

Research Article

Ligand isomerism-enabled supramolecular nanoconfinement in {P₄Mo₆} frameworks toward efficient Grotthuss-type proton transport

Rimsha Rehman[§], Mengna She[§], Chao Zhang*, Jingping Wang, and Jingyang Niu*

Henan Key Laboratory of Polyoxometalate Chemistry, College of Chemistry and Molecular Sciences, Henan University, Kaifeng 475004, China)

[§] Rimsha Rehman and Mengna She contributed equally to this work.

Received: 12 May 2026; Revised: 21 July 2026; Accepted: 27 July 2026

✉ Address correspondence to Chao Zhang, zhangchao@henu.edu.cn; Jingyang Niu, jyniu@henu.edu.cn

Cite This: *Polyoxometalates*, 2027, 6, 9140152 <https://doi.org/10.26599/POM.2026.9140152>

ABSTRACT

Constructing continuous hydrogen-bonded networks within confined microenvironments remains a critical challenge for developing high-performance crystalline proton conductors. Herein, we demonstrate a ligand isomerism-directed spatial packing strategy to construct two {P₄Mo₆}-based cobalt frameworks. Employing the linear bridging ligand 4,4'-bipyridine drives the formation of a densely packed three-dimensional (3D) coordination framework (**CoPom-3D**), severely restricting solvent-accessible free volume. Conversely, the chelating 2,2'-bipyridine blocks multi-directional extension, yielding one-dimensional (1D) coordination chains (**CoPom-1D**). Crucially, these 1D chains assemble into a 3D supramolecular architecture via strong π - π interactions, creating robust nanoconfined environments. Although capturing fewer lattice water molecules and possessing a lower intrinsic proton concentration than its 3D counterpart, this unique nanoconfinement profoundly alters the local hydrogen-bond topology, promoting a more dynamic hydrogen-bond environment. Under identical conditions of 50 °C and 95% RH, **CoPom-1D** exhibits a proton conductivity of $1.92 \times 10^{-3} \text{ S cm}^{-1}$, approximately 17 times that of **CoPom-3D** ($1.12 \times 10^{-4} \text{ S cm}^{-1}$). Arrhenius analysis yields an apparent activation energy of 0.11 eV for **CoPom-1D**,

compared with 0.49 eV for **CoPom-3D**. Together with the pronounced humidity dependence and the short water-framework O $\cdots$ O contacts, this low barrier is consistent with a predominantly Grotthuss-type proton-hopping contribution. The nanoconfined environment is proposed to facilitate local hydrogen-bond reorganization, although the microscopic water dynamics and solvent-reorganization energy were not directly measured. These findings underscore that regulating supramolecular nanoconfinement and promoting carrier mobility, rather than merely maximizing coordination dimensionality or structural proton density, provides a highly rational approach for optimizing proton transport mechanisms in polyoxometalate-based materials.

Keywords: polyoxometalates, proton conductivity, supramolecular nanoconfinement, ligand isomerism, Grotthuss mechanism

INTRODUCTION

Proton-conducting materials (PCMs) are essential components in clean-energy conversion technologies, such as proton-exchange membrane fuel cells (PEMFCs), hydrogen sensors, and electrochemical devices.[1–3] Their ability to efficiently transport protons under humid conditions allows high power density and compact design in next-generation energy systems.[4] Despite significant progress, a major challenge remains: achieving high proton conductivity while maintaining long-term structural integrity under conditions such as moderate temperatures and high relative humidity.[5–7] Many polymeric electrolytes exhibit excellent conductivity but suffer from limited structural definition, making it difficult to elucidate proton-transport pathways at the molecular level.[8–10] In contrast, crystalline proton-conducting materials offer well-defined and ordered structures, enabling the direct visualization of proton transfer pathways and facilitating a fundamental understanding of structure-property relationships that is inaccessible in amorphous systems.[11–13] Consequently, balancing flexible hydrogen-bond networks that facilitate proton mobility with rigid frameworks that provide mechanical and chemical stability poses a significant challenge.[14,15] Specifically, the rational design of confined pore microenvironments that can thermodynamically anchor water molecules while maintaining continuous, low-energy hydrogen-bonded pathways to govern specific transport mechanisms remains a formidable task.

Within the realm of crystalline proton conductors, polyoxometalate (POM)-based hybrid materials have emerged as a promising class of structurally well-defined platforms for constructing hydrated hydrogen-bond networks and regulating proton-transfer pathways.[16]

Representative POM-functionalized and POM-pillared frameworks have demonstrated that the incorporation of POM units can improve water retention, establish connected proton-conducting pathways, and support appreciable proton conductivity under humid conditions.[17,18] These representative studies establish the broader feasibility of employing POM units as structural platforms for constructing hydrated proton-conduction pathways. Beyond proton conduction, POM-based molecular, composite, catalytic, and extended-framework materials exhibit substantial structural and functional diversity.[19–23] By integrating the chemical robustness of inorganic modules with the structural diversity of organic linkers, these hybrid systems can establish well-defined pore environments and continuous hydrogen-bonding channels while maintaining structural stability within a single framework.[24–27] Among the most versatile building blocks for such assemblies are POMs, which are discrete, anionic metal-oxide clusters formed by early transition metals (e.g., Mo, W, V).[28,29] Their intrinsic characteristics, including high negative charge density, redox flexibility, and oxygen-rich surfaces, provide multiple proton-donor and acceptor sites, enabling their incorporation into charged frameworks.[30–32] The abundant oxo groups generate extensive hydrogen-bond networks that facilitate both Grotthuss (proton-hopping) and vehicular (diffusion-assisted) transport mechanisms.[33,34] Moreover, the redox and thermal stability of POMs ensure their structural integrity during hydration-dehydration cycles.[35–37] These features make POM-based hybrid materials a highly promising platform for designing structurally stable proton conductors that operate efficiently under mild conditions.[38–40] Among various POM clusters, the $\{P_4Mo_6\}$ unit is particularly attractive because of its high negative charge density and oxygen-rich surface.[41–44] These features provide multiple proton-accepting and hydrogen-bonding sites that can anchor water molecules and contribute to the formation of hydrated proton-transfer environments. This view is supported by structurally related phosphomolybdate-based proton conductors. For example, two-dimensional frameworks constructed from hourglass-type $\{M[P_4Mo_6]_2\}$ units contain hydrated structural environments and exhibit appreciable proton conductivity under humid conditions.[9,45,46] Similarly, $\{P_4Mo_6\}$ -based coordination compounds containing transition-metal nodes and lattice or coordinated water demonstrate that hydrated phosphomolybdate architectures can support water-assisted proton transport.[21,37] These representative studies illustrate how hydrated phosphomolybdate frameworks can provide suitable structural environments for proton transport, without establishing an identical water arrangement or transport pathway in the present system.[47] Recent POM-based materials provide additional evidence that confined structural environments can promote connected hydrogen-bond

networks and reduce barriers to proton transport. In particular, controlled self-assembly of metal-oxo units has been used to generate confined proton-conduction pathways with enhanced transport performance. These findings support nanoconfinement engineering as an effective approach for regulating local water environments in crystalline POM systems.[48] Recent studies have demonstrated that changes in coordination connectivity, including guest-induced dimensional crossover and post-synthetic or water-induced structural transformations, can modify framework organization and proton-conduction behavior in crystalline coordination materials.[49,50] In particular, positional isomerism of pyridyl ligands has been shown to regulate coordination modes, framework dimensionality, supramolecular assembly, and ultimately proton-conduction behavior.[51] These findings identify linker geometry and framework connectivity as key structural design parameters for regulating proton-transport environments and structure–property relationships.

However, discrete $\{P_4Mo_6\}$ clusters, despite their intrinsic proton-activity, are often water-soluble and lack continuous pathways for long-range proton transport.[52,53] To circumvent this issue, the conventional strategy is to bridge these clusters into high-dimensional (e.g., three-dimensional, 3D) coordination frameworks.[54] While such 3D architectures offer structural robustness, an overemphasis on multi-directional coordination bonds can result in densely packed lattices. Such dense packing severely restricts the available free volume, expels solvent molecules, and consequently disrupts the continuity of the hydrogen-bonding networks.[55,56] More importantly, even if such dense frameworks inherently possess a high concentration of potential proton sources, the lack of continuous, dynamic transport channels paralyzes efficient proton hopping. To address the limitations inherent in dense coordination frameworks, we hypothesized that constructing supramolecular nanoconfined environments—rather than simply increasing coordination dimensionality or indiscriminately increasing proton density—represents a more effective approach.[57] In this context, cobalt ions, due to their flexible coordination geometries, serve as versatile connectors for linking $\{P_4Mo_6\}$ units,[58] while bipyridine ligands provide a unique opportunity to regulate spatial packing and framework free volume through ligand isomerism. Specifically, linear 4,4'-bipyridine (4,4'-bpy) typically acts as a bridging ligand that promotes highly compact framework extension.[59] The chelating coordination mode of 2,2'-bpy occupies adjacent coordination sites on the secondary cobalt centers and limits the availability of these sites for multidirectional metal–ligand propagation, thereby suppressing dense 3D covalent extension.[60,61] In contrast, the spatially separated nitrogen donors of linear 4,4'-bpy allow it

to bridge different metal centers and promote extended framework connectivity. Related studies on bipyridine-based systems and ligand-isomerism-controlled coordination polymers have demonstrated that ligand geometry and coordination mode can regulate network connectivity and structural dimensionality.[62–64] In the present system, this ligand-isomerism-directed dimensional regulation favors the formation of 1D coordination chains, which subsequently assemble into a 3D nanoconfined supramolecular architecture.

Related structural-regulation strategies have also been demonstrated in crystalline proton-conducting frameworks. The assembly of multiple types of cages can generate crystalline porous architectures containing one-dimensional nanoscale channels and proton-conducting functionality, whereas ligand-directed assembly of $[\text{Mo}_2\text{O}_2\text{S}_2]^{2+}$ units can produce interlocked supramolecular architectures with efficient proton conduction.[60,65] These examples indicate that controlling cage organization, framework connectivity, and supramolecular interlocking provides effective means of regulating proton-conducting environments. In the present system, ligand isomerism represents another example of structure-guided regulation of covalent connectivity and supramolecular organization, leading to distinct proton-transport environments.

