

## Spontaneous resolution of a new diphosphonate-functionalized polyoxomolybdate

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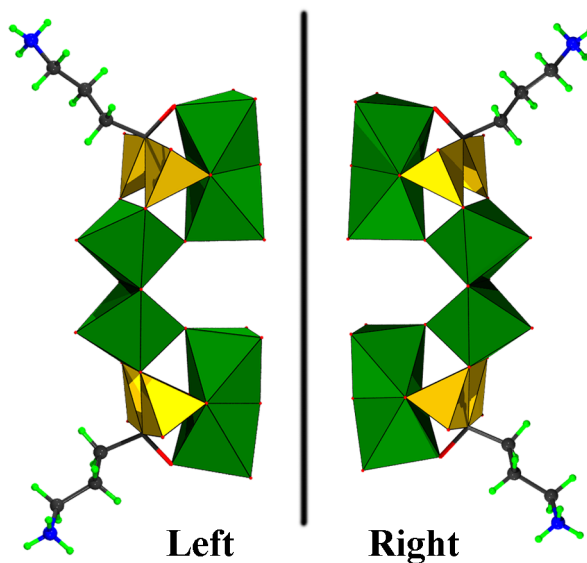


Figure S1. Polyhedral and ball-and-stick representation of polyoxoanion **1a** and **1b**.

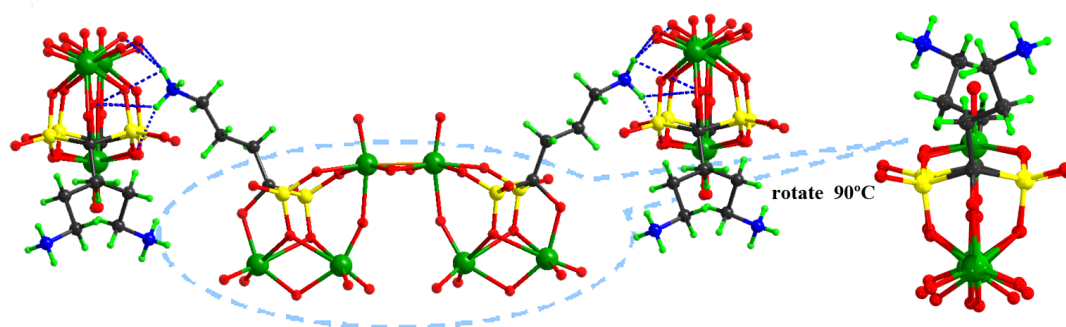
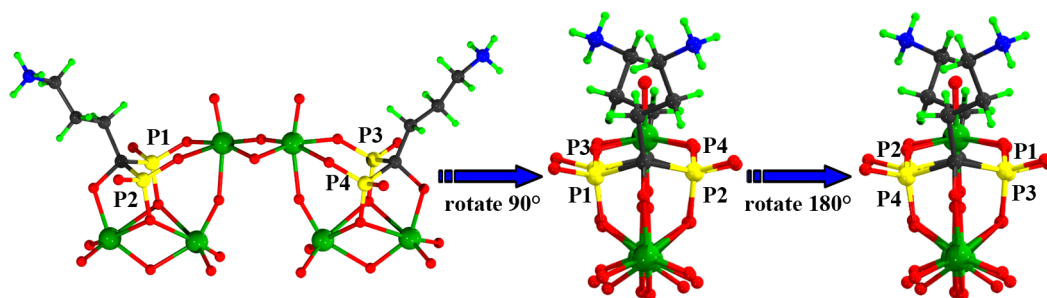
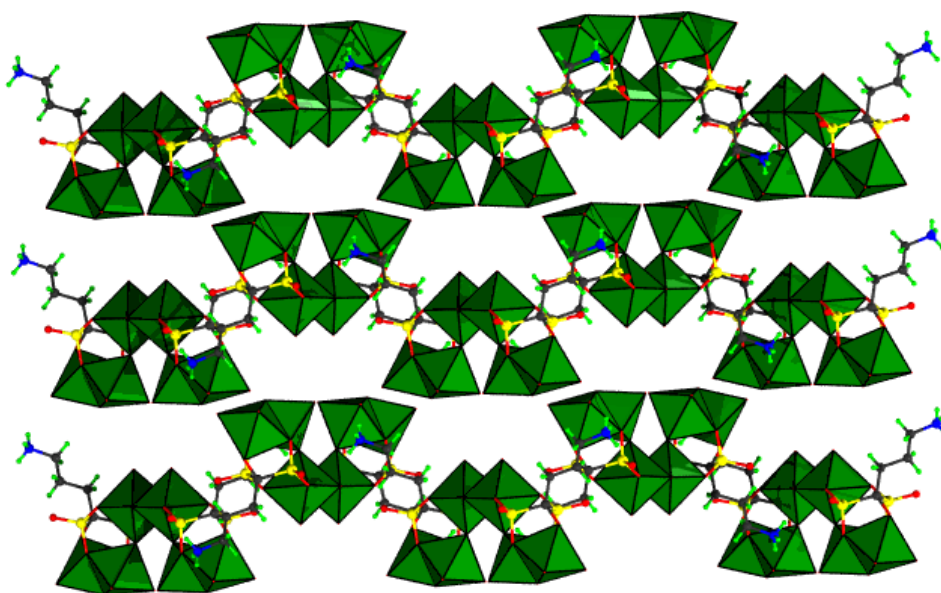


