Supplementary Materials

Two diphosphonate-functionalized asymmetric polyoxomolybdates with catalytic activity for oxidation of benzyl alcohol to benzaldehyde

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Experimental Section

Synthesis of TBA-1

2.6485 g (1.50 mmol) of compound **1** was dissolved in 40 ml distilled water with stirring, and then 2.9102 g (9.00 mmol) tetrabutylammonium bromide was added. The mixture was stirred for 10 mins. The clear solution was kept at room temperature for slow evaporation. White precipitates were isolated after one week. The precipitate is collected on a sintered glass funnel, washed with 10 ml cold water, and finally dried in air. (yield 45 % based on compound **1**). Anal. Found (%): C, 36.67; N, 3.53; Na, 1.64; Mo, 24.32; P, 5.10. IR (KBr pellet): ν = 3456 (s), 2968 (s), 2873 (s), 2112 (m), 1642 (s), 1505 (m), 1469 (m), 1386 (m), 1160 (s), 1070 (s), 1023 (m), 922 (s), 826 (m), 743 (s), 684 (m), 648 (m), 529 (m), and 485 (w) cm^{-1}.

Synthesis of TBA-2

4.2143 g (1.50 mmol) of compound **2** was dissolved in 30 ml distilled water with stirring, and then 3.8676 g (12.00 mmol) tetrabutylammonium bromide was added. The mixture was stirred for 10 mins. The clear solution was kept at room temperature for slow evaporation. White precipitates were isolated after five days. The precipitate is collected on a sintered glass funnel, washed with 10 ml cold water, and finally dried

in air. (yield 60 % based on compound **2**). Anal. Found (%): C, 25.41; N, 4.13; Na, 0.54; Mo, 27.70; P, 5.76. IR (KBr pellet): ν = 3436 (s), 3197 (s), 2953 (s), 2875 (s), 1621 (m), 1520 (w), 1460 (m), 1409 (w), 1162 (m), 1126 (m), 1060 (s), 1030 (s), 923 (s), 887 (s), 792 (s), 696 (s), 660 (m), 553 (m), and 469 (w) cm^{-1}.

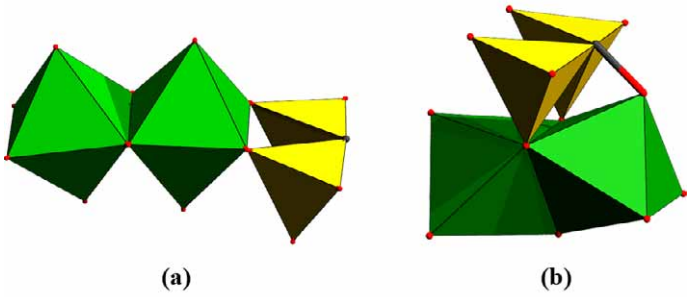


Fig. S1 Polyhedral and ball/stick drawing of $\{(Mo^{V}_2O_4)(O_3PXPO_3)\}$ (a), $\{(Mo_2O_6)(RC(O)(PO_3)_2\}$ (b) units.

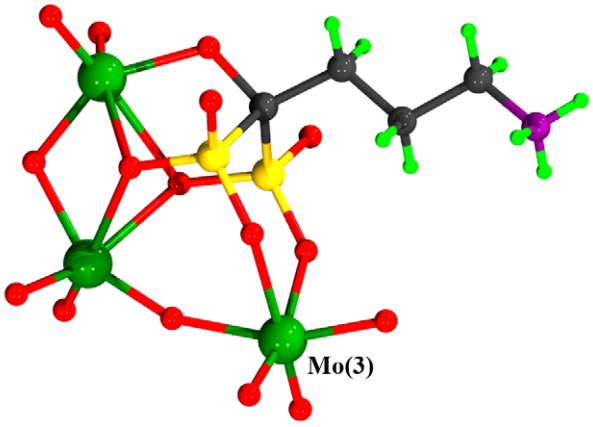


Fig. S2 The ball/stick drawing of the fragment $\{MoO_3[(Mo_2O_6)NH_3CH_2CH_2$-$CH_2C(O)(PO_3)_2]\}$.

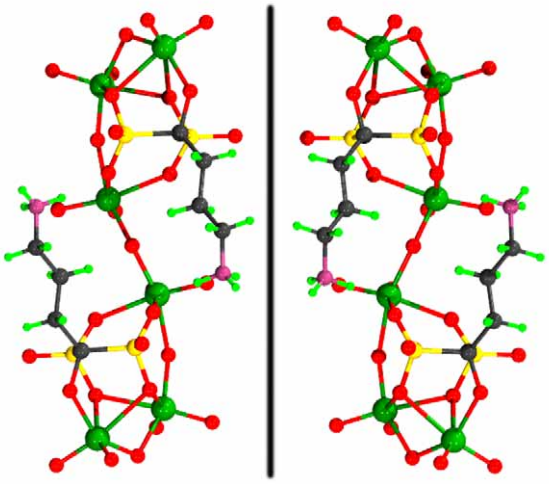


Fig. S3 Ball-and-stick representation of two enantiomers of polyoxoanion **1**.

