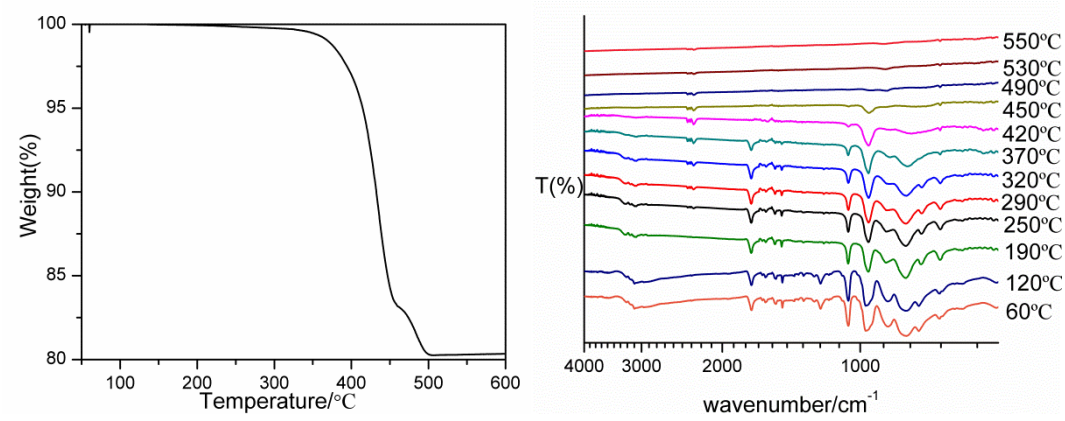
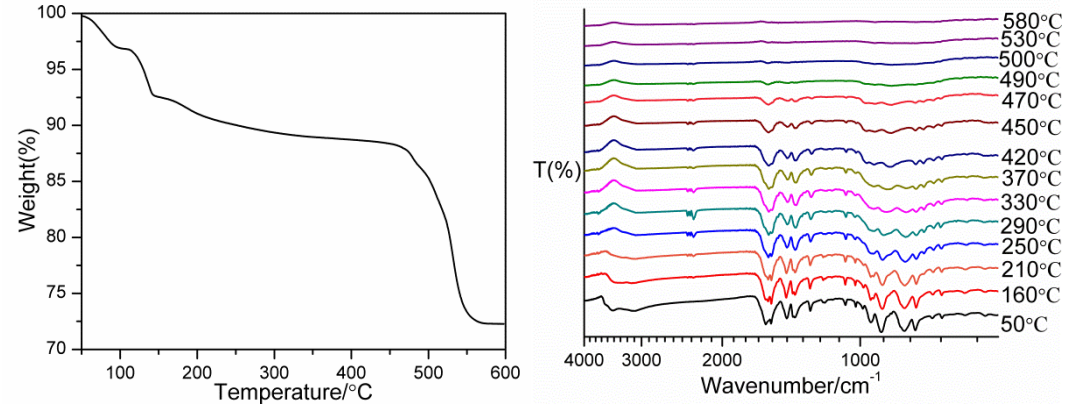
Supporting Information for

Synthesis, Crystal structure of α-Keggin heteropolymolybdates with pyridine-2,6-dicarboxylate based frameworks, and associated RhB photocatalytic degradation and 2D-IR-COS test