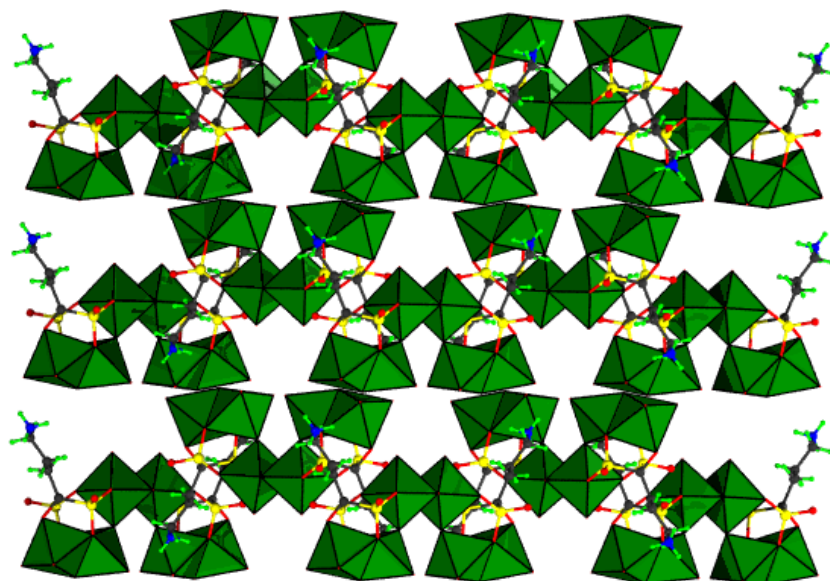
Figure S2. The “folding” of alkyls are fixed by hydrogen bonds in different direction.



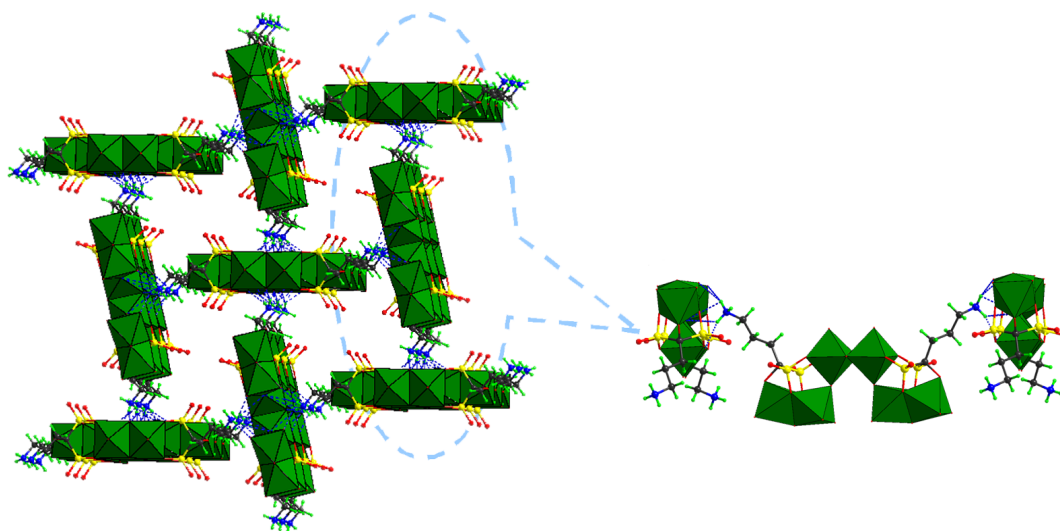
**Figure S3.** The polyoxoanion possesses a  $C_2$  symmetry.



