

Construction of inorganic macrocyclic host-guest architectures with high proton conductivity via coordination mode tuning

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ABSTRACT: Constructing an inorganic macrocycle-based host-guest system remains a formidable synthetic challenge. Herein, by tuning the coordination modes of the pyrimidine-5-carboxylic acid (Pym-5-CA) and the assembly of $[\text{Mo}_2\text{O}_2\text{S}_2]^{2+}$ units, we can obtain either an organic-templated inorganic ring architecture ($\text{H}_4[(\text{Mo}_2\text{O}_2\text{S}_2)_6(\text{OH})_{12}(\text{C}_5\text{H}_3\text{O}_2\text{N}_2)_2] \cdot 6\text{DMF} \cdot 5\text{H}_2\text{O}$, denoted as $\text{Mo}_{12}\text{-Pym-5-CA}$, (**1**)) or an inorganic-host-organic-guest complex ($[(\text{Mo}_2\text{O}_2\text{S}_2)_5(\text{OH})(\text{H}_2\text{O})_5(\text{Pym-5-CA})] \cdot 24\text{H}_2\text{O}$, $\text{Mo}_{10}@\text{Pym-5-CA}$ (**2**)). By employing a similar strategy, but with another organic guest molecule, 3-pyridine-boronic acid (3-PyBA), another host-guest complex $\text{H}[(\text{Mo}_2\text{O}_2\text{S}_2)_5(\text{OH})(\text{H}_2\text{O})_5(3\text{-PyBA})] \cdot 2\text{DMF} \cdot 16\text{H}_2\text{O}$, $\text{Mo}_{10}@\text{3-PyBA}$ (**3**) can be obtained. The host-guest structures have been characterized by multiple techniques, such as powder X-ray diffraction (PXRD), single-crystal X-ray diffraction (SC-XRD), and hydrogen nuclear magnetic resonance spectroscopy (^1H NMR). Proton conduction measurements at 70 °C and 90% RH reveal that complex **2** exhibits a proton conductivity of $8.76 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$, approximately 2.1 times higher than that of complex **1** and 1.7 times higher than that of complex **3**. This superior performance stems from the synergistic effect of its intact carboxyl groups, which serve as strong proton donors, and its well-defined hydrogen bond network. Potentiometric measurements under varying pH conditions further reveal that complex **2** exhibits a slope of 37 mV dec^{-1} , higher than those of complex **1** (28 mV dec^{-1}) and complex **3** (32 mV dec^{-1}), indicating an enhanced proton-responsive behavior. By elucidating the distinct roles of supramolecular and coordination assembly in dictating the structures and proton conduction of polyoxothiometalates (POTMs), this work establishes a direct correlation between proton transport and interfacial response. Beyond demonstrating their promise as proton-selective electrochemical interfaces, these findings provide valuable insights for the rational design next-generation proton-conductive materials.

KEYWORDS: polyoxothiometalates (POTMs), host-guest complexes, $\{\text{Mo}_{10}\}$ ring, Pym-5-CA, proton conduction

1 Introduction

Host-guest chemistry is a cornerstone of supramolecular science that explores the selective encapsulation of guest molecules within the cavities of host molecules through reversible non-covalent interactions such as hydrogen bonding, π - π stacking, and hydrophobic effects [1-7]. Most traditional host-guest systems have overwhelmingly relied on organic macrocyclic hosts like cyclodextrins, cucurbiturils, and calixarenes [8-13]. However, seldom have host-guest examples based on inorganic macrocycles been reported.

Polyoxometalates (POMs) are a type of atomically precise nanosized structures, owning strong Brønsted acidity, and tunable oxygen-rich surfaces [14-33]. Recent studies have demonstrated the remarkable potential as inorganic hosts. For instance, Cronin and colleagues reported the self-templating assembly of a $\{\text{Mo}_{24}\text{Fe}_{12}\}$ inorganic macrocycle capable of encapsulating various polyoxometalate guests, [34] including the Anderson $\{\text{FeMo}_6\}$, Keggin $\{\text{PMo}_{12}\}$, and Dawson $\{\text{P}_2\text{W}_{18}\}$ clusters. Remarkably, this system undergoes

"template-free" assembly, wherein the macrocyclic components generate the Anderson template in situ and even transform the encapsulated cluster within the macrocyclic cavity to yield a new $\{\text{Mo}_{12}\text{O}_{36}(\text{HPO}_3)_2\}$ species. The resulting host-guest assemblies further organize into a cubic cluster-of-clusters architecture with a giant unit cell volume of approximately 220 nm³, demonstrating hierarchical self-organization from molecular to supramolecular scales. Extending this concept, the same group subsequently demonstrated a ligand-directed template assembly strategy for the construction of gigantic molybdenum blue wheels, achieving precise control over ring size and nuclearity through judicious choice of templating anions [35]. More recently, Fang and co-workers demonstrated the formation of a $\{\text{Mo}_{22}\text{Fe}_8\}$ macrocycle templated by the Preyssler anion $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$ ($\{\text{P}_5\text{W}_{30}\}$), which exhibits selective polyanion binding behavior in solution [36]. In the solid state, the resulting 1:2 host-guest complex $\{\text{P}_5\text{W}_{30}\}_2 \subset \{\text{Mo}_{22}\text{Fe}_8\}$ achieves ultrahigh proton conduction ($1.7 \times 10^{-2} \text{ S cm}^{-1}$ at 368

K, 90% RH) through an extended hydrogen-bonding network. These investigations underscore the significant promise of inorganic macrocyclic chemistry. A key challenge, however, lies in the rational design of polyoxometalate (POM) macrocycles, which remains elusive due to the inherent propensity of metal-oxo units to condense into extended structures as opposed to forming well-defined rings.

Polyoxothiometalates (POTMs) represent a fascinating subclass of POMs where one or more oxo ligands are replaced by sulfide groups within the metal-oxo structures. Recently, our group has explored the assembly behavior of the $[\text{Mo}_2\text{O}_2\text{S}_2]^{2+}$ units as a versatile building block for POTMs. Our findings reveal a pronounced tendency for this unit to form cyclic ring-like architectures, making it an excellent candidate for applications in inorganic host-guest chemistry. Moreover, POTMs exhibit enhanced proton enrichment capabilities, attributable to their higher negative charge and greater hydrophilicity [37–39]. Their oxygen-rich surfaces facilitate the formation of stable hydrogen bond networks, while charge delocalization helps reduce lattice electrostatic potential, thereby promoting proton flow and enhancing mobility [40].

Herein, a planar $\{\text{Mo}_{10}\}$ supramolecular ring constructed from $[\text{Mo}_2\text{O}_2\text{S}_2]^{2+}$ units was designed as a tunable platform to investigate how assembly pathways govern material structure and function. By precisely regulating the synthesis conditions, the binding mode of the pyrimidine-5-carboxylic acid (Pym-5-CA) was directed through pH control. Under higher pH conditions, Pym-5-CA deprotonation activates it as an organic template, engaging in coordination-driven assembly with $[\text{Mo}_2\text{O}_2\text{S}_2]^{2+}$ units to yield the organic-templated inorganic ring $\{\text{Mo}_{12}\}$ (**1**). Simply by lowering the pH, the ligand transforms into a hydrogen bond donor, redirecting the assembly pathway toward supramolecular recognition and anchoring above the $\{\text{Mo}_{10}\}$ ring to form the inorganic-host-organic-guest complex $\text{Mo}_{10}@\text{Pym-5-CA}$ (**2**). This pH-controlled switch from coordination to supramolecular assembly provides an ideal model system for probing structure-activity relationships in proton conduction. To further explore the influence of guest functional-group chemistry, 3-pyridineboronic acid (3-PyBA) was introduced under identical acidic conditions, successfully yielding a second host-guest complex, $\text{Mo}_{10}@\text{3-PyBA}$ (**3**), featuring a water-mediated dynamic hydrogen bond network. The distinct proton conduction performances of **1**, **2**, and **3** were then investigated to establish a direct correlation with their programmed binding modes. Proton conduction measurements at 70 °C and 90% RH reveal that complex **2** exhibits a proton conductivity of $8.76 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$, approximately 2.1 times higher than that of complex **1** and 1.7 times higher than that of complex **3**. This superior performance highlights the synergistic effect between intact carboxyl groups ($-\text{COOH}$) as strong proton donors and the well-defined hydrogen bond network within the supramolecular host-guest architecture. Importantly, potentiometric measurements under varying pH conditions reveal that complex **2** exhibits a slope of 37 mV dec^{-1} , higher than those of complex **1** (28 mV dec^{-1}) and complex **3** (32 mV dec^{-1}). It generates pronounced electrical signals that track

proton concentration variations, directly linking proton transport with interfacial electrochemical behavior. Integrating strong proton-donating organic guests with inorganic POTM hosts featuring hydrogen bond networks effectively modulates proton conduction, highlighting a clear structure-property relationship relevant to material design.

