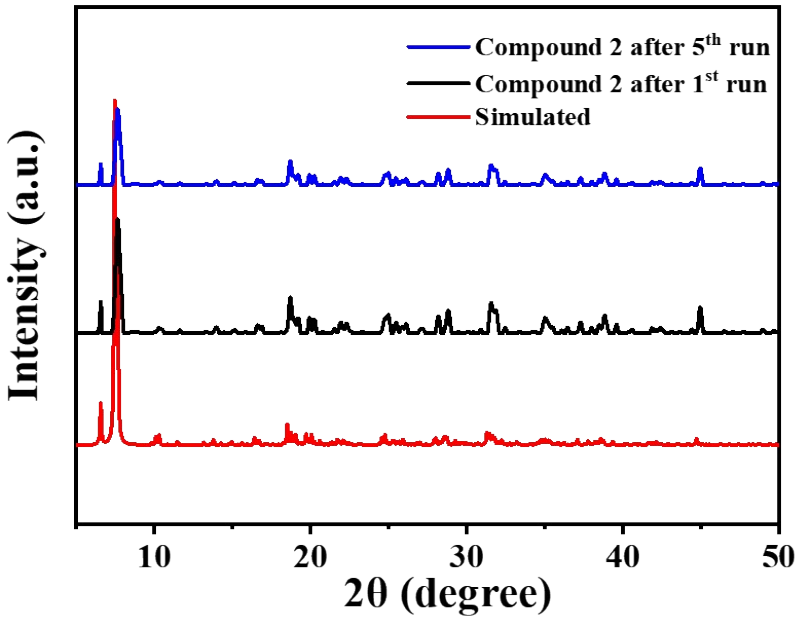
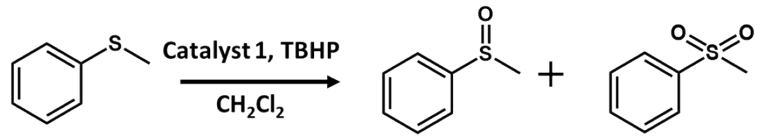


Fig. S21 The PXRD patterns, after the 1 st and the 5th cycle with catalyst **2** for cycloaddition of CO_2 reactions.

Section 5. Tables

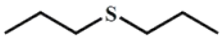
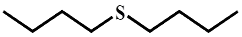
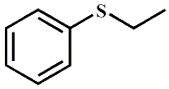
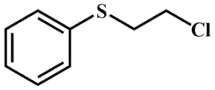
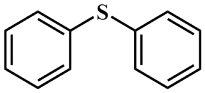
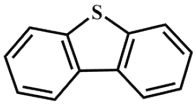
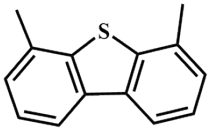
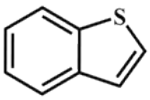
Table S1. Sul oxidation reactions of various sulfides with **1** at different conditions [a].



Entry	Oxidant	Oxidant mmol	T °C	t min	Solvent	Conv. [b] %
1	TBHP	5	55	30	CH_2Cl_2	92
2	TBHP	5	60	30	CH_2Cl_2	99
3	TBHP	5	60	20	CH_2Cl_2	97
4	TBHP	4	60	30	CH_2Cl_2	99
5	TBHP	4	60	30	methanol	65
6	TBHP	4	60	30	ethanol	81

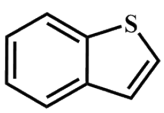
[a]Reaction conditions: substrate, 1 mmol; catalyst **1**, 0.01 mmol; solvent, 5 mL, [b]conversions were determined by GC-FID using dodecane as internal standard.

Table S2. Sul oxidation reactions of various sulfides with **1** at different conditions [a].

Entry	Substrate	t h	Conv. [b] %
1		0.5	99
2		0.5	99
3		0.5	99
4		0.5 1	76.3 99
5		1 3	77 99
6		1 7	12 73
7		1 7	8 41
8		1 12	3 35

[a]Reaction conditions: catalyst **1**, 0.01 mmol; substrate, 1 mmol; oxidant, 4 mmol; CH_2Cl_2, 5 mL, and temperature (60 °C). [b]Conversions were determined by GC-FID using dodecane as an internal standard.

Table S3. Catalytic comparison of **1** and **2** with related POM-based catalysts.