Compound **1**



Compound **2**



Compound **3**

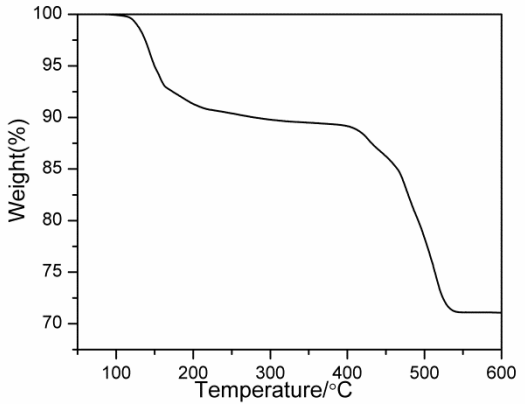
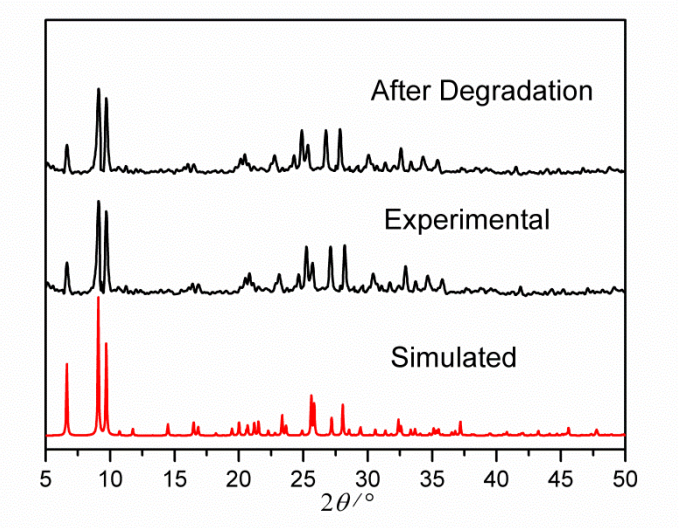
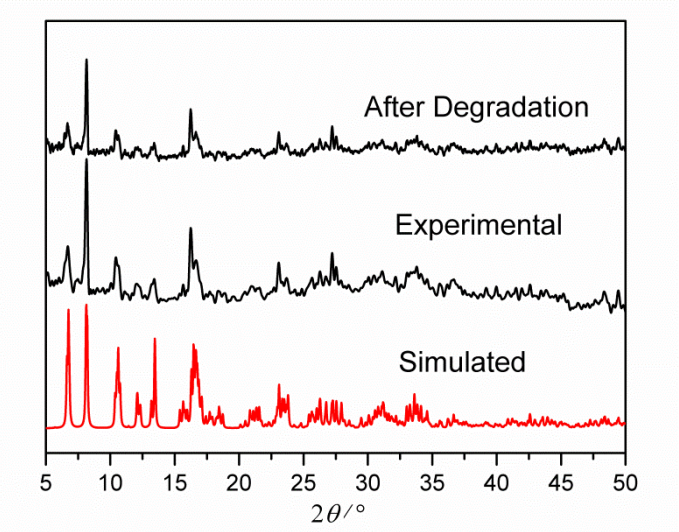


Fig. S1 Thermogravimetric curves and thermal infrared spectra for compound **1-3**

Compound **1**



Compound **2**



Compound **3**

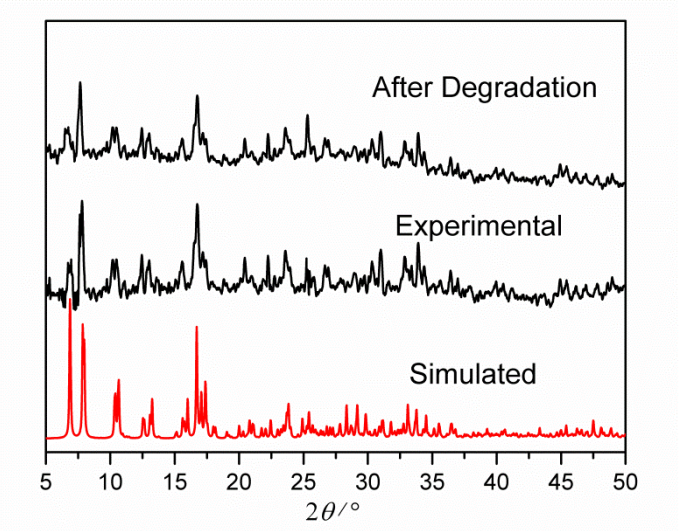
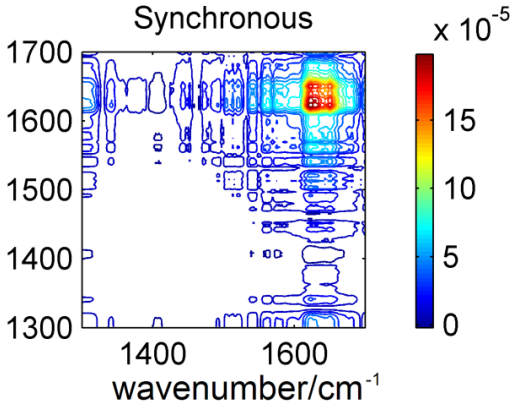
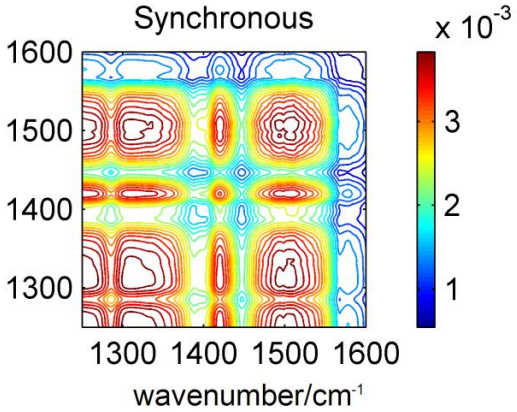


