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{VMo$_9$O$_{31}$[RC(CH$_2$O)$_3$]}$^{6-}$: the first class of triol ligand covalently-decorated Keggin-type polyoxomolybdates

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Content

Materials

All chemicals were purchased from Aladdin and were used without further purification. The water used in the experiment is high purity water.

Measurement

FT-IR spectra were recorded on a Bruker Vertex 80v spectrometer equipped with a DTGS detector (32 scans) with the resolution of 4 cm^{-1} using KBr pellets. Elemental analysis for C, H, and N was carried out on a Vario MICRO cube of Elementar Company. Elemental analysis for V and Mo was taken on a PLASMA-SPEC (I) inductively coupled plasma atomic emission spectrometer. Thermo gravimetric analysis (TGA) was carried out on a TA Instruments Q500 Thermal Analyzer with flow of nitrogen, and the temperature was set from 30 to 900 °C under a heating rate of 10 °C·min^{-1}. ^{1}H NMR and ^{51}V spectra were conducted on a Bruker AVANCE 500 MHz spectrometer. Single-crystal X-ray diffraction indexing and data collection were performed on Bruker D8 Venture diffractometer with graphite-monochromated Mo K$_\alpha$ (λ= 0.71073 Å) at 293 K. All complexes were solved by direct method and refined by full-matrix-least-squares fitting on F^2 using the SHELXTL software. All non-H atoms, except some lattice water molecules, were refined with anisotropic thermal parameters.

Synthesis

Synthesis of $(NH_4)_6\{VMo_9O_{31}[CH_3C(CH_2O)_3]\}\cdot 9H_2O$ (1). A mixture of V_2O_5 (0.36 g, 2.00 mmol), $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (2.47 g, 2.00 mmol) and $CH_3C(CH_2OH)_3$ (0.96 g, 0.80 mmol) was dissolved in 20 mL of water and the mixture was heated to 80 °C for 2 h under stirring. The formed yellow solution was cooled to room temperature and the crystals in light yellow color formed about after 1 day with the yield of 56.8% based on Mo. The pH values before and after reaction were 5.67 and 5.45, respectively. Elem. anal. Calcd. for $(NH_4)_6\{VMo_9O_{31}[CH_3C(CH_2O)_3]\}\cdot 9H_2O$: V, 2.83; Mo, 48.01; C, 3.34; H, 2.84; N, 4.67. Found: V, 2.96; Mo, 48.05; C, 3.45; H, 2.90; N, 4.64. IR (KBr, cm^{-1}): 3573, 3161, 3033, 2866, 2814, 1612, 1402, 1216, 1043, 960, 924, 838, 642, 518, and 478.

Synthesis of $(NH_4)_6\{VMo_9O_{31}[CH_3CH_2C(CH_2O)_3]\}\cdot 9H_2O$ (2). A mixture of V_2O_5 (0.36 g, 2.00 mmol), $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (2.47 g, 2.00 mmol) and $CH_3CH_2C(CH_2OH)_3$ (1.07 g, 0.80 mmol) was dissolved in 20 mL of water and the mixture solution was heated to 80 °C for 2 h. The resulted yellow solution was cooled to room temperature and the light-yellow crystals can be obtained about after 1 day with the yield of 57.8% based on Mo. The pH values before and after reaction were 5.43 and 5.39, respectively. Elem. anal. Calcd. for $(NH_4)_6\{VMo_9O_{31}[CH_3C(CH_2O)_3]\}\cdot 9H_2O$: V, 2.83; Mo, 47.68; C, 3.97; H, 2.93; N, 4.64. Found: V, 2.79; Mo, 47.64; C, 4.03; H, 2.93; N, 4.63. IR (KBr, cm^{-1}): 3556, 3130, 3026, 2876, 2824, 1612, 1400, 1205, 1043, 960, 924, 848, 640, 507, and 478.