Guided by this isomerism-directed spatial-packing strategy, we successfully synthesized and structurally characterized two new $\{\text{P}_4\text{Mo}_6\}$ -based cobalt frameworks, **CoPom-3D** and **CoPom-1D (Figure 1)**, by employing 4,4'-bpy and 2,2'-bpy as structure-directing ligands, respectively. Although both compounds are constructed from the same fundamental hourglass-type $[\text{Co}(\text{P}_4\text{Mo}_6\text{O}_{31})_2]^{10-}$ building unit, the distinct coordination behaviors of the bipyridine isomers generate markedly distinct internal microenvironments. As anticipated, **CoPom-3D** assembles into a fully connected, densely packed 3D coordination framework that severely restricts solvent-accessible space. Here, coordination dimensionality refers to the dimensionality of the metal–ligand network generated through coordination bonds, whereas supramolecular nanoconfinement describes the higher-order organization of these coordination motifs through noncovalent interactions and the nanoscale interchain spaces created by this assembly. Reduced coordination dimensionality is therefore not itself the origin of the enhanced proton transport in **CoPom-1D**. Rather, the chelating 2,2'-bpy ligand suppresses dense multidirectional covalent extension, yielding 1D coordination chains that subsequently assemble through π – π interactions into a 3D supramolecular architecture containing nanoconfined interchain voids. These confined regions provide a supramolecularly confined microenvironment that supports connected water-mediated hydrogen-bonding interactions and

may facilitate low-barrier proton transfer. Thus, dimensionality regulation serves as a structural strategy of enabling supramolecular nanoconfinement rather than as an intrinsically beneficial structural endpoint.

Most importantly, this isomerism-induced structural variation exerts a pronounced impact on the resulting proton transport mechanisms. Under identical conditions (50 °C, 95% RH), the nanoconfined **CoPom-1D** exhibits a significantly higher proton conductivity ($1.92 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$) than the densely packed **CoPom-3D** ($1.12 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$). Activation-energy analysis yields a barrier of 0.49 eV for **CoPom-3D**, consistent with a high-barrier, spatially localized proton-transfer process limited by poorly connected hydrogen-bonding pathways, whereas an ultralow value of 0.11 eV was obtained for **CoPom-1D**. This exceptional value is consistent with the proposition that the supramolecular nanoconfinement enforces a highly ordered water arrangement, significantly lowering the solvent reorganization energy and thereby supports a highly efficient Grotthuss-type transport pathway. These results strongly suggest that regulating supramolecular nanoconfinement and spatial packing density—rather than merely

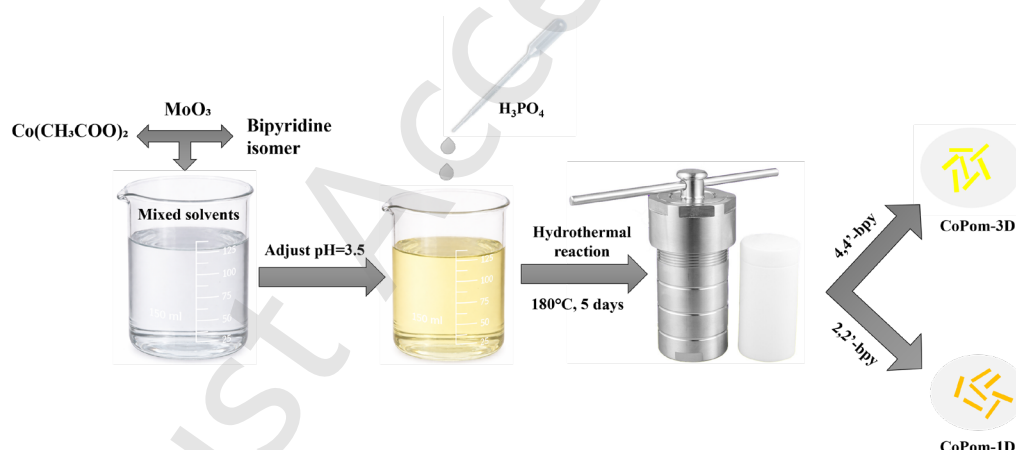


Figure 1. Schematic illustration of the ligand-isomerism-directed hydrothermal synthesis of the $\{\text{P}_4\text{Mo}_6\}$ -based cobalt frameworks, **CoPom-3D** and **CoPom-1D**, employing 4,4'-bpy and 2,2'-bpy as structure-directing ligands, respectively.

maximizing framework dimensionality—is the key to facilitating highly efficient proton-transport behavior in $\{\text{P}_4\text{Mo}_6\}$ -based hybrid materials.

EXPERIMENTAL SECTION

Materials and Physical Measurements

All solvents and reagents were purchased from commercial sources and used as received without further purification. Powder X-ray diffraction (PXRD) patterns were recorded over a

2 θ range of 5–50° on a Bruker D8 ADVANCE X-ray diffractometer equipped with monochromatized Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$). Fourier transform infrared (FT-IR) spectra were collected in the range of 4000–400 cm⁻¹ using a Bruker Tensor II spectrometer with samples prepared as KBr pellets. Thermogravimetric analysis (TGA) was performed on an SDT 650 synchronous thermal analyzer under an air atmosphere from room temperature to 800 °C at a heating rate of 10 °C min⁻¹. Inductively coupled plasma optical emission spectrometry (ICP-OES) measurements were carried out using an Agilent 5110 ICP-OES spectrometer. Proton conductivity measurements were conducted using a Solartron 1260 impedance/gain-phase analyzer equipped with a 1296 dielectric interface over a frequency range of 0.5 Hz to 1 MHz with an applied AC voltage of 100 mV. Single-crystal X-ray diffraction (SCXRD) data were collected on a Bruker D8 diffractometer with monochromatized Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved and refined using the SHELX programs[66] incorporated within the Olex2 graphical user interface.[67] A summary of the crystallographic data and refinement parameters for **CoPom-3D** and **CoPom-1D** is provided in Table S1.

Synthesis of Compounds

(C₁₀H₉N₂)₂[Co(C₁₀H₈N₂)(H₂O)₂]₂[Co(H₂P₄Mo₆O₃₁)₂]·7H₂O (CoPom-3D): This compound was synthesized using a protocol modified from that reported for [Co@{Co₁₆Mo₁₆}].[40] Briefly, Co(CH₃COO)₂ (0.5 mmol, 0.088 g), MoO₃ (0.5 mmol, 0.073 g), and 4,4'-bpy (0.4 mmol, 0.063 g) were dissolved in a mixed solvent containing 1 mL of aqueous tetrabutylammonium hydroxide (40 wt% in water), 4 mL of distilled water, and 4 mL of ethanol. The resulting mixture was stirred magnetically at room temperature for 30 min. Subsequently, the pH of the solution was adjusted to 3.5 by the addition of 0.2 mL of 85 wt % H₃PO₄ and stirring was continued for an additional 2 hours. The mixture was then transferred into a 25 mL Teflon-lined stainless-steel autoclave and heated at 180 °C for 5 days. Upon cooling naturally to room temperature, clear light-yellow block crystals were obtained (0.105 g, yield: 77% based on Mo). Elemental analysis (ICP-OES, wt%) found: P 7.13, Co 5.18, Mo 33.76; calculated: P 7.30, Co 5.20, Mo 33.90.

[Co(C₁₀H₈N₂)₂(H₂O)]₄[Co₂(H₂O)₄(P₄Mo₆O₃₁)₂]·5H₂O (CoPom-1D): This compound was synthesized using a procedure identical to that described for **CoPom-3D**, except that 2,2'-bpy (0.4 mmol, 0.062 g) was used instead of 4,4'-bpy. Upon naturally cooling to room temperature, clear light-orange block crystals were obtained (0.152 g, yield: 88% based on Mo).

Elemental analysis (ICP-OES, wt%) found: P 5.71, Co 8.22, Mo 27.19; calculated: P 5.86, Co 8.36, Mo 27.22.

Synthesis Strategy and Condition Optimization

The synthesis of **CoPom-3D** and **CoPom-1D** was achieved via a hydrothermal self-assembly strategy based on the in-situ generation of $\{P_4Mo_6\}$ POM building units from MoO_3 and H_3PO_4 , following a protocol modified from a previously reported method.[40] Phase purity and crystallinity were found to be highly sensitive to both the initial pH and reaction temperature. Systematic experiments revealed that a narrow pH window of 3.4 - 4.0 and a temperature of 180 °C are required for the successful isolation of both compounds. To examine whether the target compounds could be obtained under milder conditions, parallel exploratory reactions for **CoPom-3D** and **CoPom-1D** were performed using water-bath heating at 90 °C. Under the tested conditions, neither reaction yielded single crystals suitable for single-crystal X-ray diffraction. Thus, direct substitution of the 180 °C hydrothermal treatment with 90 °C water-bath heating is insufficient for obtaining the target single crystals using the present reaction protocol. This result does not rule out the development of a lower-temperature synthetic route through further optimization of the reaction conditions. Further details are provided in the supporting information.

RESULTS AND DISCUSSION

Crystal Structures and Spatial Packing Analysis

Single-crystal X-ray diffraction analysis reveals that **CoPom-3D** and **CoPom-1D** crystallize in the orthorhombic $Cmce$ and monoclinic $C2/c$ space groups, respectively (Table S1). Despite their distinct crystallographic symmetries, both compounds share the same fundamental inorganic building unit: the hourglass-type $[Co(P_4Mo_6O_{31})_2]^{10-}$ building block, which is constructed from two $\{P_4Mo_6\}$ clusters bridged by a central cobalt ion through six μ -O bridges. In **CoPom-3D**, the secondary cobalt centers are coordinated by linear 4,4'-bpy ligands, oxygen atoms from coordinated water molecules, and terminal oxygen atoms from adjacent phosphate groups (Figure 2). This coordination mode drives the extended connectivity in three orthogonal directions, yielding a fully connected, densely packed 3D coordination framework (Figure 2). Notably, the molecular formula of **CoPom-3D** contains protonated 4,4'-bipyridine counterions ($C_{10}H_9N_2^+$) alongside seven lattice water molecules, theoretically endowing it with a high intrinsic concentration of potential proton carriers.

