Supporting Information

Synthesis, characterization and catalytic epoxidation properties of lanthanide-stabilized peroxoisopolytungstates

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CONTENTS

Section 1 Survey of Lanthanide-containing isopolytungstates

Table S1. A detailed survey of already synthesized Ln-iso-POTs

Year	Polyanion Formula	Ref.
1971, 1974	$[Ln(W_5O_{18})_2]^{n-}$ (Ln = La, Ce^{III}, Ce^{IV}, Pr, Nd, Sm, Ho, Yb)	1
2008	$[H_6Ce_2(H_2O)Cl(W_5O_{18})_3]^{7-}$	2
2009	$[Ln_2(H_2O)_{10}W_{22}O_{71}(OH)_2]^{8-}$ (Ln = La, Ce, Tb, Dy, Ho, Er, Tm, Yb, Lu)	3
2009	$[Ln_2(H_2O)_{10}W_{28}O_{93}(OH)_2]^{14-}$ (Ln = Sm or Eu)	4
2013	$[Ln_4(WO_4)(H_2O)_{16}\{W_7O_{22}(O_2)_2\}_4]^{14-}$ (Ln = La or Pr)	5
2014	$[Ce_2(H_2O)_6W_{22}O_{72}(OH)_4]^{10-}$, $[Ce_2(H_2O)_9W_{36}O_{110}(OH)_{12}]_2^{20-}$ $[Ce_4(H_2O)_{12}W_{44}O_{144}(OH)_{12}]^{24-}$	6
2016	$[Ln_4(H_2O)_{22}W_{28}O_{94}H_2]_2^{12-}$ (Ln = Pr, Nd, Sm) $[Ln(H_2O)_4][Ln(H_2O)_5]_2[W_{22}O_{74}H_2]^{8-}$ (Ln = Gd, Tb, Er, Tm, Yb, Lu) $[Eu(H_2O)_7]_2[Eu(H_2O)_5]_2[W_{22}O_{74}H_2]^{2-}$	7