Catalyst	Substrate	Temperature (°C)/ Time (h)	Conv. [b] (%)	Ref.
1		60/12	35	This work
2		55/7	85	This work
$[Zn_{1.5}(LOH)_3] \cdot (PMo_{12}O_{40}) \cdot CH_3OH \cdot 2H_2O$		50/12	33	2

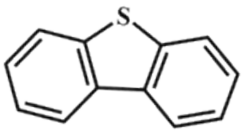
$[Co_2L'_{0.5}V_4O_{12}]$ ·3DMF·5H_2O		50/12	75	3
$[Ag_3L_2]$ $[PMo_{12}O_{40}]$ ·CH_3CN·4H_2O		50/12	13.5	4
$[Ag_4(PMo_{12}O_{40})$ $(L)_2]$ ·OH		40/12	4	5
1		60/7	73	This work
2		55/4	99	This work
$[Zn_{1.5}(LOH)_3]$ (PMo_{12}) $O_{40})$ CH_3OH·2H_2O (2)		50/12	80	2
$[Co_2L'_{0.5}V_4O_{12}]$ ·3DMF·5H_2O		50/12	93	3
$[Ag_3L_2]$ $[PMo_{12}O_{40}]$ ·CH_3CN·4H_2O		50/12	78.5	4
(en)$[Cu_3(ptz)4(H_2O)_4][Co_2Mo_{10}H_4O_{38}]$ ·24H_2O		50/12	80	6
$[Ag_4(PMo_{12}O_{40})$ $(L)_2]$ ·OH		40/12	87	5
1		60/1	77	This work
2		55/0.5	99	This work
$[Zn_{1.5}(LOH)_3]$ (PMo_{12}) $O_{40})$ CH_3OH·2H_2O (2)		50/6	99	2
(en)$[Cu_3(ptz)4(H_2O)_4]$ $[Co_2Mo_{10}H_4O_{38}]$ ·24H_2O		40/8	60.5	6
$[Ag_3L_2]$ $[PMo_{12}O_{40}]$ ·CH_3CN·4H_2O		50/4	73.9	4

Table S4. Catalytic comparison of **2** for cycloaddition of CO_2 to epoxides.

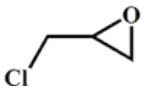
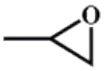
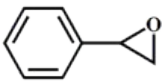
Catalyst	Substrate	P (MPa)/T (°C)/ t (h)	Conv. (%)	Ref.
2		0.5/60/7	99	This work
CPM-200-In/Mg		1.2/80/6	90.3	7
Zn-C_3N_4(25)		2/130/5	88	8
[DBUH][PFPhO]/β-CD		3/130/10	98.8	9
[Cd_3(HECTV)(bdc)$_3$] ·DMF·6H_2O		0.1/80/2	68	10
2		0.5/60/7	99	This work
CPM-200-In/Mg		1.2/80/6	87.3	7
Zn-C_3N_4(25)		2/130/5	99	8
[DBUH][PFPhO]/β-CD		3/130/10	98.7	9
2		0.5/60/12	81	This work
CPM-200-In/Mg		1.2/80/6	71.9	7
Zn-C_3N_4(25)		2/130/5	45	8
[DBUH][PFPhO]/β-CD		3/130/10	95.6	9
[Zn_3(HECTV)(OHbdc)$_3$] ·3DMF·4H_2O		0.1/80/4	65	10

Table S5. Crystallographic data and structural refinements for **1**-**2**.

Compound	**1**	**2**
Formula	C_{55} H_{58} Mo_{12} N_{12} $O_{40.50}$ P Zn_2	$C_{59}H_{99}$ Mo_{12} N_8 O_{40} P Zn_4
Formula Weight	2848.10	3004.19
T(K)	296.15	296.15
Crystal System	monoclinic	tetragonal
Space group	*C*2/c	$I4_1$cd
a(Å)	23.936(2)	32.635(2)
b(Å)	18.220(2)	32.635(2)
c(Å)	19.260(2)	34.282(3)
α (°)	90	90
β (°)	106.755(2)	90
γ (°)	90	90
V（Å^3）	8043.0(16)	36512(6)
Z	4	16
D_c（mg m^{-3}）	2.352	2.186
μ (mm^{-1})	2.504	2.719
F (000)	5500	23488
θ range (°)	1.428 -25.005	1.2-25.0
Crystal size (mm^3)	0.12×0.12×0.13	0.12×0.12×0.12
Limiting indices	-28≤h≤ 26 -21≤k≤ 21 -22≤l≤ 22	-38≤h≤ 38 -35≤k≤38 -40≤l≤40
Reflections collected	28661	128461
R(int)	0.0462	0.0514
Data/restraints/parameters	7073/12/564	16094/153/1124
GOF	1.011	1.064
R_1[a] wR_2[b] [I > 2σ(I)]	R1[a]= 0.0301 WR_2= 0.0612	R1[a]= 0.0428 WR_2= 0.0791
R_1, wR_2 (all data)	R_1=0.0253 WR_2=0.0595	R_1= 0.0339 WR_2=0.0751

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \Sigma [w (F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

Table S6. Selected bond lengths (Å) for compound **1**.