Fig. S2 The powder X-ray diffraction patterns of compound **1**-**3**

Compound **1**



Compound **2**



Compound **3**

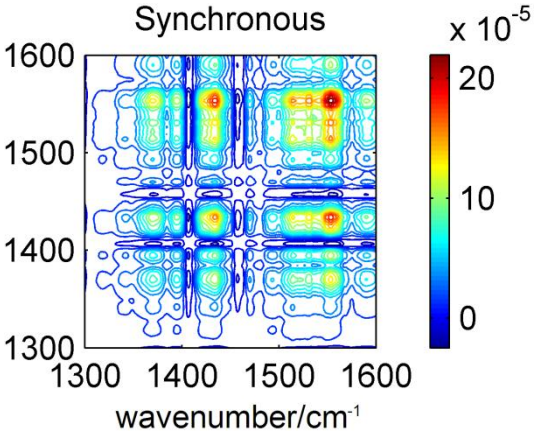


Fig. S3.1 Magnesium-dependent synchronous correlation IR spectra of compound **1-3** over a magnesium range from 0-50mT

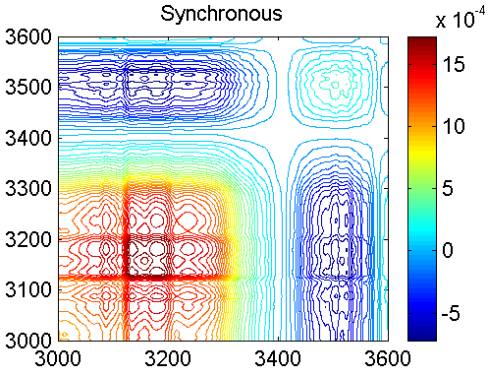
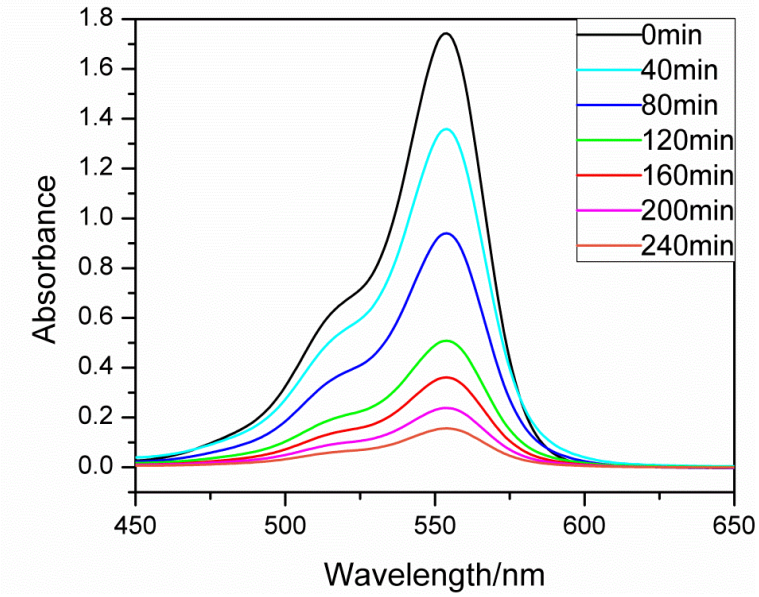


Fig. S3.2 Temperature-dependent synchronous correlation IR spectra of **2** between 3000-3600cm^{-1} over a temperature range from 323 to 393 K

As is shown in Fig**. S3.2**, obvious inductions appear at 3200 and 3550 cm^{-1}. The auto peaks around 3200 cm^{-1} are assigned to temperature-induced stretching vibrations of carboxyl O-H bond, and the auto peaks around 3550 cm^{-1}, which is much weaker, are assigned to temperature-induced stretching vibrations of pyridine N-H bond. So, the hydrogen atoms at the carboxylate O and the pyridine N are both present.