Section 2 Additional Structural Figures

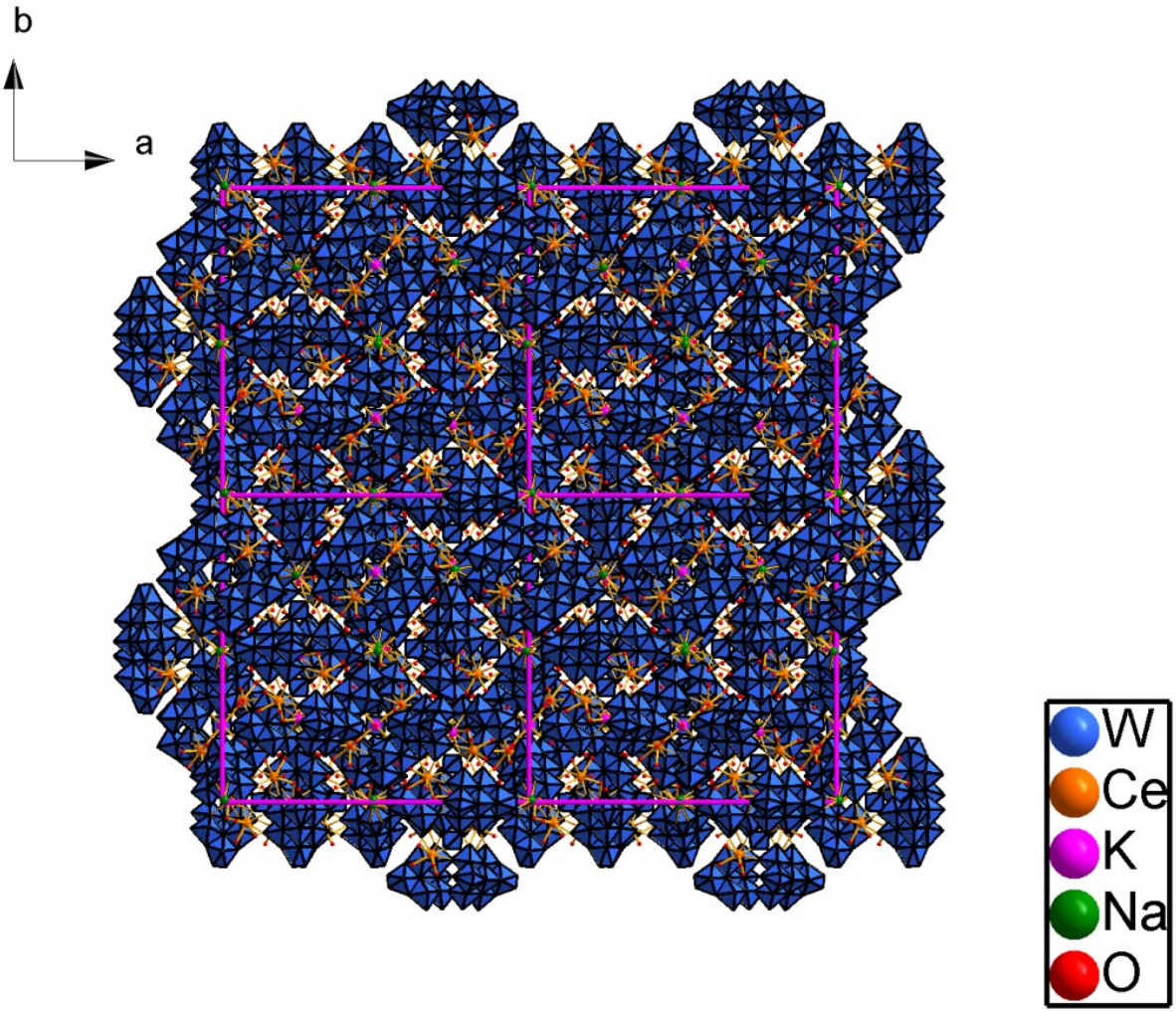


Figure S1. The 3D structure of **1** viewed along the *c* axis

Section 3 Selected bond distances of 1−5

Table S2. Selected bond distances of **1**

Bond	Length	Bond	Length	Bond	Length
W(1)-O(1)	1.773(16)	W(4)-O(14)	1.871(19)	W(7)-O(24)	1.93(2)
W(2)-W(5)	3.2201(17)	W(5)-O(6)	1.952(17)	W(8)-O(10)	1.975(18)
W(2)-O(2)	1.774(17)	W(5)-O(7)	2.083(18)	W(8)-O(11)	2.080(18)
W(2)-O(3)	1.751(15)	W(5)-O(12)	2.306(19)	W(8)-O(13)	2.357(19)
W(2)-O(4)	1.946(19)	W(5)-O(15)	1.70(2)	W(8)-O(24)	1.96(2)
W(2)-O(5)	2.259(17)	W(5)-O(16)	1.95(2)	W(8)-O(25)	1.72(2)
W(2)-O(6)	1.912(18)	W(5)-O(17)	1.95(2)	W(8)-O(26)	1.92(2)
W(2)-O(7)	2.197(18)	W(5)-O(18)	1.92(2)	W(8)-O(27)	1.91(3)
W(3)-W(8)	3.2039(18)	W(6)-O(7)	2.203(19)	Ce(1)-O(1)	2.412(16)
W(3)-O(4)	1.941(17)	W(6)-O(14)	2.27(2)	Ce(1)-O(2)	2.466(17)
W(3)-O(5)	2.213(16)	W(6)-O(16)	1.95(2)	Ce(1)-O(3)	2.496(15)
W(3)-O(8)	1.740(17)	W(6)-O(19)	1.70(2)	Ce(1)-O(8)	2.519(17)
W(3)-O(9)	1.757(17)	W(6)-O(20)	1.71(2)	Ce(1)-O(9)	2.500(17)
W(3)-O(10)	1.905(16)	W(6)-O(21)	1.92(2)	Ce(1)-O(1W)	2.68(2)
W(3)-O(11)	2.177(18)	W(7)-W(8)	3.233(2)	Ce(1)-O(2W)	2.54(2)
W(4)-O(5)	1.879(17)	W(7)-O(11)	2.262(18)	Ce(1)-O(3W)	2.48(2)
W(4)-O(7)	2.257(19)	W(7)-O(14)	2.25(2)	Ce(1)-O(4W)	2.58(2)
W(4)-O(11)	2.246(17)	W(7)-O(21)	1.94(2)	O(17)-O(18)	1.49(3)
W(4)-O(12)	1.773(18)	W(7)-O(22)	1.716(19)	O(26)-O(27)	1.49(4)
W(4)-O(13)	1.773(17)	W(7)-O(23)	1.73(2)		

Table S3. Selected bond distances of **2**

Bond	Length	Bond	Length	Bond	Length
W(1)-O(1)	1.761(16)	W(4)-O(14)	1.875(19)	W(7)-O(24)	1.94(2)
W(2)-W(5)	3.2239(14)	W(5)-O(6)	1.949(18)	W(8)-O(10)	1.967(18)
W(2)-O(2)	1.756(18)	W(5)-O(7)	2.088(16)	W(8)-O(11)	2.082(18)
W(2)-O(3)	1.746(16)	W(5)-O(12)	2.33(2)	W(8)-O(13)	2.38(2)
W(2)-O(4)	1.961(17)	W(5)-O(15)	1.71(2)	W(8)-O(24)	1.97(2)
W(2)-O(5)	2.231(17)	W(5)-O(16)	1.96(2)	W(8)-O(25)	1.71(2)
W(2)-O(6)	1.913(17)	W(5)-O(17)	1.95(2)	W(8)-O(26)	1.94(2)
W(2)-O(7)	2.179(17)	W(5)-O(18)	1.90(2)	W(8)-O(27)	1.93(3)
W(3)-W(8)	3.2031(15)	W(6)-O(7)	2.225(17)	Nd(1)-O(1)	2.404(15)
W(3)-O(4)	1.945(16)	W(6)-O14)	2.272(19)	Nd(1)-O(2)	2.449(16)
W(3)-O(5)	2.216(17)	W(6)-O(16)	1.94(2)	Nd(1)-O(3)	2.472(16)
W(3)-O(8)	1.739(17)	W(6)-O(19)	1.74(2)	Nd(1)-O(8)	2.500(17)
W(3)-O(9)	1.746(16)	W(6)-O(20)	1.744(19)	Nd(1)-O(9)	2.496(16)
W(3)-O(10)	1.907(16)	W(6)-O(21)	1.92(2)	Nd(1)-O(1W)	2.66(2)
W(3)-O(11)	2.171(18)	W(7)-W(8)	3.236(2)	Nd(1)-O(2W)	2.530(19)