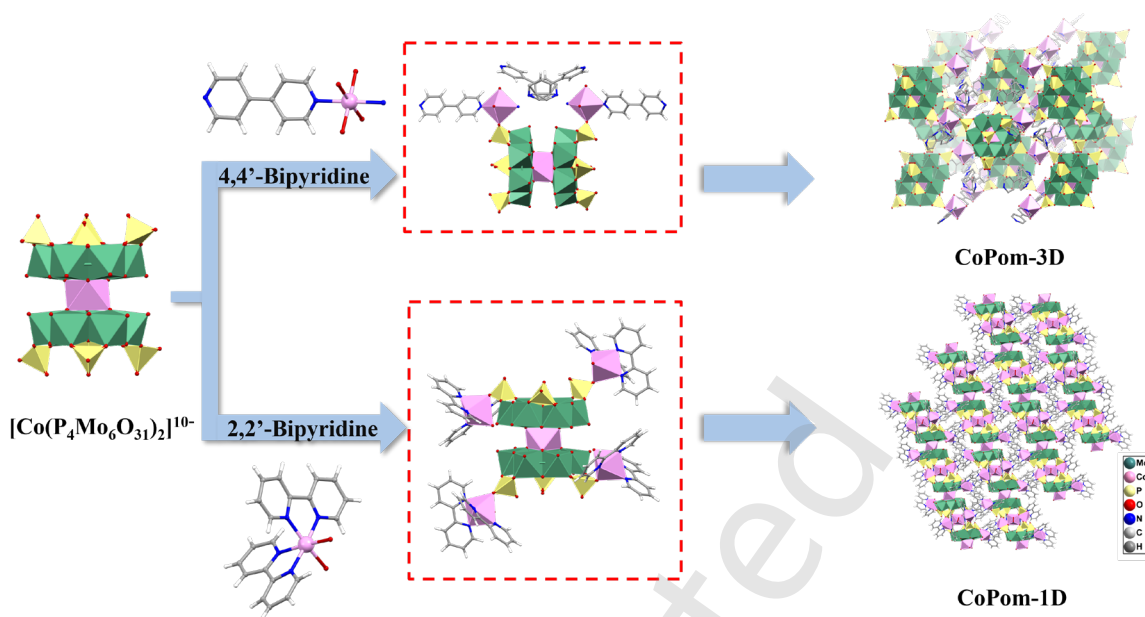


Figure 2. Structural representations of the coordination architectures derived from the hourglass-type $[\text{Co}(\text{P}_4\text{Mo}_6\text{O}_{31})_2]^{10-}$ building unit and bipyridine isomers. The linear 4,4'-bipyridine linker drives the formation of a densely packed 3D coordination framework (**CoPom-3D**), whereas the chelating 2,2'-bipyridine ligand yields 1D coordination chains that further assemble into a 3D supramolecular architecture containing nanoconfined interchain voids (**CoPom-1D**). Color scheme: Mo, green; Co, pink; P, yellow; O, red; N, blue; C, gray; and H, white.

However, this extensive cross-linking leaves minimal free volume within the lattice, severely restricting the formation of continuous hydrogen-bonded water networks and effectively immobilizing these carriers, despite the presence of 7 lattice water molecules per formula unit. The Co–O and Co–N bond lengths are 2.021(4)–2.198(4) Å and 2.164(8)–2.179(8) Å, respectively, while the O–Co–O bond angles range from 82.89(18)° to 180.0°. The 180.0° value is imposed by crystallographic symmetry and therefore has no associated ESD. Within the $\{\text{P}_4\text{Mo}_6\}$ core, the Mo–O bond lengths are 1.675(4)–2.318(3) Å, and the Mo–O–Mo and P–O–Mo bond angles are 81.67(12)–114.16(16)° and 123.8(2)–137.3(3)°, respectively (**Tables S2 and S3**).

In contrast, within **CoPom-1D**, the 2,2'-bpy ligands coordinate in a chelating mode to Co(II) ions, occupying adjacent coordination sites on the cobalt centers (**Figure 2**). These cobalt centers are further coordinated by oxygen atoms from a $\{\text{PO}_4\}$ group and coordinated water molecules (**Figure 2**), forming distorted octahedral geometries. Similar to **CoPom-3D**, the relevant bond lengths and angles in **CoPom-1D**—including the Co–O, Co–N, and Mo–O bond lengths are 1.942(14)–2.214(12) Å, 2.090(15)–2.174(14) Å, and 1.666(11)–2.306(9) Å, respectively. The O–Co–O, Mo–O–Mo, and P–O–Mo bond angles range from 27.8(9)° to

180.0°, 81.9(4)° to 113.7(4)°, and 125.1(6)° to 139.9(7)°, respectively. The 180.0° value is imposed by crystallographic symmetry (**Tables S4** and **S5**). Because the chelating 2,2'-bpy ligands effectively blockade multiple coordination sites on the secondary cobalt centers, they prevent multi-directional covalent extension. As a result, the structural connectivity propagates only along one crystallographic direction via POM-Co linkages, generating 1D infinite coordination chains (**Figure 2**). Crucially, these low-dimensional chains assemble into a robust 3D supramolecular architecture driven by strong hydrogen-bonding interactions and π - π stacking between adjacent bipyridine rings.

Beyond providing the supramolecular interactions that assemble the 1D chains into a 3D architecture, the π - π -stacked bipyridine groups may also indirectly regulate the proton-conduction microenvironment by defining relatively rigid aromatic interfaces around the interchain voids. Compared with these less hydrophilic aromatic regions, the oxygen-rich {P₄Mo₆} surfaces provide more polar hydrogen-bonding and proton-accepting sites. This chemical contrast may preferentially localize confined water near the oxygen-rich POM surfaces, while the surrounding aromatic boundaries restrict the dimensions and configurational space of the hydrated region. Such confinement would not necessarily immobilize the water molecules. Rather, it may maintain close water-framework contacts while still permitting local water reorientation and exchange of hydrogen-bonding partners. A spatially constrained but locally reorganizable hydrogen-bonding environment may reduce the extent of local hydrogen-bond rearrangement associated with successive proton-transfer events and thereby contribute to the low apparent activation barrier of **CoPom-1D**. Because the orientation and dynamics of the confined water and the associated solvent reorganization energy were not directly measured, this interpretation remains a structure-supported mechanistic model.

In **CoPom-1D**, the lattice-water oxygen atom forms short O $\cdots$ O contacts of 2.595(13), 2.715(18), 2.806(24), and 2.873(13) Å with neighboring framework oxygen atoms, together with a longer contact of 3.059(19) Å. These distances are consistent with plausible local hydrogen-bonding interactions and indicate closely spaced proton-donor and proton-acceptor sites within the nanoconfined region. Related POM-based proton conductors have demonstrated that framework connectivity and local hydrogen-bonding environments can substantially influence proton conductivity and the proposed transport mechanism.[68,69] The short O $\cdots$ O contacts observed in **CoPom-1D** do not independently prove the existence of a continuous or dynamically operating proton-conduction pathway. Nevertheless, when

considered together with the pronounced humidity dependence and low activation energy, they provide structural evidence supporting a proton-transfer process consistent with a predominantly Grotthuss-type contribution. Structural parameters indicate that these water clusters are thermodynamically anchored to the framework via extensive hydrogen-bonding interactions, rather than merely being physically trapped. In contrast, the highly congested coordination framework in **CoPom-3D** provides insufficient free volume, precluding the formation of continuous hydrogen-bonded pathways. This structural contrast illustrates how limiting dense multidirectional covalent extension can enable the formation of a supramolecular architecture containing nanoconfined interchain spaces. The resulting nanoconfined environment in **CoPom-1D** may support better-connected water-mediated hydrogen-bonding interactions than the densely packed **CoPom-3D** framework. This structural organization is consistent with the enhanced proton conductivity and low apparent activation energy of **CoPom-1D**, although the microscopic solvent mobility and solvent-reorganization energy were not directly measured.: intentionally blocking covalent dimensionality can paradoxically yield superior supramolecular porosity and highly ordered solvent microenvironments. The resulting nanoconfined environment in **CoPom-1D** has significant implications for proton transport, suggesting that enhanced hydrogen-bond continuity and solvent mobility can effectively outcompete a high static concentration of protons and solvent molecules in governing macroscopic proton transport and minimizing solvent reorganization energy.

Physicochemical Characterizations

To confirm the phase purity and structural integrity of the synthesized compounds, powder X-ray diffraction (PXRD) and Fourier-transform infrared (FT-IR) spectroscopy were performed. The experimental PXRD patterns of both **CoPom-3D** and **CoPom-1D** match well with the simulated patterns generated from their respective single-crystal data (**Figures S1 and S2**). Minor variations in peak intensities are typical of preferred orientation effects in crystalline powders and do not indicate structural impurities. This excellent agreement confirms that the bulk synthesized samples are of high phase purity. Correspondingly, the FT-IR spectra of both compounds exhibit highly similar absorption profiles due to their identical inorganic building units and structurally related isomeric ligands (**Figures S5 and S6**). Taking **CoPom-1D** as a representative example, a broad absorption band in the region of 3560-3059 cm^{-1} is assigned to O–H stretching vibrations of coordinated and hydrogen-bonded water molecules. The peaks observed at 2920-2850 cm^{-1} are attributed to C–H stretching vibrations

of organic ligands. A strong band near 1650 cm^{-1} corresponds to $\nu(\text{C}=\text{N})/\nu(\text{C}=\text{C})$ stretching vibrations of the coordinated bipyridine ligands, confirming successful metal-ligand coordination. The intense bands in the range $1100\text{--}1000\text{ cm}^{-1}$ are assigned to asymmetric P–O stretching vibrations from phosphate groups, while absorptions below 800 cm^{-1} are characteristic of Mo=O and Mo–O–Mo vibrations (**Figure S6**), indicating the preservation of the $\{\text{P}_4\text{Mo}_6\}$ POM framework.

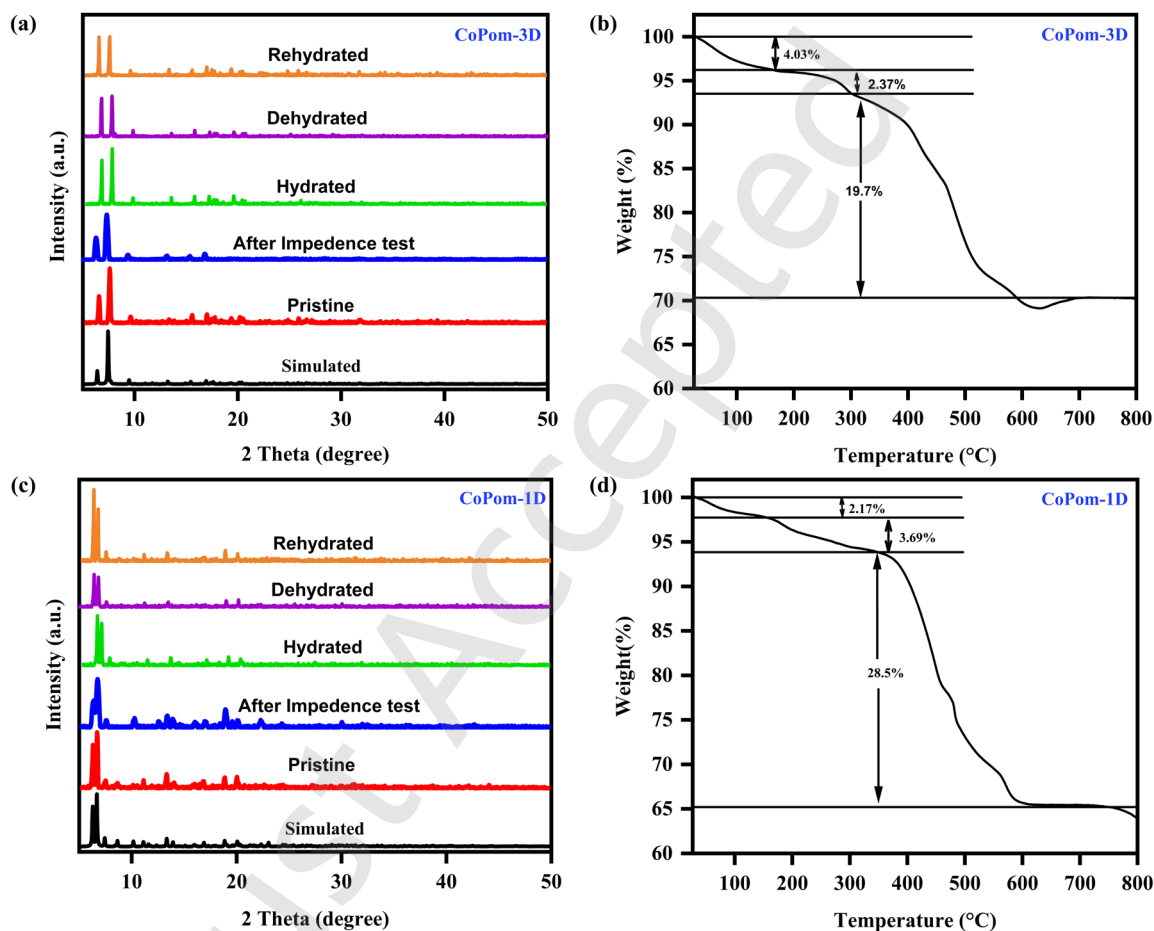


Figure 3. Structural stability and thermal profiles of the synthesized frameworks. (a, c) PXRD patterns of **CoPom-3D** and **CoPom-1D**, respectively, recorded during hydration–dehydration–rehydration cycles, confirming their structural robustness. (b, d) TGA curves of **CoPom-3D** and **CoPom-1D**, respectively, illustrating their distinct water-release behaviors.