Synthesis of $(NH_4)_6\{VMo_9O_{31}[HOCH_2C(CH_2O)_3]\}\cdot 9H_2O$ (3). A mixture of V_2O_5 (0.36 g, 2.00 mmol), $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (2.47 g, 2.00 mmol) and $HOCH_2C(CH_2OH)_3$ (1.09 g, 0.80 mmol) in 20 mL of water was heated to 80 °C for 2 h. The yellow solution was cooled to room temperature and was kept for about 1 day to obtain light-yellow crystals with the yield of 55.0% based on Mo. The pH values before and after reaction were 5.76 and 5.38, respectively. Elem. anal. Calcd. for $(NH_4)_6\{VMo_9O_{31}[CH_3C(CH_2O)_3]\}\cdot 9H_2O$: V, 2.81; Mo, 47.63; C, 3.31; H, 2.81; N, 4.63. Found: V, 2.78; Mo, 47.32; C, 3.68; H, 2.85; N, 4.63. IR (KBr, cm^{-1}): 3514, 3137, 3024, 2876, 2802, 1614, 1398, 1240, 1020, 960, 648, 516, and 476.

Single-crystal X-ray diffraction data for compounds 1−3

Table S1 The summary of crystal data and structure refinements for compounds **1−3**.

	1	2	3
Formula	$(NH_4)_6\{VMo_9O_{31}[CH_3C(CH_2O)_3]\}\cdot 9H_2O$	$(NH_4)_6\{VMo_9O_{31}[CH_3CH_2C(CH_2O)_3]\}\cdot 9H_2O$	$(NH_4)_6\{VMo_9O_{31}[HOCH_2C(CH_2O)_3]\}\cdot 9H_2O$
F. W.	1797.92	1811.94	1813.92
S. G.	$Cmc2_1$	$P-1$	$Cmc2_1$
a (Å)	13.858(5)	10.497(1)	13.876(1)
b (Å)	15.952(4)	10.558(1)	16.020(1)
c (Å)	20.649(5)	21.911(1)	20.658(1)
α (deg)	90	95.23(1)	90
β (deg)	90	102.32(1)	90
γ (deg)	90	97.400(1)	90
V (Å^3)	4565(2)	2335(1)	4593(1)
Z	4	2	4
D_c (g cm^{-3})	2.616	2.577	2.686
$F(000)$	3472	1752	3504
Reflections coll./unique	28379/5411	73589/10651	23232/5282
R_{int}	0.0234	0.0265	0.0328
GOF on F^2	1.141	1.116	1.075
R_1^a [$I > 2\sigma(I)$]	0.0168	0.0322	0.0260
wR_2^b(all data)	0.0488	0.0830	0.0677

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

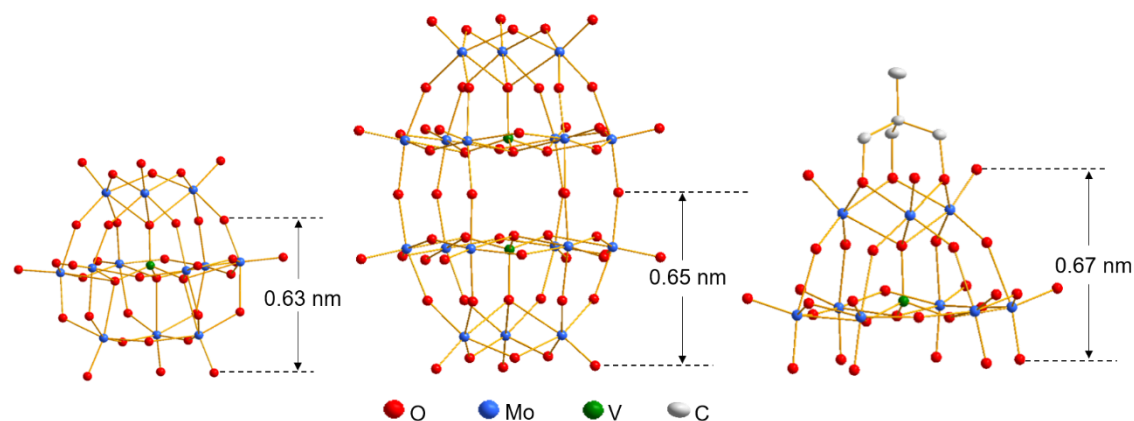## Size comparison of the same part in different structures

Fig. S1 Ball-and-stick representations of left: Keggin-type $[VMo_{12}O_{40}]^{3-}$, middle: Dawson-type $[V_2Mo_{18}O_{62}]^{6-}$ and right: polyanion **1a** $\{VMo_9O_{31}[CH_3C(CH_2O)_3]\}^{3-}$, showing the influence of triol ligand on the size of the cluster.