W(4)-O(5)	1.902(18)	W(7)-O(11)	2.263(19)	Nd(1)-O(3W)	2.465(19)
W(4)-O(7)	2.253(18)	W(7)-O(14)	2.248(19)	Nd(1)-O(4W)	2.53(2)
W(4)-O(11)	2.258(18)	W(7)-O(21)	1.94(2)	O(17)-O(18)	1.43(3)
W(4)-O(12)	1.772(18)	W(7)-O(22)	1.719(19)	O(26)-O(27)	1.46(4)
W(4)-O(13)	1.763(18)	W(7)-O(23)	1.75(2)		

Table S4. Selected bond distances of **3**

Bond	Length	Bond	Length	Bond	Length
W(1)-O(1)	1.785(17)	W(4)-O(14)	1.88(2)	W(7)-O(24)	1.94(2)
W(2)-W(5)	3.2309(17)	W(5)-O(6)	1.98(2)	W(8)-O(10)	1.99(2)
W(2)-O(2)	1.762(18)	W(5)-O(7)	2.08(2)	W(8)-O(11)	2.09(2)
W(2)-O(3)	1.744(17)	W(5)-O(12)	2.30(2)	W(8)-O(13)	2.40(2)
W(2)-O(4)	1.959(19)	W(5)-O(15)	1.72(2)	W(8)-O(24)	1.98(2)
W(2)-O(5)	2.250(18)	W(5)-O(16)	1.96(2)	W(8)-O(25)	1.75(2)
W(2)-O(6)	1.89(2)	W(5)-O(17)	1.96(3)	W(8)-O(26)	1.93(2)
W(2)-O(7)	2.19(2)	W(5)-O(18)	1.91(3)	W(8)-O(27)	1.95(3)
W(3)-W(8)	3.2112(18)	W(6)-O(7)	2.22(2)	Sm(1)-O(1)	2.369(17)
W(3)-O(4)	1.938(19)	W(6)-O(14)	2.26(2)	Sm(1)-O(2)	2.422(18)
W(3)-O(5)	2.222(18)	W(6)-O(16)	1.97(2)	Sm(1)-O(3)	2.455(17)
W(3)-O(8)	1.733(18)	W(6)-O(19)	1.74(2)	Sm(1)-O(8)	2.477(19)
W(3)-O(9)	1.754(17)	W(6)-O(20)	1.76(2)	Sm(1)-O(9)	2.478(17)
W(3)-O(10)	1.911(19)	W(6)-O(21)	1.92(2)	Sm(1)-O(1W)	2.67(3)
W(3)-O(11)	2.168(19)	W(7)-O(11)	2.27(2)	Sm(1)-O(2W)	2.49(2)
W(4)-O(5)	1.885(19)	W(7)-O(14)	2.27(2)	Sm(1)-O(3W)	2.45(2)
W(4)-O(7)	2.27(2)	W(7)-O(21)	1.95(2)	Sm(1)-O(4W)	2.52(2)
W(4)-O(11)	2.28(2)	W(7)-O(22)	1.72(2)	O(17)-O(18)	1.43(4)
W(4)-O(12)	1.79(2)	W(7)-O(23)	1.76(2)	O(26)-O(27)	1.50(4)
W(4)-O(13)	1.75(2)				

Table S5. Selected bond distances of **4**

Bond	Length	Bond	Length	Bond	Length
W(1)-O(1)	1.786(15)	W(4)-O(14)	1.894(18)	W(7)-O(24)	1.96(2)
W(2)-W(5)	3.2242(15)	W(5)-O(6)	1.969(17)	W(8)-O(10)	1.98(2)
W(2)-O(2)	1.752(17)	W(5)-O(7)	2.099(18)	W(8)-O(11)	2.074(18)
W(2)-O(3)	1.747(17)	W(5)-O(12)	2.33(2)	W(8)-O(13)	2.39(2)
W(2)-O(4)	1.955(19)	W(5)-O(15)	1.74(2)	W(8)-O(24)	1.96(2)
W(2)-O(5)	2.232(18)	W(5)-O(16)	1.96(2)	W(8)-O(25)	1.71(2)
W(2)-O(6)	1.902(17)	W(5)-O(17)	1.94(2)	W(8)-O(26)	1.93(2)
W(2)-O(7)	2.182(19)	W(5)-O(18)	1.90(2)	W(8)-O(27)	1.93(3)
W(3)-W(8)	3.2073(16)	W(6)-O(7)	2.22(2)	Tb(1)-O(1)	2.348(15)
W(3)-O(4)	1.937(17)	W(6)-O(14)	2.24(2)	Tb(1)-O(2)	2.406(16)
W(3)-O(5)	2.226(18)	W(6)-O(16)	1.95(2)	Tb(1)-O(3)	2.444(16)

