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Proton conductive watery channels constructed by Anderson polyanions and lanthanide coordination cations

Jun Miao, a Yiwei Liu, a Qun Tang, a Danfeng He, a Guocheng Yang, b Zhan Shi, a Shuxia Liu a,∗ and Qingyin Wu a

A 3D inorganic-organic hybrid proton conductor, [Sm(H2O)3(CO2CH3NH3)+][Al(OH)3Mo6O33]·10H2O (1), has been synthesized by using coordination cations, [Sm(H2O)3(gly)3]+ (gly = CO2CH3NH3+), and polyoxocations, [Al(OH)3Mo6O33]3+ (AlMo3). The polyoxocations ([AlMo3]) and the coordination cations ([Sm(H2O)3(gly)3]+) stack to form a 3D supramolecular network structure containing 1D channels along c axis by electrostatic force and H-bonded interaction. Significantly, the 1D channels are water-filled with a high water content (both Sm co-ordinated and in lattice). Dynamic adsorption measurement was implemented at 1atm, 95% relative humidity (RH). The water adsorption amount (6.52 wt% at 25 °C and 5.68 wt% at 80 °C) consistent with the number of lattice water molecules of 1 suggests that water chains were retained at elevated temperatures (80 °C) under 95% RH. Alternating-current (AC) impedance measurements of 1 reveal an outstanding conductivity for 1 is 4.53× 10−3 S·cm−1 at 80 °C under 95% RH. The activation energy of 1 calculated from Arrhenius plots of the proton conductivity is 1.09 eV, which indicated that the protons transfer by vehicle mechanism.

Introduction

Inspired by the application of proton conductor in fuel cells, many researchers are interested in developing solid proton-conducting materials with conductivity of 10−3 S·cm−1 or above.1−4 Recently, much attention has been paid toward the syntheses of inorganic-organic hybrids for proton conduction.5,9 In general, these materials require proton carriers given by acid or hydroxyl groups and proton-conducting pathways composed of hydrophilic channels or hydrogen-bond networks.10,11 Both a large amount and a high mobility of proton carriers are required to provide good proton conductivity.12 The proton transport may occur through water molecules and hydroxonium ions which moved directionally in the pathway. Alternatively, protons may transfer between water molecules and hydroxonium ions through the hydrogen-bonded chains.13−19 Polyoxometalates (POMs) are a subset of anionic early transition-metal oxide clusters with unique physical and chemical properties.20−23 The applications of these POMs have attracted considerable attention in catalysis, medicine, materials science, or nanotechnology.24−27 Due to the fact that POMs have discrete and mobile ionic structures, these solids possess strong Bronsted acidity and “pseudoliquid phase” behaviour.28,29 It is worth noting that these properties in acid-base catalysis are generally correlated with proton conductivities of solids.30,31 Hence, POMs have been regarded as attractive candidates for proton conduction. In 1979, Nakamura first reported H2PM12O40·29H2O (M = Mo, W) as a proton conductor.32 Since then, developments on the conductivity of POMs have concentrated upon transition metal-substituted heteropolyacids (HPAs) and POM-MOFs.30,31,33−39 In these compounds, the conductivity generally arises from guest water and coordinated water as proton donors or carriers; furthermore, it could also be caused by the characteristics of a “pseudoliquid phase” with high proton mobility. However, HPAs are water-soluble, and disfavor of determined proton transfer pathways limits their development in high proton conduction.

A couple of years ago, a large number of porous ionic crystals based on polyoxometalates and molecular cations (macroocations) were reported.40−43 As transferable inorganic building blocks, POMs have been applied in the preparation of functional materials based on ionic networks.38,39,43 Solubility and aggregation state of POM-based ionic crystals can be finely tuned by the choice of sizes, shapes, charges, and ligands of the constituent ions.40 Polyanions and macroocations can form hydrophilic channels in the ionic crystals by strong electrostatic force which is suitable for accommodating guest molecules in crystal lattice.43 Despite the promising advancement in channel-selective sorption,40−43 there are still some challenges and opportunities to develop the porous ionic crystals for proton...
conduction. Guest (water) molecules in the channels to form a facile proton conduction pathway make them potential candidates for proton-conducting materials. However, there have hitherto been rare reports of POM-based ionic crystals for proton conduction.\textsuperscript{38,39,44-46}