Compound **2**



Compound **3**

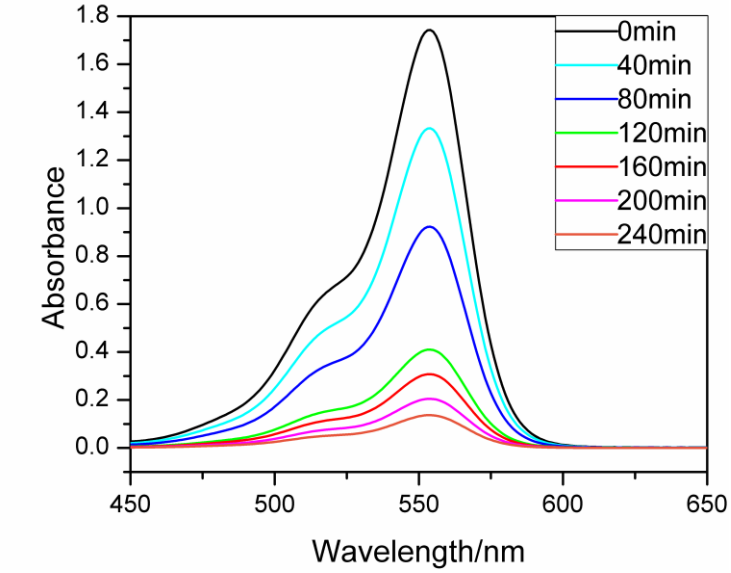


Fig. S4.1 The UV-vis absorption spectra change of **2** and **3**

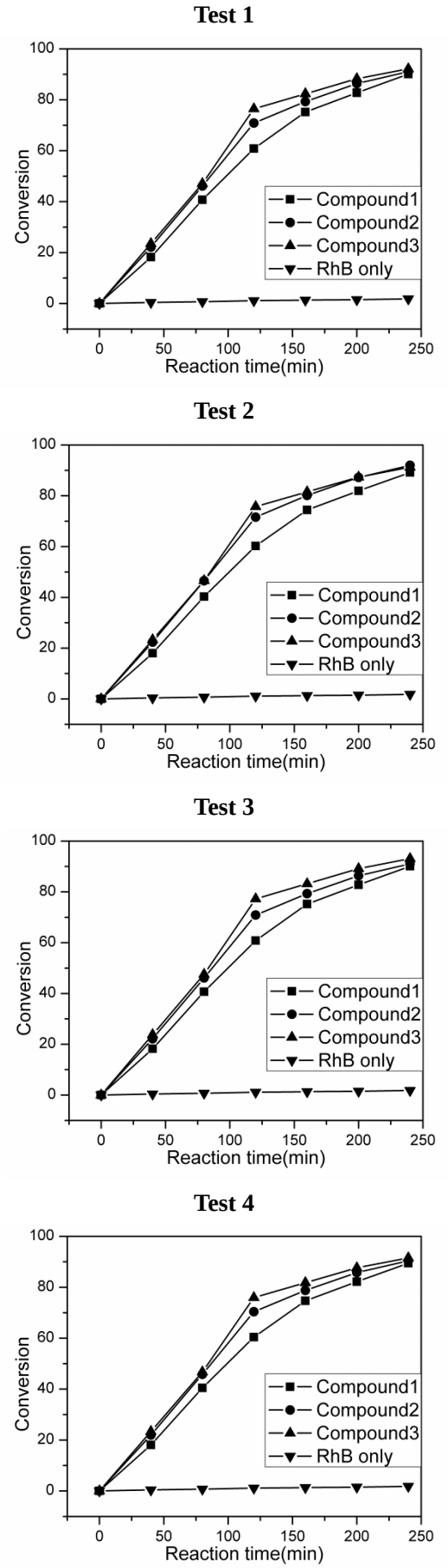


Fig. S4.2 Plots of the conversions of RhB versus reaction time of **1-3** in 4 repeatability tests.

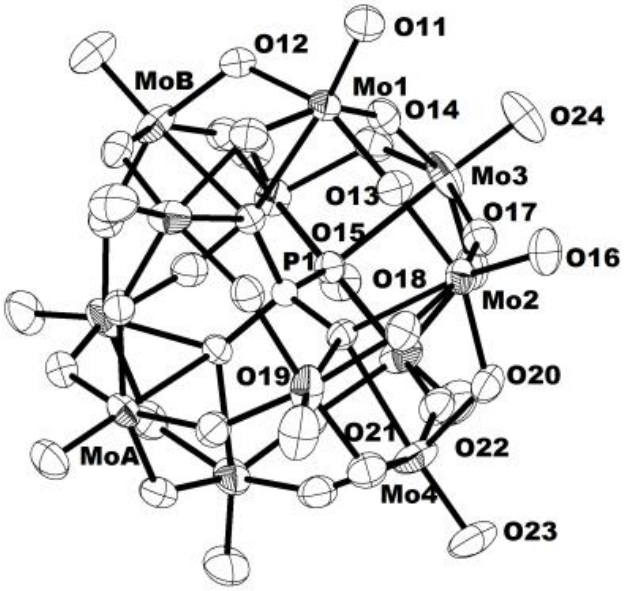


Fig. S5.1 Crystal structure of $[PMo_{12}O_{40}]^{3-}$ (Symmetry codes: A: -y+1, x-y, z; B: -x+y+1, -x+1, z)