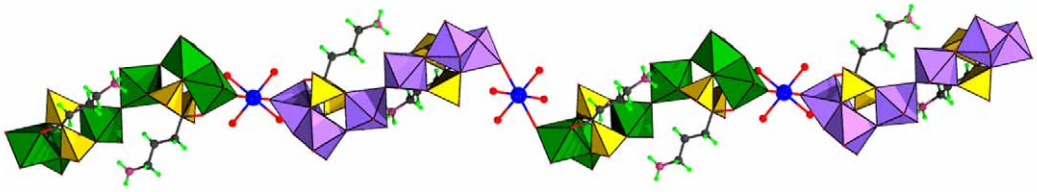


Fig. S4 Polyhedral and ball-and-stick representation of the R- and S- polyoxoanions **1** are alternately arranged and connected by Na^{+} cations to 1D chain.

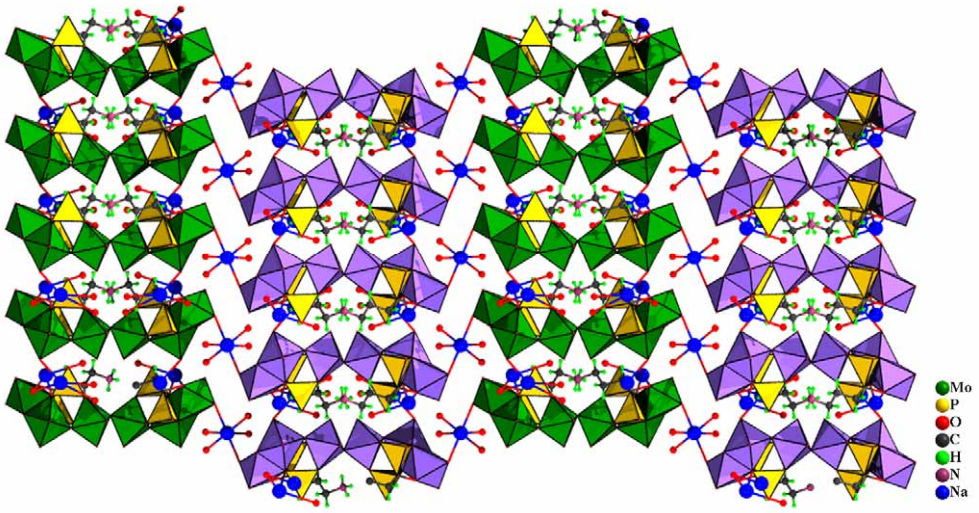


Fig. S5 Polyhedral and ball-and-stick representation of the 3D framework in compound **1** viewed from a axis.

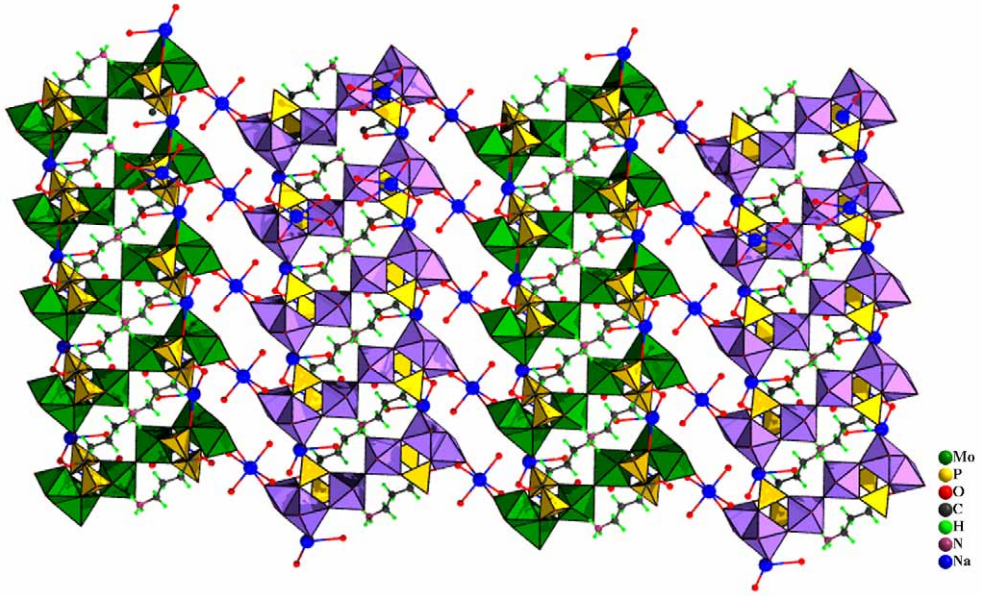


Fig. S6 Polyhedral and ball-and-stick representation of the 3D framework in compound **1** viewed from b axis.