In this work, an ionic network based on Anderson POM, [Sm(H$_2$O)$_6$(CO$_2$CH$_3$NH$_3$)$_2$][Al(OH)$_6$Mo$_6$O$_{18}$]·10H$_2$O (1), was synthesized and characterized. The single crystal was obtained by slow crystallization at room temperature from acidic (pH ≈ 2.6) aqueous solutions. Single crystal X-ray diffraction analysis revealed that compound 1 is constructed by [Sm(H$_2$O)$_6$(CO$_2$CH$_3$NH$_3$)$_2$]$^{3+}$ and [Al(OH)$_6$Mo$_6$O$_{18}$]$^{3-}$ possessing a high water content (both Sm coordinated and in the lattice), and significantly, the other characteristic of 1 is the presence of repetitive array of water molecules in 1D channels. Both features are considered to be beneficial for proton conduction. The outstanding conductivity of 4.53×10$^{-3}$ S cm$^{-1}$ for 1 was achieved at 80 °C under 95% RH. The effect of the glycine ligand on the conductivity properties was also investigated.

**Experimental**

**Materials**

All chemicals were used as purchased without further purification. Elemental analyses were performed on a Perkin–Elmer 240C elemental analyzer and a PLASMASPEC(I) ICP atomic emission spectrometer. IR spectra were recorded in the range 400–4000 cm$^{-1}$ on an Alpha Centaur FT/IR spectrophotometer using KBr pellets. TG analyses were performed on a Perkin–Elmer TGA7 instrument in flowing N$_2$ with a heating rate of 10°C/min. Powder X-ray diffraction measurements were performed on a Rigaku D/MAX-3 instrument with Cu KR radiation in the angular range 2θ = 5°–50° at 293 K.

**Synthesis of [Sm(H$_2$O)$_6$(gly)$_2$][Al(OH)$_6$Mo$_6$O$_{18}$]·10H$_2$O and preparation of La(H$_2$O)$_6$[Al(OH)$_6$Mo$_6$O$_{18}$]·4H$_2$O**

[Sm(H$_2$O)$_6$(CO$_2$CH$_3$NH$_3$)$_2$][Al(OH)$_6$Mo$_6$O$_{18}$]·10H$_2$O (1) was synthesized using reported synthetic methods.\textsuperscript{47} Na$_2$MoO$_4$·2H$_2$O (0.90 g, 3.7 mmol) was added to 15 mL acetic acid solution (volume ratio of water: acetic acid= 2:1). The mixture and a 30 mL aqueous solution of AlCl$_3$·6H$_2$O (0.36 g, 1.5 mmol) was mixed. Then a 10 mL water solution of glycine (0.09 g, 1.2 mmol) and SmCl$_3$·6H$_2$O (0.22 g, 0.6 mmol) was added. The pH of the resulting mixture was adjusted with dilute hydrochloric acid to about 2.6 and it was stirred for half an hour. A large amount of colorless block crystals formed after 4 hours collected in about 61% yield (based on Mo).

Elemental Anal. Calc. for C$_{36}$H$_{36}$AlSmMo$_6$O$_{38}$: C, 32.6; H, 2.46; N, 1.90; Al, 1.83; Sm, 10.21; Mo, 39.07. Found: C, 32.2; H, 3.18; N, 1.96; Al, 1.61; Sm, 9.48; Mo, 36.44%. IR (KBr, cm$^{-1}$): 3384 (br), 1587 (m), 1472 (s), 1424 (m), 1338 (m), 1111 (m), 952 (m), 890 (s), 650 (s), 582 (m), 446 (m).