To further evaluate the structural stability and water tolerance of the frameworks, systematic hydration–dehydration–rehydration cycle experiments were performed and monitored via PXRD and FT-IR. Specifically, the samples were immersed in deionized water at room temperature for 24 hours to achieve full hydration (or rehydration), while dehydration

was carried out by heating the samples at 150 °C for 24 hours in a vacuum oven. As shown in **Figure 3a** and **3c**, the PXRD patterns remain essentially unchanged after these rigorous treatments, with no observable peak shifts or formation of impurity phases. This clearly demonstrates that both frameworks maintain their crystallinity and structural integrity, confirming excellent water stability and reversible structural behavior. FT-IR spectra (**Figures S9** and **S10**) further support these observations. The broad O–H stretching band (3000–3600 cm⁻¹) decreases significantly after dehydration and is fully restored upon rehydration, indicating reversible water uptake, while the characteristic bands in the fingerprint region remain unchanged, confirming the preservation of the coordination skeleton.

Having established the phase purity and structural robustness of the frameworks, thermogravimetric analysis (TGA) was subsequently employed to elucidate the distinct thermal behaviors and water microenvironments that directly govern proton transport. The TGA curve of **CoPom-3D** exhibits an initial weight loss of approximately 4.03% below 200 °C, corresponding to the removal of seven lattice water molecules (calc. 3.71%) (**Figure 3b**). A second weight loss step of about 2.37% (200–300 °C) is attributed to the release of four coordinated water molecules from the cobalt coordination sphere (calc. 2.12%). At higher temperatures (300–530 °C), a significant weight loss of 19.7% occurs, corresponding to the decomposition of the organic bipyridine ligands (calc. 18.5%). The transient mass fluctuation near 600–700 °C is attributed to the temporary reduction of metal species by local carbonaceous residue, followed by their complete re-oxidation in the air atmosphere. Above 700 °C, the curve stabilizes, indicating the formation of stable metal oxide residues (mainly consisting of molybdenum, cobalt, and phosphate oxides), with an experimental residual mass of 70.24% (calc. 69.86%). In contrast, for **CoPom-1D**, an initial weight loss of 2.17% below 150 °C corresponds to the removal of five lattice water molecules (calc. 2.13%), and a further 3.69% loss (150–330 °C) is attributed to the release of eight coordinated water molecules (calc. 3.41%) (**Figure 3d**). At higher temperatures (330–600 °C), a significant weight loss of 28.5% is observed, corresponding to the decomposition of the organic bipyridine ligands (calc. 29.5%). Above 600 °C, the mass generally stabilizes, indicating the formation of stable metal oxide residues, leaving a final residue of 63.96% (calc. 63.77%). It should be noted that the termination temperatures for the dehydration processes slightly differ between the two compounds (~300 °C for **CoPom-3D** and ~350 °C for **CoPom-1D**).

The distinct dehydration behaviors observed in the TGA profiles offer valuable insights into the water microenvironments within the two frameworks. The lattice water in **CoPom-1D**

is released below 150 °C, whereas that in **CoPom-3D** is released below 200 °C. This earlier release indicates lower thermal retention of lattice water in **CoPom-1D** under the applied TGA conditions and may be consistent with less strongly constrained framework–water interactions. Because TGA is a temperature-programmed measurement, it does not directly quantify equilibrium water-binding energies, molecular residence times, water diffusion, reorientation rates, or proton-carrier mobility.

Structurally, the short O···O contacts and nanoconfined void geometry maintain close proximity between the lattice water molecules and the oxygen-rich framework sites.[70] Within this confined environment, less strongly anchored water molecules may undergo local reorientation and exchange hydrogen-bonding partners more readily, without requiring long-range translational diffusion. The framework may therefore help maintain the spatial connectivity of the water-mediated hydrogen-bond network while permitting local hydrogen-bond reorganization. Such local reorganization may reduce the extent of hydrogen-bond rearrangement associated with successive proton-transfer events. The pronounced humidity dependence and low activation energy of **CoPom-1D** are consistent with this interpretation, although the molecular dynamics of the confined water were not directly measured in the present study.

Consequently, this system highlights a structural trade-off between a higher static concentration of potential proton carriers in **CoPom-3D** and a nanoconfined hydrogen-bond environment in **CoPom-1D** that is consistent with more facile local reorganization and lower-barrier proton transfer. The subsequent electrochemical impedance measurements evaluate how these contrasting structural environments affect macroscopic proton conductivity.

Proton Transport Behavior and Mechanistic Insights

The presence of extensive oxygen-rich frameworks and confined lattice water molecules in both compounds motivated an in-depth investigation into their solid-state proton-transport properties. Following a standard evaluation protocol, powdered samples were pressed into dense pellets (3 mm in diameter) under a pressure of 0.5 MPa for 30 seconds. Both sides of the pellets were coated with silver paste to ensure optimal electrical contact. Proton conductivity was then measured using AC impedance spectroscopy over a frequency range of 0.5 Hz to 1

MHz under controlled temperature and relative-humidity conditions, as detailed in the Supporting Information.

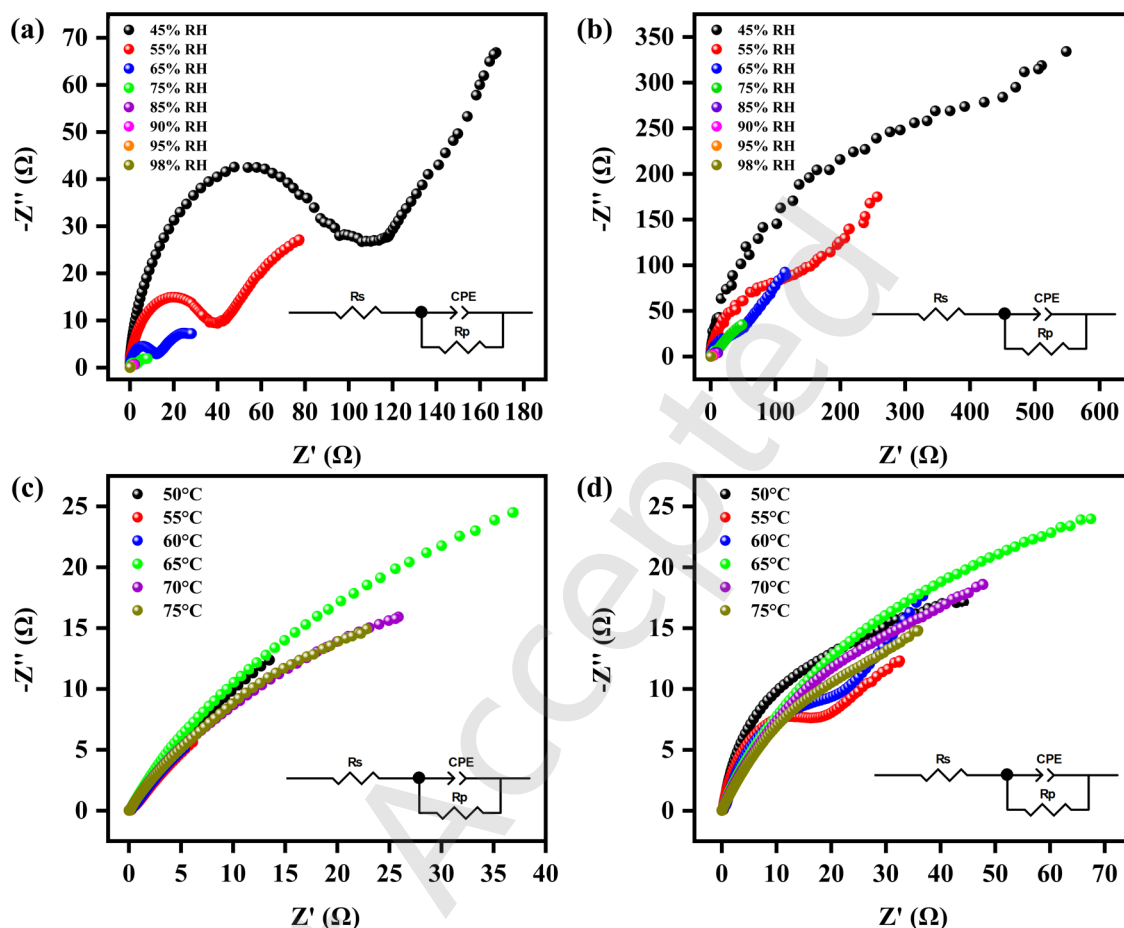


Figure 4. Nyquist plots of the synthesized frameworks under controlled humidity and temperature conditions. (a, b) Humidity-dependent Nyquist plots of **CoPom-3D** and **CoPom-1D**, respectively, recorded at 50 °C. (c, d) Temperature-dependent Nyquist plots of **CoPom-3D** and **CoPom-1D**, respectively, recorded at 98% RH. The inset in each panel shows the equivalent circuit $R_s + (R_p \parallel CPE)$ used for fitting the impedance spectra.

