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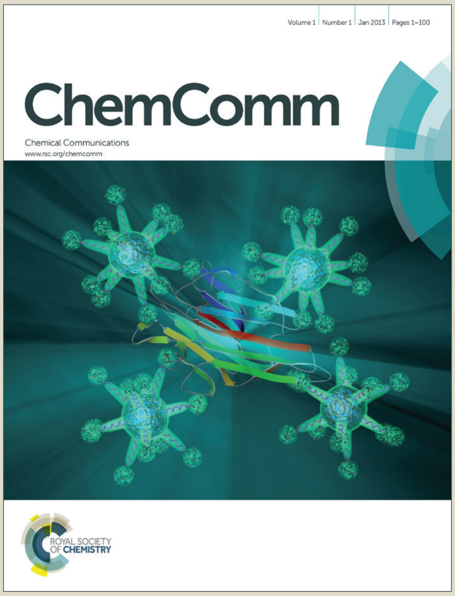

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Polyoxometalate-Functionalized Metal-Organic Frameworks with Improved Water Retention and Uniform Proton-Conducting Pathways in Three Orthogonal Directions

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Polyoxometalate-functionalized metal-organic frameworks featuring uniform proton-conducting pathways in three orthogonal directions, good water retention and stability were prepared. The proton conductivity of the hybrid material was observed to increase by 5 orders of magnitude comparing to the parent material HKUST-1.

Metal−organic frameworks (MOFs) are versatile crystalline porous materials constructed from metal ions or clusters and organic ligands via coordination bonds.[1] The extraordinary degree of variability for both the organic and inorganic components of MOFs provide endless topological diversities and aesthetically fascinating structures.[2] More importantly, the crystalline nature of MOFs enables direct visualization of structure for systematic design and exact analysis of a structure-activity relationship. Customization of the material to yield desired physical and chemical properties can be implemented by the judicious selection of organic ligands and metal centers or the incorporation of specific guest molecules. Relative to the immense effort directed at gas storage,[3] sensing,[4] and catalysis[5] etc., proton conduction has received little attention.[6] Recently, proton-conducting MOFs have been obtained by introducing acidic and/or hydrophilic units or proton carriers into nano-channels to form efficient proton transfer pathways for their potential application in fuel cells.[7] However, the stability (thermal and solvent stability, especially in water) and water retention of most MOFs is a limitation for their further modification and application.[8] In addition, the proton-conducting pathways in the large majority of hitherto reported proton-conductive MOFs are low dimensional (1-D or 2-D),[7a-f, 9] which will result in highly anisotropic conductivities.[10] Construction of 3-D H-bonding networks with high symmetry in ordered channels would remit or eliminate the anisotropic conductivity and lead to a high conductivity of the bulk sample.[11]

Here, we choose a cubic symmetry MOF, HKUST-1 with a space group *Fm-3m*, as a promising candidate.[12] Key to the study is to incorporate appropriate proton donors and/or carriers into the three orthogonal uniform channels to construct 3-D H-bonding networks (Figure 1). Keggin-type polyoxometalates, with quasi-spherical architecture and abundant exterior oxygen atoms, are the most stable, available, and widely studied species among all types of POMs.[13] The polyanions are usually surrounded by plenty of water molecules through strong H-bonding affinity in the crystalline state. Hence, loading Keggin-type POMs into the ordered channels of MOFs would provide more hopping sites in the cavities and improve the stability and hydrophilicity of MOFs. The hybrid material might be a potentially excellent proton-conductor.

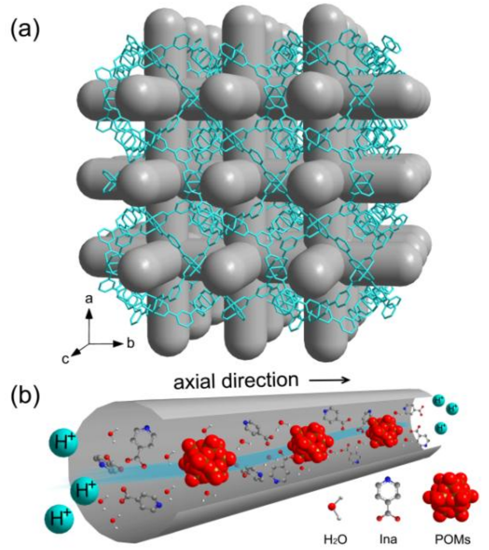

Fig. 1 Schematic of (a) the uniform proton-conducting pathways (gray cylinders) along a, b, and c axes in HKUST-1, and (b) the proton-conducting pathway constructed by POMs, Ina and water molecules arranged alternately in the nano-channels.