Preparation method of La(H$_2$O)$_6$[Al(OH)$_6$Mo$_6$O$_{18}$]·4H$_2$O is presented according to literature.\textsuperscript{48}

**Crystal Structure determination**

The reflection intensity data of 1 was collected on a SMART CCD diffractometer equipped with graphite monochromatic Mo KR radiation (λ = 0.71073 Å) at 293 K. The linear absorption coefficients, scattering factors for the atoms, and anomalous dispersion corrections were taken from International Tables for X-ray Crystallography. The structure was solved by the direct method and refined by the full-matrix least squares method on F$_2$ using the SHELXTL crystallographic software package. All H atoms were placed geometrically for I. Anisotropic thermal parameter was used to refine all non-hydrogen atoms. Large Max. (Positive) Residual Density 4.84 eÅ$^{-3}$ in the crystal structure is near Sm1 and O14 with a distance of 2.434 Å and 1.472 Å, respectively. Thus, it is not suitable to be assigned as any atoms, which can be interpreted as Fourier truncation errors. The crystal data and structure refinement results of compound 1 are summarized in Table 1.

**Table 1 Crystal data and structure refinement parameters for 1.**

<table>
<thead>
<tr>
<th></th>
<th>La(H$_2$O)$_6$[Al(OH)$_6$Mo$<em>6$O$</em>{18}$]·4H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>C$<em>{36}$H$</em>{36}$AlMo$<em>6$O$</em>{38}$Sm</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
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<tr>
<td>Space group</td>
<td>C2/c</td>
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<tr>
<td>θ Range (°)</td>
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<tr>
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<td>33.101(13)</td>
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<td>b (Å)</td>
<td>10.690(4)</td>
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<tr>
<td>c (Å)</td>
<td>11.876(4)</td>
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<tr>
<td>β (°)</td>
<td>106.485(8)</td>
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<tr>
<td>V (Å$^3$)</td>
<td>4029(3)</td>
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<td>Z</td>
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<tr>
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<td>D$_0$ (g cm$^{-3}$)</td>
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<td>Absorption coefficient (mm$^{-1}$)</td>
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<td>Total data collected</td>
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<td>Unique data</td>
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<tr>
<td>R$_{int}$</td>
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<tr>
<td>Goodness-of-fit</td>
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<tr>
<td>R$_1$ [I &gt; 2σ(I)]$^a$</td>
<td>0.0768</td>
</tr>
<tr>
<td>wR$_2$ [I &gt; 2σ(I)]$^b$</td>
<td>0.2058</td>
</tr>
</tbody>
</table>

$^a$ R$_1$ = ∑||F$_o$||−|∑|F$_c$|/∑|F$_o$|.

$^b$ wR$_2$ = (∑w(F$_o^2$−F$_c^2$)$^2$)/∑w(F$_o^2$)$^2$.$^2$.

**Vapour sorption Measurements**

The water sorption measurements were performed with Micromeritics ASAP 2020 surface area and porosity analyser and Hiden Isochema Intelligent Gravimetric Analyser (IGA-100B).

The sample (~100 mg) was outgassed to a constant weight at 90°C under a high vacuum (<10$^{-6}$ mbar) prior to measurement of the isotherms. The saturated vapour pressure of the sorbent (water) at 298 K is 31.8 mbar. High purity N$_2$ (99.999%) was used as carrier gas for the adsorption of H$_2$O. The total flow rate throughout the experiments was kept constant at 500 ± 1 cm$^3$ min$^{-1}$, while the pressure was maintained constant at 1000 ± 1 mbar and the temperature variation was < 0.1°C. The purge
The process was performed by outgassing with the rate of 10 mbar min\(^{-1}\). The temperatures of 298 K and 353 K were maintained constant-temperature water bath.

**Conductivity characterization**

Impedance measurements of the products were performed on a PARSTAT 2273 (AMETEK Instruments, USA) electrochemical workstation. The product was compressed to a disc under a pressure of 30 MPa at room temperature. The diameter was 10 mm and the thickness was 3.8 mm. Two copper sheets were attached to the faces of the disc. Copper slices and copper wires were used as electrodes and lines, respectively. The proton conductivity was measured using a cell: copper|sample|copper. Measurements controlled by using an HDHWHS-50 incubator were taken in the temperature range of 25~80 °C with 95% relative humidity. ZSimpWin software was used to extrapolate impedance data results by means of an equivalent circuit simulation to complete the Nyquist plot and obtain the resistance values.