Initially, humidity-dependent impedance measurements were conducted at 50 °C (**Figures 4a and 4b**). As the relative humidity increased from 45% to 95%, both compounds exhibited a dramatic enhancement in proton conductivity, underscoring the indispensable role of adsorbed water molecules in mediating proton transfer within the solid-state matrix. Under 50 °C and 95% RH, **CoPom-1D** exhibits a proton conductivity of $1.92 \times 10^{-3} \text{ S cm}^{-1}$, placing it within the $10^{-3} \text{ S cm}^{-1}$ range reported for several representative POM-based crystalline proton conductors, although direct quantitative ranking is limited by differences in measurement conditions (**Table S6**). **CoPom-1D** exhibits competitive proton conductivity within the reported $\{\text{P}_4\text{Mo}_6\}$ family under relatively mild conditions and has the lowest activation energy among the representative materials included in **Table S7**. As summarized in **Table S7**, **CoPom-1D** exhibits a proton conductivity of $1.92 \times 10^{-3} \text{ S cm}^{-1}$ at 50 °C and 95% RH, which is within the $10^{-3} \text{ S cm}^{-1}$ range reported for several representative $\{\text{P}_4\text{Mo}_6\}$ -based proton conductors. Although higher proton conductivities have been reported under more demanding temperature and humidity conditions, **CoPom-1D** displays competitive proton conductivity under relatively mild measurement conditions. In comparison, **CoPom-3D** exhibits a much lower conductivity of $1.12 \times 10^{-4} \text{ S cm}^{-1}$ under the same conditions. Because these conductivity values were measured under different experimental conditions, **Table S7** is intended to provide contextual

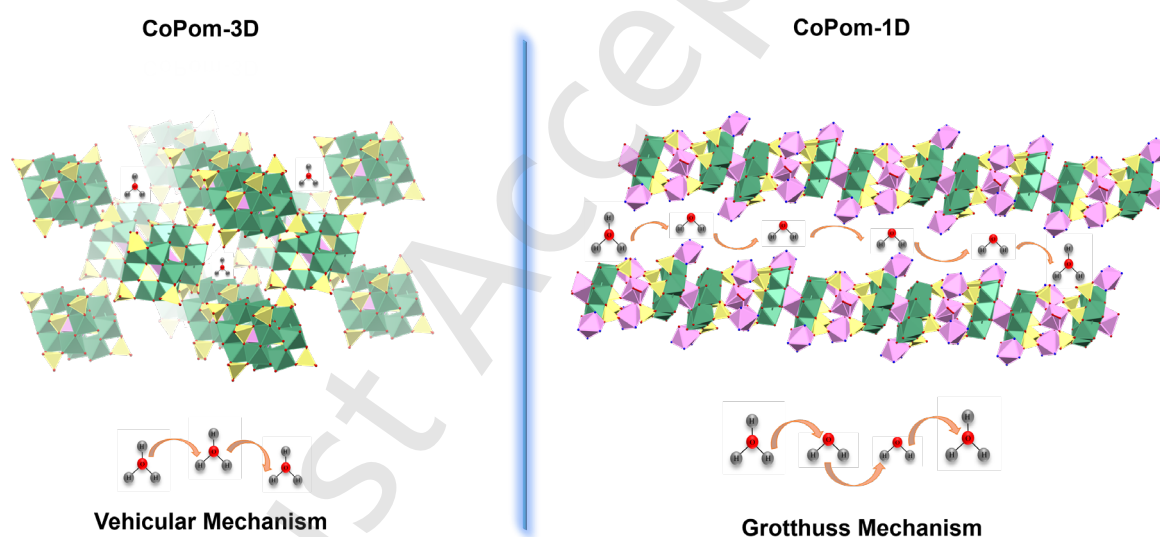


Figure 5. Schematic illustration of the proposed proton-transport pathways. The nanoconfined **CoPom-1D** architecture is consistent with a localized Grotthuss-type proton-transfer pathway, whereas in the densely packed **CoPom-3D** framework, minimal free volume and poorly connected hydrogen-bonding pathways restrict local proton transfer and prevent the formation of an efficient long-range transport pathway.

benchmarking rather than a strict ranking of proton-conduction performance. The activation-energy values listed in **Table S7** further show that **CoPom-1D** has the lowest apparent activation energy among the representative materials compared. This conductivity comparison supports a relationship between the nanoconfined interchain environment and the enhanced proton-transport performance of **CoPom-1D**: the highly dynamic nanoconfined water network in **CoPom-1D** effectively compensates for the lower static proton concentration and densely packed water molecules in **CoPom-3D**.

The superior performance of **CoPom-1D** over **CoPom-3D** can be attributed to several synergistic factors (**Figure 5**), rooted in their distinct structural and microenvironmental characteristics. First, regarding structural channels and nanoconfinement, the markedly different conductivity values are consistent with the spatial packing analysis. **CoPom-3D** is a densely packed 3D coordination framework where multi-directional covalent extension severely restricts the available free volume, effectively trapping its intrinsic protons and leaving minimal space for solvent accommodation and reorganization. In sharp contrast, while **CoPom-1D** is constructed from 1D coordination chains, its specific supramolecular packing (driven by π - π stacking and hydrogen bonding) creates expansive, nanoconfined interchain voids. This unique confinement architecture allows for the formation of robust and continuous water networks, which are essential for long-range proton transport via efficient hopping.

Second, the electrochemical results directly corroborate the water-microenvironment analysis derived from our TGA studies. **CoPom-1D** therefore contains fewer lattice water molecules and lacks the protonated bipyridinium species present in **CoPom-3D**, establishing a lower static inventory of water and potential proton-donating species; however, this compositional difference alone does not directly describe the microscopic mobility or hydrogen-bond reorganization of confined water. In solid-state conductors, the kinetically advantageous mobility of water clusters in **CoPom-1D** compensates for its lower static carrier concentration, facilitating more rapid reorganization of the hydrogen-bond network. Conversely, the tightly bound water and intrinsic protons in the rigid 3D framework of **CoPom-3D** experience significant steric restriction, leading to sluggish proton mobility and lower macroscopic conductivity. These results indicate that the static inventory of lattice water and potential proton-donating species is not the sole determinant of conductivity in this pair of materials; hydrogen-bond connectivity and local proton-transfer accessibility also play important roles.

Finally, temperature-dependent conductivity measurements were performed to further elucidate the proton-transport mechanisms (**Figure 4c** and **4d**). As expected, the conductivity in both frameworks increases with temperature, indicating a thermally activated proton-transfer process. The relatively high activation energy of **CoPom-3D** (0.49 eV), together with its minimal free volume and poorly connected hydrogen-bonding pathways, is consistent with a high-barrier proton-transfer process. Local proton hopping between neighboring donors and acceptor sites may occur, but long-range transport is strongly limited by the discontinuity of the available proton-transfer pathways. Under these structural constraints, translational

diffusion of H_3O^+ or larger hydrated protonic species is unlikely. The low proton conductivity of **CoPom-3D** is therefore attributed to limited hydrogen-bond connectivity and restricted local proton-transfer accessibility, rather than to a dominant vehicular mechanism. In contrast, the very low E_a of 0.11 eV for **CoPom-1D** strongly suggests a low barrier, hopping-dominated proton-transport pathway that is consistent with Grotthuss-type proton transfer. The superior performance of **CoPom-1D** over **CoPom-3D** can be attributed to several synergistic structural factors (**Figure 5**). **CoPom-3D** is a densely packed 3D coordination framework in which multidirectional covalent extension severely restricts solvent-accessible free volume and limits the formation of connected hydrogen-bonding pathways. In contrast, **CoPom-1D** is constructed from 1D coordination chains that further assemble through π - π stacking and hydrogen bonding into a supramolecular architecture containing nanoconfined interchain regions. These confined regions provide short water-framework $\text{O}\cdots\text{O}$ contacts and a better-connected local hydrogen-bonding environment, which are consistent with more accessible proton transfer under humid conditions. Temperature-dependent conductivity measurements yielded apparent activation energies of 0.49 eV for **CoPom-3D** and 0.11 eV for **CoPom-1D**. The value obtained for **CoPom-1D** is lower than those of the representative $\{\text{P}_4\text{Mo}_6\}$ -based proton conductors summarized in **Table S7**. Because the literature values were obtained for different materials and under different measurement conditions, this comparison is intended to provide contextual benchmarking rather than a strict ranking. More importantly, **CoPom-1D** and **CoPom-3D** contain the same fundamental hourglass-type $\{\text{P}_4\text{Mo}_6\}$ building unit and were evaluated using the same experimental protocol. Their markedly different apparent activation energies therefore indicate that ligand-directed spatial packing and the resulting proton-transfer environment influence the energetic requirements for macroscopic proton conduction.

The low apparent activation energy of **CoPom-1D** is consistent with the combined influence of the oxygen-rich $\{\text{P}_4\text{Mo}_6\}$ surface and the nanoconfined interchain environment. The terminal and bridging oxygen sites of the $\{\text{P}_4\text{Mo}_6\}$ cluster provide numerous proton-accepting and hydrogen-bonding sites, while the confined interchain regions contain short water-framework $\text{O}\cdots\text{O}$ contacts that provide plausible local proton-transfer connections. This spatial arrangement may help maintain close donor-acceptor proximity and facilitate local hydrogen-bond reorganization, thereby reducing the extent of structural rearrangement required during successive proton-transfer events. Collectively, these structural features are consistent with a low-barrier, predominantly Grotthuss-type contribution to proton transport. Because the microscopic proton-transfer free-energy landscape and confined-water dynamics

were not directly measured, this explanation is presented as a structure-supported mechanistic interpretation rather than direct proof of the origin of the 0.11 eV activation energy. Despite its lower lattice-water content and the absence of protonated bipyridinium species, **CoPom-1D** exhibits approximately 17-fold higher proton conductivity than **CoPom-3D** under identical conditions (50 °C, 95% RH), together with a substantially lower apparent activation energy (0.11 eV vs. 0.49 eV). These observations suggest that, for this material pair, proton conductivity is influenced more by hydrogen-bond connectivity and local proton-transfer accessibility than by the static amount of lattice water or proton-donating species. Instead, the nanoconfined interchain geometry and short water–framework O $\cdots$ O contacts support a better-connected water-mediated hydrogen-bonding environment, while the electrochemical results are consistent with hydrogen-bond connectivity and the ease of proton transfer playing more consequential roles under the measurement conditions. The microscopic mobility of the confined water was not directly measured. Proton transfer through water-mediated hydrogen-bond networks involve coupled changes in the proton position and the local coordination and orientation of surrounding water molecules. Previous *ab initio* and molecular-simulation studies have shown that nanoconfinement can modify hydrogen-bond connectivity and proton-transfer pathways.[71–74] However, these effects depend strongly on pore geometry and interfacial chemistry rather than universally enhancing water mobility.