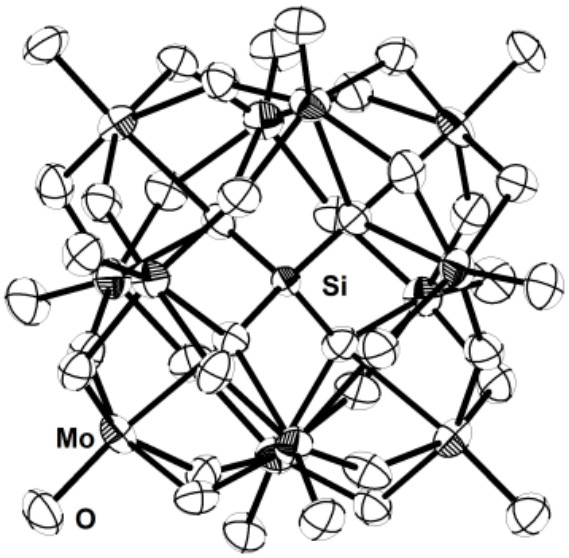


Fig. S5.2 Crystal structure of $[SiMo_{12}O_{40}]^{4-}$

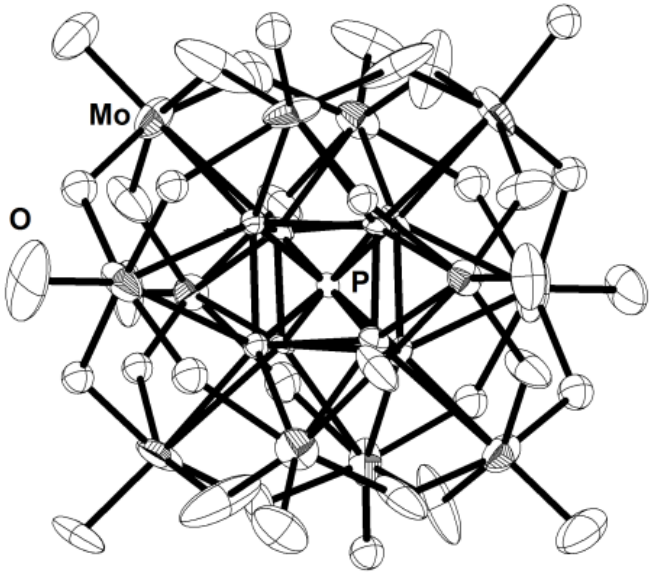


Fig. S5.3 Crystal structure of $[PMo_{12}O_{40}]^{3-}$, removed unnecessary split O for clarity.