IR and TGA data for compounds 1−3
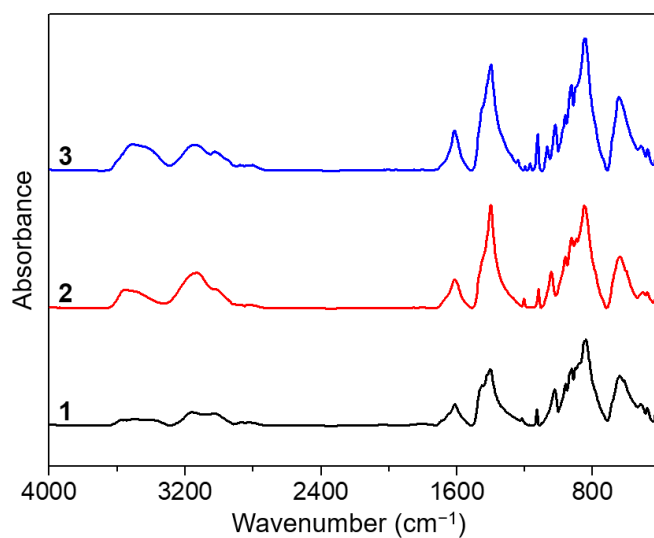
Fig. S2 IR spectra of compounds **1−3** with the formulas of $(NH_4)_6\{VMo_9O_{31}[CH_3C(CH_2O)_3]\}\cdot 9H_2O$ (**1**), $(NH_4)_6\{VMo_9O_{31}[CH_3CH_2C(CH_2O)_3]\}\cdot 9H_2O$ (**2**) and $(NH_4)_6\{VMo_9O_{31}[HOCH_2C(CH_2O)_3]\}\cdot 9H_2O$ (**3**) in KBr.

Table S2 The summary for detailed assignments of IR spectra of **1−3**.