**Figure S4.** Polyhedral and ball-and-stick representation of 3D supramolecular framework in compound **1a** viewed from a axis.



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



**Figure S6.** Polyhedral and ball-and-stick representation of 3D supramolecular framework in compound **1a** viewed from c axis.

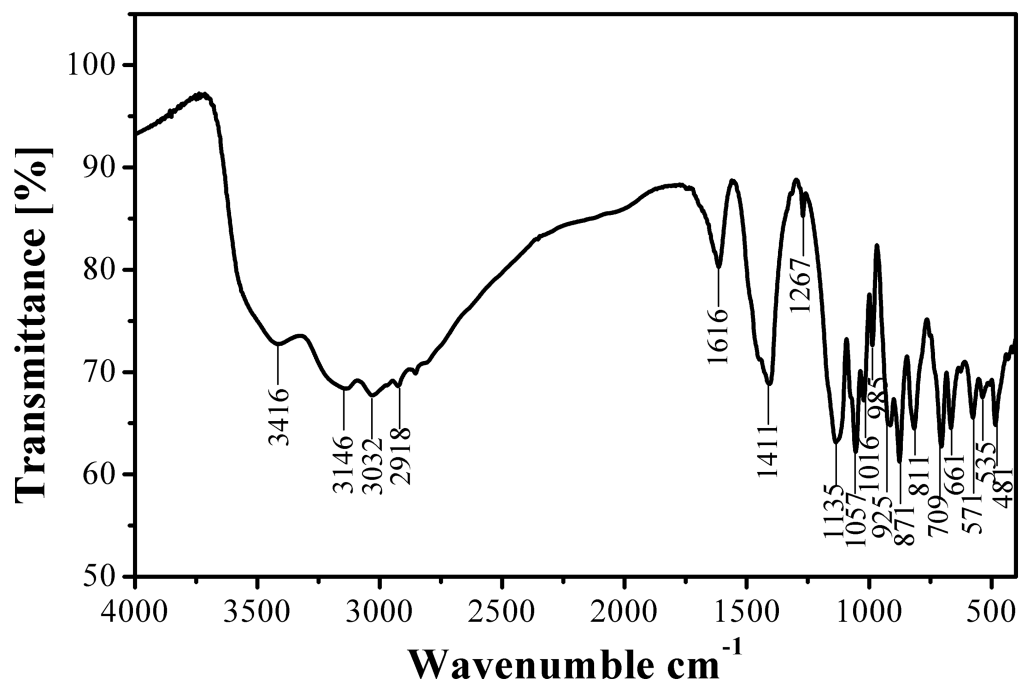


Figure S7. IR spectrum for compound 1.