Mo(1)-O(3)	1.687(2)	Mo(4)-O(14)	1.677(2)
Mo(1)-O(1)	1.857(2)	Mo(4)-O(13)	1.930(2)
Mo(1)-O(5)	1.874(2)	Mo(4)-O(10)	1.935(2)
Mo(1)-O(2)	1.979(2)	Mo(4)-O(15)	1.935(2)
Mo(1)-O(4)	1.990(2)	Mo(4)-O(19)#1	1.961(2)
Mo(1)-O(6)	2.450(2)	Mo(4)-O(11)	2.470(2)
Mo(2)-O(9)	1.687(2)	Mo(5)-O(16)	1.680(2)
Mo(2)-O(8)	1.869(2)	Mo(5)-O(12)	1.873(2)
Mo(2)-O(10)	1.877(2)	Mo(5)-O(13)	1.877(2)
Mo(2)-O(4)	1.934(2)	Mo(5)-O(17)	1.989(2)
Mo(2)-O(20)#1	2.016(2)	Mo(5)-O(2)#1	2.002(2)
Mo(2)-O(11)	2.434(2)	Mo(5)-O(6)#1	2.441(2)
Mo(3)-O(7)	1.675(2)	Mo(6)-O(18)	1.690(2)
Mo(3)-O(8)	1.914(2)	Mo(6)-O(15)	1.853(2)
Mo(3)-O(5)	1.920(2)	Mo(6)-O(19)	1.868(2)
Mo(3)-O(12)	1.935(2)	Mo(6)-O(17)	1.966(2)
Mo(3)-O(1)#1	1.971(2)	Mo(6)-O(20)	2.016(2)
Mo(3)-O(6)#1	2.458(2)	Mo(6)-O(11)#1	2.455(2)
Zn(1)-N(2)	2.046(3)	P(1)-O(6)#1	1.536(2)
Zn(1)-N(1)	2.073(3)	P(1)-O(6)	1.536(2)
Zn(1)-O(17)	2.089(2)	P(1)-O(11)#1	1.536(2)
Zn(1)-O(2)#1	2.206(2)	P(1)-O(11)	1.536(2)
Zn(1)-O(4)#1	2.218(2)	Zn(1)-O(20)	2.318(2)

Table S7. Selected bond angles (°) for compound **1**.

O(3)-Mo(1)-O(1)	102.76(11)	O(7)-Mo(3)-O(8)	102.01(11)
O(3)-Mo(1)-O(5)	101.83(11)	O(7)-Mo(3)-O(5)	102.36(11)
O(1)-Mo(1)-O(5)	93.75(10)	O(8)-Mo(3)-O(5)	85.52(9)
O(3)-Mo(1)-O(2)	100.87(10)	O(7)-Mo(3)-O(12)	103.18(11)
O(1)-Mo(1)-O(2)	91.38(10)	O(8)-Mo(3)-O(12)	91.15(9)
O(5)-Mo(1)-O(2)	154.98(9)	O(5)-Mo(3)-O(12)	154.38(9)
O(3)-Mo(1)-O(4)	101.52(10)	O(7)-Mo(3)-O(1)#1	101.82(11)
O(1)-Mo(1)-O(4)	155.33(9)	O(8)-Mo(3)-O(1)#1	156.16(9)
O(5)-Mo(1)-O(4)	85.52(9)	O(5)-Mo(3)-O(1)#1	88.94(9)
O(2)-Mo(1)-O(4)	79.76(9)	O(12)-Mo(3)-O(1)#1	83.91(9)
O(3)-Mo(1)-O(6)	173.52(10)	O(7)-Mo(3)-O(6)#1	173.01(9)
O(1)-Mo(1)-O(6)	74.65(8)	O(8)-Mo(3)-O(6)#1	83.59(8)
O(5)-Mo(1)-O(6)	84.35(8)	O(5)-Mo(3)-O(6)#1	82.10(8)
O(2)-Mo(1)-O(6)	73.45(8)	O(12)-Mo(3)-O(6)#1	72.29(8)
O(4)-Mo(1)-O(6)	80.75(8)	O(1)#1-Mo(3)-O(6)#1	72.68(8)
O(9)-Mo(2)-O(8)	103.35(10)	O(14)-Mo(4)-O(13)	103.16(11)
O(9)-Mo(2)-O(10)	100.94(10)	O(14)-Mo(4)-O(10)	102.60(11)
O(8)-Mo(2)-O(10)	92.43(10)	O(13)-Mo(4)-O(10)	90.93(9)
O(9)-Mo(2)-O(4)	103.08(10)	O(14)-Mo(4)-O(15)	102.87(11)
O(8)-Mo(2)-O(4)	87.63(9)	O(13)-Mo(4)-O(15)	84.49(9)
O(10)-Mo(2)-O(4)	155.30(9)	O(10)-Mo(4)-O(15)	154.50(9)
O(9)-Mo(2)-O(20)#1	97.66(10)	O(14)-Mo(4)-O(19)#1	101.67(11)
O(8)-Mo(2)-O(20)#1	158.39(9)	O(13)-Mo(4)-O(19)#1	155.13(9)
O(10)-Mo(2)-O(20)#1	88.47(9)	O(10)-Mo(4)-O(19)#1	84.85(9)
O(4)-Mo(2)-O(20)#1	82.71(9)	O(15)-Mo(4)-O(19)#1	88.84(9)