1 (cm^{-1})	**2** (cm^{-1})	**3** (cm^{-1})	Assignments
3573, 3161, 3033	3556, 3130, 3026	3514, 3137,3024	O−H and N−H str.
2866, 2814	2876, 2824	2876, 2802	C−H str.
1612	1612	1614	O−H bending
1402	1400	1398	C−H bending
1216, 1043	1205, 1043	1240,1020	C−O
960	960	960	Mo=O
924, 838	924, 848	925, 842	Mo−O−Mo
642, 518, 478	640, 507, 478	648, 516, 476	V−O
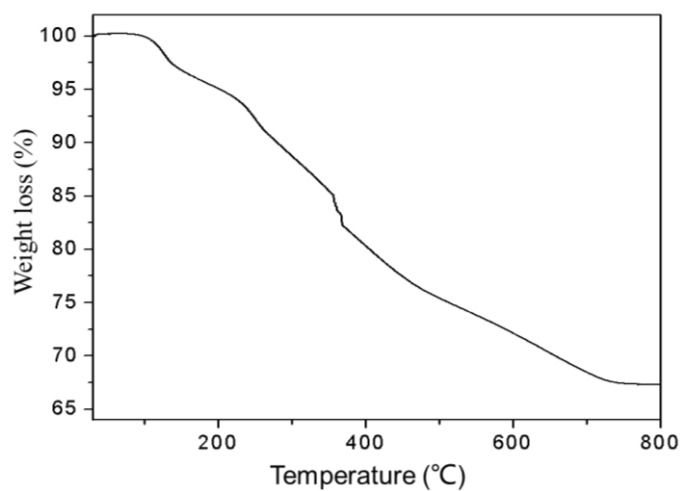
Fig. S3 TGA curve of compound **1** with formula of $(NH_4)_6\{VMo_9O_{31}[CH_3C(CH_2O)_3]\}\cdot 9H_2O$.
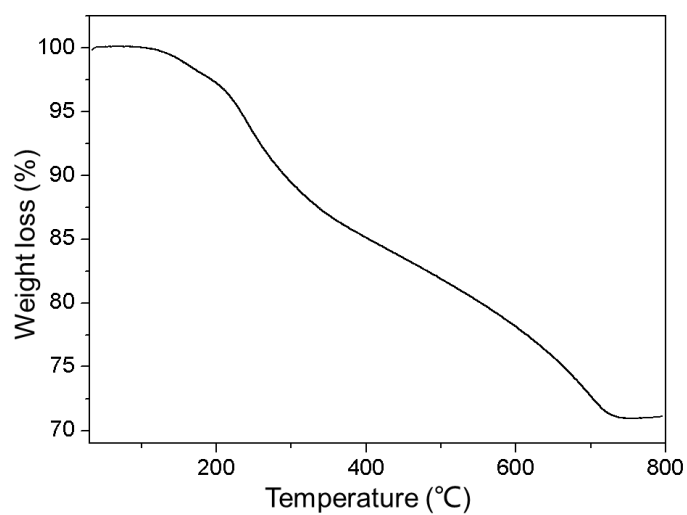
Fig. S4 TGA curve of compound **2** with formula of $(NH_4)_6\{VMo_9O_{31}[CH_3CH_2C(CH_2O)_3]\}\cdot 9H_2O$.
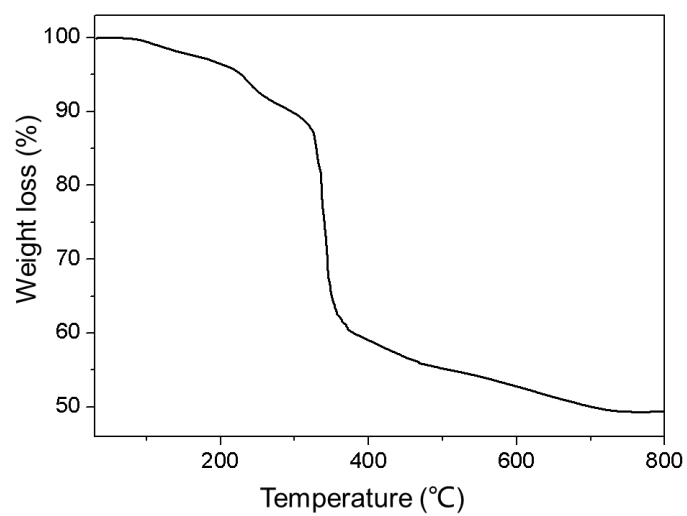
Fig. S5 TGA curve of compound **3** with formula of $(NH_4)_6\{VMo_9O_{31}[HOCH_2C(CH_2O)_3]\}\cdot 9H_2O$.
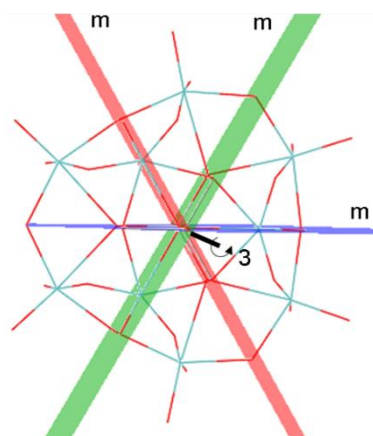
Symmetry of polyanion 1a

Fig. S6 The wireframe drawing of polyanion **1a** showing the C_{3v} symmetry with one 3-fold axis and three mirrors through the rotation axis.