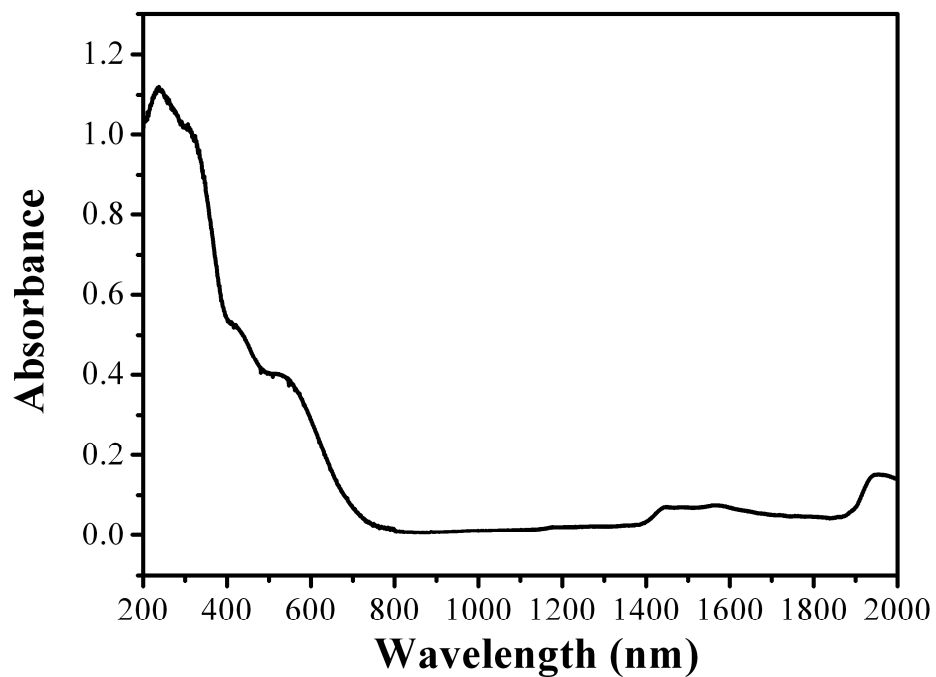
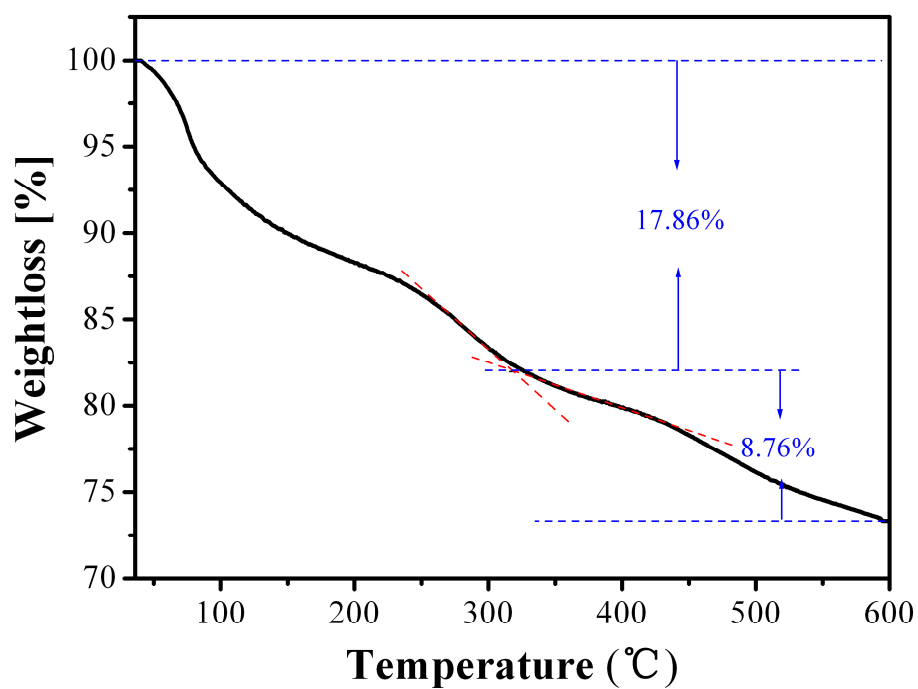
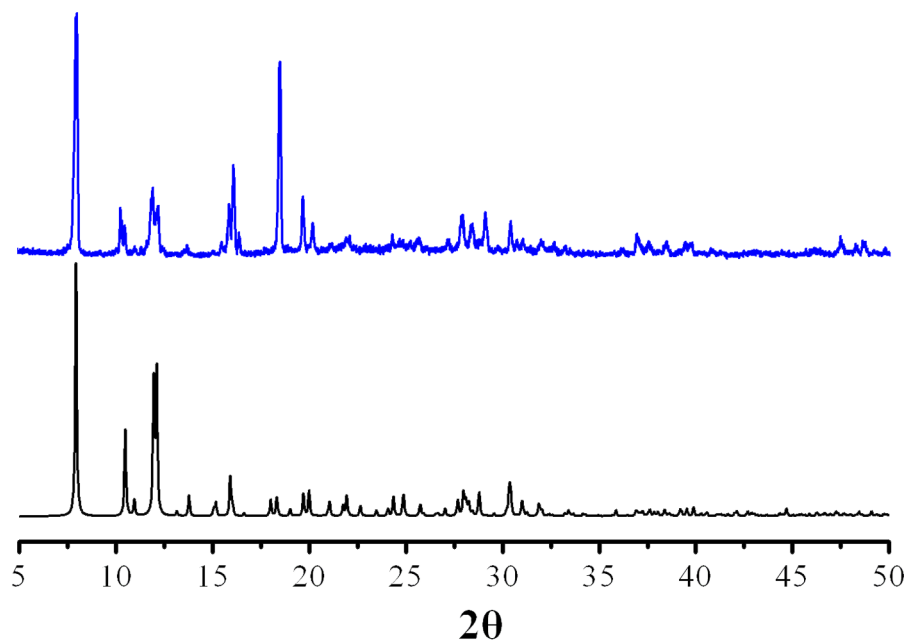