O(9)-Mo(2)-O(11)	169.48(9)	O(14)-Mo(4)-O(11)	171.59(10)
O(8)-Mo(2)-O(11)	86.04(8)	O(18)-Mo(6)-O(17)	102.26(11)
O(10)-Mo(2)-O(11)	73.58(8)	O(15)-Mo(6)-O(17)	87.56(10)
O(4)-Mo(2)-O(11)	81.79(8)	O(19)-Mo(6)-O(17)	154.45(9)
O(20)#1-Mo(2)-O(11)	73.50(8)	O(18)-Mo(6)-O(20)	98.99(10)
O(16)-Mo(5)-O(12)	101.87(11)	O(15)-Mo(6)-O(20)	156.78(9)
O(16)-Mo(5)-O(13)	103.05(11)	O(19)-Mo(6)-O(20)	88.41(9)
O(12)-Mo(5)-O(13)	93.76(10)	O(17)-Mo(6)-O(20)	80.37(9)
O(16)-Mo(5)-O(17)	102.34(11)	O(18)-Mo(6)-O(11)#1	170.87(10)
O(12)-Mo(5)-O(17)	155.15(9)	O(15)-Mo(6)-O(11)#1	85.60(9)
O(13)-Mo(5)-O(17)	86.16(9)	O(19)-Mo(6)-O(11)#1	73.68(8)
O(16)-Mo(5)-O(2)#1	99.27(11)	O(17)-Mo(6)-O(11)#1	81.09(8)
O(12)-Mo(5)-O(2)#1	90.16(10)	O(20)-Mo(6)-O(11)#1	73.04(8)
O(13)-Mo(5)-O(2)#1	156.01(9)	N(2)-Zn(1)-N(1)	92.67(12)
O(17)-Mo(5)-O(2)#1	80.54(9)	N(2)-Zn(1)-O(17)	166.80(11)
O(16)-Mo(5)-O(6)#1	171.07(10)	N(1)-Zn(1)-O(17)	92.73(10)
O(12)-Mo(5)-O(6)#1	73.65(8)	N(2)-Zn(1)-O(2)#1	116.74(11)
O(13)-Mo(5)-O(6)#1	85.12(8)	N(1)-Zn(1)-O(2)#1	101.94(11)
O(17)-Mo(5)-O(6)#1	81.59(8)	O(17)-Zn(1)-O(2)#1	73.78(8)
O(2)#1-Mo(5)-O(6)#1	73.30(8)	N(2)-Zn(1)-O(4)#1	85.36(10)
P(1)-O(6)-Mo(5)#1	126.23(12)	N(1)-Zn(1)-O(4)#1	169.74(10)
P(1)-O(6)-Mo(1)	125.52(12)	O(17)-Zn(1)-O(4)#1	91.36(8)
P(1)-O(6)-Mo(3)#1	127.07(11)	O(2)#1-Zn(1)-O(4)#1	70.23(8)
P(1)-O(11)-Mo(2)	125.19(12)	N(2)-Zn(1)-O(20)	95.75(11)
P(1)-O(11)-Mo(6)#1	125.35(12)	N(1)-Zn(1)-O(20)	120.01(10)
Mo(2)-O(11)-Mo(6)#1	91.69(7)	O(17)-Zn(1)-O(20)	71.14(8)
P(1)-O(11)-Mo(4)	126.96(11)	O(2)#1-Zn(1)-O(20)	125.42(8)
O(13)-Mo(4)-O(11)	83.49(8)	O(4)#1-Zn(1)-O(20)	70.23(8)
O(10)-Mo(4)-O(11)	71.84(8)	O(6)#1-P(1)-O(6)	109.20(17)
O(15)-Mo(4)-O(11)	82.71(8)	O(6)#1-P(1)-O(11)#1	110.78(11)
O(19)#1-Mo(4)-O(11)	71.90(8)	O(6)-P(1)-O(11)#1	108.59(11)
O(18)-Mo(6)-O(15)	102.94(11)	O(6)#1-P(1)-O(11)	108.59(11)
O(18)-Mo(6)-O(19)	102.12(11)	O(6)-P(1)-O(11)	110.78(11)
O(15)-Mo(6)-O(19)	94.33(10)	O(11)#1-P(1)-O(11)	108.91(17)

Table S8. Selected bond lengths (Å) for compound **2**.