2 Experimental

Synthesis of complexes 1-2

H₄[(Mo₂O₂S₂)₆(OH)₁₂(C₅H₃O₂N₂)₂]·6DMF·5H₂O (1**); [(Mo₂O₂S₂)₅(OH)₁₀(H₂O)₅(C₅H₄N₂O₂)]·24H₂O (**2**).** Pyrimidine-5-carboxylic acid (0.025 g, 0.20 mmol) and potassium chloride (0.05 g) were dissolved in 10 mL of deionized water with vigorous stirring for 5 minutes. Subsequently, 5 mL of an aqueous solution containing $[\text{Mo}_2\text{O}_2\text{S}_2]^{2+}$ ions was added dropwise to the mixture. The pH of the resulting solution was adjusted to 7.5 using a 1 mol/L potassium carbonate (K_2CO_3) solution, affording a clear orange solution. After stirring the reaction mixture at room temperature for 1 hour, it was filtered. The filtrate was allowed to evaporate slowly at room temperature over one week, generating yellow long strip-like crystals, which were complex **1**. The pH was adjusted to 4.5 to obtain the yellow blocky crystal complex **2**.

Elemental analysis calcd (%) for **1**: H, 2.76; Mo, 42.47; S, 14.19; C, 12.40; N, 5.17. Found: H, 2.72; Mo, 42.45; S, 14.16; C, 12.38; N, 5.15. Elemental analysis calcd (%) for **2**: H, 3.22; Mo, 42.52; S, 14.21; C, 2.66; N, 1.24.

Found: H, 3.21; Mo, 42.50; S, 14.19; C, 2.65; N, 1.22.

Synthesis of complex 3

H[(Mo₂O₂S₂)₅(OH)₁₀(H₂O)₅(C₅H₆BN₂O₂)]·2DMF·16H₂O. A mixture of 3-pyridineboronic acid (0.025 g, 0.20 mmol) and nickel chloride (0.2 g) was dissolved in a mixed solvent of 10 mL deionized water and 2 mL N,N-dimethylformamide (DMF) with vigorous stirring for 5 minutes. Subsequently, 3 mL of a solution containing $[\text{Mo}_2\text{O}_2\text{S}_2]^{2+}$ ions was added dropwise to the aforementioned mixture. The pH of the system was adjusted to 4.5 using 1 mol/L K_2CO_3 solution, resulting in a clear orange solution. After stirring at room temperature for 1 hour, the mixture was filtered. The filtrate was allowed to evaporate slowly at room temperature for one week, yielding yellow needle-shaped crystals. Elemental analysis calcd (%) for **3**: H, 3.09; Mo, 40.22; S, 13.44; C, 5.54; N, 1.76. Found: H, 3.08; Mo, 40.20; S, 13.43; C, 5.52; N, 1.74.

3 Results and discussion

A pH-controlled strategy was devised to modulate the protonation state of the organic ligand, thereby switching its binding mode from coordination to supramolecular interaction and enabling controlled construction of diverse POTM-based architectures. The controllable self-assembly behavior of the dimeric $[\text{Mo}_2\text{O}_2\text{S}_2]^{2+}$ unit with pyrimidine-5-carboxylic acid (Pym-5-CA) and 3-pyridine-boronic acid (3-PyBA) under varying pH conditions was elucidated through in-situ synthesis and structural analysis. To investigate the decisive influence of assembly pathways on material structure, Pym-5-CA was selected as an organic template, and its binding mode was precisely directed through

controlled synthesis conditions. Examination of single-crystal X-ray diffraction (SC-XRD) data (see Supporting Information Tables S1-S3) reveals a distinct coordination mode at higher pH (~ 7.5). Under these conditions, the carboxyl group ($-\text{COOH}$) of Pym-5-CA undergoes deprotonation and forms a robust Mo-O coordination bond with a length of approximately 2.3 Å. This results in the formation of an organic-templated inorganic ring architecture, $\text{Mo}_{12}\text{-Pym-5-CA}$, wherein a $\{\text{Mo}_{12}\}$ ring, assembled from six $\mu_2\text{-OH}$ bridged $[\text{Mo}_2\text{O}_2\text{S}_2]^{2+}$ units, chelates two Pym-5-CA ligands within its cavity. The structure is further stabilized by a significant $\pi \cdots \pi$ stacking interaction between the heteroaromatic rings of the ligands, with an interplanar distance of about 3.6 Å. Ligand steric constraints lead to an octahedral coordination geometry for Mo1 and Mo7, while the remaining metal centers adopt a pyramid geometric configuration (Fig. 1 (a)). The crystal structure thus confirms that at higher pH, deprotonated Pym-5-CA anchors within the $\{\text{Mo}_{12}\}$ ring through coordination bonds, yielding a stable coordination-dominated architecture.

Lowering the pH was designed to retain the carboxyl proton, redirecting the assembly toward supramolecular interactions. In contrast, the assembly under mildly acidic conditions (pH ~ 4.5) yields a structurally distinct inorganic-host-organic-guest complex, host-guest complex, $\text{Mo}_{10}\text{@Pym-5-CA}$. At this lower pH, Pym-5-CA remains in its neutral $-\text{COOH}$ form and is anchored above the cavity of the pre-assembled $\{\text{Mo}_{10}\}$ ring through the $\text{O15} \cdots \text{H15} \cdots \text{O13}$ hydrogen bond ($[d(\text{H15} \cdots \text{O15}) = 2.09 \text{ Å}], \angle \text{O15} - \text{H15} \cdots \text{O13} = 156.7^\circ$), as detailed in Fig. 1(b) and Table S4 (Supporting

Information). A simplified schematic in Fig. 1(e) illustrates this spatial host-guest arrangement. The $-\text{COOH}$ proton of the guest forms a highly directional hydrogen bond with a bridging oxygen atom on the $\{\text{Mo}_{10}\}$ ring, constituting a discrete and robust supramolecular synthon. The $\{\text{Mo}_{10}\}$ ring itself is composed of five $[\text{Mo}_2\text{O}_2\text{S}_2]^{2+}$ units interconnected by $\mu_2\text{-OH}$ bridges, forming a cyclic structure with an internal cavity diameter of approximately 5.0 Å (Fig. 1(c)). The structural stability of this assembly is augmented by the coordination of water molecules to adjacent molybdenum centers (Fig. S1). The alternating shared edges and faces form an octahedral ring, and two octahedra with the same building units are connected by S-S edges (Fig. S2). As shown in the top-view representation in Fig. 1(d), the size complementarity between the $\{\text{Mo}_{10}\}$ host cavity and the Pym-5-CA guest is evident. The crystallographic analysis substantiates this supramolecular design, showing that the neutral carboxyl group anchors above the $\{\text{Mo}_{10}\}$ ring through directional hydrogen bonding, thereby achieving a clean switch from coordination-dominated to hydrogen bond-dominated assembly.