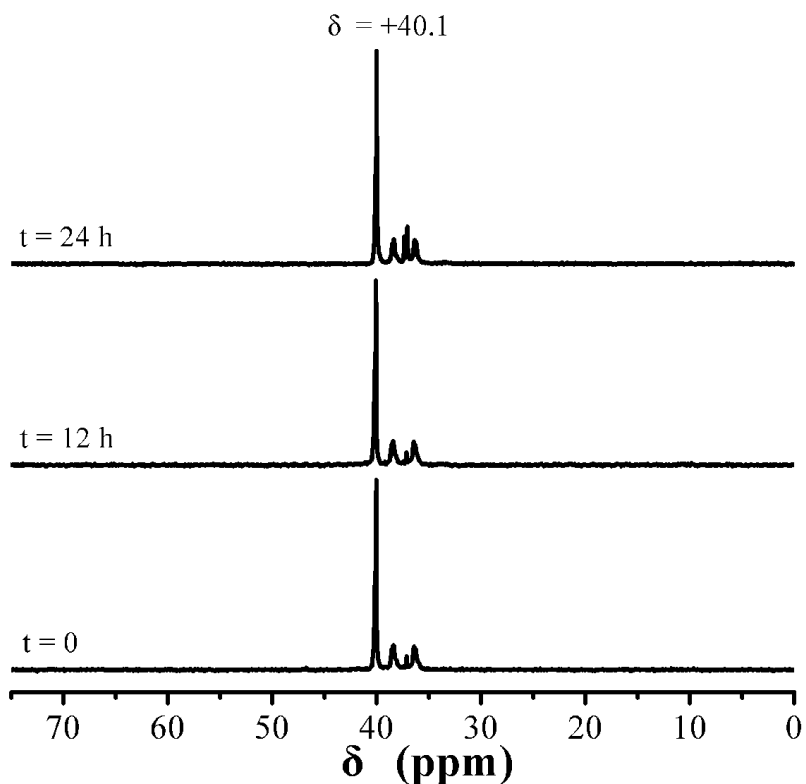
Figure S8. The UV-Vis spectrum for compound 1 in the solid state.



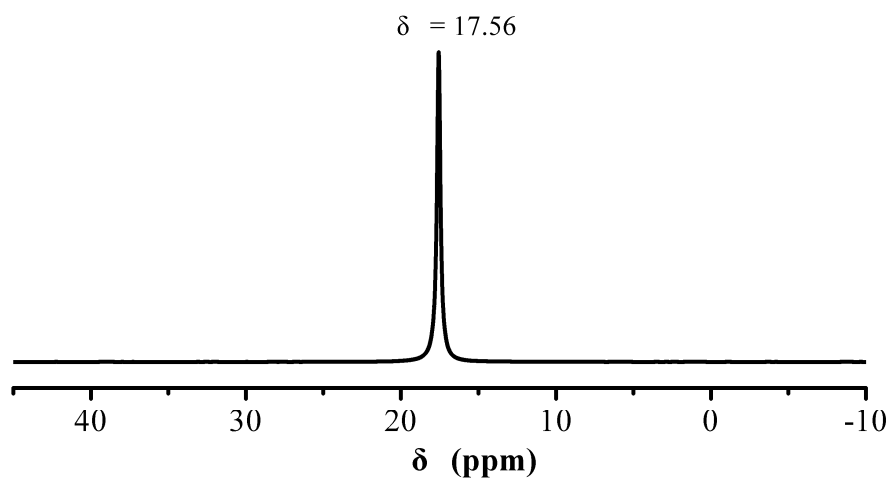
**Figure S9.** The TG curve of **1** exhibits three weight loss stages in the temperature ranges 35-600 °C. The first and second weight loss is 17.86% in the temperature range 35-330 °C, corresponding to the release of all the  $\text{NH}_4^+$  ions and lattice water molecules in **1** (17.89%). And after 330 °C, polyoxoanion **1** would be decomposed.