Mo(1)-O(7)	1.682(9)	Mo(4)-O(18)	1.668(10)
Mo(1)-O(9)	1.807(8)	Mo(4)-O(39)	1.951(9)
Mo(1)-O(8)	1.808(8)	Mo(4)-O(16)	1.955(9)
Mo(1)-O(35)	1.987(8)	Mo(4)-O(17)	2.014(10)
Mo(1)-O(6)	2.009(9)	Mo(4)-O(19)	2.077(9)
Mo(2)-O(3)	1.690(9)	Mo(5)-O(21)	1.678(9)
Mo(2)-O(15)	1.827(8)	Mo(5)-O(17)	1.829(9)
Mo(2)-O(2)	1.832(8)	Mo(5)-O(22)	1.833(9)
Mo(2)-O(35)	2.005(8)	Mo(5)-O(24)	2.011(9)
Mo(2)-O(6)	2.012(9)	Mo(5)-O(23)	2.022(9)
Mo(3)-O(14)	1.681(9)	Mo(6)-O(37)	1.684(10)
Mo(3)-O(13)	1.948(9)	Mo(6)-O(33)	1.824(9)
Mo(3)-O(39)	1.970(9)	Mo(6)-O(27)	1.828(9)
Mo(3)-O(16)	1.978(9)	Mo(6)-O(24)	1.973(9)
Mo(3)-O(15)	2.013(9)	Mo(6)-O(23)	1.992(9)

Mo(7)-O(4)	1.661(9)	Mo(10)-O(30)	1.666(9)
Mo(7)-O(5)	1.952(9)	Mo(10)-O(29)	1.943(8)
Mo(7)-O(12)	1.954(9)	Mo(10)-O(28)	1.955(9)
Mo(7)-O(33)	2.018(9)	Mo(10)-O(10)	1.969(8)
Mo(7)-O(11)	2.095(9)	Mo(10)-O(8)	2.040(9)
Mo(7)-O(32)	2.508(8)	Mo(10)-O(36)	2.491(8)
Mo(7)-Mo(8)	2.6262(15)	Mo(11)-O(20)	1.673(9)
Mo(8)-O(1)	1.653(9)	Mo(11)-O(25)	1.964(9)
Mo(8)-O(13)	1.957(8)	Mo(11)-O(40)	1.978(8)
Mo(8)-O(12)	1.975(9)	Mo(11)-O(22)	2.007(9)
Mo(8)-O(5)	1.983(8)	Mo(11)-O(19)	2.097(8)
Mo(8)-O(2)	2.016(8)	Mo(11)-O(38)	2.516(8)
Mo(8)-O(34)	2.517(8)	Mo(12)-O(29)	1.941(8)
Mo(9)-O(31)	1.659(10)	Mo(12)-O(25)	1.979(9)
Mo(9)-O(10)	1.948(9)	Mo(12)-O(40)	1.980(8)
Mo(9)-O(28)	1.956(9)	Mo(12)-O(9)	2.031(9)
Mo(9)-O(27)	2.004(9)	P(1)-O(36)	1.539(9)
Mo(9)-O(11)	2.100(9)	P(1)-O(34)	1.547(8)
Zn(1)-N(1)	1.936(11)	P(1)-O(38)	1.554(9)
Zn(1)-O(35)	1.967(8)	P(1)-O(32)	1.562(9)
Zn(1)-O(40)	1.968(8)	Zn(3)-N(5)	1.980(10)
Zn(1)-O(39)	1.981(9)	Zn(3)-O(28)	1.986(10)
Zn(2)-O(12)	1.957(9)	Zn(4)-O(6)	1.946(9)
Zn(2)-O(16)	1.973(9)	Zn(4)-N(2)#1	1.962(10)
Zn(2)-N(3)	1.987(10)	Zn(4)-O(5)	1.969(9)
Zn(2)-O(24)	1.995(8)	Zn(4)-O(10)	2.007(9)
Zn(3)-O(25)	1.942(9)	Zn(3)-O(23)	1.965(8)
Mo(12)-O(26)	1.683(9)		

Table S9. Selected bond angles (°) for compound **2**.

O(7)-Mo(1)-O(9)	103.6(5)	O(3)-Mo(2)-O(15)	104.0(4)
O(7)-Mo(1)-O(8)	104.1(4)	O(3)-Mo(2)-O(2)	104.2(4)
O(9)-Mo(1)-O(8)	97.3(4)	O(15)-Mo(2)-O(2)	97.1(4)
O(7)-Mo(1)-O(35)	103.8(4)	O(3)-Mo(2)-O(35)	103.3(4)
O(9)-Mo(1)-O(35)	88.6(4)	O(15)-Mo(2)-O(35)	88.5(4)
O(8)-Mo(1)-O(35)	149.2(4)	O(2)-Mo(2)-O(35)	149.6(4)
O(7)-Mo(1)-O(6)	103.6(4)	O(3)-Mo(2)-O(6)	103.5(4)
O(9)-Mo(1)-O(6)	150.4(4)	O(15)-Mo(2)-O(6)	149.9(4)
O(8)-Mo(1)-O(6)	87.2(4)	O(2)-Mo(2)-O(6)	87.9(4)
O(35)-Mo(1)-O(6)	73.7(3)	O(35)-Mo(2)-O(6)	73.3(3)
O(7)-Mo(1)-Mo(2)	100.4(3)	O(3)-Mo(2)-Mo(1)	100.0(3)
O(9)-Mo(1)-Mo(2)	124.8(3)	O(15)-Mo(2)-Mo(1)	124.3(3)
O(8)-Mo(1)-Mo(2)	123.7(3)	O(2)-Mo(2)-Mo(1)	124.4(3)
O(35)-Mo(1)-Mo(2)	37.2(2)	O(35)-Mo(2)-Mo(1)	36.8(2)
O(6)-Mo(1)-Mo(2)	37.6(2)	O(6)-Mo(2)-Mo(1)	37.5(3)
O(14)-Mo(3)-O(13)	100.2(4)	O(18)-Mo(4)-O(39)	107.6(5)
O(14)-Mo(3)-O(39)	106.0(4)	O(18)-Mo(4)-O(16)	106.0(4)
O(13)-Mo(3)-O(39)	152.6(3)	O(39)-Mo(4)-O(16)	93.8(4)
O(14)-Mo(3)-O(16)	106.2(4)	O(18)-Mo(4)-O(17)	100.7(5)
O(13)-Mo(3)-O(16)	87.6(4)	O(39)-Mo(4)-O(17)	151.0(4)