W(3)-O(8)	1.763(18)	W(6)-O(19)	1.75(2)	Tb(1)-O(8)	2.432(19)
W(3)-O(9)	1.760(16)	W(6)-O(20)	1.74(2)	Tb(1)-O(9)	2.457(16)
W(3)-O(10)	1.906(17)	W(6)-O(21)	1.93(2)	Tb(1)-O(1W)	2.66(2)
W(3)-O(11)	2.195(19)	W(7)-O(11)	2.254(19)	Tb(1)-O(2W)	2.48(2)
W(4)-O(5)	1.896(18)	W(7)-O(14)	2.27(2)	Tb(1)-O(3W)	2.44(2)
W(4)-O(7)	2.240(18)	W(7)-O(21)	1.94(2)	Tb(1)-O(4W)	2.48(2)
W(4)-O(11)	2.259(17)	W(7)-O(22)	1.73(2)	O(17)-O(18)	1.40(3)
W(4)-O(12)	1.795(19)	W(7)-O(23)	1.74(2)	O(26)-O(27)	1.45(4)
W(4)-O(13)	1.767(18)				

Table S6. Selected bond distances of **5**

Bond	Length	Bond	Length	Bond	Length
W(1)-O(1)	1.770(16)	W(4)-O(14)	1.877(19)	W(7)-O(24)	1.92(2)
W(2)-W(5)	3.2169(16)	W(5)-O(6)	1.950(18)	W(8)-O(10)	1.960(19)
W(2)-O(2)	1.767(17)	W(5)-O(7)	2.117(18)	W(8)-O(11)	2.063(18)
W(2)-O(3)	1.743(16)	W(5)-O(12)	2.31(2)	W(8)-O(13)	2.36(2)
W(2)-O(4)	1.951(18)	W(5)-O(15)	1.74(2)	W(8)-O(24)	1.98(2)
W(2)-O(5)	2.226(17)	W(5)-O(16)	1.95(2)	W(8)-O(25)	1.70(2)
W(2)-O(6)	1.899(18)	W(5)-O(17)	1.93(2)	W(8)-O(26)	1.95(2)
W(2)-O(7)	2.149(18)	W(5)-O(18)	1.94(2)	W(8)-O(27)	1.95(3)
W(3)-W(8)	3.1990(17)	W(6)-O(7)	2.237(19)	Er(1)-O(1)	2.377(16)
W(3)-O(4)	1.944(16)	W(6)-O(14)	2.23(2)	Er(1)-O(2)	2.427(17)
W(3)-O(5)	2.226(16)	W(6)-O(16)	1.94(2)	Er(1)-O(3)	2.460(17)
W(3)-O(8)	1.731(18)	W(6)-O(19)	1.74(2)	Er(1)-O(8)	2.488(18)
W(3)-O(9)	1.776(17)	W(6)-O(20)	1.72(2)	Er(1)-O(9)	2.456(17)
W(3)-O(10)	1.885(17)	W(6)-O(21)	1.91(2)	Er(1)-O(1W)	2.67(2)
W(3)-O(11)	2.162(18)	W(7)-O(11)	2.278(19)	Er(1)-O(2W)	2.51(2)
W(4)-O(5)	1.891(17)	W(7)-O(14)	2.27(2)	Er(1)-O(3W)	2.45(2)
W(4)-O(7)	2.250(19)	W(7)-O(21)	1.95(2)	Er(1)-O(4W)	2.50(2)
W(4)-O(11)	2.245(17)	W(7)-O(22)	1.745(19)	O(17)-O(18)	1.41(3)
W(4)-O(12)	1.784(19)	W(7)-O(23)	1.75(2)	O(26)-O(27)	1.53(4)
W(4)-O(13)	1.778(19)				

Section 4 The bond valence sum calculations

Table S7. The BVS calculation results of all the oxygen atoms in **1**−**5**

Atom	BVS				
	1	**2**	**3**	**4**	**5**
O1	1.97	1.97	1.90	1.85	1.86
O2	1.90	1.94	1.93	1.93	1.82
O3	1.99	1.95	1.97	1.91	1.89
O4	1.86	1.82	1.84	1.85	1.84
O5	1.95	1.92	1.94	1.92	1.94
O6	1.92	1.93	1.92	1.91	1.96
O7	1.97	1.96	1.95	1.96	1.95
O8	1.98	1.96	1.99	1.86	1.92
O9	1.93	1.94	1.90	1.85	1.76
O10	1.88	1.90	1.84	1.87	1.98
O11	1.94	1.93	1.89	1.92	1.98
O12	1.83	1.81	1.76	1.89	1.78
O13	1.78	1.80	1.84	1.77	1.76
O14	1.92	1.91	1.89	1.87	1.93
O15	1.79	1.75	1.67	1.65	1.62
O16	1.83	1.83	1.76	1.80	1.85
O17	0.87	0.91	0.90	0.94	0.97
O18	0.96	1.04	1.02	1.05	0.94
O19	1.79	1.61	1.61	1.59	1.62
O20	1.75	1.60	1.52	1.61	1.71
O21	1.93	1.93	1.92	1.90	1.92
O22	1.72	1.71	1.71	1.65	1.60
O23	1.66	1.57	1.53	1.61	1.56
O24	1.86	1.81	1.78	1.78	1.84
O25	1.69	1.74	1.59	1.77	1.78
O26	1.00	0.94	0.97	0.97	0.91
O27	1.01	0.96	0.82	0.97	0.90
O1W	0.24	0.22	0.20	0.18	0.17
O2W	0.35	0.32	0.34	0.30	0.25
O3W	0.41	0.38	0.38	0.33	0.30
O4W	0.31	0.31	0.31	0.30	0.26