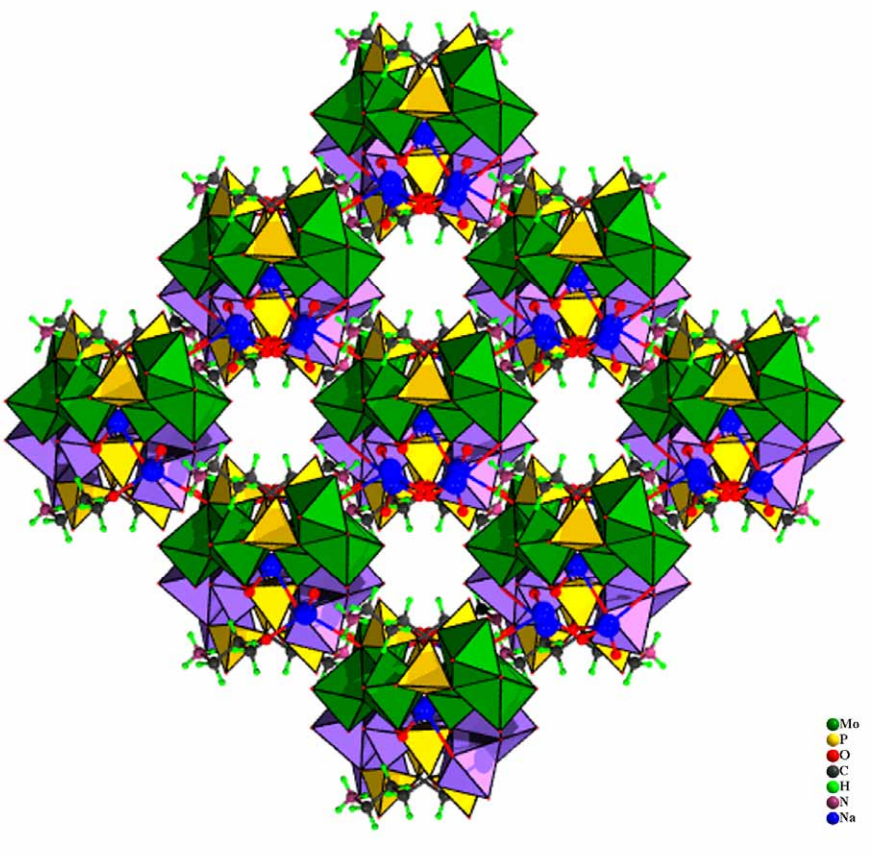


Fig. S7 Polyhedral and ball-and-stick representation of the 3D framework in compound **1** viewed from c axis.

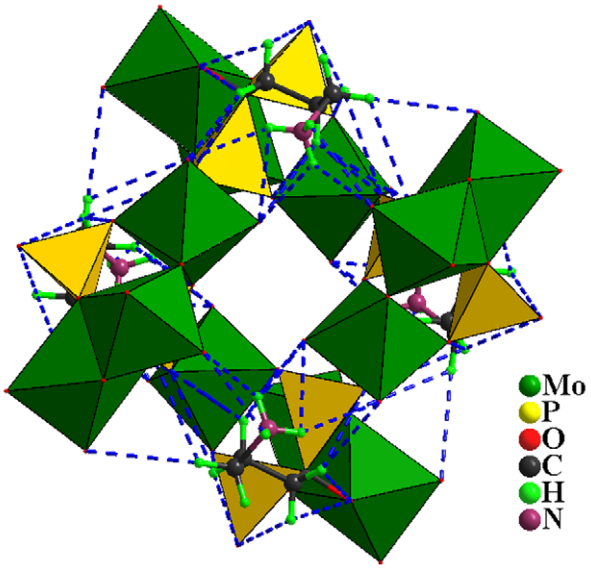


Fig. S8 The intramolecular hydrogen bonds between alkyls and oxygen atoms of polyoxoanion in compound 2.

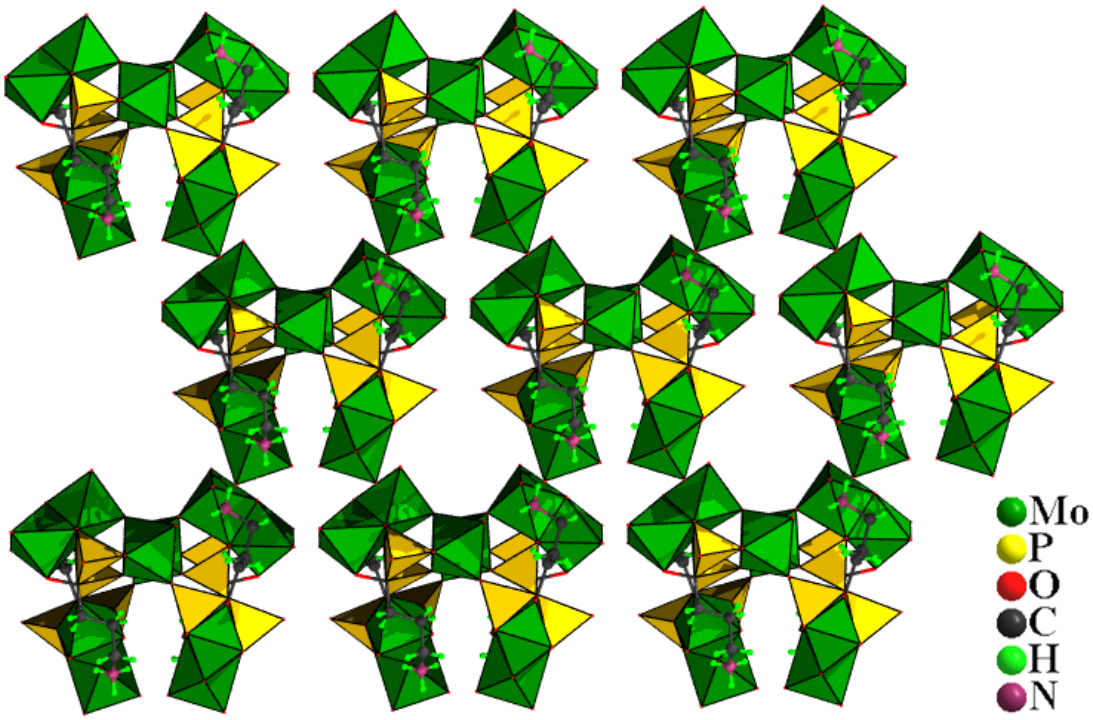


Fig. S9 Polyhedral and ball-and-stick representation of 3D supramolecular structure in compound **2** viewed from a axis.