O(39)-Mo(3)-O(16)	92.5(4)	O(16)-Mo(4)-O(17)	84.5(4)
O(14)-Mo(3)-O(15)	99.4(4)	O(18)-Mo(4)-O(19)	98.2(4)
O(13)-Mo(3)-O(15)	84.6(4)	O(39)-Mo(4)-O(19)	83.9(4)
O(39)-Mo(3)-O(15)	83.6(3)	O(16)-Mo(4)-O(19)	155.2(4)
O(16)-Mo(3)-O(15)	154.2(3)	O(17)-Mo(4)-O(19)	85.8(4)
O(14)-Mo(3)-Mo(4)	100.7(3)	O(18)-Mo(4)-Mo(3)	101.7(4)
O(13)-Mo(3)-Mo(4)	134.4(3)	O(39)-Mo(4)-Mo(3)	48.2(3)
O(39)-Mo(3)-Mo(4)	47.6(3)	O(16)-Mo(4)-Mo(3)	48.4(3)
O(16)-Mo(3)-Mo(4)	47.7(3)	O(17)-Mo(4)-Mo(3)	131.8(3)
O(15)-Mo(3)-Mo(4)	130.6(2)	O(19)-Mo(4)-Mo(3)	131.7(3)
O(21)-Mo(5)-O(17)	103.3(5)	O(37)-Mo(6)-O(33)	104.0(4)
O(21)-Mo(5)-O(22)	103.3(5)	O(37)-Mo(6)-O(27)	103.7(5)
O(17)-Mo(5)-O(22)	98.8(4)	O(33)-Mo(6)-O(27)	97.6(4)
O(21)-Mo(5)-O(24)	102.3(5)	O(37)-Mo(6)-O(24)	101.9(5)
O(17)-Mo(5)-O(24)	88.2(4)	O(33)-Mo(6)-O(24)	87.5(4)
O(22)-Mo(5)-O(24)	151.1(4)	O(27)-Mo(6)-O(24)	151.7(4)
O(21)-Mo(5)-O(23)	102.9(5)	O(37)-Mo(6)-O(23)	102.5(4)
O(17)-Mo(5)-O(23)	150.7(4)	O(33)-Mo(6)-O(23)	150.7(4)
O(22)-Mo(5)-O(23)	87.8(4)	O(27)-Mo(6)-O(23)	87.9(4)
O(24)-Mo(5)-O(23)	73.5(3)	O(24)-Mo(6)-O(23)	75.0(3)
O(21)-Mo(5)-Mo(6)	99.3(4)	O(37)-Mo(6)-Mo(5)	98.8(4)
O(17)-Mo(5)-Mo(6)	124.2(3)	O(33)-Mo(6)-Mo(5)	124.2(3)
O(22)-Mo(5)-Mo(6)	124.5(3)	O(27)-Mo(6)-Mo(5)	125.2(3)
O(24)-Mo(5)-Mo(6)	36.9(2)	O(24)-Mo(6)-Mo(5)	37.8(2)
O(23)-Mo(5)-Mo(6)	37.6(2)	O(23)-Mo(6)-Mo(5)	38.3(2)
O(4)-Mo(7)-O(5)	106.2(5)	O(1)-Mo(8)-O(13)	101.0(4)
O(4)-Mo(7)-O(12)	106.0(4)	O(1)-Mo(8)-O(12)	104.9(4)
O(5)-Mo(7)-O(12)	94.3(4)	O(13)-Mo(8)-O(12)	88.0(4)
O(4)-Mo(7)-O(33)	100.0(5)	O(1)-Mo(8)-O(5)	104.9(4)
O(5)-Mo(7)-O(33)	153.0(4)	O(13)-Mo(8)-O(5)	153.0(3)
O(12)-Mo(7)-O(33)	84.3(4)	O(12)-Mo(8)-O(5)	92.7(4)
O(4)-Mo(7)-O(11)	96.4(4)	O(1)-Mo(8)-O(2)	100.4(4)
O(5)-Mo(7)-O(11)	84.9(4)	O(13)-Mo(8)-O(2)	85.0(3)
O(12)-Mo(7)-O(11)	156.8(3)	O(12)-Mo(8)-O(2)	154.6(3)
O(33)-Mo(7)-O(11)	86.0(4)	O(5)-Mo(8)-O(2)	82.9(4)
O(4)-Mo(7)-O(32)	169.1(4)	O(1)-Mo(8)-O(34)	173.2(4)
O(5)-Mo(7)-O(32)	80.0(3)	O(13)-Mo(8)-O(34)	74.1(3)
O(12)-Mo(7)-O(32)	82.0(3)	O(12)-Mo(8)-O(34)	79.8(3)
O(33)-Mo(7)-O(32)	73.1(3)	O(5)-Mo(8)-O(34)	79.5(3)
O(11)-Mo(7)-O(32)	75.0(3)	O(2)-Mo(8)-O(34)	74.8(3)
O(4)-Mo(7)-Mo(8)	100.9(4)	O(1)-Mo(8)-Mo(7)	99.1(3)
O(5)-Mo(7)-Mo(8)	48.6(2)	O(13)-Mo(8)-Mo(7)	134.8(3)
O(12)-Mo(7)-Mo(8)	48.4(3)	O(12)-Mo(8)-Mo(7)	47.7(3)
O(33)-Mo(7)-Mo(8)	132.0(2)	O(5)-Mo(8)-Mo(7)	47.6(3)
O(11)-Mo(7)-Mo(8)	133.3(3)	O(2)-Mo(8)-Mo(7)	130.1(2)
O(32)-Mo(7)-Mo(8)	89.8(2)	O(34)-Mo(8)-Mo(7)	87.68(19)
O(31)-Mo(9)-O(10)	106.7(5)	O(30)-Mo(10)-O(29)	100.4(4)
O(31)-Mo(9)-O(28)	106.2(4)	O(30)-Mo(10)-O(28)	105.9(4)
O(10)-Mo(9)-O(28)	93.4(4)	O(29)-Mo(10)-O(28)	88.1(4)
O(31)-Mo(9)-O(27)	100.9(4)	O(30)-Mo(10)-O(10)	104.7(4)
O(10)-Mo(9)-O(27)	151.5(4)	O(29)-Mo(10)-O(10)	153.6(3)
O(28)-Mo(9)-O(27)	85.5(4)	O(28)-Mo(10)-O(10)	92.8(4)
O(31)-Mo(9)-O(11)	97.6(4)	O(30)-Mo(10)-O(8)	98.3(4)