In **CoPom-1D**, the nanoconfined interchain geometry, oxygen-rich {P₄Mo₆} surfaces, and short water–framework O $\cdots$ O contacts provide a structural basis for maintaining closely spaced proton-donor and proton-acceptor sites. This spatial organization may reduce the extent of local hydrogen-bond rearrangement required during successive proton-transfer events and is therefore consistent with the low apparent activation energy and pronounced humidity dependence. Nevertheless, neither the microscopic reorientation dynamics of the confined water nor the solvent-reorganization energy was directly measured or calculated in the present study. The proposed role of water-network reorganization should therefore be regarded as a structure-supported and literature-supported mechanistic interpretation rather than direct experimental evidence for the dynamic behavior of confined water in **CoPom-1D**.

Consequently, the substantially higher conductivity of **CoPom-1D** despite its lower lattice-water content indicates that the static inventory of lattice water and potential proton-donating species alone does not determine conductivity in this pair of materials. Instead, hydrogen-bond connectivity and the kinetic accessibility of proton transfer appear to play more consequential roles. To evaluate the short-term operational stability of **CoPom-1D**, its proton

conductivity was measured periodically at 2 h intervals over a 12 h period under constant conditions of 50 °C and 95% RH. As shown in **Figure S17**, the conductivity remained essentially constant throughout the measurement period, with only minor fluctuations and no systematic decrease. This result demonstrates stable proton-conduction performance over 12 h under the investigated conditions and is consistent with the retention of the water-mediated proton-transport pathway. To place the proton-transport behavior of **CoPom-1D** in a broader context, comparison with recently reported $\{\text{AlMo}_{14}\text{O}_{44}\}$ -based supramolecular proton conductors provides a useful benchmark. The two reported $\{\text{AlMo}_{14}\text{O}_{44}\}$ -based compounds exhibit proton conductivities of 3.89×10^{-2} and $4.76 \times 10^{-2} \text{ S cm}^{-1}$, respectively, at 85 °C and 98% RH, with activation energies of 0.56 and 0.55 eV. Their proton transport was assigned predominantly to a vehicular mechanism. Because these conductivity values were obtained under different experimental conditions, the comparison is not intended to establish superior proton conductivity. Instead, it highlights the mechanistic distinction between the reported vehicular systems and **CoPom-1D**. Although **CoPom-1D** exhibits a lower conductivity ($1.92 \times 10^{-3} \text{ S cm}^{-1}$ at 50 °C and 95% RH), it shows a markedly lower activation energy (0.11 eV). Together with the short water–framework $\text{O} \cdots \text{O}$ contacts observed in the crystal structure and the pronounced humidity dependence of proton conductivity, this low activation energy is consistent with the proposed Grotthuss-type proton-transfer pathway in the nanoconfined environment.[74] The present design principle can be placed in the broader context of related crystalline proton conductors. In porous nonmetal organic frameworks, proton conductivity has been shown to depend strongly on water uptake within one-dimensional polar pore channels, illustrating how pore chemistry and confined hydration can regulate proton transport.[75] In POM-based materials, controlled self-assembly has likewise been employed to generate confined proton-conduction pathways, while recent reviews identify hydrated transport microenvironments and continuous hydrogen-bond networks as recurring design principles.[16,48] These precedents place the present ligand-isomerism-induced nanoconfinement strategy within a broader class of structure-guided design strategies for regulating proton transport, without implying that its specific structural mechanism is universally applicable. Overall, these results indicate that, in this pair of materials, hydrogen-bond connectivity and carrier mobility can outweigh the static number of potential proton carriers in governing macroscopic proton conductivity.

CONCLUSION

In summary, we have successfully constructed two new $\{P_4Mo_6\}$ -based cobalt frameworks through a ligand-isomerism-directed hydrothermal assembly strategy. By employing linear 4,4'-bpy and chelating 2,2'-bpy as structure-directing agents, the identical anionic hourglass-type $[Co(P_4Mo_6O_{31})_2]^{10-}$ building units were transformed into a densely packed 3D coordination framework (**CoPom-3D**) and a 3D supramolecular architecture assembled from 1D coordination chains (**CoPom-1D**), respectively. Comprehensive structural and thermal analyses reveal that although **CoPom-1D** possesses a lower lattice water content and lacks the intrinsic protonated ligands found in **CoPom-3D**, its unique supramolecular nanoconfinement facilitates a more flexible and dynamically reorganizable hydrogen-bond network. As a result, **CoPom-1D** exhibits a superior proton conductivity of $1.92 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$ at 50 °C and 95% RH, which ranks among the highest for POM-based crystalline conductors and is nearly an order of magnitude higher than that of the dense **CoPom-3D** framework ($1.12 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$). The markedly different apparent activation energies of **CoPom-1D** and **CoPom-3D** indicate a strong relationship between ligand-directed spatial packing and the energetic requirements for macroscopic proton transport. The structural and electrochemical results are consistent with a predominantly Grotthuss-type contribution in **CoPom-1D**, although direct characterization of proton and confined-water dynamics will be required to establish the microscopic mechanism conclusively. These findings suggest that suppressing dense multidirectional covalent extension, creating supramolecularly confined proton-transport microenvironments, and regulating water-mediated hydrogen-bonding environments may provide broadly applicable design principles for improving POM-based proton conductors.

Acknowledgement

This work was supported by the National Natural Science Foundation of China (Grant No. 21701040). The authors acknowledge the use of a large language model for language editing and improving the clarity of the manuscript. The authors retain full responsibility for the experimental design, data interpretation, and the final content presented in this work.

Conflict of Interest

The authors declare no conflict of interest.

REFERENCES

- [1] Kreuer, K.-D. Proton Conductivity: Materials and Applications. *Chem. Mater.*, **1996**, *8*, 610–641.
- [2] Haile, S.M.; Chisholm, C.R.I.; Sasaki, K.; Boysen, D.A.; Uda, T. Solid Acid Proton Conductors: From Laboratory Curiosities to Fuel Cell Electrolytes. *Faraday Discuss.*, **2007**, *134*, 17–39.
- [3] Horike, S.; Umeyama, D.; Kitagawa, S. Ion Conductivity and Transport by Porous Coordination Polymers and Metal–Organic Frameworks. *Acc. Chem. Res.*, **2013**, *46*, 2376–2384.
- [4] Peighambaroust, S.J.; Rowshanzamir, S.; Amjadi, M. Review of the Proton Exchange Membranes for Fuel Cell Applications. *Int. J. Hydrog. Energy*, **2010**, *35*, 9349–9384.
- [5] Sadakiyo, M.; Yamada, T.; Honda, K.; Matsui, H.; Kitagawa, H. Control of Crystalline Proton-Conducting Pathways by Water-Induced Transformations of Hydrogen-Bonding Networks in a Metal–Organic Framework. *J. Am. Chem. Soc.*, **2014**, *136*, 7701–7707.
- [6] Yoon, M.; Srirambalaji, R.; Kim, K. Homochiral Metal–Organic Frameworks for Asymmetric Heterogeneous Catalysis. *Chem. Rev.*, **2012**, *112*, 1196–1231.
- [7] Paille, G.; Gomez-Mingot, M.; Roch-Marchal, C.; Lassalle-Kaiser, B.; Mialane, P.; Fontecave, M.; Mellot-Draznieks, C.; Dolbecq, A. A Fully Noble Metal-Free Photosystem Based on Cobalt-Polyoxometalates Immobilized in a Porphyrinic Metal–Organic Framework for Water Oxidation. *J. Am. Chem. Soc.*, **2018**, *140*, 3613–3618.
- [8] Wang, C.; Su, T.; Zang, H.-Y.; Su, Z.-M. Rational Design and Progress of Molybdenum-Oxo Clusters. *Mater. Chem. Front.*, **2023**, *7*, 1912–1942.
- [9] Du, Z.-Y.; Chen, Z.; Kang, R.-K.; Han, Y.-M.; Ding, J.; Cao, J.-P.; Jiang, W.; Fang, M.; Mei, H.; Xu, Y. Two 2D Layered P₄Mo₆ Clusters with Potential Bifunctional Properties: Proton Conduction and CO₂ Photoreduction. *Inorg. Chem.*, **2020**, *59*, 12876–12883.
- [10] Li, J.-N.; Du, Z.-Y.; Li, N.-F.; Han, Y.-M.; Zang, T.-T.; Yang, M.-X.; Liu, X.-M.; Wang, J.-L.; Mei, H.; Xu, Y. Two Three-Dimensional Polyanionic Clusters [M(P₄Mo₆)₂] (M = Co, Zn) Exhibiting Excellent Photocatalytic CO₂ Reduction Performance. *Dalton Trans.*, **2021**, *50*, 9137–9143.
- [11] Horike, S.; Umeyama, D.; Inukai, M.; Itakura, T.; Kitagawa, S. Coordination-Network-Based Ionic Plastic Crystal for Anhydrous Proton Conductivity. *J. Am. Chem. Soc.*, **2012**, *134*, 7612–7615.
- [12] Liu, Y.-R.; Chen, Y.-Y.; Zhao, H.-Y.; Li, G. Exploration of Single-Crystal Proton Conduction in Ordered Networks. *Coord. Chem. Rev.*, **2024**, *499*, 215516.
- [13] Yamada, T.; Otsubo, K.; Makiura, R.; Kitagawa, H. Designer Coordination Polymers: Dimensional Crossover Architectures and Proton Conduction. *Chem. Soc. Rev.*, **2013**, *42*, 6655–6669.
- [14] Biradha, K.; Goswami, A.; Moi, R.; Saha, S. Metal–Organic Frameworks as Proton Conductors: Strategies for Improved Proton Conductivity. *Dalton Trans.*, **2021**, *50*, 10655–10673.
- [15] Ma, X.-Q.; Xiao, H.-P.; Chen, Y.; Lai, Q.-S.; Li, X.-X.; Zheng, S.-T. Polyoxometalate-Based Macrocycles and Their Assembly. *Coord. Chem. Rev.*, **2024**, *510*, 215818.
- [16] Zhang, H.; Wang, Y.; Shi, Y.; Zhang, Y.; Yang, Y.; Wang, Y.; Cui, Y.; Guo, J.; Zhang, P.; Sun, L.; Zhang, J. Recent Advances in Polyoxometalate-Based Proton Conducting Materials: Design Strategies, Conduction Mechanisms, Structure–Function Relationships and Future Perspectives. *Nano Res.*, **2025**, *18*, 94907743.
- [17] Liu, Y.; Yang, X.; Miao, J.; Tang, Q.; Liu, S.; Shi, Z.; Liu, S. Polyoxometalate-Functionalized Metal–Organic Frameworks with Improved Water Retention and