This pair of structural analogues, constructed from the same ligand via distinct assembly routes, provides an ideal model system for probing structure-activity relationships in proton conduction. To extend this model system and probe how functional group identity influences supramolecular recognition, 3-PyBA, bearing a boronic acid group ($-\text{B}(\text{OH})_2$), was introduced under the same acidic conditions, successfully yielding a second host-guest complex, $\text{Mo}_{10}\text{@3-PyBA}$. Structural analysis of the resulting host-

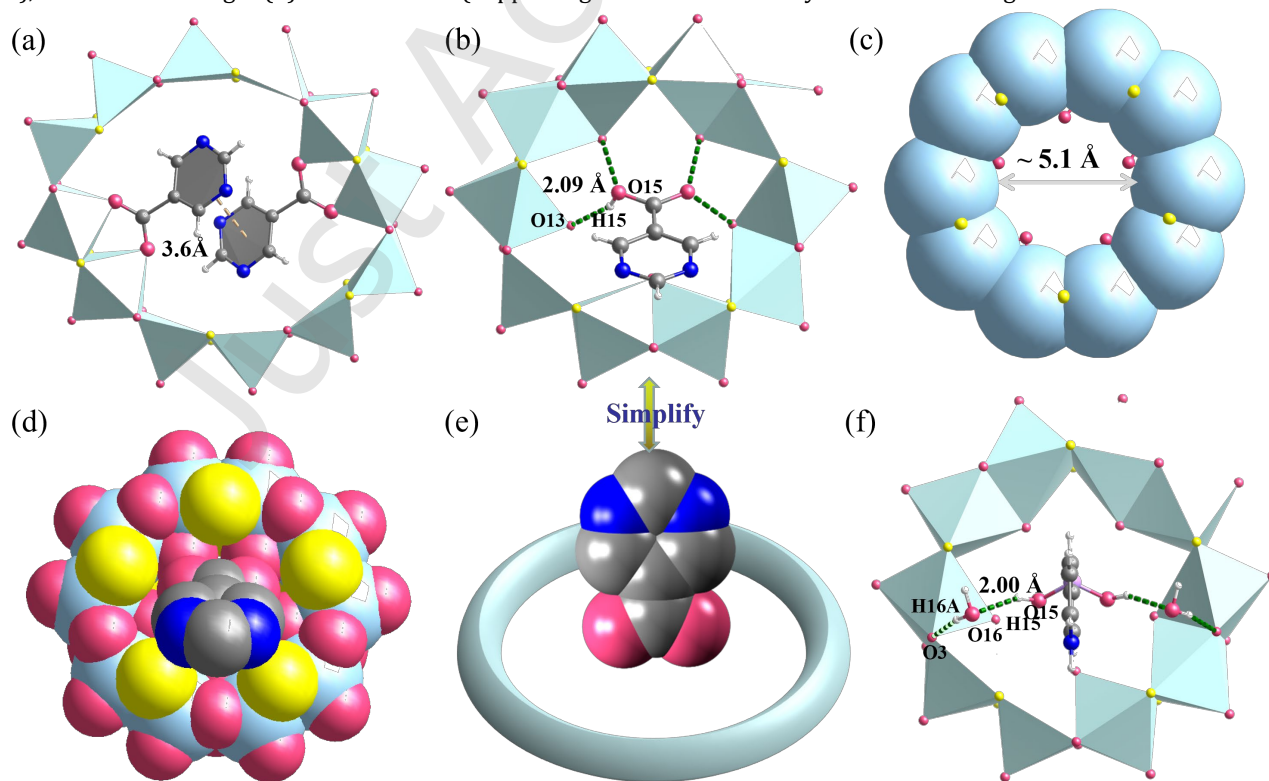


Figure 1 (a) The structure diagram of $\text{Mo}_{12}\text{-Pym-5-CA}$; (b) The structure diagram of $\text{Mo}_{10}\text{@Pym-5-CA}$; (c) $\{\text{Mo}_{10}\}$ ring annular cavity; (d) Spatial fill view of $\text{Mo}_{10}\text{@Pym-5-CA}$; (e) A simplified diagram of the structure of $\text{Mo}_{10}\text{@Pym-5-CA}$; (f) The structure diagram of $\text{Mo}_{10}\text{@3-PyBA}$. Color code: Mo, light

blue; N, blue; O, rose red; C, grayish black.

guest complex $\text{Mo}_{10}@3\text{-PyBA}$ reveals that while its $-\text{B}(\text{OH})_2$ group also engages in hydrogen bonding with the $\{\text{Mo}_{10}\}$ ring, the resulting interaction network differs significantly from that of the $-\text{COOH}$ group. Given its dual capacity as both a hydrogen bond donor and acceptor, the $-\text{B}(\text{OH})_2$ group in this system primarily functions as a hydrogen bond donor, engaging in a bridging interaction via a water molecule to enhance stability. In this arrangement, the water molecule (O16) acts as both a hydrogen-bond acceptor and donor, thereby mediating the host-guest interaction. Specifically, it accepts an $\text{O15-H15} \cdots \text{O16}$ hydrogen bond from the $-\text{B}(\text{OH})_2$ group of the 3-PyBA ligand ($[d(\text{H15} \cdots \text{O16}) = 2.01 \text{ \AA}, \angle \text{O15-H15} \cdots \text{O16} = 157.8^\circ]$) and simultaneously donates an $\text{O16-H16A} \cdots \text{O3}$ hydrogen bond to the terminal oxygen atom (O3) of the polyoxomolybdate ring ($[d(\text{H16A} \cdots \text{O3}) = 1.93 \text{ \AA}, \angle \text{O16-H16A} \cdots \text{O3} = 168.1^\circ]$). The complete hydrogen-bond geometry is summarized in Table S4 (Supporting Information). Oxygen sites on the ring form $\text{O-H} \cdots \text{O}$ hydrogen bonds with the same bridge oxygen sites (Fig. 1(f)). Although the hydrogen-bond geometries at both ends of this water-mediated bridge approach ideal values, the introduction of a bridging water molecule increases the dynamic character and configurational entropy of the

supramolecular assembly. Consequently, the overall host-guest binding in $\text{Mo}_{10}@3\text{-PyBA}$ is less robust compared to the direct, single hydrogen-bond motif observed in $\text{Mo}_{10}@\text{Pym-5-CA}$. This series of structural differences clearly reveals the role transformation of ligands from structural building units to spatially confined objects under pH regulation, as well as the corresponding evolution of interaction patterns from coordination bond dominance to hydrogen bond dominance. Meanwhile, the $-\text{COOH}$ and $-\text{B}(\text{OH})_2$ groups exhibit differentiated hydrogen bond properties on the same $\{\text{Mo}_{10}\}$ supramolecular platform, providing a key basis for understanding the functional group effects in supramolecular assembly.

To systematically investigate the characteristics of hydrogen bond interactions across different assembly modes, Hirshfeld surface analyses were performed on all three complexes. As illustrated in Fig. 2, the d_{norm} maps of $\{\text{Mo}_{12}\}$ -Pym-5-CA, $\text{Mo}_{10}@\text{Pym-5-CA}$, and $\text{Mo}_{10}@3\text{-PyBA}$ each exhibit pronounced concave regions corresponding to close intermolecular contacts. These features quantitatively confirm the critical role of hydrogen bonding in directing the spatial assembly. Specifically, in the supramolecular pathway, the three-dimensional network of $\text{Mo}_{10}@\text{Pym-5-CA}$ is