O(10)-Mo(9)-O(11)	84.0(4)	O(29)-Mo(10)-O(8)	84.4(3)
O(28)-Mo(9)-O(11)	155.8(4)	O(28)-Mo(10)-O(8)	155.6(4)
O(27)-Mo(9)-O(11)	85.5(4)	O(10)-Mo(10)-O(8)	84.0(3)
O(31)-Mo(9)-Mo(10)	101.4(4)	O(30)-Mo(10)-O(36)	171.0(4)
O(10)-Mo(9)-Mo(10)	48.3(2)	O(29)-Mo(10)-O(36)	74.1(3)
O(28)-Mo(9)-Mo(10)	47.8(3)	O(28)-Mo(10)-O(36)	81.3(3)
O(27)-Mo(9)-Mo(10)	132.3(3)	O(10)-Mo(10)-O(36)	80.0(3)
O(11)-Mo(9)-Mo(10)	131.9(3)	O(8)-Mo(10)-O(36)	74.3(3)
O(20)-Mo(11)-O(25)	105.2(4)	O(30)-Mo(10)-Mo(9)	99.7(4)
O(20)-Mo(11)-O(40)	104.9(4)	O(29)-Mo(10)-Mo(9)	135.2(3)
O(25)-Mo(11)-O(40)	94.1(3)	O(28)-Mo(10)-Mo(9)	47.9(3)
O(20)-Mo(11)-O(22)	100.7(4)	O(10)-Mo(10)-Mo(9)	47.6(3)
O(25)-Mo(11)-O(22)	84.3(4)	O(8)-Mo(10)-Mo(9)	131.2(2)
O(40)-Mo(11)-O(22)	153.8(4)	O(36)-Mo(10)-Mo(9)	89.1(2)
O(20)-Mo(11)-O(19)	97.5(4)	O(26)-Mo(12)-O(29)	101.1(4)
O(25)-Mo(11)-O(19)	156.7(3)	O(26)-Mo(12)-O(25)	105.5(4)
O(40)-Mo(11)-O(19)	85.0(3)	O(29)-Mo(12)-O(25)	87.2(4)
O(22)-Mo(11)-O(19)	86.3(4)	O(26)-Mo(12)-O(40)	106.1(4)
O(20)-Mo(11)-O(38)	170.2(4)	O(29)-Mo(12)-O(40)	151.4(3)
O(25)-Mo(11)-O(38)	82.2(3)	O(25)-Mo(12)-O(40)	93.6(3)
O(40)-Mo(11)-O(38)	80.5(3)	O(26)-Mo(12)-O(9)	100.1(4)
O(22)-Mo(11)-O(38)	73.4(3)	O(29)-Mo(12)-O(9)	84.5(3)
O(19)-Mo(11)-O(38)	74.7(3)	O(25)-Mo(12)-O(9)	154.2(3)
O(20)-Mo(11)-Mo(12)	99.6(3)	O(40)-Mo(12)-O(9)	82.5(3)
O(25)-Mo(11)-Mo(12)	48.4(3)	O(26)-Mo(12)-Mo(11)	100.8(3)
O(40)-Mo(11)-Mo(12)	48.4(2)	O(29)-Mo(12)-Mo(11)	133.9(2)
O(22)-Mo(11)-Mo(12)	132.0(3)	O(25)-Mo(12)-Mo(11)	47.9(3)
O(19)-Mo(11)-Mo(12)	133.0(2)	O(40)-Mo(12)-Mo(11)	48.3(2)
O(38)-Mo(11)-Mo(12)	90.0(2)	O(9)-Mo(12)-Mo(11)	130.2(2)
N(1)-Zn(1)-O(35)	105.3(4)	O(12)-Zn(2)-O(16)	98.2(4)
N(1)-Zn(1)-O(40)	121.2(4)	O(12)-Zn(2)-N(3)	126.4(5)
O(35)-Zn(1)-O(40)	109.1(4)	O(16)-Zn(2)-N(3)	108.4(4)
N(1)-Zn(1)-O(39)	109.2(4)	O(12)-Zn(2)-O(24)	108.4(4)
O(35)-Zn(1)-O(39)	111.7(4)	O(16)-Zn(2)-O(24)	110.4(4)
O(40)-Zn(1)-O(39)	100.4(3)	N(3)-Zn(2)-O(24)	104.6(5)
O(25)-Zn(3)-O(23)	110.6(4)	O(6)-Zn(4)-N(2)#1	108.7(4)
O(25)-Zn(3)-N(5)	125.6(4)	O(6)-Zn(4)-O(5)	111.5(4)
O(23)-Zn(3)-N(5)	105.7(5)	N(2)#1-Zn(4)-O(5)	124.3(4)
O(25)-Zn(3)-O(28)	98.2(4)	O(6)-Zn(4)-O(10)	110.5(4)
O(23)-Zn(3)-O(28)	107.4(4)	N(2)#1-Zn(4)-O(10)	102.1(4)
N(5)-Zn(3)-O(28)	108.1(5)	O(5)-Zn(4)-O(10)	98.1(4)
O(36)-P(1)-O(34)	111.0(3)	O(36)-P(1)-O(32)	108.8(5)
O(36)-P(1)-O(38)	109.1(5)	O(34)-P(1)-O(32)	108.2(5)
O(34)-P(1)-O(38)	108.5(5)	O(38)-P(1)-O(32)	111.2(3)
P(1)-O(32)-Mo(7)	126.0(5)	P(1)-O(36)-Mo(10)	127.9(5)
P(1)-O(34)-Mo(8)	128.3(4)	P(1)-O(38)-Mo(11)	125.9(5)