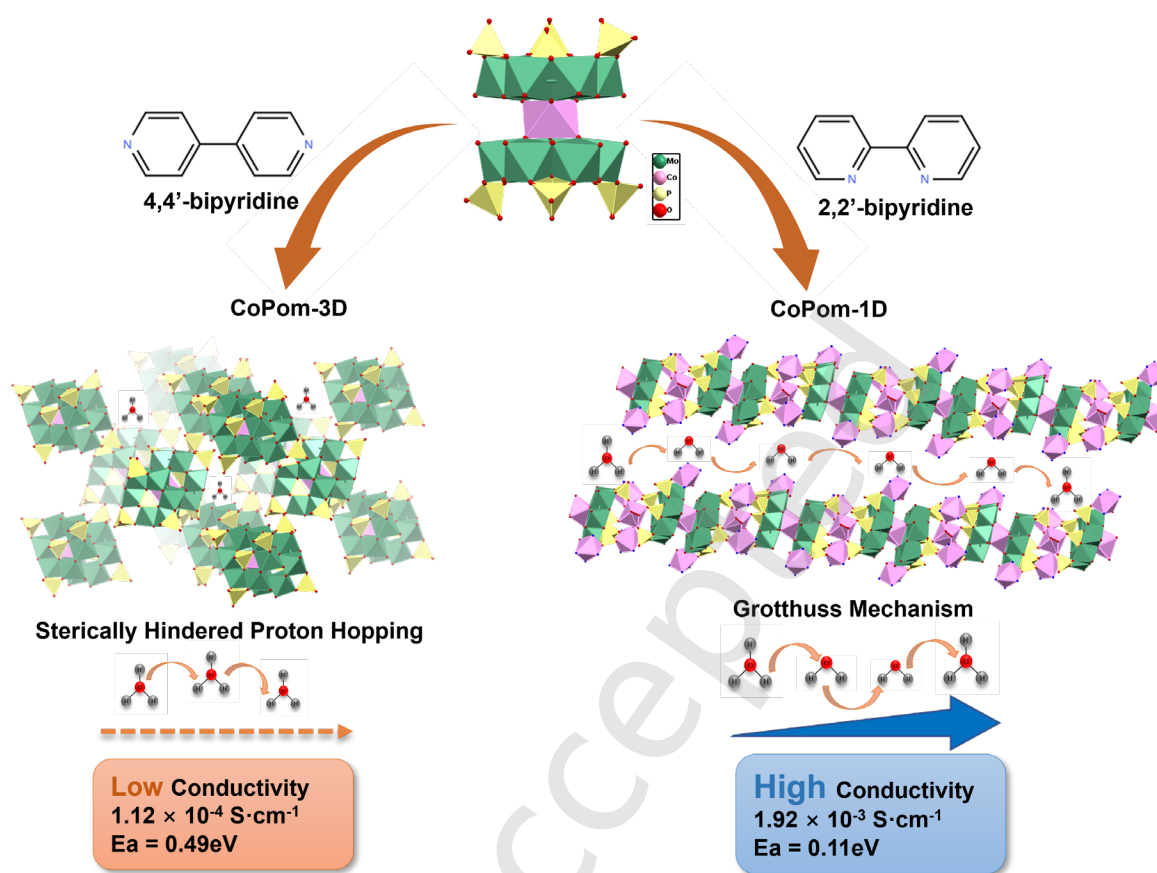
- Uniform Proton-Conducting Pathways in Three Orthogonal Directions. *Chem Commun*, **2014**, 50, 10023–10026.
- [18] Zhou, E.; Qin, C.; Huang, P.; Wang, X.; Chen, W.; Shao, K.; Su, Z. A Stable Polyoxometalate-Pillared Metal–Organic Framework for Proton-Conducting and Colorimetric Biosensing. *Chem. – Eur. J.*, **2015**, 21, 11894–11898.
- [19] Song, Y.-F.; Tsunashima, R. Recent Advances on Polyoxometalate-Based Molecular and Composite Materials. *Chem. Soc. Rev.*, **2012**, 41, 7384–7402.
- [20] Wang, S.-S.; Yang, G.-Y. Recent Advances in Polyoxometalate-Catalyzed Reactions. *Chem. Rev.*, **2015**, 115, 4893–4962.
- [21] Sun, J.-Y.; Wang, Z.-L.; Zhang, Z.; Liu, G.-C.; Wang, X.-L. Hydrothermal Synthesis, Structure, and Catalytic Properties of a (4,6)-Connected Framework Constructed from Keggin-Type Polyoxometalate Units and Tetranuclear Copper Complexes. *Polyoxometalates*, **2024**, 3, 9140039.
- [22] Zheng, Y.; Sun, J.; Zhang, Z.; Li, X.; Liu, G.; Sun, C.; Wang, X. A 3D Supramolecular Framework with Electron-Deficient-Carboxylate-Functionalized [γ -Mo₈O₂₆]-Subunits for Catalytic Epoxidation of Alkenes and Electrochemical Detection of Sunset Yellow. *J. Mol. Struct.*, **2025**, 1337, 142176.
- [23] Song, H.; Guo, M.-S.; Wang, J.-F.; Liu, Y.-Q.; Bi, H.-X.; Du, J.; An, W.-T.; Ma, Y.-Y.; Han, Z.-G. Reduced Phosphomolybdate as Photoassisted Electrochemical Crystalline Sensor for Trace Cr(VI) Detection. *Polyoxometalates*, **2024**, 3, 9140065.
- [24] Gao, Z.-X.; Sun, S.; Li, B.; Cheng, D.-M.; Wang, Y.-H.; Zang, H.-Y.; Li, Y.-G. Design and Synthesis of Phosphomolybdate Coordination Compounds Based on {P₄Mo₆} Structural Units and Their Proton Conductivity. *Tungsten*, **2023**, 5, 67–74.
- [25] Zhang, H.; Yu, K.; Li, J.; Wang, C.; Lv, J.; Chen, Z.; Cai, H.; Zhou, B. The Highest Connected Pure Inorganic 3D Framework Assembled by {P₄Mo₆} Cluster and Alkali Metal Potassium. *RSC Adv.*, **2015**, 5, 3552–3559.
- [26] Li, W.; Zhu, J.-N.; Shen, N.-N.; Xiong, W.-W.; Huang, X.-Y. Assembling [M(P₄Mo₆)₂] (M = Na, Mn, Na/Cu) Dimeric Clusters via Transition Metal/Sodium Ions into 0D to 3D Phosphomolybdates. *CrystEngComm*, **2019**, 21, 971–980.
- [27] Yang, L.; Zhang, Z.; Zhang, C.; Wang, X. A Bifunctional POM-based Cu-viologen Complex with Mixed Octamolybdate Clusters for Rapid Oxidation Desulfurization and Effective Photogeneration of Hydrogen. *Rare Met.*, **2024**, 43, 236–246.
- [28] Soria-Carrera, H.; Atrián-Blasco, E.; Martín-Rapún, R.; Mitchell, S.G. Polyoxometalate–Peptide Hybrid Materials: From Structure–Property Relationships to Applications. *Chem. Sci.*, **2023**, 14, 10–28.
- [29] Long, D.; Tsunashima, R.; Cronin, L. Polyoxometalates: Building Blocks for Functional Nanoscale Systems. *Angew. Chem. Int. Ed.*, **2010**, 49, 1736–1758.
- [30] Luo, Y.-H.; Yi, L.-Q.; Lu, J.-N.; Dong, L.-Z.; Lan, Y.-Q. A Stable Polyoxometalate-Based Porous Coordination Polymer with High Proton Conductivity. *CrystEngComm*, **2018**, 20, 6077–6081.
- [31] Maji, T.K.; Matsuda, R.; Kitagawa, S. A Flexible Interpenetrating Coordination Framework with a Bimodal Porous Functionality. *Nat. Mater.*, **2007**, 6, 142–148.
- [32] El Hajj, F.; Patinec, V.; Triki, S.; Handel, H.; Marchivie, M. Isomerism as a Remarkable Tool for the Design of New Potentially Bridging Macrocyclic Ligands: Synthesis and Characterization of the [Cu(4-L1)](NO₃)₂·2H₂O Polymeric Chain (4-L1=mono-N (4-Picolyl)Cyclen). *Inorg. Chem. Commun.*, **2010**, 13, 1314–1316.
- [33] Shigematsu, A.; Yamada, T.; Kitagawa, H. Wide Control of Proton Conductivity in Porous Coordination Polymers. *J. Am. Chem. Soc.*, **2011**, 133, 2034–2036.
- [34] Sadakiyo, M.; Yamada, T.; Kitagawa, H. Rational Designs for Highly Proton-Conductive Metal–Organic Frameworks. *J. Am. Chem. Soc.*, **2009**, 131, 9906–9907.

- [35] Umeyama, D.; Horike, S.; Inukai, M.; Hijikata, Y.; Kitagawa, S. Confinement of Mobile Histamine in Coordination Nanochannels for Fast Proton Transfer. *Angew. Chem. Int. Ed.*, **2011**, *50*, 11706–11709.
- [36] Zhang, S.; Lu, Y.; Sun, X.-W.; Li, Z.; Dang, T.-Y.; Zhang, Z.; Tian, H.-R.; Liu, S.-X. Purely Inorganic Frameworks Based on Polyoxometalate Clusters with Abundant Phosphate Groups: Single-Crystal to Single-Crystal Structural Transformation and Remarkable Proton Conduction. *Chem. Commun.*, **2020**, *56*, 391–394.
- [37] Hu, Q.; Li, K.; Chen, X.; Liu, Y.; Yang, G. Polyoxometalate Catalysts for the Synthesis of N-Heterocycles. *Polyoxometalates*, **2024**, *3*, 9140048.
- [38] Agmon, N. The Grotthuss Mechanism. *Chem. Phys. Lett.*, **1995**, *244*, 456–462.
- [39] Kreuer, K. On the Complexity of Proton Conduction Phenomena. *Solid State Ion.*, **2000**, *136–137*, 149–160.
- [40] Li, C.; Jiang, H.-Y.; Wang, J.-L.; Kang, R.-K.; Mei, H.; Xu, Y. An Isolated Doughnut-like Molybdenum(V) Cobalto-Phosphate Cluster Exhibiting Excellent Photocatalytic Performance for Carbon Dioxide Conversion. *Dalton Trans.*, **2022**, *51*, 9616–9621.
- [41] Liu, W.-J.; Dong, L.-Z.; Li, R.-H.; Chen, Y.-J.; Sun, S.-N.; Li, S.-L.; Lan, Y.-Q. Different Protonic Species Affecting Proton Conductivity in Hollow Spherelike Polyoxometalates. *ACS Appl. Mater. Interfaces*, **2019**, *11*, 7030–7036.
- [42] Deng, W.; Zhu, Z.; Sun, Y.; Xu, H.; Liu, S.; Wen, H. Recent Advances in {P₄Mo₆}-Based Polyoxometalates. *Polyoxometalates*, **2024**, *3*, 9140071.
- [43] Wang, G.; Li, J.; Shang, L.; He, H.; Cui, T.; Chai, S.; Zhao, C.; Wu, L.; Li, H. Nanostructured Polymer Composite Electrolytes with Self-Assembled Polyoxometalate Networks for Proton Conduction. *CCS Chem.*, **2022**, *4*, 151–161.
- [44] Bi, H.-X.; Guo, M.-S.; Du, J.; Ma, Y.-Y.; Han, Z.-G. Polyoxometalate Chemistry of {M[P₄Mo₆]₂}: From Structure Assembly to Functional Application. *Coord. Chem. Rev.*, **2024**, *518*, 216092.
- [45] Li, Y.-J.; Li, C.-X.; Zhou, S.-B.; Wei, J.-Y.; Fang, Q.; Hu, X.-L.; Liu, B.-L.; Su, Z.-M. Two-Dimensional Layer {P₄Mo₆} Clusters Constructed with N-Ligands for Bifunctional Properties of Proton Conduction and Supercapacitors. *Inorg. Chem.*, **2025**, *64*, 443–451.
- [46] Zhang, Y.-Q.; Zhou, L.-Y.; Ma, Y.-Y.; Dastafkan, K.; Zhao, C.; Wang, L.-Z.; Han, Z.-G. Stable Monovalent Aluminum(I) in a Reduced Phosphomolybdate Cluster as an Active Acid Catalyst. *Chem. Sci.*, **2021**, *12*, 1886–1890.
- [47] Ji, N.-N.; Shi, Z.-Q.; Xie, X.-X.; Li, G. Polyoxometalate-Based Hydrogen-Bonded Organic Frameworks as a New Class of Proton Conducting Materials. *CrystEngComm*, **2020**, *22*, 8161–8165.
- [48] Liu, Q.; Li, J.; Liu, S.; Yu, S.; Chen, Z.; Ma, J.; Chen, Y.; Zang, H.-Y. Carboxylate-Directed Self-Assembly of [Mo₂O₄]²⁺ Units for Enhanced Proton Conduction. *Inorg. Chem.*, **2025**, *64*, 16623–16631.
- [49] Oruganti, Y.; Kim, D.; Lim, D.-W. Dimensional Crossover and Proton Conductivity in Copper-Based Coordination Polymers by Coordinative Guest Insertion. *Cryst. Growth Des.*, **2024**, *24*, 1612–1618.
- [50] Goswami, A.; Ghorai, A.; Pal, D.; Banerjee, S.; Biradha, K. Proton Conducting Metal-Organic Frameworks (MOFs) via Post Synthetic Transmetalation and Water Induced Structural Transformations. *Chem. – Eur. J.*, **2024**, *30*, e202402165.
- [51] Zhu, J.; Zhu, P.; Mei, J.; Xie, J.; Guan, J.; Zhang, K.-L. Proton Conduction and Luminescent Sensing Property of Two Newly Constructed Positional Isomer-Dependent Redox-Active Mn(II)-Organic Frameworks. *Polyhedron*, **2021**, *200*, 115139.