Table S8. The BVS calculation results of W and Ln in **1−5**

Atom	BVS				
	1	2	3	4	5
W1	5.90	6.09	5.71	5.69	5.97
W2	5.96	5.95	5.97	6.00	6.03
W3	6.06	6.11	6.10	5.93	6.09
W4	6.00	5.96	5.94	5.83	5.90
W5	6.51	6.47	6.35	6.30	6.28
W6	6.30	5.96	5.84	5.92	6.14
W7	6.08	5.96	5.86	5.89	5.83
W8	6.40	6.32	6.01	6.35	6.33
Ln1	3.38	3.13	3.17	2.89	2.56

Table S9. The bond valence sum range of all the oxygen atoms on **1−5**

BVS range	Number				
	1	**2**	**3**	**4**	**5**
1.9~2.0	44	44	36	28	32
1.7~1.9	40	36	36	44	44
1.5~1.7	8	12	20	20	16
0.6~1.2	16	16	16	16	16
<0.6	16	16	16	16	16

The bond-valence sum calculations show that all W, and Ln centers are in the +6, and +3 oxidation states, respectively. To balance the charges of **1−5**, thirty-two protons should be added, respectively. In order to locate these protons accurately, the bond valence sum calculations of all the oxygen atoms on POM fragments are carried out (Table S7). According to the results in Table S9, the oxidation states 124 O atoms in $[Ln_4(WO_4)(H_2O)_{16}\{W_7O_{22}(O_2)_2\}_4]^{14-}$ of **1−5** can be divided into 5 groups according to their bond valence sums. So, the multiply protons cannot be located in polyoxometalates units by X-ray diffraction, and this assumption is reasonable in consideration of rich basic surface oxygen atoms and the high negative charges of polyoxoanion. Moreover, the phenomenon of multiple protons delocalized on the whole polyoxoanions is very common in POM chemistry.[8]