The proton conductivity calculated as

\[ \sigma = \left( \frac{1}{R} \right) \cdot \left( \frac{h}{S} \right) \]

where \( R \) is the resistance, \( h \) is the thickness, and \( S \) is the area of the disc.

Linear fitting of was used from the equation below:

\[ \sigma T = \sigma_0 \exp(-E_a/k_B T) \]

where \( \sigma \) is the ionic conductivity, \( \sigma_0 \) is the preexponential factor, \( k_B \) is the Boltzmann constant, and \( T \) is the temperature.

**Results and discussion**

**Synthesis and structural study**

Compound 1 was synthesized at a relatively low reaction pH (~2.6). At this pH, the carboxylic acid groups are expected to be deprotonated, whereas the primary amine groups are protonated.

As shown in Fig. 1, the ionic crystal is composed of \([\text{Al(OH)}_6\text{Mo}_6\text{O}_{18}]^5\) polyanions, \([\text{Sm(H}_2\text{O)}_5(\text{CO}_2\text{CH}_2\text{NH}_3)_2]^3\) coordination cations and lattice water molecules. Sm\(^{3+}\) coordinates with five oxygen atoms from water molecules and four carboxyl O atoms from two glycine ligands with distorted tricapped trigonal prism coordination geometry. The polyoxometalates and macrocations lined up to form columns respectively by H-bonded interaction, which were alternately arranged in a honeycomb structure by electrostatic force (Fig. S8, ESI†). The distance between the oxygen atoms of the coordinated water molecules in the macrocations is 6.32 Å, and the oxygen atoms of the polyoxometalates in the adjacent column is 7.41 Å. The spaces between the columns were occupied with the lattice water molecules. Hence, the polyanions and the coordination cations stack to form a 3D supramolecular network structure containing 1D channels along c axis by electrostatic force and H-bonded interaction.

Significantly, 1D channels are lined exclusively by three of the five coordinated water molecules (H\(_2\)O\(_{15A}\), H\(_2\)O\(_{15B}\), H\(_2\)O\(_{17}\)) of \([\text{Sm(H}_2\text{O)}_5(\text{gly})_2]^3\) forming hydrophilic inner surface with Anderson-type polyanions by H-bonded interaction. Besides, the crucial feature of 1 is the presence of repetitive array of water molecules in the 1D channels. Among five lattice water molecules (O\(_{1w}-O_{5w}\)) of the asymmetric unit of 1, four (O\(_{2w}-O_{5w}\)) of them are involved in the formation of the water chains in 1D channels (Fig. 1 and Fig. S9, ESI†). In addition, structural analysis of 1 suggests the presence of protonated primary amines in [Sm(H\(_2\)O\(_5\)(gly)\(_2\)]\(^{3+}\).
Dynamic adsorption study

In general, ionic crystals based on POMs and macrocations possess unique guest sorption properties. Thus, guest sorption property of 1 was investigated. Water sorption isotherm is present in Fig. S3 indicating that 1 can provide water uptake capacity of 6.15 wt%. 

Thermogravimetric analysis revealed that loss of lattice waters occurred from room temperature to 97 °C (Fig. S2, ESI†). It suggests that repetitive array of water molecules in the 1D channels may be broken. However, the dehydrated samples (at 97 °C for 4 hours) exposed to 95% RH at 25 °C and 80 °C for 60 minutes were fully hydrated. It was confirmed powder X-ray diffraction (Fig. 2) and dynamic adsorption measurement (Fig. 3). Dynamic adsorption measurement was implemented at 1atm, 95% RH and representative temperatures (25 and 80 °C) using N2 as carrier gas. As indicated in Figure 3, 1 showed a rapid adsorption process of water molecules in the initial 40 minutes and reached adsorption equilibrium within 60 minutes. The total water adsorption amount is 6.51 wt% (3.62 mmol g−1) at 25 °C and 5.68 wt% (3.16 mmol g−1) at 80 °C. This value is equivalent to approximate 6 water molecules per formula unit in accord with the number of lattice water molecules of 1 suggesting water chains still exist at elevated temperatures (80 °C) under 95% RH. Powder X-ray Diffraction (PXRD) results indicated the structure of dehydrated 1 is different from that of 1, suggesting that framework of the ionic crystal may distort and even collapse in lack of guest molecules. However, PXRD spectra of rehydrated 1 is similar with that of simulated 1, indicating rehydrated 1 maintained the same structure as the single-crystal as shown in PXRD results. This phenomenon can result from large electrostatic interaction between host–guest in that POMs possess electronegative oxygen atoms at the molecular surface.