- [52] Li, X.; Chai, S.; Li, H. Polyoxometalate-Based Reticular Materials for Proton Conduction: From Rigid Frameworks to Flexible Networks. *Dalton Trans.*, **2024**, 53, 6488–6495.
- [53] Lim, D.-W.; Kitagawa, H. Rational Strategies for Proton-Conductive Metal–Organic Frameworks. *Chem. Soc. Rev.*, **2021**, 50, 6349–6368.
- [54] Zhu, Y.-J.; Cui, Y.-M.; Wang, N.-H.; Sun, J.; Wu, X.-S.; Han, X.; Wang, X.; Su, Z.-M. Construct Ordered Proton Channels in Polyoxometalate-Based Metal–Organic Frameworks for Enhancing Proton Conduction. *Inorg. Chem.*, **2025**, 64, 19113–19119.
- [55] Li, W.-H.; Deng, W.-H.; Wang, G.-E.; Xu, G. Conductive MOFs. *EnergyChem*, **2020**, 2, 100029.
- [56] Ramaswamy, P.; Wong, N.E.; Shimizu, G.K.H. MOFs as Proton Conductors—Challenges and Opportunities. *Chem Soc Rev*, **2014**, 43, 5913–5932.
- [57] Bureekaew, S.; Horike, S.; Higuchi, M.; Mizuno, M.; Kawamura, T.; Tanaka, D.; Yanai, N.; Kitagawa, S. One-Dimensional Imidazole Aggregate in Aluminium Porous Coordination Polymers with High Proton Conductivity. *Nat. Mater.*, **2009**, 8, 831–836.
- [58] Zhang, W.-S.; Wang, G.-Q.; Wang, Y.-X.; Yang, Y.-L.; Bai, X.; Cui, H.; Lu, Y.; Liu, S.-X. A Multifunctional Cobalt–Organic Framework for Proton Conduction and Selective Sensing of Fe^{3+} Ions. *Dalton Trans.*, **2023**, 52, 4407–4414.
- [59] Dubskikh, V.A.; Kolosov, A.A.; Lysova, A.A.; Samsonenko, D.G.; Lavrov, A.N.; Kovalenko, K.A.; Dybtsev, D.N.; Fedin, V.P. A Series of Metal–Organic Frameworks with 2,2'-Bipyridyl Derivatives: Synthesis vs. Structure Relationships, Adsorption, and Magnetic Studies. *Molecules*, **2023**, 28, 2139.
- [60] Ma, X.-Q.; Liu, Y.-F.; Yang, G.-P.; Kong, X.-J.; Li, X.-X.; Zheng, S.-T. An Unusual Crystalline Porous Framework Constructed from Multitypes of Cages with Proton Conduction Property and Heterogeneous Catalytic Activity for Pyrazole Synthesis. *Inorg. Chem.*, **2024**, 63, 12240–12247.
- [61] Sun, J.-Y.; Sun, S.-Y.; Zhang, Z.; Li, M.-T.; Liu, G.-C.; Wang, X.-L. A 4,4-Connected 2D POM-Based Complex with Synergistic Mixed-Valence $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$ for Mild and Efficient Catalytic Oxidation of Phenols. *J. Mater. Chem. A*, **2026**, 14, 15000–15007.
- [62] Cheng, P.-C.; Kuo, P.-T.; Liao, Y.-H.; Xie, M.-Y.; Hsu, W.; Chen, J.-D. Ligand-Isomerism Controlled Structural Diversity of Zn(II) and Cd(II) Coordination Polymers from Mixed Dipyrityladipoamide and Benzenedicarboxylate Ligands. *Cryst. Growth Des.*, **2013**, 13, 623–632.
- [63] Chen, W.-T.; Wang, M.-S.; Liu, X.; Guo; Huang, J.-S. Investigations of Group 12 (IIB) Metal Halide/Pseudohalide-Bipy Systems: Syntheses, Structures, Properties, and TDDFT Calculations (Bipy = 2,2'-Bipyridine or 4,4'-Bipyridine). *Cryst. Growth Des.*, **2006**, 6, 2289–2300.
- [64] Ma, X.-Y.; Bi, H.-X.; Zhang, X.-J.; Du, J.; Ma, Y.-Y.; Han, Z.-G. Effect of Bridging Units on the Detection Performance of $\text{Cd}\{\text{P}_4\text{Mo}_6\}_2$ -Based Electrochemical Sensors for Trace Chromium(VI) and Tetracycline. *Polyoxometalates*, **2025**, 4, 9140090.
- [65] Wang, L.; Li, J.; Liu, X.; Liu, Q.; Li, J.; Liang, S.; Zang, H.-Y. Ligand-Directed Assembly of $[\text{Mo}_2\text{O}_2\text{S}_2]^{2+}$ into Interlocked Architectures with Efficient Proton Conduction. *Chin. Chem. Lett.*, **2025**, 111698.
- [66] Sheldrick, G.M. Crystal Structure Refinement with *SHELXL*. *Acta Crystallogr. Sect. C Struct. Chem.*, **2015**, 71, 3–8.
- [67] Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. *OLEX2*: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Crystallogr.*, **2009**, 42, 339–341.

- [68] Zheng, D.-W.; Xu, H.; Sun, Y.-J.; Zhu, Z.-H.; Wang, X.-L.; Liu, S.-J.; Su, Z.-M. Tuning Proton Conduction Mechanism via Metal Cation Node in Isostructural Polyoxometalate Frameworks. *J. Mol. Struct.*, **2026**, 1368, 146308.
- [69] Wang, H.-Y.; Li, S.-R.; Wang, X.; Long, L.-S.; Kong, X.-J.; Zheng, L.-S. Enhanced Proton Conductivity of Mo₁₅₄-Based Porous Inorganic Framework. *Sci. China Chem.*, **2021**, 64, 959–963.
- [70] Li, X.-X.; Li, C.-H.; Hou, M.-J.; Zhu, B.; Chen, W.-C.; Sun, C.-Y.; Yuan, Y.; Guan, W.; Qin, C.; Shao, K.-Z.; Wang, X.-L.; Su, Z.-M. Ce-Mediated Molecular Tailoring on Gigantic Polyoxometalate {Mo₁₃₂} into Half-Closed {Ce₁₁Mo₉₆} for High Proton Conduction. *Nat. Commun.*, **2023**, 14, 5025.
- [71] Marx, D. Proton Transfer 200 Years after von Grotthuss: Insights from Ab Initio Simulations. *ChemPhysChem*, **2006**, 7, 1848–1870.
- [72] Fumagalli, L.; Esfandiar, A.; Fabregas, R.; Hu, S.; Ares, P.; Janardanan, A.; Yang, Q.; Radha, B.; Taniguchi, T.; Watanabe, K.; Gomila, G.; Novoselov, K.S.; Geim, A.K. Anomalously Low Dielectric Constant of Confined Water. *Science*, **2018**, 360, 1339–1342.
- [73] Shi, B.; Pang, X.; Li, S.; Wu, H.; Shen, J.; Wang, X.; Fan, C.; Cao, L.; Zhu, T.; Qiu, M.; Yin, Z.; Kong, Y.; Liu, Y.; Zhang, M.; Liu, Y.; Pan, F.; Jiang, Z. Short Hydrogen-Bond Network Confined on COF Surfaces Enables Ultrahigh Proton Conductivity. *Nat. Commun.*, **2022**, 13, 6666.
- [74] Ren, W.-B.; Li, B.; Cui, Y.; Chen, X.; Liu, Q.; Chen, Y.; Chen, Z.; Wang, Y.; Zang, H.-Y. Synthesis of {AlMo₁₄O₄₄}-Based Supramolecular Structures with High Proton Conductivity. *Inorg. Chem.*, **2024**, 63, 20307–20313.
- [75] O'Shaughnessy, M.; Lim, J.; Glover, J.; Neale, A.R.; Day, G.M.; Hardwick, L.J.; Cooper, A.I. Nonmetal Organic Frameworks Exhibit High Proton Conductivity. *J. Am. Chem. Soc.*, **2025**, 147, 15429–15434.

TOC Graph



Ligand isomerism dictates framework dimensionality and proton transport pathways. The 1D structure enables superior proton conduction via a Grotthuss mechanism, whereas the 3D framework exhibits lower conductivity due to localized, sterically hindered proton hopping.