Section 5 Experimental Section

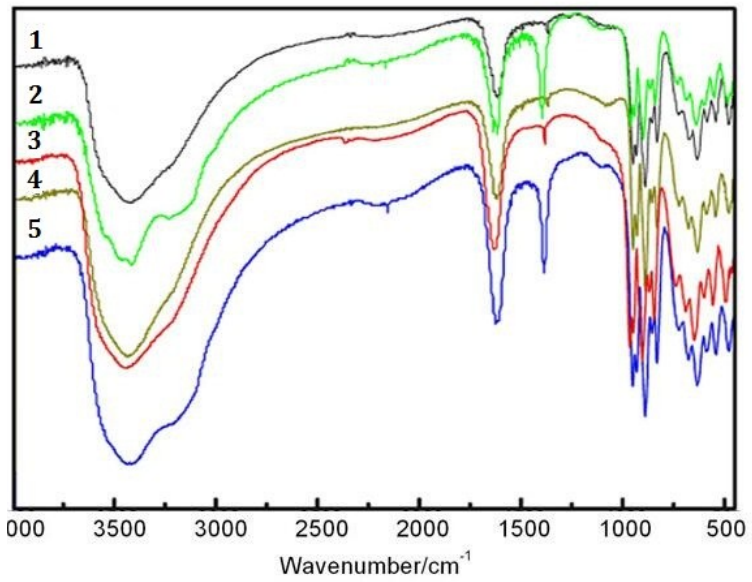


Figure S2. IR spectrum of **1−5**

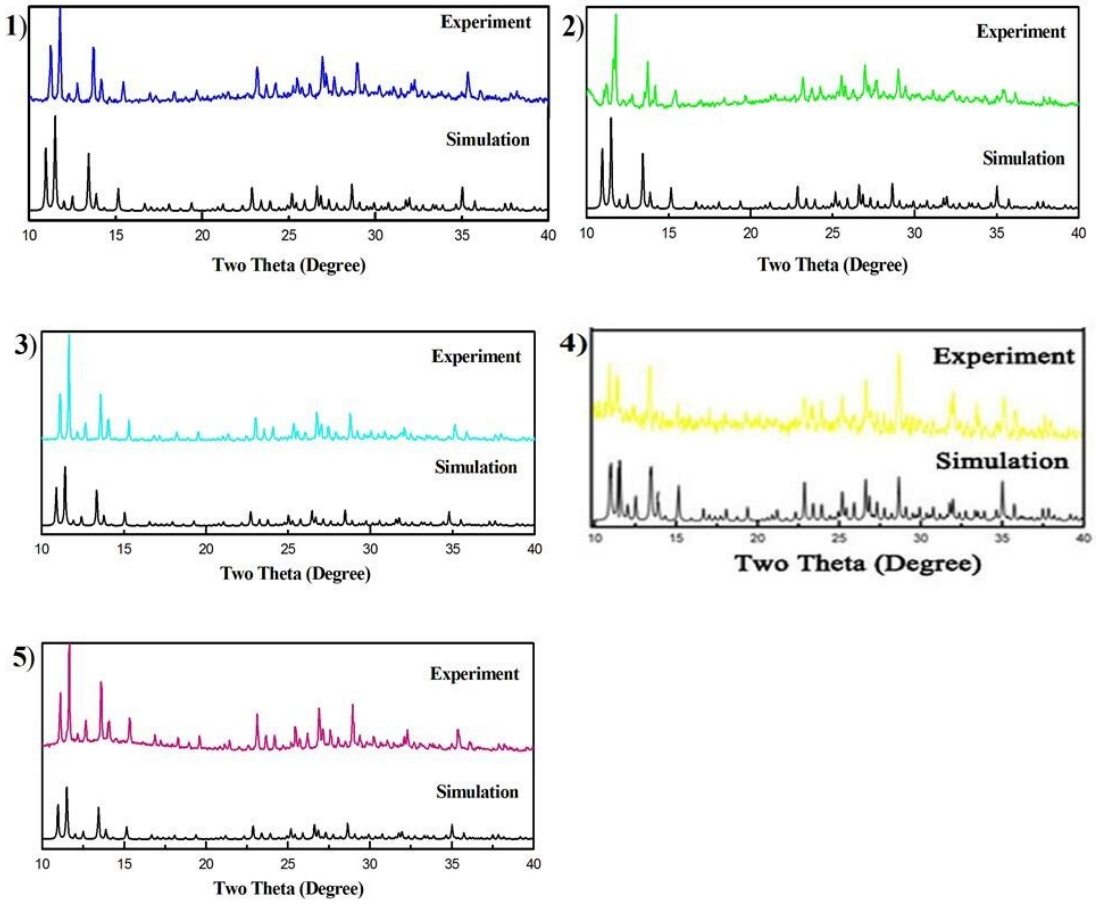


Figure S3. The experimental and simulated XRPD pattern of **1**−**5**.

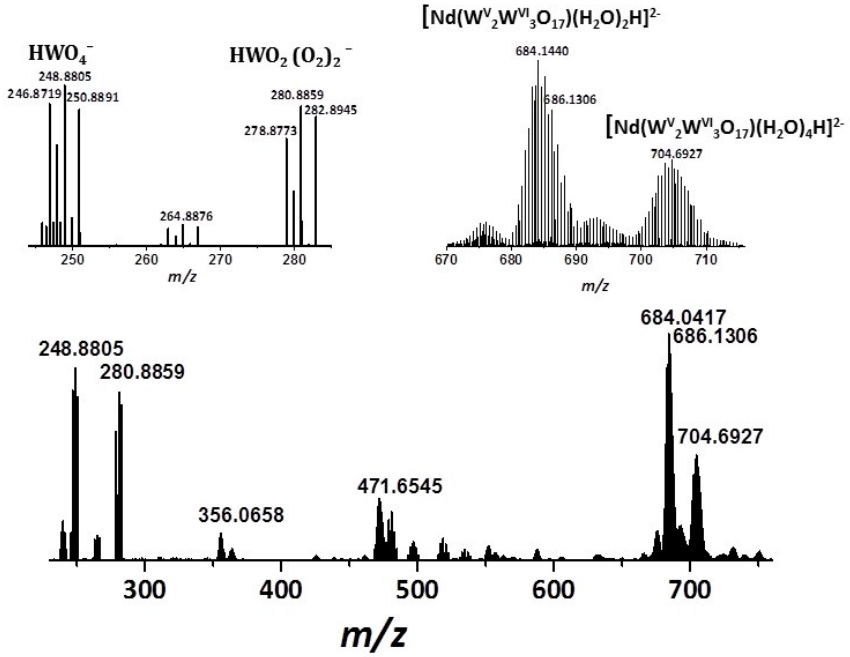


Fig. S4. The negative-mode ESI mass spectrum in water solution of **2** in the m/z=230-940 range

Table S10. Detected species in the electrospray mass spectrum of 2

m/z		peak assignment
experimental	calculated	
248.8805	248.8455	HWO_4^-
280.8859	280.8443	$HWO_2(O_2)_2^-$
686.1306	686.2351	$[Nd(W^V_2W^{VI}_3O_{17})(H_2O)_2H]^{2-}$
704.6927	704.2505	$[Nd(W^V_2W^{VI}_3O_{17})(H_2O)_4H]^{2-}$