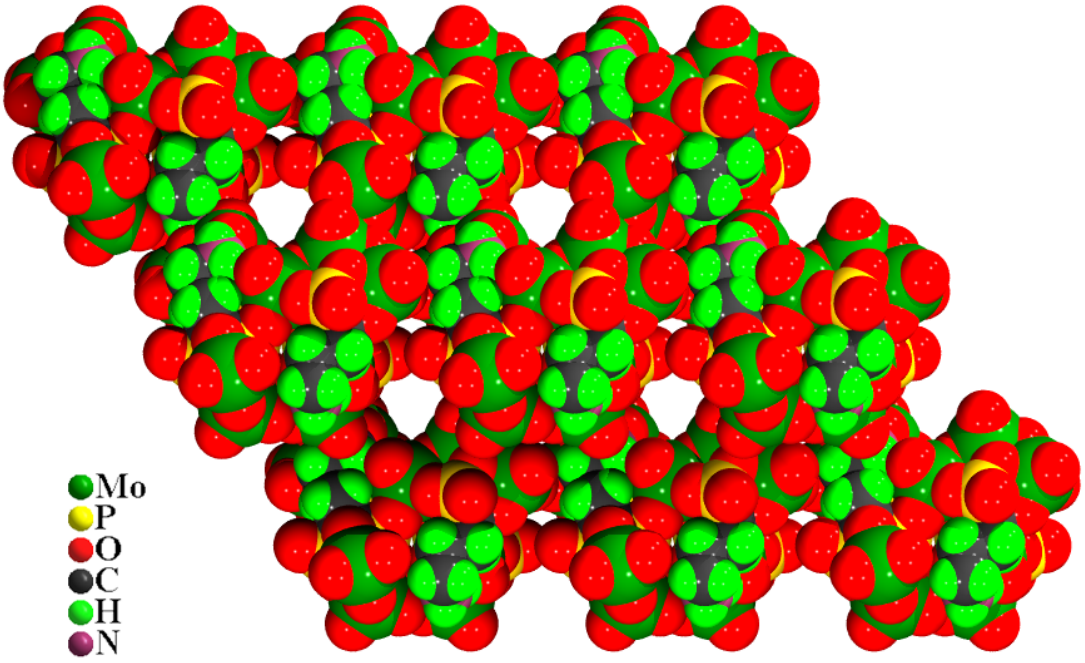


Fig. S10 A polyhedral space-filling diagram of 3D supramolecular structure in compound **2** with approximately channels along b xis.

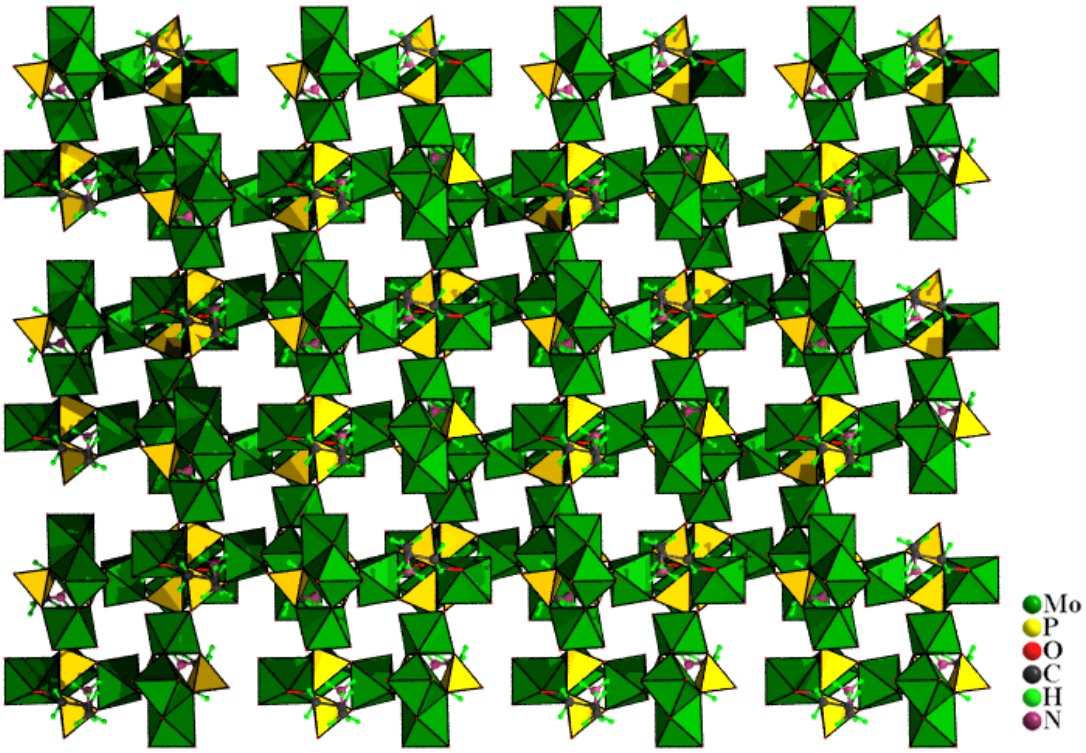
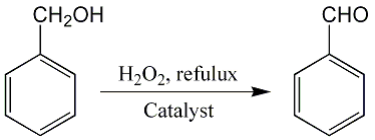


Fig. S11 Polyhedral and ball-and-stick representation of 3D supramolecular structure in compound **2** viewed from c axis.