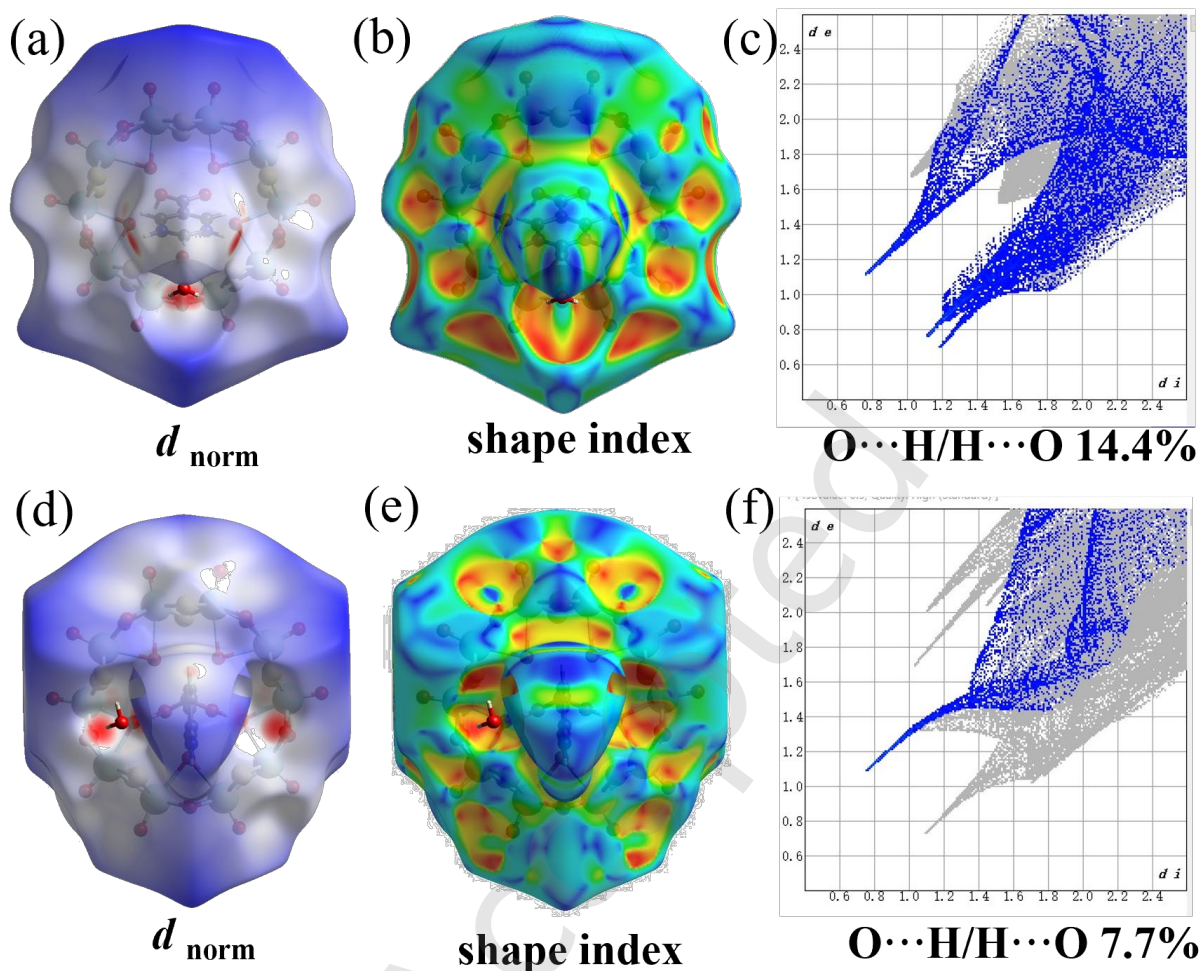


Figure 2 Hirshfeld surface analyses: (a-c) d_{norm} map, shape index map, and 2D fingerprint plot of $\text{Mo}_{10}@\text{Pym-5-CA}$; (d-f) corresponding plots for $\text{Mo}_{10}@\text{3-PyBA}$.

primarily mediated by hydrogen bonds formed between nitrogen atoms of the ligand and the $\mu_2\text{-O}$ groups of $\{\text{Mo}_{10}\}$ ring (Fig. S4). Its two-dimensional fingerprint plot reveals that $\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$ contacts account for 14.4% of the total intermolecular interactions (Fig. 2(a)-(c)). This relatively high hydrogen bonding ratio indicates a densely distributed and well-oriented hydrophilic surface on the $\{\text{Mo}_{10}\}$ ring, which is expected to facilitate the capture of water molecules and provide continuous pathways for proton migration. In contrast, the assembly of $\text{Mo}_{10}@\text{3-PyBA}$ proceeds through a more elaborate two-step pathway. The initial stage involves analogous hydrogen bonding interactions that give rise to a two-dimensional layer. Subsequently, uncoordinated water and DMF molecules intercalate between these layers, where their oxygen atoms bridge adjacent $\{\text{Mo}_{10}\}$ units, thereby extending the structure into a three-dimensional network (Fig. S5). This structural arrangement is consistent with its lower

$\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$ contact ratio of 7.7%, which is approximately 6.7% lower than that observed for $\text{Mo}_{10}@\text{Pym-5-CA}$ (Fig. 2(d)-(f)). The reduced hydrogen bond contribution quantitatively reflects the more dynamic, water-mediated binding inherent to the boronic acid system. Notably, the coordination-assembled complex $\{\text{Mo}_{12}\}\text{-Pym-5-CA}$ exhibits a fundamentally distinct hydrogen bonding profile. In this coordination assembly mode, since Pym-5-CA is directly embedded in the $\{\text{Mo}_{12}\}$ cluster framework in a deprotonated carboxylate anion form through strong coordination bonds, the number of sites that can act as hydrogen bond acceptors is significantly reduced (Fig. S3). Hirshfeld surface analysis shows that the contribution rate of $\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$ contacts in this structure further drops to approximately 3.0%, which is significantly lower than that of the two supramolecular structures (Fig. S6). This phenomenon confirms that although the formation of coordination bonds enhances the structural stability, it sacrifices to some extent the

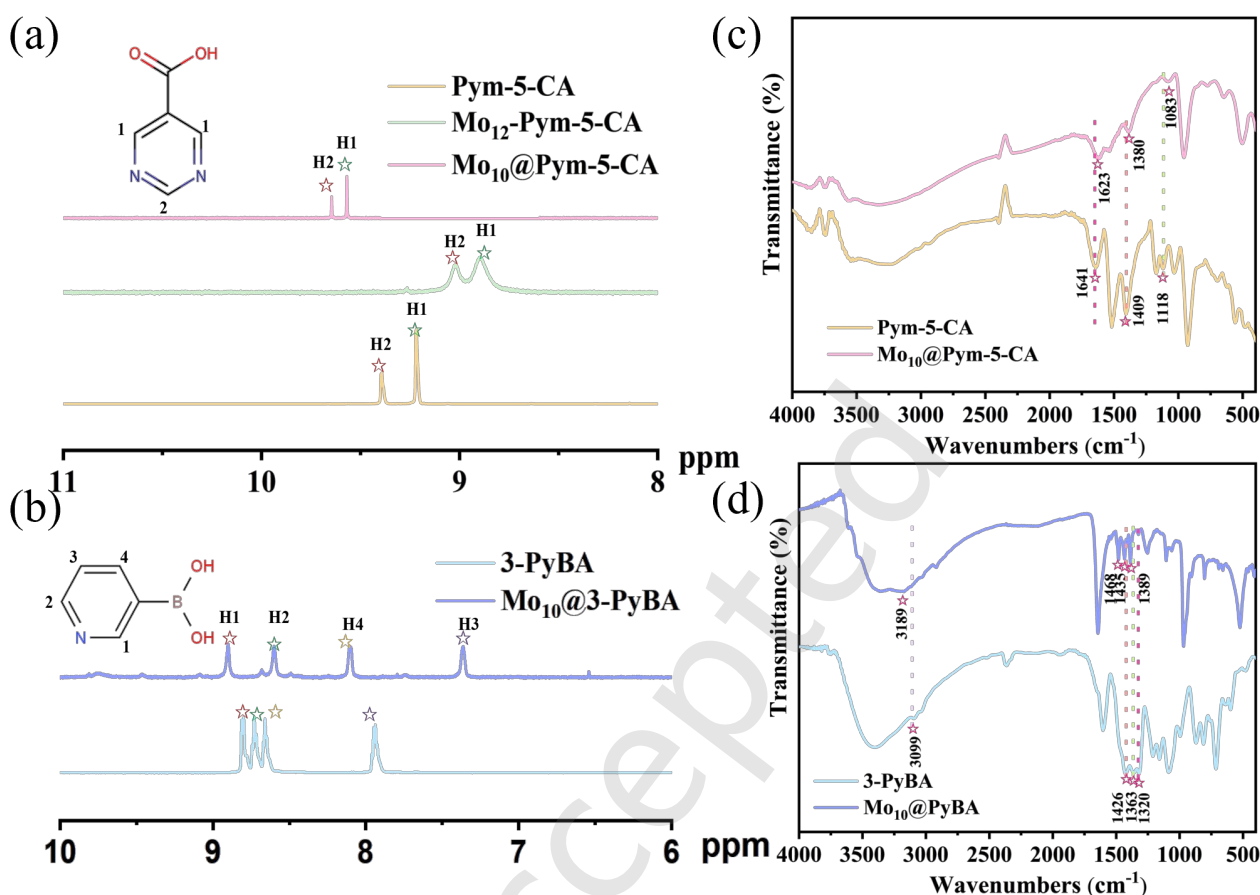


Figure 3 (a-b) ^1H NMR spectra of Mo_{12} -Pym-5-CA, Mo_{10} @Pym-5-CA and Mo_{10} @3-PyBA; (c-d) FT-IR spectra of Mo_{10} @Pym-5-CA and Mo_{10} @3-PyBA.

ability of the system to construct a hydrogen bond network.

