Supplementary Information

$[Ni(C_{17}H_{20}N_4)_4][H_5PMo^{VI}_8V^{IV}_4O_{40}(V^{IV}O)_2]\cdot 8H_2O$: confinement of heteropoly anions in Ni-containing rigid concave surfaces with high catalytic activity in the oxidation of styrene

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Contents:

Details for catalytic activity experiments:

The oxidation of styrene was performed in a 50 ml double necked round bottom flask fitted in a water cooled condenser and a magnetic stirrer. 13 mmol styrene, 15 ml solvent (CH_3CN) and 100 mg title compound were mixed in the flask and kept the temperature at 333 K, then 36 mmol dilute hydrogen peroxide (30%) was added to the flask. The mixture was analyzed by a gas chromatograph (GC-6890, FID; 30 m × 0.32 mm capillary column) after 3h reaction. The major products obtained were benzaldehyde and small amount of epoxide and benzoic acid with the conversion of styrene was 90% and the selectivity of benzaldehyde, epoxide and benzoic acid in the oxidation of styrene were 69.7%, 3.9% and 26.4%, respectively.

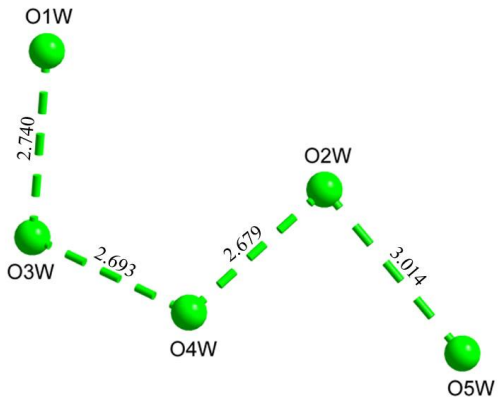


Fig. S1 A view of the discrete acyclic water pentamer in **1**.

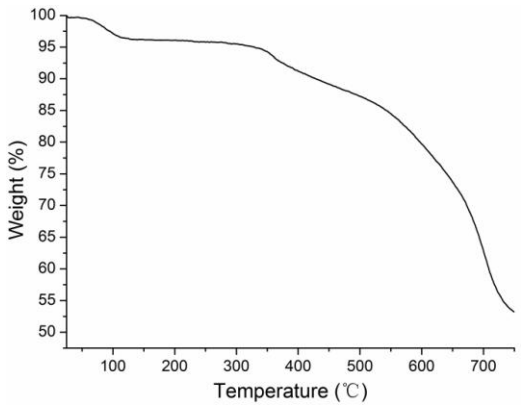
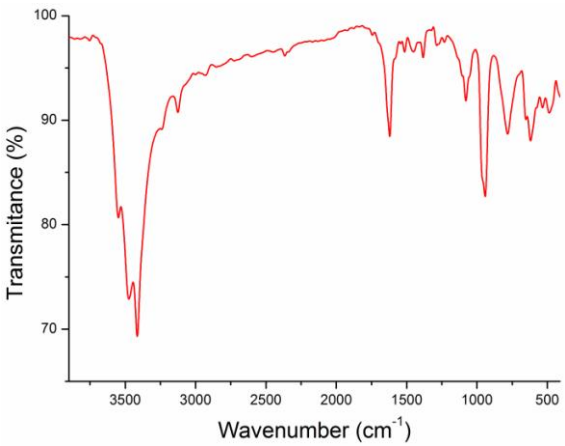


Fig. S2 The TG curve of compound **1**.



IR spectrum: 3414cm^{-1}, ν(O-H); 1619 cm^{-1},1383 cm^{-1}, ν(C-C), ν(C-N); 1081 cm^{-1}, ν(P-O); 940 cm^{-1}, ν(Mo=O); 781 cm^{-1}, ν(Mo-O-Mo); 620 cm^{-1}, ν(Mo-O)

Fig. S3 IR spectra of compound **1**.

Table S1 The O···O distances and O···O···O angles in water pentamer of **1**.

O1W···O3W	2.740(14)Å	O4W···O2W	2.679(10)Å
O3W···O4W	2.693(78)Å	O2W···O5W	3.014(13)Å
O1W···O3W···O4W	101.136(376)°	O4W···O2W···O5W	86.623(337)°
O3W···O4W···O2W	101.608(308)°		

Table S2 Selected bond lengths (Å) for 1

Mo(1)-O(15)	1.690(3)	Ni(1)-N(5)#1	2.098(4)
Mo(1)-O(7)	1.788(3)	Ni(1)-N(5)	2.098(4)
Mo(1)-O(13)	1.827(3)	Ni(1)-O(19)#2	2.105(4)
Mo(1)-O(18)#1	2.056(2)	Ni(1)-O(21)	2.113(4)
Mo(1)-O(22)	2.064(3)	V(1)-O(1)	1.606(4)
Mo(1)-O(17)	2.436(3)	V(1)-O(6)	1.932(3)
Mo(2)-O(9)	1.697(3)	V(1)-O(7)#1	1.944(3)
Mo(2)-O(6)	1.792(3)	V(1)-O(16)	1.954(3)
Mo(2)-O(14)	1.815(3)	V(1)-O(12)#1	1.971(3)
Mo(2)-O(18)	2.071(2)	V(2)-O(2)	1.594(3)
Mo(2)-O(22)	2.085(3)	V(2)-O(14)	1.934(3)

Mo(2)-O(17)	2.437(3)	V(2)-O(11)	1.940(3)
Mo(3)-O(4)	1.695(3)	V(2)-O(10)	1.944(3)
Mo(3)-O(11)	1.798(3)	V(2)-O(13)	1.953(3)
Mo(3)-O(12)	1.800(3)	V(3)-O(21)	1.621(4)
Mo(3)-O(8)#1	2.049(2)	V(3)-O(20)	1.895(2)
Mo(3)-O(20)	2.082(3)	V(3)-O(20)#1	1.895(2)
Mo(3)-O(5)#1	2.459(2)	V(3)-O(8)#1	1.976(3)
Mo(4)-O(3)	1.695(3)	V(3)-O(8)	1.976(3)
Mo(4)-O(10)	1.792(3)	V(4)-O(19)	1.622(4)
Mo(4)-O(16)	1.831(3)	V(4)-O(18)	1.894(3)
Mo(4)-O(20)	2.047(3)	V(4)-O(18)#1	1.894(3)
Mo(4)-O(8)	2.070(2)	V(4)-O(22)#1	1.979(2)
Mo(4)-O(5)	2.440(3)	V(4)-O(22)	1.979(2)
P(1)-O(5)	1.534(3)	O(5)-Mo(3)#1	2.459(2)
P(1)-O(5)#1	1.534(3)	O(7)-V(1)#1	1.944(3)
P(1)-O(17)	1.537(3)	O(8)-Mo(3)#1	2.049(2)
P(1)-O(17)#1	1.537(3)	O(12)-V(1)#1	1.971(3)
Ni(1)-N(4)#1	2.082(4)	O(18)-Mo(1)#1	2.056(2)
Ni(1)-N(4)	2.082(4)	O(19)-Ni(1)#3	2.105(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z-1/2 #2 x,y-1,z #3 x,y+1,z