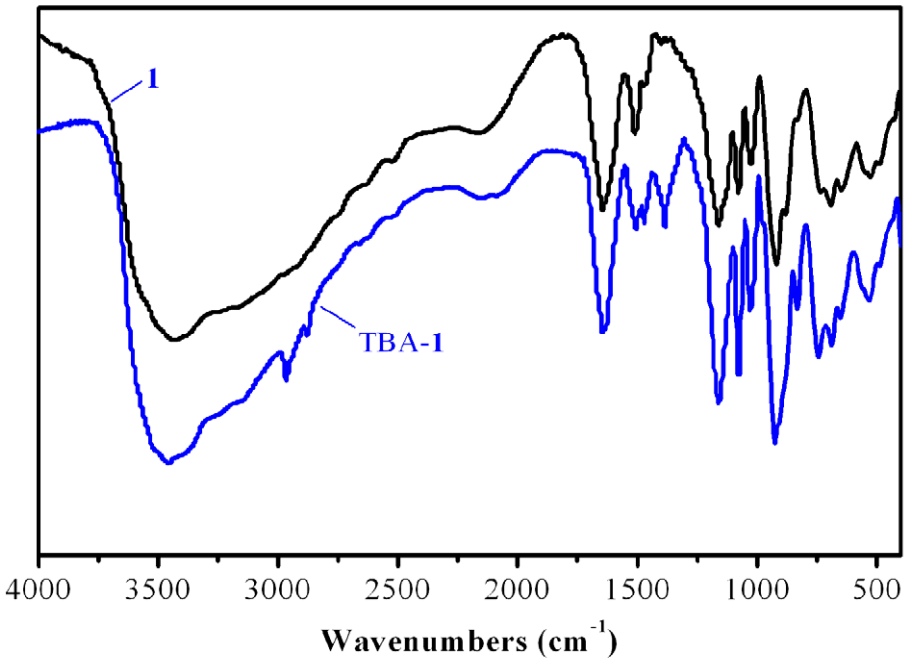
Fig. S12 Different stages of the probe reactions: (a) Before reaction; (b) at the end of reaction (H_2O_2 was unused up); (c) the end of reaction after adding 10 ml of ether.

Table S1. Oxidation of benzyl alcohol to benzaldehyde with hydrogen peroxide

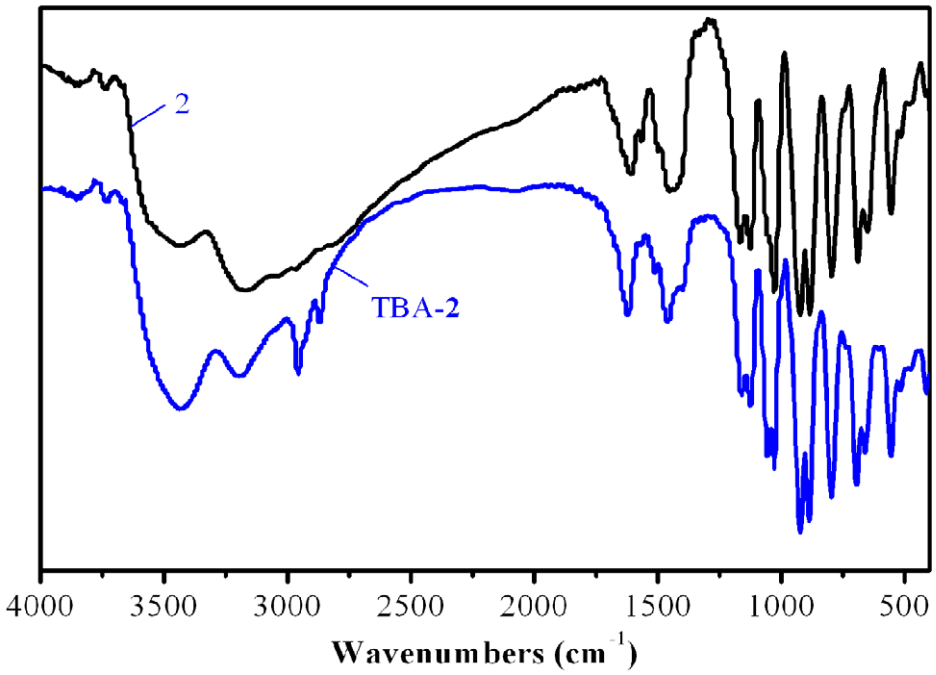


Entry	Catalyst	Amount of catalyst/g	$C_6H_5CH_2OH/H_2O_2$ molar ratio	Reaction time/h	Conversion (%)	Selectivity (%)
1	TBA-1[a]		1:1.6	4.3	10.6	51.9
2		0.1	1:1.6	0.5	28.8	93.6
3		0.1	1:1.6	1.0	40.2	91.2
4		0.1	1:1.6	2.0	55.2	89.5
5		0.1	1:1.6	4.3	72.5	87.1
6	Recycled 1	0.1	1:1.6	4.3	56.5	74.9
7	Recycled 2	0.1	1:1.6	4.3	55.2	74.0
8	TBA-2[a]		1:2	5.5	15.5	49.4
9		0.2	1:2	1.0	48.7	94.6
10		0.2	1:2	2.0	61.3	88.8
11		0.2	1:2	4.0	74.8	84.2
12		0.2	1:2	5.5	81.5	82.4
13	Recycled 1	0.2	1:2	5.5	72.6	62.4
14	Recycled 2	0.2	1:2	5.5	70.8	66.3