**Figure S10.** The experimental (blue) and Simulated (black) PXR D patterns of compound 1.



**Figure S11.** The  $^{31}\text{P}$  NMR spectra of compound **1** with time in  $\text{D}_2\text{O}$ . The  $^{31}\text{P}$  NMR spectra of compound **1** in  $\text{D}_2\text{O}$  exhibits one main signal at  $\delta = +40.1$ , which is inconsistent with the results of the solid state  $^{31}\text{P}$  NMR spectra of compound **1** (in which two resonances ( $\delta = +26.74$  ppm,  $\delta = +22.23$  ppm) with almost equal relative intensity were exhibited). This means P1, P2, P3 and P4 in polyoxoanion **1** could be of the same chemical environment in  $\text{D}_2\text{O}$ . In other words, the chirality of polyoxoanion **1** can not be retained in  $\text{D}_2\text{O}$ . This restriction of “folding” alkyls induced chiral polyoxometalate can only exist in the solid state. The weak signals at  $\delta = +38.4$ ,  $\delta = +37.1$  and  $\delta = +36.3$  ppm may come from impurity or intergradation of the polyoxoanion.

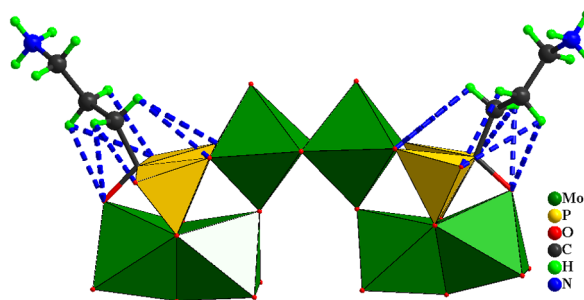


**Figure S12.** The  $^{31}\text{P}$  NMR spectrum of pure alendronic acid in  $\text{D}_2\text{O}$  at the same pH as the solutions of the title compound.



## Hydrogen bonds

Intramolecular hydrogen bonds in the polyoxoanion:



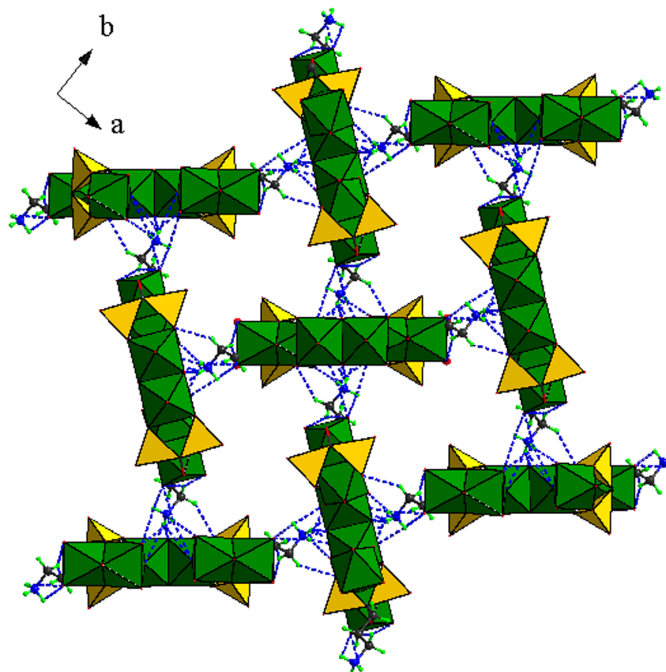
**Figure S13.** The intramolecular hydrogen bonds in the polyoxoanion. They range from 2.610 Å to 3.171 Å.<sup>1-4</sup> These hydrogen bonds help to stabilise the structure of polyoxoanion.