Hydrogen nuclear magnetic resonance (^1H NMR) spectroscopy was employed to determine whether the three complexes' binding modes persist in solution. The interactions of the $\{\text{Mo}_{10}\}$ rings and $\{\text{Mo}_{12}\}$ ring structures with heteroaromatic acid ligands were systematically investigated in deuterated dimethyl sulfoxide ($\text{DMSO}-d_6$). The spectra reveal markedly different binding modes and dynamic properties among the three complexes. As shown in Fig. 3a, the pyrimidine protons in Mo_{12} -Pym-5-CA show an upfield shift for both H1 and H2 signals, a convergence of their chemical shifts, and significant line broadening. These features align precisely with the coordination mode, indicating that the ligand rigidly fixed to the cluster framework exhibits restricted motion and a homogenized chemical environment. Under the fixed conformation of ligands, protons at different sites on the pyrimidine ring show chemical shift convergence due to the homogenization of spatial orientation and electronic effects. Meanwhile, the rigid connection formed between the ligand and the $\{\text{Mo}_{12}\}$ skeleton through strong coordination bonds and its slow exchange kinetic process leads to the broadening of spectral lines. Collectively, these NMR characteristics provide direct experimental support for the model in which the ligand is integrated as a structural component within the cluster framework. Notably, Mo_{10} @Pym-5-CA displays a

fundamentally distinct NMR signature. The H1 proton adjacent to the $-\text{COOH}$ group undergoes a pronounced downfield shift ($\Delta\delta \approx +0.3$ ppm, Fig. 3(a)). This marked deshielding is characteristic of a complexation-induced effect, providing direct evidence that the $-\text{COOH}$ group acts as a hydrogen bond donor, forming a directional $\text{O}-\text{H} \cdots \text{O}$ hydrogen bond with a bridging oxygen atom of the $\{\text{Mo}_{10}\}$ ring. The overall nuclear magnetic resonance signal of Mo_{10} @Pym-5-CA varies significantly with sharp peaks, confirming the definite host-guest interaction mode observed in solid-state structures[41]. In contrast, the NMR spectrum of Mo_{10} @3-PyBA displays more complex features. While the H1 proton adjacent to the $-\text{B}(\text{OH})_2$ group also undergoes a downfield shift ($\Delta\delta \approx +0.1$ ppm), confirming hydrogen bonding interaction between the $-\text{B}(\text{OH})_2$ group and a bridging oxygen site, the relatively small shift magnitude coupled with pronounced peak broadening reflects the dynamic character of this interaction (Fig. 3(b)). This behavior is consistent with the known properties of the $-\text{B}(\text{OH})_2$ functional group. The two hydroxyl groups of $-\text{B}(\text{OH})_2$ can act cooperatively as hydrogen bond donors, while also likely undergoing rapid association-dissociation equilibria, resulting in overall weaker and more flexible binding compared to the $-\text{COOH}$ group. Simultaneously, a definite upfield shift was observed in the distal ligand protons (such as H2, H3, and H4), which is likely due to the specific spatial orientation generated

between the aromatic ring and the $\{Mo_{10}\}$ ring skeleton of the guest molecule after binding, thereby triggering a secondary ring current shielding effect. These NMR results confirm at the solution level the fundamental differences in intermolecular forces across the three assembly modes. From the strong and definite hydrogen bond interaction in $Mo_{10}@Pym-5-CA$, to the weak and dynamic hydrogen bond combination in $Mo_{10}@3-PyBA$, and then to the rigid fixation achieved through coordination bonds in $Mo_{12}-Pym-5-CA$. This gradient in binding strength, precisely matching the hierarchy observed in Hirshfeld analysis, confirms that pH-controlled assembly successfully achieves the targeted interaction modes.

Fourier-transform infrared (FT-IR) spectroscopy was employed to probe the intermolecular interactions within the three complexes. As shown in Fig. S7, the supramolecular complexes $Mo_{10}@Pym-5-CA$ and $Mo_{10}@3-PyBA$ both exhibit characteristic absorption bands between 400 and 1100 cm^{-1} , attributable to the $\{Mo_{10}\}$ ring skeleton. Strong peaks at 956 and 969 cm^{-1} are assigned to the $\nu(Mo=O)$ stretching mode. Peaks at 652 and 658 cm^{-1} correspond to $\nu(Mo-OH-Mo)$ vibrations, while bands at 505 and 523 cm^{-1} are ascribed to $\nu(Mo-S-Mo)$ vibrations. Notably, the positions of the $\nu(Mo-OH-Mo)$ stretching vibration in both complexes are shifted relative to those reported for the host $\{Mo_{10}\}$ ring [42], indicating modulation of the bridging environment upon guest inclusion. These shifts confirm that guest inclusion fine-tunes the bridging oxygen environment through hydrogen bond interactions, consistent with the 1H NMR deshielding effects. In contrast, the coordination compound $\{Mo_{12}\}-Pym-5-CA$ displays distinctly different IR features. The $\nu(Mo=O)$ frequency shifts to approximately 973 cm^{-1} , and the $\nu(Mo-OH-Mo)$ vibration appears near 667 cm^{-1} . These shifts confirm the pronounced influence of coordination bonding on the electronic structure of the molybdenum-oxo framework. The larger shift magnitude reflects the stronger electronic perturbation expected from the coordination-based design, correlating with the rigid 1H NMR signals. Furthermore, the characteristic $\nu(C=O)$ peak of the neutral $-COOH$ group (~ 1700 cm^{-1}) is absent. Instead, asymmetric $\nu_{as}(COO^-)$ and symmetrical $\nu_s(COO^-)$ stretching vibrations of the

carboxylate ion are observed at 1590 and 1430 cm^{-1} , respectively, with a separation ($\Delta\nu$) of about 160 cm^{-1} , which is indicative of a monodentate coordination mode. For the supramolecular complex $Mo_{10}@Pym-5-CA$, significant red shifts are observed relative to the free $Pym-5-CA$ ligand across several key vibrations. The C-O stretch (1083 cm^{-1}), the C=O stretch (1623 cm^{-1}), and the in-plane C-H bending of the aromatic ring (1380 cm^{-1}) (Fig. 3(c)). These shifts confirm the involvement of the $-COOH$ group in hydrogen bonding interactions with the host. In $Mo_{10}@3-PyBA$, the O-H stretching vibration of the $-B(OH)_2$ group is broadened and shifted to around 3200 cm^{-1} , while the B-O stretches appear at 1389 and 1435 cm^{-1} (Fig. 3(d)). These features suggest the formation of a dynamic hydrogen bonding network involving the $-B(OH)_2$ group. The IR spectral shifts not only confirm specific host-guest recognition in the supramolecular complexes but also trace the continuous evolution from hydrogen bonded association to coordinative integration within the $\{Mo_{12}\}$ framework. This progression provides key spectroscopic evidence for understanding the distinct nature of interactions governed by different assembly pathways.

Having established the molecular-level interactions, the next question was how the differences between the three complexes propagate to larger length scales. Multiscale solution-structure analysis was performed using dynamic light scattering (DLS) and small-angle X-ray scattering (SAXS) to probe the hierarchical assembly behavior of $Mo_{12}-Pym-5-CA$, $Mo_{10}@Pym-5-CA$, and $Mo_{10}@3-PyBA$ at the nanoscale. The DLS data reveal an approximately order-of-magnitude variation in hydrodynamic diameters among the three complexes. $Mo_{12}-Pym-5-CA$ exists as monodisperse particles with an average diameter of ~ 15 nm, consistent with discrete clusters stabilized by coordination bonds (Fig. 4(a)). The small, monodisperse size accords with the discrete, rigid nature inferred from crystallography and spectroscopy. In contrast, $Mo_{10}@Pym-5-CA$ and $Mo_{10}@3-PyBA$ form larger assembled structures with diameters of ~ 141 nm and ~ 235 nm, respectively. These increased dimensions reflect the capacity of supramolecular interactions to drive higher-order aggregation. The notably larger size observed for $Mo_{10}@3-PyBA$ suggests that the water-bridged hydrogen bonding