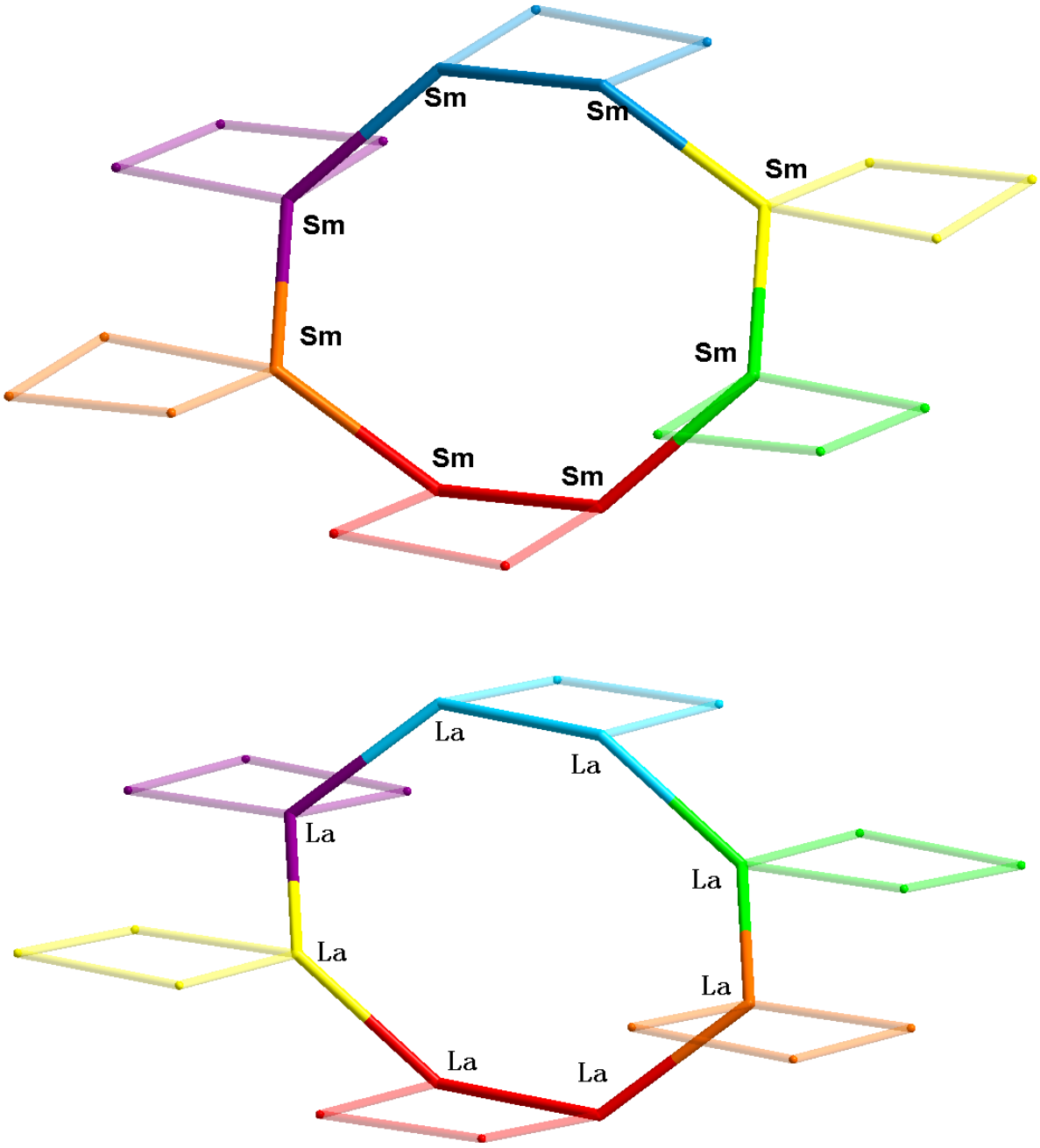


Fig. S5.4 Octanucler metallamacrocycle $Ln_8(pdc)_8$ in compound **2** (along [011] direction) and **3** (along [100] direction), Ln-O-C-O-Ln bonds are simplified as Ln-Ln bonds

Tab. S1.1 Selected Bond Distances (Å) and Angles (deg) of **1**[a]

Mo(1)-O(11)	1.665(6)	Mo(3)-O(14)	1.893(6)	Mo(1)$^{\#1}$-O(15)-Mo(1)	88.5(2)	O(12)-Mo(1)-O(15)	72.96(19)
Mo(1)-O(12)	1.907(6)	Mo(3)-O(17)	1.960(6)	Mo(1)$^{\#}$1-O(15)-Mo(1)$^{\#2}$	88.5(2)	O(13)-Mo(1)-O(15)	83.0(2)
Mo(1)-O(12)$^{\#1}$	1.913(6)	Mo(3)-O(18)$^{\#2}$	1.888(6)	Mo(1)$^{\#2}$-O(15)-Mo(1)	88.5(2)	O(14)-Mo(1)-O(13)	84.7(2)
Mo(1)-O(13)	1.925(6)	Mo(3)-O(19)$^{\#2}$	2.453(5)	Mo(1)-O(12)-Mo(1)$^{\#2}$	125.5(3)	O(14)-Mo(1)-O(15)	83.3(2)
Mo(1)-O(14)	1.913(6)	Mo(3)-O(21)$^{\#2}$	1.926(6)	Mo(2)-O(13)-Mo(1)	150.6(3)	O(19)$^{\#1}$-P(1)-O(15)	109.4(2)
Mo(1)-O(15)	2.434(5)	Mo(3)-O(24)	1.672(6)	Mo(3)-O(14)-Mo(1)	153.9(3)	O(19)$^{\#1}$-P(1)-O(19)	109.5(2)
Mo(2)-O(13)	1.875(6)	Mo(4)-O(19)	2.420(5)	O(11)-Mo(1)-O(12)	102.3(3)	O(19)$^{\#1}$-P(1)-O(19)$^{\#2}$	109.5(2)
Mo(2)-O(16)	1.691(6)	Mo(4)-O(20)	1.907(6)	O(11)-Mo(1)-O(12)$^{\#1}$	101.4(3)	O(19)$^{\#2}$-P(1)-O(15)	109.4(2)
Mo(2)-O(17)	1.855(6)	Mo(4)-O(21)	1.911(6)	O(11)-Mo(1)-O(13)	101.9(3)	O(19)-P(1)-O(15)	109.4(2)
Mo(2)-O(18)	1.957(6)	Mo(4)-O(22)	1.915(6)	O(11)-Mo(1)-O(14)	102.7(3)	O(19)-P(1)-O(19)$^{\#2}$	109.5(2)
Mo(2)-O(19)	2.419(5)	Mo(4)-O(22)$^{\#1}$	1.910(6)	O(11)-Mo(1)-O(15)	172.5(3)	P(1)-O(15)-Mo(1)	126.31(16)
Mo(2)-O(20)	1.942(6)	Mo(4)-O(23)	1.682(6)	O(12)$^{\#1}$-Mo(1)-O(13)	88.6(2)	P(1)-O(15)-Mo(1)$^{\#1}$	126.31(16)
P(1)-O(15)	1.531(9)	P(1)-O(19)$^{\#1}$	1.531(5)	O(12)$^{\#1}$-Mo(1)-O(14)	155.8(2)	P(1)-O(15)-Mo(1)$^{\#2}$	126.31(16)
P(1)-O(19)	1.531(5)	P(1)-O(19)$^{\#2}$	1.531(5)	O(12)$^{\#1}$-Mo(1)-O(15)	72.88(19)	P(1)-O(19)-Mo(2)	125.5(3)
				O(12)-Mo(1)-O(12)$^{\#1}$	87.5(4)	P(1)-O(19)-Mo(3)$^{\#1}$	125.8(3)
				O(12)-Mo(1)-O(13)	155.8(2)	P(1)-O(19)-Mo(4)	126.0(3)
				O(12)-Mo(1)-O(14)	89.2(2)		

[a] Symmetry transformations used to generate equivalent atoms for for **1**: #1 -y+1, x-y, z; #2 -x+y+1, -x+1, z.