[a] Reaction conditions: 2.0 ml (20 mmol) of benzyl alcohol, aqueous 30% hydrogen peroxide, reflux

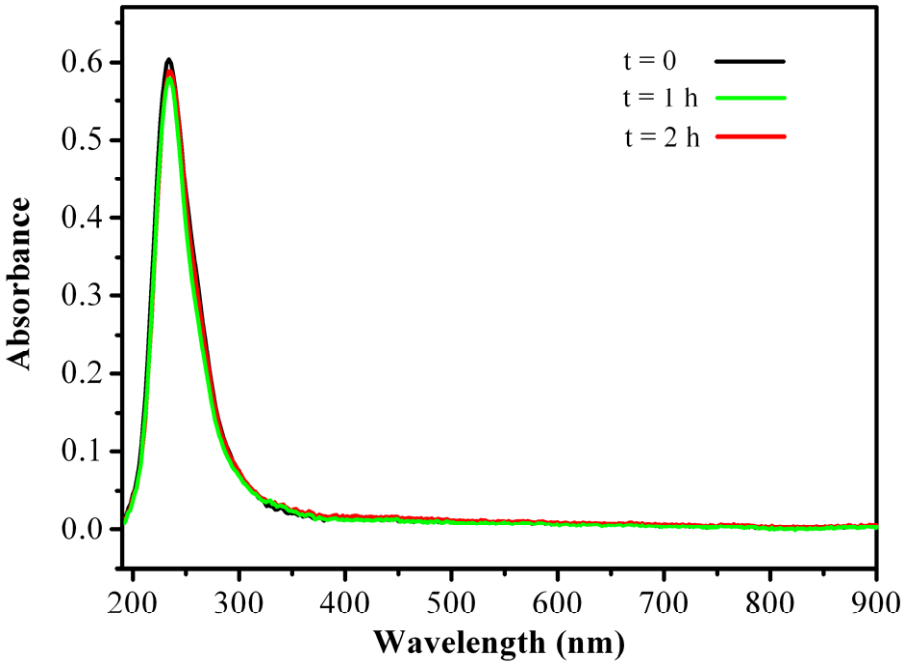


(a)

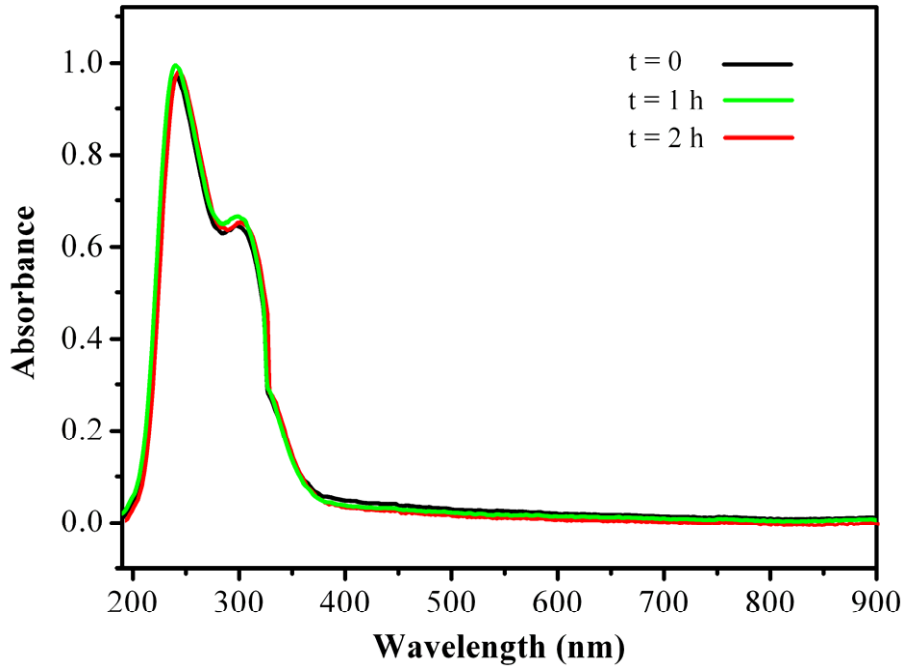


(b)

Fig. S13 IR spectrum for compounds **1** (a), **2** (b).



(a)



(b)

Fig. S14 The UV-Vis spectrum for compounds **1** (a) and **2** (b) in aqueous solution.