Proton Conductivity Study

Compound 1 possesses 1D channels with water molecules that interact with the coordinated water molecules and Anderson-type polyanion. These structural characteristics prompted us to investigate its proton conduction property. Then we measured water-assisted proton conduction in 1 which operates at low temperature (25–80 °C). AC impedance measurements of 1 were carried out using a two-probe method with Cu-pressed electrodes over the temperature range from 25 to 80 °C under 95% RH. The conductivities were determined from the Nyquist plots. Real (Z’) and imaginary (Z’’) parts of the impedance spectrum are shown in Fig. 4. The semi-circle in the high-frequency region corresponds to bulk and grain boundary resistance, whereas the tail at low frequency is consistent with mobile ions that are blocked by the electrode–electrolyte interface. The proton conductivity for 1 was found to be 4.85×10−6 S·cm−1 at 25 °C. The conductivity increases with increasing temperature and reaches 4.53×10−3 S·cm−1 upon the sample at 80 °C for 2 hours and subsequently water-equilibrated (Fig. 4). PXRD results indicated sample 1 maintained the same structure as the single-crystal before and after the proton-conductive measurements (Fig. 2).

![Fig. 3 Variation of H2O uptake over time for 1 at 298 K (blue) and 353 K (red) under flowing N2.](image1)

![Fig. 4 Nyquist plots for 1 at 25°C (a) and 80°C (g) under 95% relative humidity.](image2)
hybrid complexes based on POM, \{[M(H$_2$O)$_{12}$](HINO)$_4$(PMo$_{12}$O$_{40}$)\}_n (M = Co, Ni; HINO = isonicotinic acid N-oxide)\textsuperscript{38} and \{[Cu$_2$(L)$_2$(H$_2$O)$_2$](Cu(dmf)$_4$(SiW$_{12}$O$_{40}$))9H$_2$O\}_n \{L = N,N-bis(2-hydroxy-3-methoxyphenyl)methylidene]hydrazine hydrate\textsuperscript{39} samples. Besides, it is comparable to those of ring-shaped organic–inorganic hybrid polyoxomolybdate, [N(CH$_3$)$_2$]$_{1.5}$K$_2$Na$_2$[H$_2$C(Mo$_6$O$_7$S$_2$)$_3$(Se$_4$O$_7$)$_3$(OH)$_4$] 25H$_2$O\textsuperscript{34} and Na$_2$[H$_2$[N(CH$_3$)$_2$PO$_3$]$_3$]Mo$_6$O$_{19}$(OH)(H$_2$O)$_4$]$_4$·18H$_2$O\textsuperscript{37}. In addition, we studied the time dependent proton conductivity of 1 at 80 °C under 95% RH for further application in fuel cells. Compound 1 showed similar proton conductivity even after 48 hours with a negligible loss of conductivity (Fig. 5 (b)). This result demonstrates the durability of the material for conduction, which is essential for practical applications.