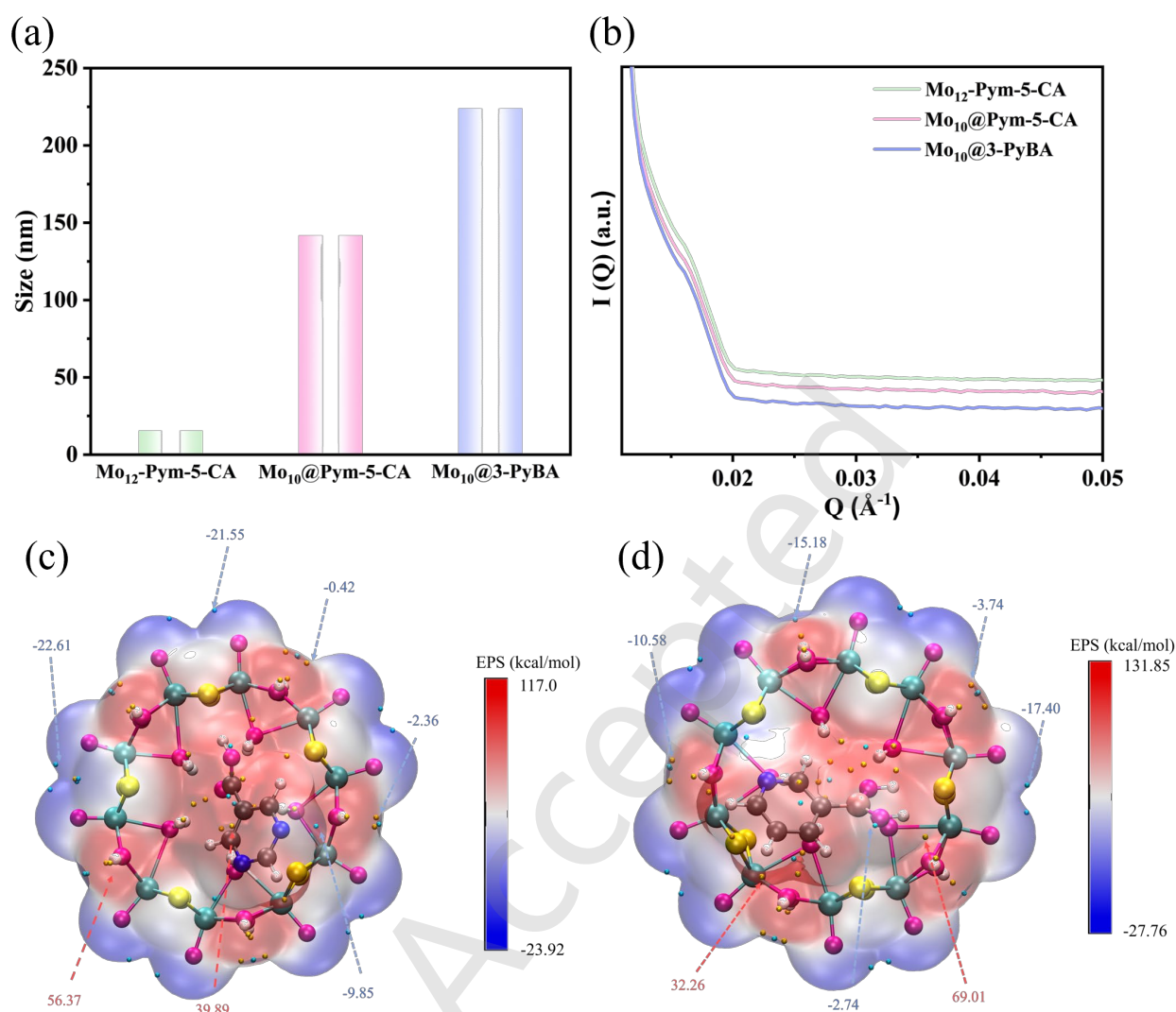


Figure 4 (a) DLS spectra of Mo₁₂-Pym-5-CA, Mo₁₀@Pym-5-CA, and Mo₁₀@3-PyBA, (b) SAXS spectra of Mo₁₂-Pym-5-CA, Mo₁₀@Pym-5-CA, and Mo₁₀@3-PyBA, (c-d) Calculated MESP maps of the anionic clusters in Mo₁₀@Pym-5-CA and Mo₁₀@3-PyBA, showing the surface charge distributions (red = electron-rich, blue = electron-deficient).

network associated with the boronic acid guest may promote a more extended or loosely packed assembly morphology under the measured conditions.

SAXS analysis provides further insight into the structural organization. All three complexes exhibit a scattering peak in the low-*q* region ($q \approx 0.016 \text{ \AA}^{-1}$), corresponding to a characteristic long period of approximately 400 nm (Fig. 4(b)). This feature indicates that the primary structural units are capable of further assembly into higher-order aggregates. Notably, the intensity of this peak follows a monotonic decrease. The order is Mo₁₂-Pym-5-CA > Mo₁₀@Pym-5-CA > Mo₁₀@3-PyBA. This trend reflects a systematic reduction in both electron-density contrast and the degree of long-range order within the assembled structures. The progression moves from rigid, homogeneous coordination clusters to tightly packed assemblies constructed by direct hydrogen-bonding networks, and finally to the most loosely packed and disordered structures. These latter structures rely on dynamic water-bridged connections.

Thermogravimetric analysis (TGA) quantitatively revealed the hierarchical release process of guest molecules in the three complexes and the differences in their thermal stability. As shown in Fig. S8, the order of thermal stability of the three complexes is Mo₁₂-Pym-5-CA (coordination bond) > Mo₁₀@Pym-5-CA (carboxyl hydrogen bond) > Mo₁₀@3-PyBA (boric acid hydrogen bond). The differences in decomposition temperature and weight loss steps directly confirm the decisive influence of different interactions and functional groups on the thermal stability of the material. For detailed analysis, please refer to the supplementary information. The crystal structures of the three complexes were characterized by powder X-ray diffraction (PXRD). As shown in Fig. S9, the PXRD spectra measured in the experiment all present sharp diffraction peaks. By tracking their peak positions and intensities, it was found that they all perfectly coincident with the standard spectra based on single crystal structure simulation. This fully proves that the obtained samples are highly crystalline pure phases. The morphologies of three

crystals were observed from the SEM image (Fig. S10-12).

To probe the dynamic stability of the supramolecular assemblies in a competitive environment, an ultraviolet-visible absorption (UV-Vis) solvent competition method was developed. This approach employs dimethyl sulfoxide (DMSO) solvent-competition experiments monitored in real time by UV-Vis spectroscopy (Fig. S13). $\text{Mo}_{10}@\text{Pym-5-CA}$ displays a discernible stability threshold. Only above a DMSO concentration of 50% does a spectral change become apparent. This change consists of a mild decrease in absorbance accompanied by a slight red shift (Fig. S13a). This behavior corresponds to the gradual, partial disassembly of its direct hydrogen bonding network. The high stability threshold confirms the robustness of the direct hydrogen bond network designed for the carboxyl system, consistent with its higher TGA

stability and well-defined ^1H NMR signals. In contrast, $\text{Mo}_{10}@\text{3-PyBA}$ undergoes rapid spectral collapse even at low DMSO concentrations, characterized by a sharp intensity drop, significant baseline elevation, and a pronounced red shift (Fig. S13b). This behavior unequivocally reveals the instantaneous rupture of its dynamic water-bridged connection, followed by uncontrolled aggregation of the released polyoxometalate clusters. These results lead to the conclusion that the superior strength of direct versus water-bridged hydrogen bonds is fundamental to macroscopic stability. This insight offers valuable guidance for rationally regulating the properties of supramolecular functional materials.

The molecular electrostatic potential (MESP) diagram is an effective tool for predicting the reaction sites of electrophilic, nucleophilic attack reactions and hydrogen bond interactions. It provides key insights into the surface potential distribution of $\text{Mo}_{10}@\text{Pym-5-CA}$ and $\text{Mo}_{10}@\text{3-PyBA}$ (Fig. 4(c)-(d)). Analysis shows that the electron-rich region (negative potential region) is an electrophilic attack or proton (H^+) preferred adsorption site, while the electron-deficient region is a nucleophilic attack or proton release or transfer site [43]. It can be seen from the figure that the bridged oxygen atoms in the $\{\text{Mo}_{10}\}$ ring are displayed as distinct red areas. The carboxyl hydrogen atom of the ligand Pym-5-CA and 3-PyBA are shown as blue areas. This theoretically predicts and confirms that the occurrence of hydrogen bond interactions

is highly possible, and indicates the specific binding sites, further confirming the form of interaction between the two structural subjects and guests. Meanwhile, this complementary distribution creates a favorable landscape for proton transfer, with the electron-rich regions serving as proton acceptor sites and the electron-deficient regions as proton donor sites, thereby establishing the electronic foundation for the proton conduction performance evaluated below.