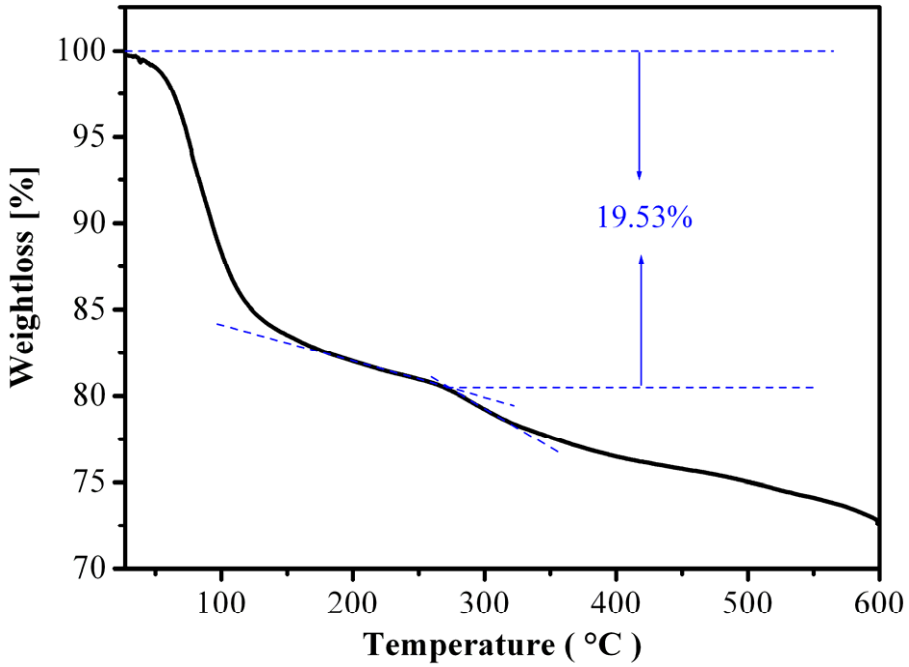


Fig. S15 The TG curve of **1** exhibits two weight loss stages in the temperature ranges 30-600°C. The first weight loss is 19.53% in the temperature range 30-270°C, corresponding to the release of all the lattice and coordinated water molecules in **1**. And after 270°C, polyoxoanion **1** would be decomposed.

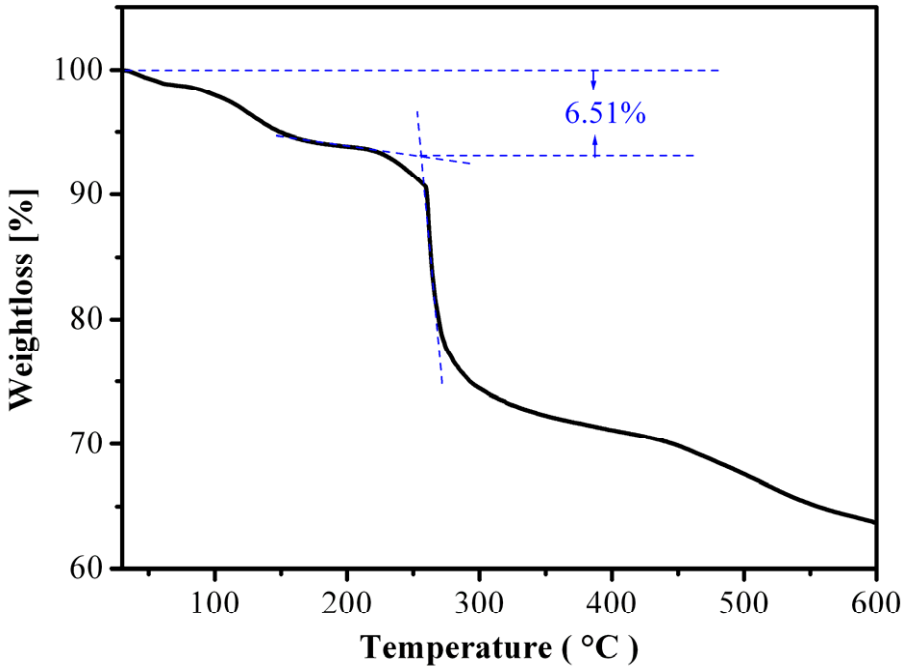


Fig. S16 The TG curve of **2** exhibits three weight loss stages in the temperature ranges 30-600°C. The first and secondary weight loss is 6.51% in the temperature range 30-257°C, corresponding to the release of all the NH_4^+ ions and lattice water molecules in **2**. And after 257°C, polyoxoanion **2** would be decomposed.