By preparing a similar compound using amine-free cations,\textsuperscript{38} the proton conductivity of 1 was compared with the compound, La(H$_2$O)$_2$[Al(OH)$_2$Mo$_6$O$_{16}$] 4H$_2$O (La(H$_2$O)$_2$[AlMo$_6$]) to confirm necessity of primary amine groups for proton conduction. The contrasting compound, La(H$_2$O)$_2$[AlMo$_6$] consists of one-dimensional chains, built from alternating [AlMo$_6$]$_{3+}$ polyanions and [La(H$_2$O)$_2$]$_{3+}$ cations, and lattice water molecules, as shown in Fig. S10. There are extensive hydrogen bonds among surface of oxygen atoms of the Anderson-type polyanions, coordinated waters, and lattice water molecules (Fig. S10, ESI\textsuperscript{5}). AC impedance measurement of La(H$_2$O)$_2$[AlMo$_6$] was carried out from 25 to 80 °C under 95% RH. The result showed that conductivity value of 1 at 80 °C under 95% RH is higher than La(H$_2$O)$_2$[AlMo$_6$] with conductivity of 1.7×10$^{-6}$ S·cm$^{-1}$. It can be concluded that in this case the protonated primary amines play a vital role in high proton conductivity.

Two predominant mechanisms are widely accepted for proton conduction: Grothuss mechanism and vehicle mechanism.\textsuperscript{5, 12} The transport of protons between relatively stationary hosts is termed as Grothuss mechanism, alternatively by other moveable species (OH\textsuperscript{−}, H$_2$O, H$_2$O$^+$, NH$_3$\textsuperscript{+}, HS\textsuperscript{−} etc.) is termed as vehicle mechanism.\textsuperscript{49} Such processes have been identified primarily by activation energies obtained through Arrhenius plots. Generally, when the activation energy value of a material is greater than 0.6 eV, we can typically attribute it to vehicle transfer via water molecules.\textsuperscript{50}

![Fig. 5] (a) Dependence of the conductivity on humidity of 1 at 80 °C; (b) Time-dependent proton conductivity of 1 at 80 °C under 95% RH.

![Fig. 6] Dependence of log(σ/S·cm$^{-1}$) on temperature under 98% RH for 1(black) and La(H$_2$O)$_2$[AlMo$_6$](red).

![Fig. 7] Arrhenius plot of 1 showing the dependence of proton conductivity on temperature.

The activation energy of 1 calculated from Arrhenius plot of the proton conductivity is 1.09 eV (Fig. 7), which indicated that vehicle mechanism is typically attributed to protons transfer. The determined structure of 1 allows insight into proton transport mechanism: [Sm(H$_2$O)$_{3}$(CO$_2$CH$_2$NH$_3$)$_2$]$^{3+}$ coordination cations as Bronsted acid donate protons to water molecules which act as vehicles (H$_2$O$^+$, H$_2$O$^-$ etc.). Crystalline HPAs in many respects behave like solutions, designated by the term “pseudoliquid phase”.\textsuperscript{28, 29} In the circumstances, solid POMs behave like concentrated solutions of H$^+(H_2O)_m$, which
in the hydrophilic channels move along one definite direction, while lattice water molecules move along the opposite direction to complete proton transport. Thus, water chains exhibited in the channels can effectively transport protons dissociated from the protonated primary amines.

Conclusions

The hydrophilic environment of the 1D channels in as-prepared POM-based ionic crystal, created by the coordinated water molecules of macrocations and polyanions, provides stable proton transfer pathway; good proton conductivity was achieved above 10^3 S·cm⁻¹ at 80 °C under 95% RH. Activation energy (Ea) for proton transfer in the I is 1.09 eV, typical of vehicle mechanism of proton conduction. High water content is retained when the starting sample exposed to 95% RH at 80 °C, although compound I is dehydrated at 97 °C or below. The proton conductivity of I was compared with a similar amine-free compound, indicating that the protons dissociated by the protonated primary amines play a vital role in high proton conductivity. Moreover, the crystallinity which enables molecular-level structure determination of I obtained by X-ray techniques allows insight into proton transport mechanism. As a consequence, POM-based inorganic-organic hybrids with water chains and additional protons will likely become an important class of proton conductive materials in the future.

Acknowledgements

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Notes and references

Graphical Abstract:

Proton conductive watery channels constructed by Anderson polyanions and lanthanide coordination cations

An ionic network based on Anderson POM featuring water chains in 1D channels exhibits outstanding proton conductivity.