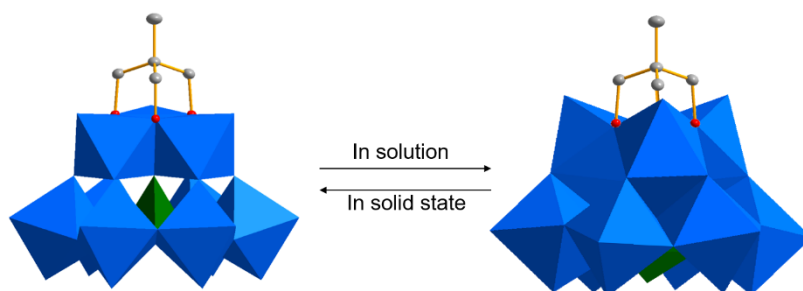**Transformation between A- and B-type polyanion**

Fig. S7 Combined polyhedral and ball-and-stick representation of polyanion **1a**, showing the different existing state in solution and solid state.
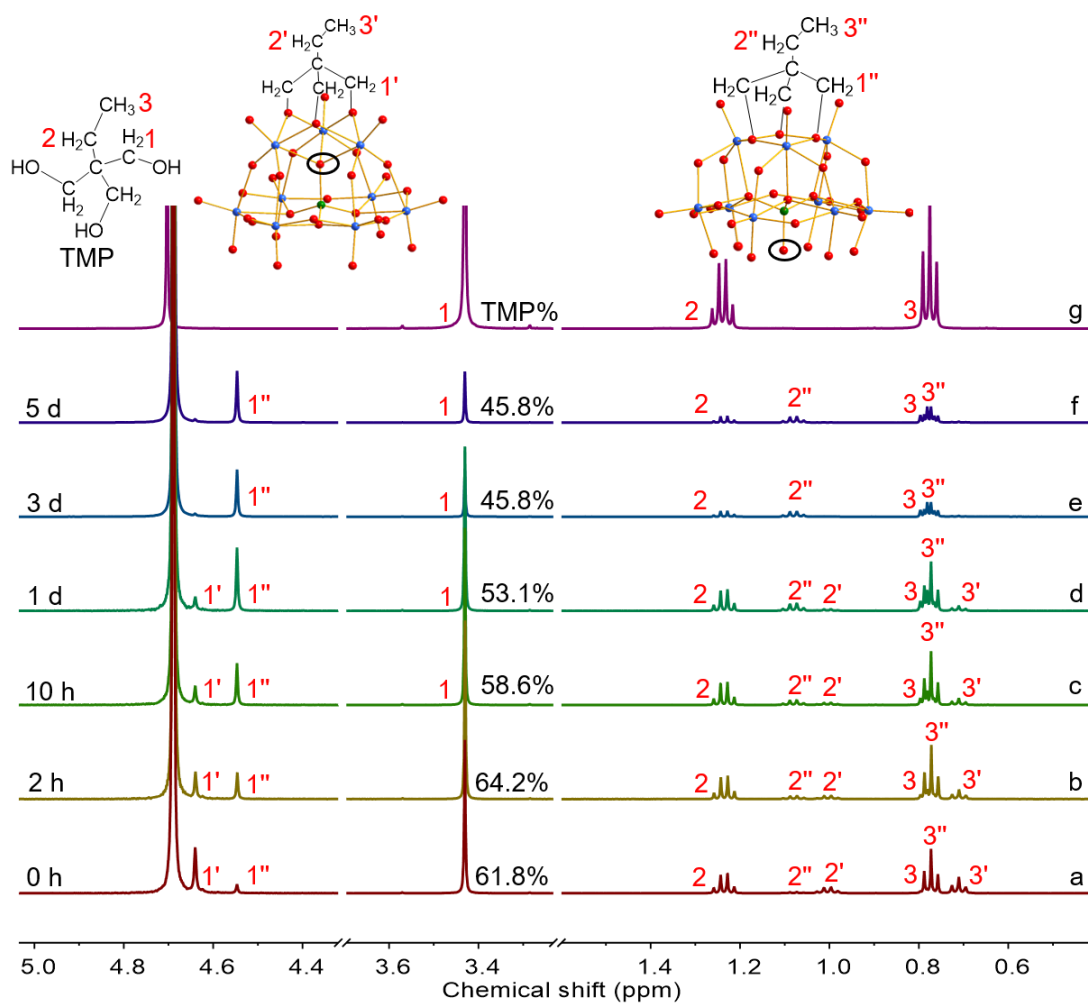
¹H NMR data for compounds 2 and 3

Fig. S8 ¹H MNR spectra of compound **3** in D_2O at various time: (a) 0 h, (b) 2 h, (c) 10 h, (d) 1 d, (e) 3 d, (f) 5 d and (g) trimethylolpropane (TMP). The temperature of the measurement is 25 °C. The different positions of the O atom in A- and B-type structures are marked with black circles.