Table S10. Hydrogen bonds for compound **1** [Å and °].

D-H···A	D-H	H···A	D···A	D-H···A
N5-H5…O20	0.8600	1.9800	2.838(4)	177.00
C4-H4…O5	0.9300	2.5400	3.458(6)	168.00
C8-H8A…O19	0.9700	2.4300	3.210(4	137.00
C10-H10…O3	0.9300	2.4200	3.210(4)	143.00
C14-H14…O1	0.9300	2.4600	3.367(7)	167.00
C17-H17B…O	0.9700	2.4600	3.406(5)	165.00
C21-H21…O9	0.9300	2.4000	3.064(5)	129.00

Table S11. Hydrogen bonds for compound **2** [Å and °].

D-H···A	D-H	H···A	D···A	D-H···A
N4-H4···O29	0.8600	1.9400	2.801(15)	176.00
N6-H6···O13	0.8600	1.9300	2.789(16)	179.00
C9-H9···O40	0.9300	2.5900	3.324(16)	136.00
C10- H10···O17	0.9300	2.5800	3.335(19)	138.00
C5A- H5AA···O21	0.9700	2.5400	3.50(2)	171.00
C10A-H10A···O21	0.9700	2.4800	3.24(2)	134.00
C14-H14··· O29	0.9300	2.4400	3.31(2)	156.00
C18- H18···O12	0.9300	2.5600	3.23(2)	129.00
C21A-H21A···O30	0.9700	2.2400	3.18(2)	163.00
C23-H23···O13	0.9300	2.5100	3.27(2)	140.00
C27-H27··· O25	0.9300	2.4600	3.19(2)	135.00

Section 6. Reference

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