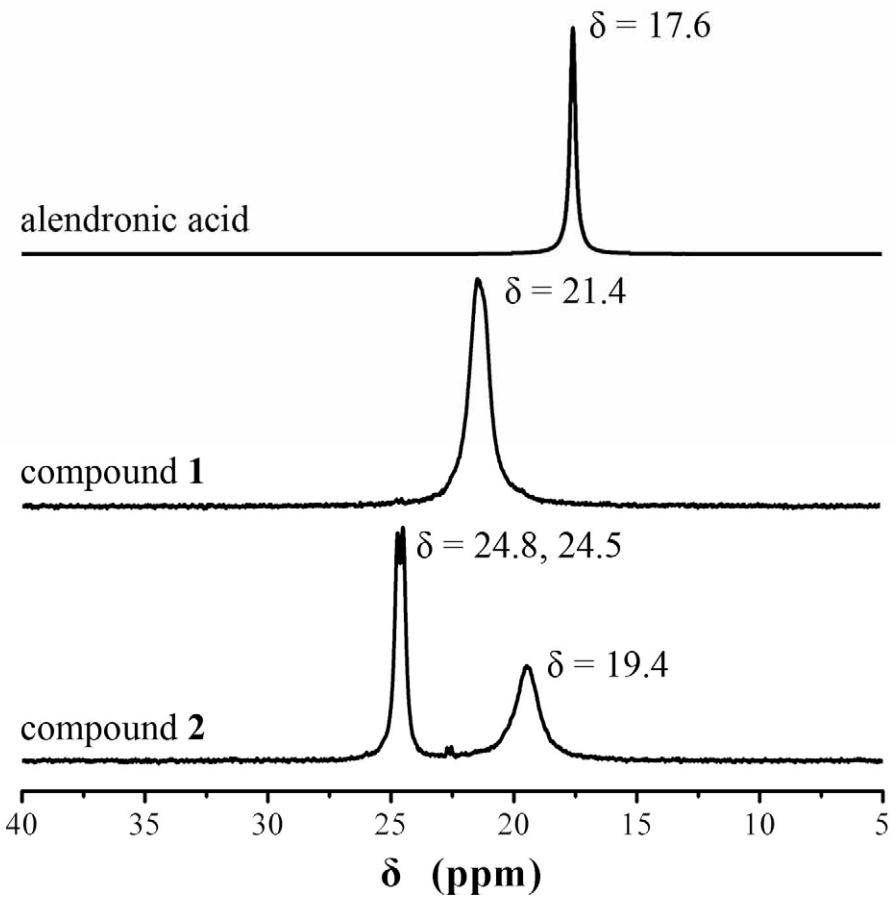


Fig. S17 The ^{31}P NMR spectrum of pure alendronic acid, compounds **1** and **2** in D_2O.

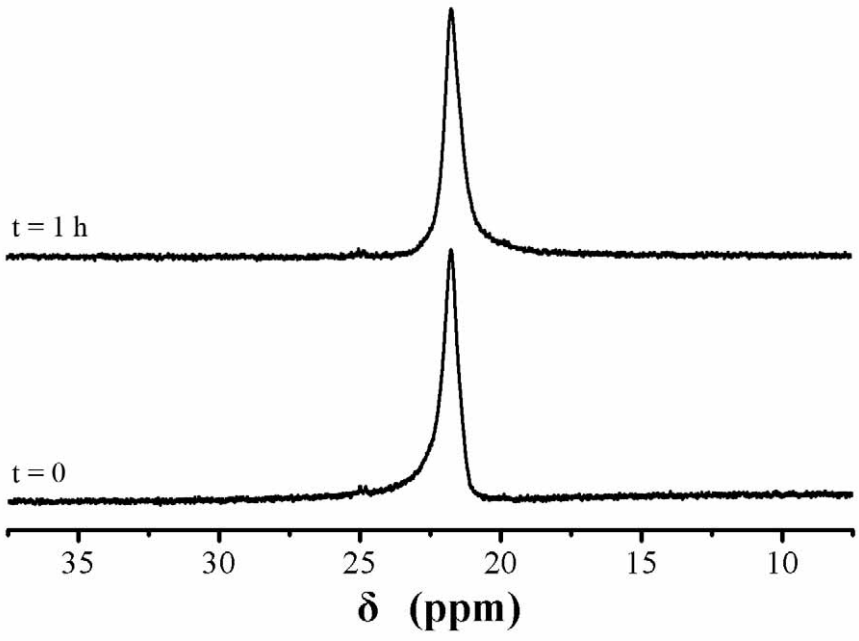


Fig. S18 The ^{31}P NMR spectrum of **TBA-1** with time in D_2O.

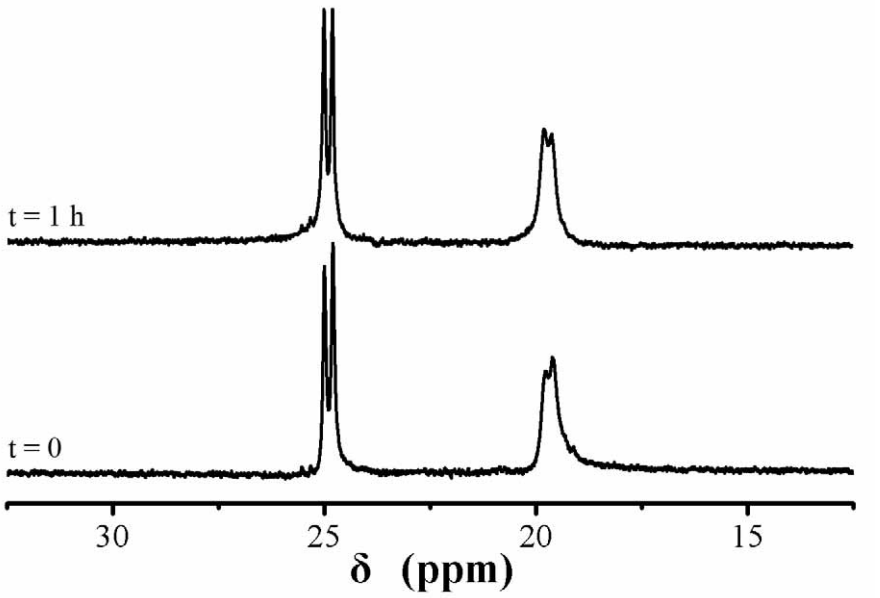


Fig. S19 The ^{31}P NMR spectrum of **TBA-2** with time in D_2O.