Proton conduction performance

As an important type of proton-conducting material, POTMs have been widely applied in the field of electronic devices due to their relatively low effective negative surface charge density [44]. We studied the proton conduction characteristics through an AC impedance spectroscopy analysis system and calculated the conductivity value by measuring the real (Z') and imaginary (Z'') components. Considering the significant impact of environmental humidity on proton conduction efficiency, we measured the electrical conductivity of materials with relative humidity ranging from 50% to 90% RH under a constant temperature of 30 °C. As shown in Fig. 5(a) and Fig. S15a-c, the proton conductivities of all three materials exhibit significant enhancement with increasing relative humidity. This humidity-dependent behavior confirms that water molecules play a crucial role in the proton conduction process, consistent with the involvement of hydrogen bond networks identified in the structural characterization. Notably, $\text{Mo}_{10}@\text{Pym-5-CA}$ (complex **2**) demonstrates superior performance, achieving a remarkable increase in conductivity from $4.11 \times 10^{-6} \text{ S cm}^{-1}$ to $1.09 \times 10^{-3} \text{ S cm}^{-1}$. Under identical conditions, $\text{Mo}_{12}\text{-Pym-5-CA}$ (complex **1**) and $\text{Mo}_{10}@\text{3-PyBA}$ (complex **3**) show comparatively lower conductivity enhancements, rising from $2.66 \times 10^{-7} \text{ S cm}^{-1}$ to $2.39 \times 10^{-4} \text{ S cm}^{-1}$ and from $2.72 \times 10^{-7} \text{ S cm}^{-1}$ to $3.34 \times 10^{-4} \text{ S cm}^{-1}$, respectively. The final conductivity of complex **2** exceeds that of complexes **1** and **3** by nearly an order of magnitude, highlighting its exceptional structural advantages for proton conduction. The complete carboxyl group ($-\text{COOH}$) in complex **2** not only provides a rich source of strong acid properties, but its supramolecular assembly mode also forms a hydrogen bond network conducive to proton transport. In contrast, complex **1** lost its main

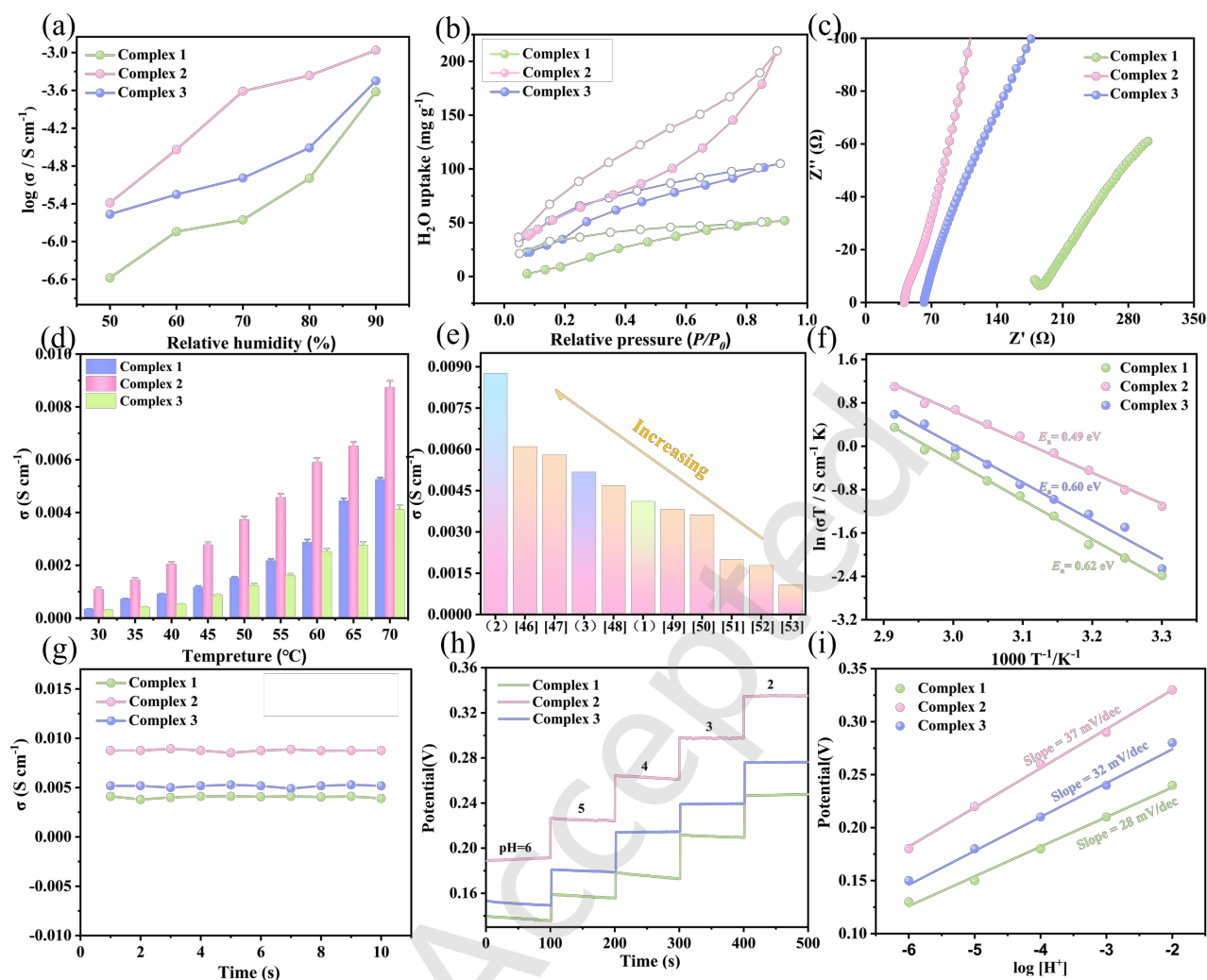


Figure 5 (a) humidity-dependent proton conductivity at 30 °C; (b) Water uptake isotherms of complexes 1-3 are measured at 30 °C; (c) Nyquist plots of complexes 1-3 at 70 °C (90% RH); (d) temperature-dependent proton conductivity of three clusters; (e) Literature comparison of proton conductivity; (f) Arrhenius plots of the proton conductivity of both clusters; (g) 10 hour constant temperature and humidity 90% RH cycle; (h) The potential-time response curves of the selective electrode in different pH buffer solutions; (i) Nernst calibration curve.

proton source due to carboxyl deprotonation, and the rigid coordination framework restricted the recombination of the hydrogen bond network. Although complex 3 retains the boric acid group, its weak acidity and dynamic hydrogen bond characteristics limit the proton conduction efficiency. The results of the water vapor adsorption experiment further confirmed this structure-performance relationship. As shown in Fig. 5(b), under the condition of $P/P_0 = 0.90$, the water adsorption capacity of complex 2 reached 209.88 mg/g, which was significantly higher than that of complexes 1 and 3. This significant difference indicates that the supramolecular structure of complex 2 can more effectively accommodate water molecules and construct a continuous hydrated hydrogen bond network, thereby providing an ideal channel for its outstanding proton conduction performance. The above results fully demonstrate the significant advantages of the supramolecular strategy that retains the complete carboxyl functional group in the construction of highly efficient proton-conducting materials. As another key influencing factor, researchers also conducted temperature-

dependent proton conductivity tests on the two complexes. As shown in Fig. 5(c)-(d) and Fig. S14a-c, under 90% RH conditions, the proton conductivity (σ) values of complexes 1-3 all exhibit an increasing trend in thermal response. At 70 °C, the σ of the three complexes increased to $4.11 \times 10^{-3} \text{ S cm}^{-1}$, $8.76 \times 10^{-3} \text{ S cm}^{-1}$, and $5.18 \times 10^{-3} \text{ S cm}^{-1}$, respectively, which was attributed to the acceleration of proton transfer with the increase of temperature [45]. Complex 2 exhibits a proton conductivity approximately 2.1 times higher than that of complex 1 and 1.7 times higher than that of complex 3. We conducted detailed impedance spectrum analyses on complexes 1-3 fitted their electrochemical behaviors through an equivalent circuit model, as shown in Fig. S16a-c. Notably, the electrical conductivity of all samples exhibited typical proton conduction characteristics that increased with the rise of humidity and temperature, and the electrical conductivity values of the three complexes were significantly better than those of most POM-based materials reported in recent years (Fig. 5(e)) [46-53]. Previous studies have shown that proton transport in most reported POM-based materials primarily