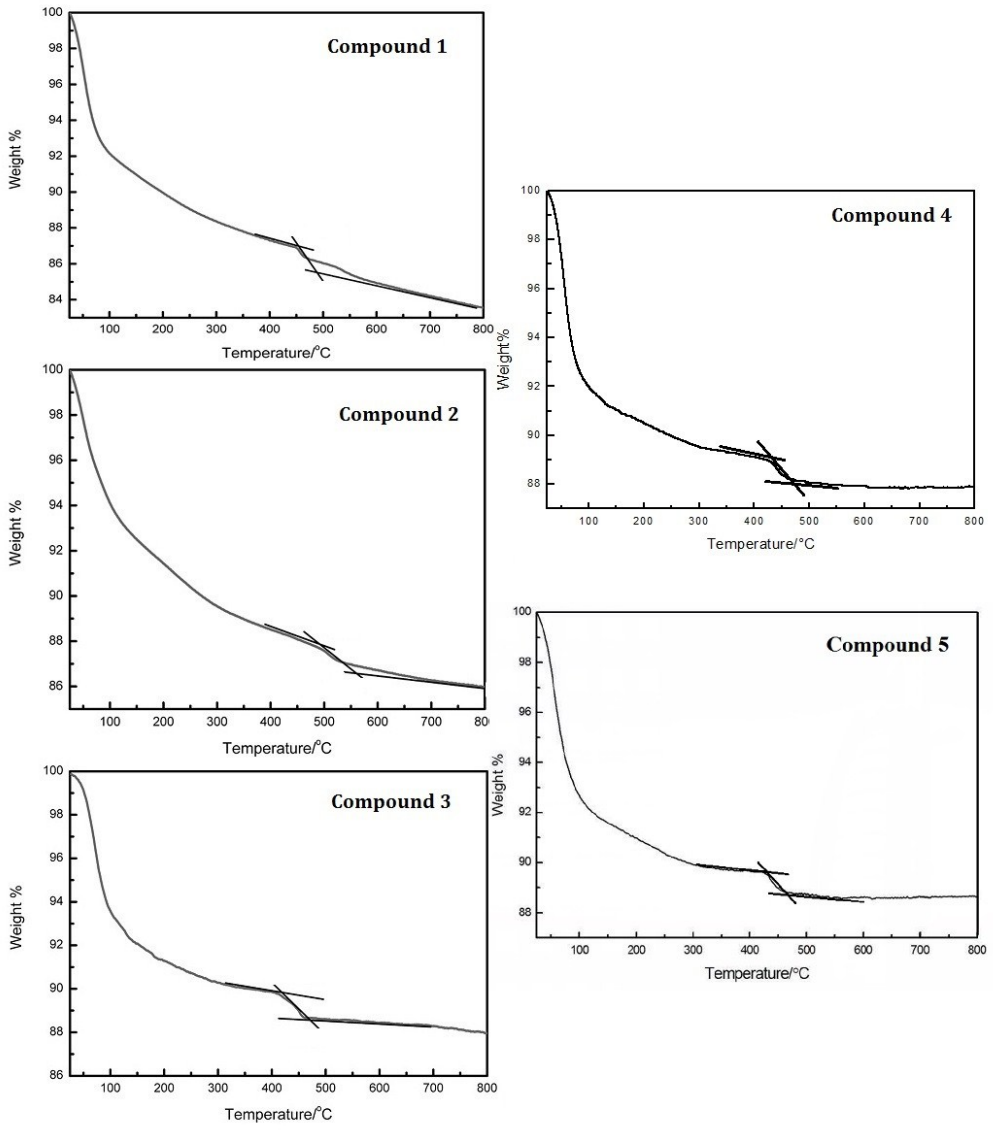


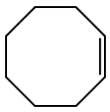
Figure S5. TG curve of **1**−**5** in a N_2 atmosphere in the range of 25–800 ºC.

Thermal gravimetric analyses (TGA) were performed under N_2 atmosphere from 25 to 800 ºC (Fig. S6). All the compounds display two weight loss steps. In the case of **1**, the first weight loss of 12.97% (calcd. 11.71 %) is from 25 to 455 ºC, which is assigned to the liberation of about 105 crystal water molecules, 48 coordinated water molecules and the dehydration of 32 protons. The second weight loss of 1.47% (calcd. 1.48%) from 455 to 490 ºC corresponds to the removal of one oxygen atom in each peroxo group. For **2**, the first weight loss of 12.07% (calcd. 11.69 %) is from 25 to 490 ºC, which is assigned to the liberation of about 105 crystal water molecules, 48 coordinated water molecules and the dehydration of 32 protons. The second weight loss of 1.35% (calcd. 1.47%) from 490 to 560 ºC corresponds to the removal of one oxygen atom in each peroxo group. For **3**, the first weight loss of 10.12% (calcd. 11.65 %) is from 25 to 415 ºC, which is assigned to the liberation of about 105 crystal water molecules, 48 coordinated water molecules and the dehydration of 32 protons. The second weight loss of 1.36% (calcd. 1.47%) from 415 to 460 ºC corresponds to the removal of one oxygen atom in each peroxo group. For **4**, the first

weight loss of 11.72% (calcd. 11.61 %) is from 25 to 430 ºC, which is assigned to the liberation of about 105 crystal water molecules, 48 coordinated water molecules and the dehydration of 32 protons. The second weight loss of 1.32% (calcd. 1.46%) from 430 to 475 ºC corresponds to the removal of one oxygen atom in each peroxo group. For **5**, the first weight loss of 11.30% (calcd. 11.56 %) is from 25 to 425 ºC, which is assigned to the liberation of about 105 crystal water molecules, 48 coordinated water molecules and the dehydration of 32 protons. The second weight loss of 1.37% (calcd. 1.46%) from 425 to 470 ºC corresponds to the removal of one oxygen atom in each peroxo group.

Section 6 Catalytic properties

Table S11. Epoxidation of cyclooctene with H_2O_2 under different conditions.

Entry	catalyst	Substrate	Solvent	Conversion (%)[b]
1	**2**		acetonitrile	95.8
2	$Nd(NO_3)_3 \cdot 6H_2O$		acetonitrile	4.1
3	$Na_2WO_4 \cdot 2H_2O$		acetonitrile	3.9
4	**2**		ethanol	48.3
5	**2**		chloroform	4.3
6	**2**		dichloromethane	3.7
7	**2**		ethyl acetate	6.5

[a] Reaction conditions: catalyst (1 μmol); cyclooctene (1 mmol); H_2O_2 (2 mmol); solvent (5 mL); Time (1.5h). [b] Determined by gas chromatography (GC) analyses based on initial substrate.

Table S12. Catalytic results for the oxidation of cyclohexene in the presence of different POM catalysts.