Tab. S1.2 Selected Bond Distances (Å) and Angles (deg) of **2**[a]

Sm(1)-O(33)	2.443(10)	Sm(2)-O(29)	2.480(10)	Sm(3)-O(25)	2.542(10)	Sm(4)-O(21)	2.472(10)
Sm(1)-O(34)	2.536(13)	Sm(2)-O(30)	2.493(15)	Sm(3)-O(26)	2.453(8)	Sm(4)-O(22)$^{\#3}$	2.359(8)
Sm(1)-O(35)	2.552(10)	Sm(2)-O(31)	2.627(17)	Sm(3)-O(27)	2.451(10)	Sm(4)-O(23)	2.408(9)
Sm(1)-O(36)	2.441(8)	Sm(2)-O(32)	2.470(11)	Sm(3)-O(28)	2.454(9)	Sm(4)-O(24)	2.411(10)
Sm(1)-O(10)$^{\#2}$	2.458(8)	Sm(2)-O(8)$^{\#4}$	2.395(7)	Sm(3)-O(1)$^{\#1}$	2.414(8)	Sm(4)-O(2)	2.440(8)
Sm(1)-O(11)	2.453(8)	Sm(2)-O(9)	2.447(8)	Sm(3)-O(5)	2.477(8)	Sm(4)-O(3)	2.418(8)
Sm(1)-O(12)	2.464(8)	Sm(2)-O(39)	2.403(8)	Sm(3)-O(6)	2.509(8)	Sm(4)-O(4)	2.382(7)
Sm(1)-O(37)	2.467(9)	Sm(2)-O(46)	2.367(9)	Sm(3)-O(7)	2.484(7)	Sm(4)-N(4)	2.519(8)
Sm(1)-N(1)	2.519(9)	Sm(2)-N(2)	2.542(9)	Sm(3)-N(3)	2.570(8)		
O(2)-Sm(4)-O(21)	71.7(3)	O(22)$^{\#3}$-Sm(4)-O(2)	86.4(3)	O(24)-Sm(4)-O(2)	80.5(4)	O(4)-Sm(4)-N(4)	145.7(3)
O(2)$^{\#3}$-Sm(4)-N(4)	63.2(3)	O(22)$^{\#3}$-Sm(4)-O(21)	79.3(4)	O(24)-Sm(4)-O(3)	84.0(4)	O(4)-Sm(4)-O(2)	119.9(3)
O(22)-Sm(4)-N(4)	74.3(3)	O(23)-Sm(4)-O(24)	129.7(4)	O(24)-Sm(4)-O(21)	121.3(5)	O(4)-Sm(4)-O(23)	68.7(3)
O(22)$^{\#3}$-Sm(4)-O(23)	72.0(3)	O(23)-Sm(4)-O(2)	147.2(4)	O(24)-Sm(4)-N(4)	75.4(3)	O(4)-Sm(4)-O(3)	102.1(3)
O(22)$^{\#3}$-Sm(4)-O(24)	149.6(3)	O(23)-Sm(4)-O(21)	80.0(4)	O(3)-Sm(4)-N(4)	64.1(3)	O(4)-Sm(4)-O(24)	72.0(3)
O(22)$^{\#3}$-Sm(4)-O(3)	82.3(3)	O(23)-Sm(4)-O(3)	75.1(4)	O(3)-Sm(4)-O(2)	127.2(3)		
O(22)$^{\#3}$-Sm(4)-O(4)	137.6(3)	O(23)-Sm(4)-N(4)	129.5(3)	O(4)-Sm(4)-O(21)	78.9(4)		

[a] Symmetry transformations used to generate equivalent atoms for **2**: #1 -x+1,-y+1,-z+1; #2 -x,-y+2,-z+2; #3 -x,-y+2,-z+1; #4 -x,-y+1,-z+2 .