**Table S1.** Intramolecular hydrogen bonds in the polyoxoanion

C2-H2A...O7	2.616 Å	C2-H2A...O13	2.708 Å
C2-H2B...O3	3.022 Å	C2-H2B...O12	3.171 Å
C3-H3A...O7	2.690 Å	C3-H3A...O10	2.974 Å
C3-H3B...O10	2.610 Å		

Intermolecular hydrogen bonds:

1) The intermolecular hydrogen bonds between polyoxoanions:

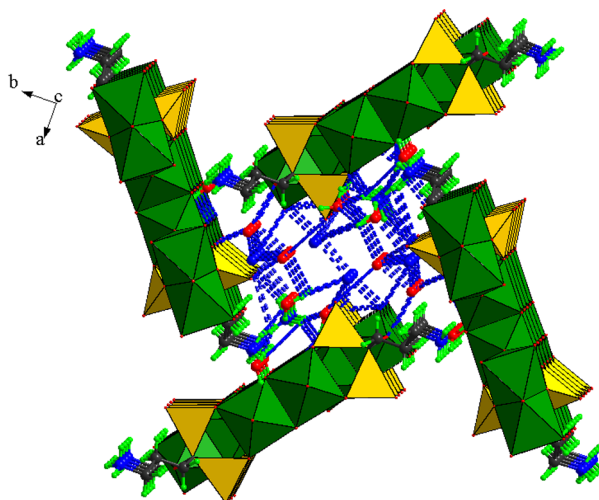


**Figure S14.** The intermolecular hydrogen bonds between polyoxoanions. The hydrogen bonds are in the range of 1.965-2.962 Å.<sup>1-4</sup> The hydrogen bonds restrict the folding alkyls of polyoxoanion in different direction, thus made the symmetry of polyoxoanion reduced from the  $C_{2v}$  (“W-shaped” structure) to  $C_2$ . Chirality of polyoxoanion have been realized. And then these hydrogen bonds linked the adjacent homochiral polyoxoanions to form a 3D homochiral supramolecular structure. Therefore, spontaneous resolution of the title chiral polyoxoanions have been observed.

**Table S2.** The intermolecular hydrogen bonds between polyoxoanions.

N1–H1A···O6	2.010 Å	N1–H1A···O11	2.648 Å
N1–H1A···O1	2.962 Å	N1–H1A···O4	2.961 Å
N1–H1B···O1	2.682 Å	N1–H1B···O15	1.965 Å
N1–H1C···O11	2.835 Å	N1–H1C···O4	2.838 Å
C4–H4A···O12	2.882 Å	C4–H4B···O2	2.834 Å
C4–H4B···O4	2.789 Å	C3–H3A···O15	2.595 Å

2) The intermolecular hydrogen bonds between polyoxoanions,  $\text{NH}_4^+$  and lattice water molecules:



**Figure S15.** Partial intermolecular hydrogen bonds between polyoxoanions,  $\text{NH}_4^+$  and lattice water molecules. Owing to some  $\text{NH}_4^+$  and lattice water molecules disordered, partial intermolecular hydrogen bonds between polyoxoanions,  $\text{NH}_4^+$  and lattice water molecules have been studied. The hydrogen bonds are in the range of 1.770-2.975 Å.<sup>1-4</sup>  $\text{NH}_4^+$  and lattice water molecules occupy the supramolecular channels, and interact each other and polyoxoanions by hydrogen bonds to stabilise the supramolecular channels.

**Table S3.** Partial intermolecular hydrogen bonds between polyoxoanions,  $\text{NH}_4^+$  and lattice water molecules.

N2–H2C···O7W	2.879 Å	N2–H2C···O6W	1.869 Å
N2–H2D···O10	2.944 Å	N2–H2E···O10	2.973 Å
N2–H2E···O7W	1.955 Å	N2–H2F···O10	1.894 Å
O5W–H5B···O6W	2.933 Å	O5W–H5B···O5	2.678 Å
O5W–H5B···O2W	2.984 Å	O5W–H5B···N4A	2.937 Å
O6W–H6A···O2	2.426 Å	O6W–H6A···N4A	1.770 Å
O6W–H6B···N2	2.616 Å	O7W–H7A···O14	2.539 Å
O7W–H7B···N2	1.975 Å		

## References

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