relies on hydrogen-bonding networks constructed by lattice water molecules, guest species, or proton-donating functional groups. However, their proton conductivity is often limited by insufficient proton sources, discontinuous proton-transport pathways, or poor structural stability under highly humid conditions. In contrast, the superior proton-conducting performance of complex **2** can be attributed to the synergistic effect of the abundant proton-donating carboxyl groups, the well-organized supramolecular host-guest architecture, and the continuous hydrogen-bonding network incorporating confined water molecules. The proton conduction activation energy (E_a) of the three complexes was obtained by fitting the variable-temperature conductivity data at 90% RH through the Arrhenius equation. As shown in Fig. 5(f), the activation energies of complexes **1-3** are 0.62 eV, 0.49 eV, and 0.60 eV, respectively. Based on the analysis of activation energy data and structural characteristics, the three complexes exhibit different proton conduction mechanisms. The activation energy of complex **2** (0.49 eV) indicates that its conduction process involves both the Grotthuss mechanism (proton jumping) and the Vehicle mechanism (mass carrier migration)[54,55], but the Vehicle mechanism is dominant. Complex **1** (0.62 eV) and complex **3** (0.60 eV) mainly exhibit the Vehicle mechanism. This mechanism difference is highly consistent with its structural characteristics. The complete carboxyl group and hydrogen bond network in complex **2** provide certain conditions for proton jumping, while the absence of a proton source in complex **1** and the weak acidity of the boronic acid group in complex **3** both limit the effective operation of the Grotthuss mechanism, making it more dependent on the Vehicle mechanism based on the diffusion of hydrated ions. In this mechanism, the number of carriers and their transport speed become the key factors determining conductivity. The high-temperature environment significantly enhanced the conductivity of the three compounds by promoting proton migration. Among them, the synergistic effect of carrier migration and proton jumping assisted by hydrogen bond networks jointly constitutes its excellent proton conduction basis. It is worth noting that compared with complexes **1** and **3**, complex **2** exhibits a more outstanding proton conduction ability, which is attributed to its unique structural advantages. The complete carboxyl functional group provides a strong proton source, the ordered supramolecular host-guest structure forms a continuous conductive path, and the stable framework and hydrogen bond network work in synergy to jointly enhance the proton conduction efficiency. This comparison result fully demonstrates that, under the premise of maintaining structural stability, constructing an ordered hydrogen bond network rich in strong proton sources is the key to obtaining efficient proton-conducting materials. Even after 10 hours of continuous testing, the proton conductivity of the three complexes did not decrease significantly, indicating that they have high stability in proton conductivity (Fig. 5(g)). To further evaluate the stability of the material, we conducted XRD and IR tests on the tested samples (Fig. S17-S18). The results show that the main spectral characteristics are highly consistent with those of the original samples, confirming that the three compounds can all maintain their

structural integrity under the test conditions. In addition, to explore its conductive nature, we conducted time-dependent current characteristic tests on complexes **1-3** using the Hebb-Wagner direct current polarization method [56]. Under a constant bias voltage of 0.1 V, the resistance values of the three were measured to be as high as $5.81 \times 10^7 \Omega$, $1.72 \times 10^8 \Omega$ and $5.55 \times 10^8 \Omega$, respectively (Fig. S19a-c). Such a high resistance value clearly indicates that among these three compounds, protons are the dominant charge carriers, while the contribution of electronic conductors can be ignored.

Since both complex **2** and complex **3** contain a large number of crystalline water molecules and hydrogen protons, they both exhibit high proton conduction efficiency. The excellent proton conduction properties of **2** and **3** can be attributed to the rapid transport of protons carried by water molecules as carriers. Compared with **3**, **2** has stronger hydrogen bond interactions and a greater water absorption capacity. This combination of structural features, systematically elucidated throughout this work, endows complex **2** with both outstanding proton conduction performance and a lower activation energy, fully validating the design strategy of preserving intact carboxyl groups within a supramolecular host-guest architecture. Fig. S20a-b, respectively, present schematic diagrams of the possible proton conduction mechanisms of complexes **2** and **3**.

To further correlate proton transport with interfacial electrochemical behavior, the pH-responsive characteristics of the three complexes were systematically investigated (Fig. 5(h)-(i)). All complexes exhibit stable and well-defined potential responses upon stepwise variation of pH. The electrolyte acidity was adjusted over a range corresponding to proton activities from 1.0×10^{-2} to 1.0×10^{-6} M (pH $\approx$ 2-6), enabling quantitative evaluation of the potential response as a function of $\log[H^+]$. Complex **2** exhibits a slope of 37 mV dec^{-1} , higher than those of complex **1** (28 mV dec^{-1}) and complex **3** (32 mV dec^{-1}). This trend parallels that observed in proton conductivity, suggesting a positive correlation between proton transport and potentiometric response [57,58]. For complex **2**, the presence of intact carboxyl groups provides accessible proton sources, while the supramolecular host-guest structure facilitates proton exchange through a relatively continuous hydrogen-bonding network at the interface. These results indicate that structural features governing proton transport can also influence interfacial electrochemical response, linking bulk conduction behavior with potentiometric signal generation. In contrast, the deprotonated carboxylate in complex **1** eliminates the primary proton source, and the water-bridged dynamic hydrogen bonds in complex **3** introduce additional kinetic barriers for interfacial charge transfer.

Conclusion

In conclusion, a planar $\{Mo_{10}\}$ supramolecular ring constructed from $[Mo_2O_2S_2]^{2+}$ units was strategically designed as a tunable assembly platform to investigate how assembly pathways govern material structure and proton conduction performance. By precisely regulating the synthesis conditions, the binding mode of the Pym-5-CA was

directed through pH control. At higher pH, carboxyl deprotonation triggered coordination-driven assembly into the {Mo₁₂} framework **1**, whereas under mildly acidic conditions, the neutral carboxyl group served as a hydrogen bond donor anchoring above the {Mo₁₀} ring to form the supramolecular host-guest complex **2**. This pair of structural analogues, derived from the same ligand via distinct assembly routes, provides an ideal model system for probing structure-activity relationships. Building upon this supramolecular platform, the introduction of 3-PyBA under identical acidic conditions yielded a second host-guest complex **3**, specifically designed to probe the influence of guest functional-group chemistry—contrasting the strong proton-donating -COOH with the weakly acidic and dynamically binding-B(OH)₂- on supramolecular recognition and proton transport. Systematic structure-property investigations reveal that the supramolecular host-guest architecture with intact -COOH groups (complex **2**) achieves superior proton conduction performance compared to both the coordination framework (complex **1**) and the boronic acid-functionalized analogue (complex **3**). This enhancement arises from the synergistic effect between the strong proton-donating carboxyl groups and the well-defined, direct hydrogen-bonding network that facilitates continuous proton transport. Furthermore, the pH-responsive potentiometric measurements demonstrate a positive correlation between bulk proton conduction and interfacial electrochemical signal transduction, with complex **2** exhibiting the highest sensitivity among the three systems. These results demonstrate the great potential of [Mo₂O₂S₂]²⁺-based supramolecular assemblies in proton conduction. Future work will focus on exploring diverse heteroaromatic acid ligands with tailored functional groups to further optimize host-guest interactions and develop superior proton-conducting materials.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing author(s) report(s) no conflict of interests in this work.

Author contribution statement

L. Wang, designed engineered the compounds and wrote the paper; J. Li. and Z. Liang, performed the experiments; H. Zang. and S. Liang, provided guidance on the experiments and paper writing. All authors contributed to the general discussion.

Use of AI statement

None.

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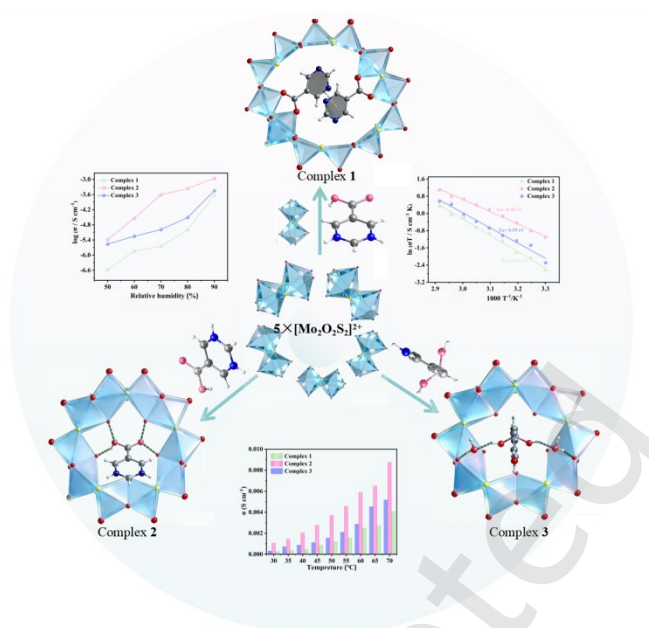
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Assembled from $[\text{Mo}_2\text{O}_2\text{S}_2]^{2+}$ units via pH-controlled modulation of ligand coordination modes, the $\{\text{Mo}_{10}\}$ -based host-guest architecture with intact -COOH groups (complex **2**) achieves a proton conductivity 2.1 times higher than that of the coordination framework (complex **1**) and 1.7 times higher than that of the boronic acid-functionalized host-guest analogue (complex **3**).