Tab. S2.1 H-Bond Distances (Å) and Angles (deg) of Coordinate and free H_2O molecule in **2**[a], H atoms add by Platon 1.15 and Olex2 1.1

No.	Type	Donor	---H....	Acceptor	D - H	H...A	D...A	D- H...A
1		O(21)	--H(21B)	..O(58)	0.85	2.38	2.9734	127
2	Intra	O(23)	--H(23A)	..O(11)	0.85	1.82	2.6542	168
3		O(23)	--H(23B)	..O(60)	0.85	1.96	2.8002	171
4		O(24)	--H(24A)	..O(59)	0.85	2.54	2.8342	101
5		O(24)	--H(24B)	..O(59)	0.85	2.33	2.8342	119
6	Intra	O(25)	--H(25A)	..O(39)	0.85	2.07	2.864	155
7		O(25)	--H(25B)	..O(41)	0.85	2.55	3.0519	119
8	Intra	O(26)	--H(26A)	..O(2)	0.85	1.96	2.7081	147
9		O(26)	--H(26B)	..O(57)	0.85	2.03	2.8813	177
10	Intra	O(27)	--H(27A)	..O(39)	0.85	2.11	2.8218	140
11		O(27)	--H(27B)	..O(53)	0.85	2.07	2.8417	150
12		O(29)	--H(29A)	..O(51)	0.85	2.26	2.8477	126
13	Intra	O(29)	--H(29B)	..O(7)	0.85	1.86	2.681	163
14		O(30)	--H(30B)	..O(54)	0.85	2.18	2.7972	129
15		O(31)	--H(31A)	..O(55)	0.85	1.97	2.8175	175
16	Intra	O(32)	--H(32A)	..O(12)	0.85	2.28	2.8222	121
17	Intra	O(32)	--H(32B)	..O(31)	0.85	2.43	3.1952	150
18	Intra	O(33)	--H(33A)	..O(9)	0.85	1.86	2.6644	158
19		O(33)	--H(33B)	..O(56)	0.85	1.96	2.7952	167
20		O(34)	--H(34A)	..O(62)	0.85	2.07	2.8998	166
21	Intra	O(35)	--H(35A)	..O(35)	0.85	2.19	2.8853	139
22	Intra	O(37)	--H(37A)	..O(3)	0.85	1.92	2.7697	174
23		O(37)	--H(37B)	..O(41)	0.85	1.96	2.791	164
24		O(38)	--H(38A)	..O(25)	0.85	2.12	2.8396	143
25		O(38)	--H(38B)	..O(88)	0.85	2.42	3.1866	150
26		O(40)	--H(40A)	..O(28)	0.85	1.91	2.6618	147
27		O(40)	--H(40B)	..O(54)	0.85	1.99	2.8289	170
28		O(41)	--H(41A)	..O(65)	0.85	2.33	3.1728	169
29		O(41)	--H(41B)	..O(25)	0.85	2.27	3.0519	153

"Cacl-OH" of Wingx and "Hadd" of Olex2 are used to place the hydrogen theoretically, but still there are some hydrogen atoms cannot be placed in sensible positions. According to the CIF of reference #8 (http://pubs.acs.org/doi/suppl/10.1021/ic801846h/suppl_file/ic801846h_si_002.cif), these hydrogen atoms are reserved.

Tab. S2.2 H-Bond Distances (Å) and Angles (deg) of Coordinate and free H_2O molecule in **3**[a], H atoms add by Platon 1.15 and Olex2 1.1

No.	Type	Donor	---H....	Acceptor	D - H	H...A	D...A	D - H...A
1	Intra	O(36)	--H(1)	..O(33)	0.9	1.95	2.7729	148
2		O(34)	--H(34A)	..O(7)	0.85	2.42	3.0028	126
3		O(34)	--H(34B)	..O(8)	0.85	2.50	3.2683	151
4		O(35)	--H(35A)	..O(13)	0.85	2.41	2.9998	127
5		O(35)	--H(35A)	..O(17)	0.85	2.5	3.065	125
6		O(35)	--H(35B)	..F(42)	0.85	2.36	2.8523	117
7		O(36)	--H(36)	..O(4)	0.85	2.58	3.1262	123
8		O(37)	--H(37B)	..O(16)	0.85	2.15	2.96	158
9		O(38)	--H(38A)	..O(19)	0.85	2.21	2.8055	127
10		O(38)	--H(38A)	..O(7)	0.85	2.45	3.2568	159
11		O(38)	--H(38B)	..F(42)	0.85	2.37	2.8532	117
12		O(39)	--H(39A)	..O(1A)	0.85	2.57	3.1948	131
13		O(39)	--H(39A)	..O(2)	0.85	2.27	2.9313	135
14	Intra	O(40)	--H(40A)	..O(30)	0.85	1.94	2.7671	164
15		O(40)	--H(40B)	..O(9)	0.85	2.32	3.16	168
16		O(40)	--H(40B)	..O(10)	0.85	2.56	3.0096	114
18		O(41)	--H(41B)	..O(11)	0.85	2.26	2.6987	112

"Cacl-OH" of Wingx and "Hadd" of Olex2 are used to place the hydrogen theoretically, but still there are some hydrogen atoms cannot be placed in sensible positions. According to the CIF of reference #8 (http://pubs.acs.org/doi/suppl/10.1021/ic801846h/suppl_file/ic801846h_si_002.cif), these hydrogen atoms are reserved.