Entry	Catalyst	Time (h)	Solvent	Conv. (yields) (%)	Ref.
1	$[\gamma\text{-}SiW_{10}O_{34}]^{4-}$	2	CH_3CN	99	9
2	$[\gamma\text{-}1,2\text{-}H_2SiV_2W_{10}O_{40}]^{4-}$	24	CH_3CN/t BuOH	93	10
3	PW_{12}	5	CH_3CN	78	11
4	PW_{12}/MIL-101	5	CH_3CN	76	11
5	$[Fe^{III}_2(NaOH_2)_2(P_2W_{15}O_{56})_2]^{16-}$	30	CH_3CN	98	12
6	$[(PO_4)\{WO(O_2)_2\}_4]^{3-}$	3	C_6H_6	99	13
7	$[(PO_4)\{WO(O_2)_2\}_2\{WO(O_2)_2(H_2O)\}]^{3-}$	3	C_6H_6	93	13
8	$K_{11}[Pr\{PW_{11}O_{39}\}_2]$	3	*tert*-Butanol	79	13
9	$K_{11}[Sm\{PW_{11}O_{39}\}_2]$	3	*tert*-Butanol	81	13
10	*Cetyl*-PrW_{10}	6	$CHCl_3$	29.5	14

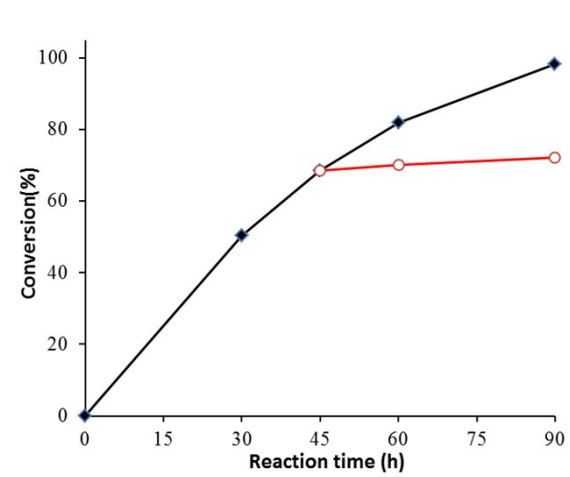


Figure S6. The effect of reaction time on the conversion over (The reaction results in red line after 45min was conducted with catalyst removed).

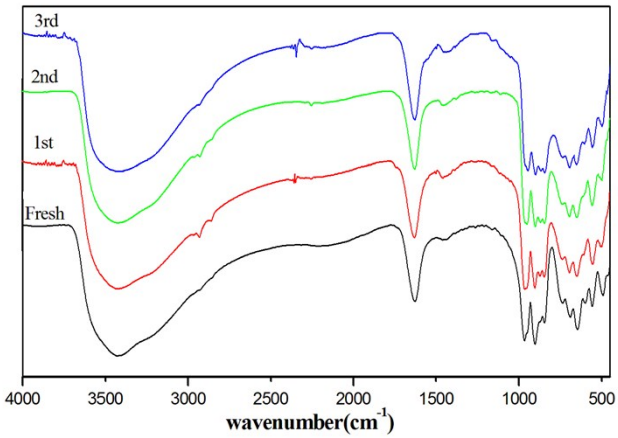


Figure S7. IR spectra of **2** before and after the recycling tests

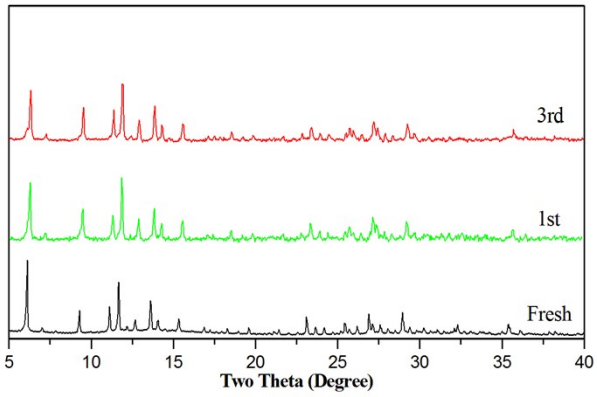


Figure S8.The XRPD of **2** before and after the recycling tests

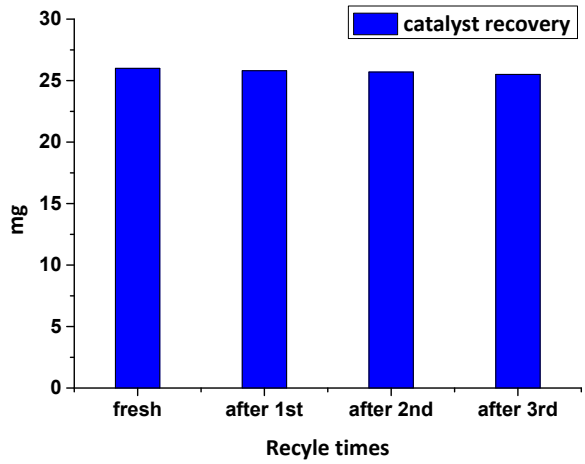


Figure S9. The weight of the catalyst **2** recycling for epoxidation of cyclooctene. Reaction conditions: catalyst (1 μmol); cyclooctene (1 mmol); H_2O_2 (2 mmol); MeCN (5 mL); reaction temperature (75 °C); time (1.5h).

Section 7 References

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