Fig. S9 ^{1}H MNR spectra of compound **3** in D_2O at various time: (a) 0 h, (b) 2 h, (c) 10 h, (d) 1 d, (e) 3 d, (f) 5 d and (g) pentaerythrotol (PET). The temperature of the measurement is 25 °C. The different positions of the O atom in A- and B-type structures are marked with black circles.
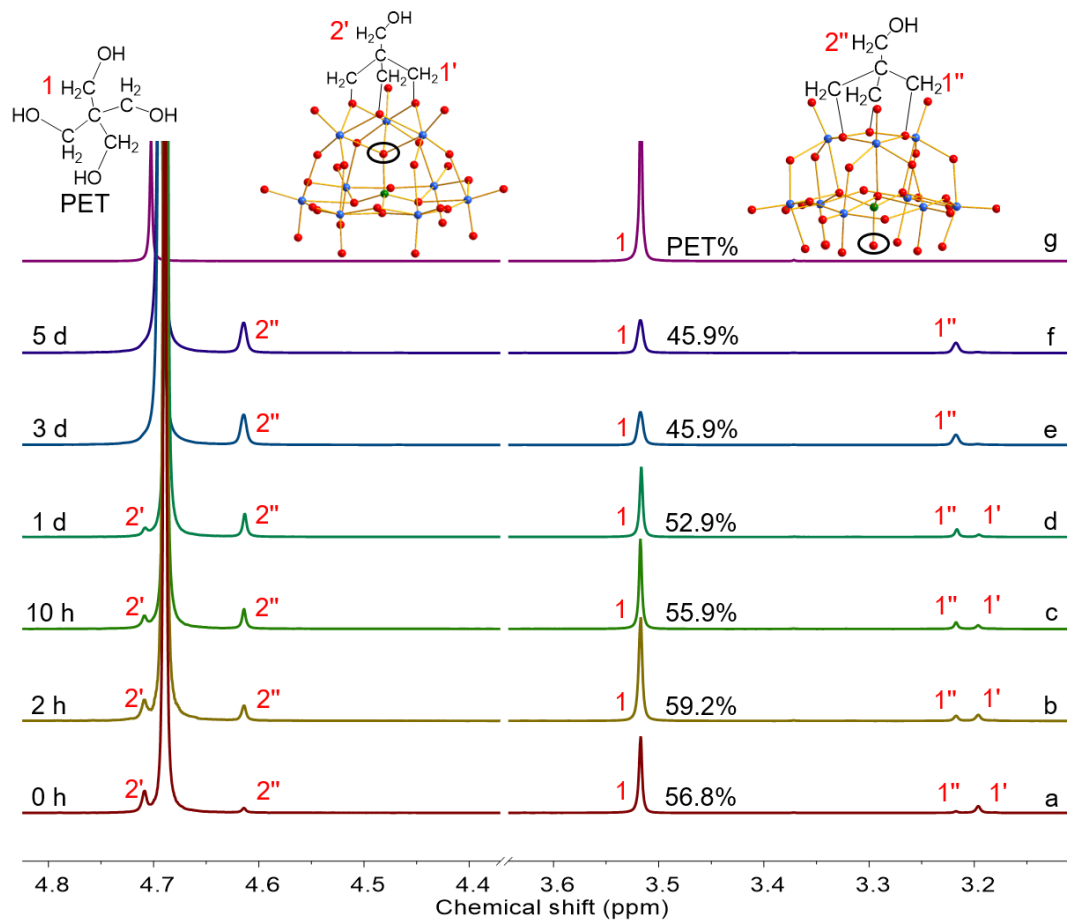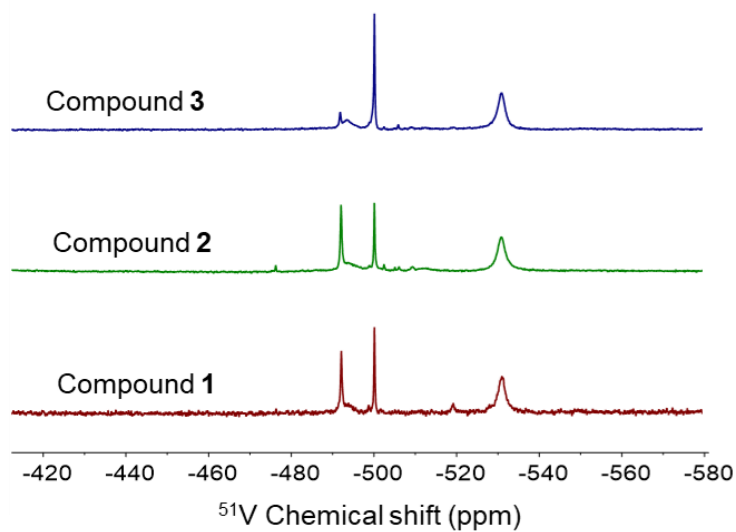
[51]V NMR data for compounds 1−3

Fig. S10 [51]V MNR spectra of compounds **1−3** in D_2O at 25 °C.

Calculation for E_a.

The E_a of proton conduction was calculated from the following equation:

$$\ln(\sigma T) = \ln A - \frac{E_a}{k}\frac{1}{T}$$

where σ is the conductivity with the unit of S/cm, T is the temperature in Kelvin, k is the Boltzmann constant. After plotting $\ln(\sigma T)$ as a function of inverse temperature, the slope of the fitted line would be $-\frac{E_a}{k}$.

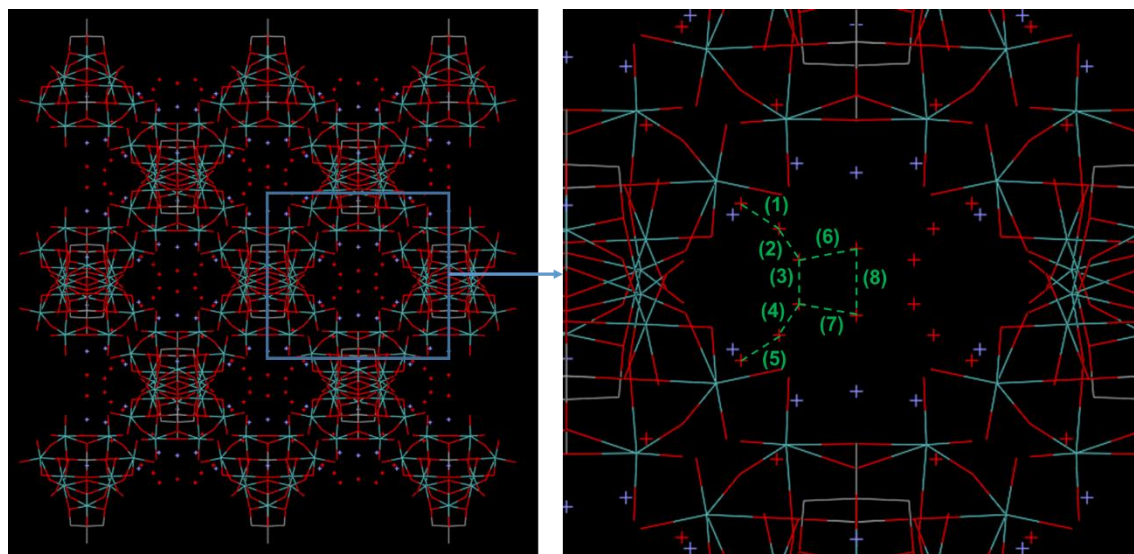**The distances of lattice water molecules in compound 1.**

Fig. S11 Left: the packing drawing of compound **1** along c axis; right: the amplification of the rectangle area in the left figure. The red stars represent the O atoms of water molecules. The dashed lines in green color represent distance between the neighboring water molecules and their values are (1) 10.783 Å, (2) 12.971 Å, (3) 10.379 Å, (4) 7.758 Å, (5) 9.982 Å, (6) 7.355 Å, (7) 7.355 Å, and (8) 10.447 Å, respectively.