Owing to the strongest acidity of phosphotungstic acid ($H_3PW_{12}O_{40}$; HPW) among the common Keggin units,[13b] we choose compound $[Cu_{12}(BTC)_8(H_2O)_{12}][H_3PW_{12}O_{40}]\cdot nH_2O$

(denoted as NENU-3, H_3BTC=1,3,5-benzentricaboxylate) for proton-conducting investigation, which is reported by us previously.[14] The host matrix $[Cu_{12}(BTC)_8(H_2O)_{12}]\cdot nH_2O$ (HKUST-1) without POMs is used for comparison. Alternating current (AC) impedance measurements revealed that NENU-3 gave a more than 3 orders of magnitude enhancement in proton conductivity (4.76×10^{-5} S cm^{-1}, Figure S1) comparing to HKUST-1 (1.08×10^{-8} S cm^{-1}, Figure S2) at 90 ℃ and 70% relative humidity (RH), which demonstrated that the incorporation of HPW exerts a key role in facilitating the internal proton transfer.

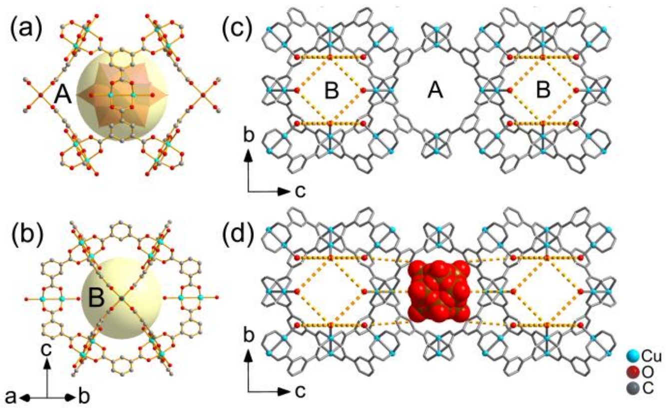

Fig. 2 The structure of (a) Pore A, (b) Pore B, (c) HKUST-1, and (d) NENU-3 and the hydrogen-bonding array formed between POMs and coordinated water molecules.

For efficient proton conduction, continuous H-bonding networks are important. In HKUST-1, two kinds of pores (labeled as A and B, Figure 2) interconnecting with each other alternately construct 3-D nano-channels. A detailed structural analysis suggests their different affinity to water molecules. As shown in Figure 2b, there are 12 open Cu sites pointing into the internal space of pore B, to which water or other desired molecules can be coordinated. In contrast, the surfaces of pore A are mainly constructed by aromatic rings with no open coordination sites pointing inside, which implies a more hydrophobic nature. Interestingly, owing to the optimum match of size and symmetry, hydrophilic HPW anions selectively inhabit hydrophobic pore A rather than pore B in NENU-3. Considering the strong affinity of HPW to water molecules, NENU-3 would be more hydrophilic than HKUST-1. To examine the capacity for inclusion of water molecules of NENU-3 and HKUST-1, we measured their water adsorption isotherms. As shown in Figure 3, NENU-3 and HKUST-1 showed similar adsorption behavior at 25 ℃. Both of them adsorbed large amount of water under 40% RH. However, it is worth noting that the solvent accessible void volume of HKUST-1 and NENU-3 are 50.1% and 23.9% (calculated by PLATON), respectively. In other words, although about one half of the inner space is filled after HPW is incorporated, the water content of NENU-3 (~58 water molecules per formula) and HKUST-1 (~52 water molecules per formula) are almost equal at 70% RH. Together these results hint that the inner cavities of HKUST-1 are not full filled after the water adsorption equilibrium reached, there is still residual space. Owing to the hydrophobic nature of pore A, we conclude that, in POMs-free frameworks, adsorbed guest water molecules are more inclined to reside in pore B to interact with coordinated water by hydrogen bonds. Only rare amount of free water molecules drift in pore A, which well explain the poor proton conductivity of HKUST-1. In contrast, more continuous H-bonding networks are constructed by the impregnation of HPW in NENU-3.

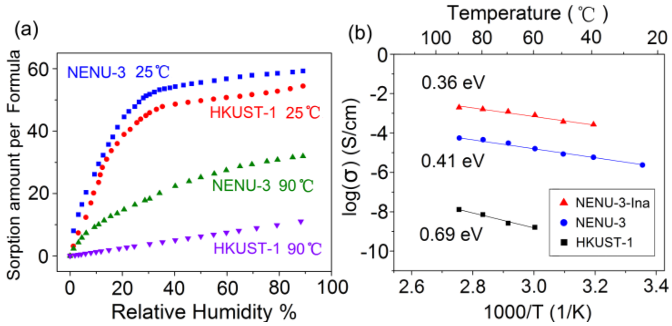

Fig. 3 (a) Water vapor adsorption isotherms of NENU-3 and HKUST-1 at 25 ℃ and 90 ℃, respectively. (b) Arrhenius plots of proton conductivities for NENU-3-Ina, NENU-3 and HKUST-1 at 70% RH, respectively.

Among reported water-mediated MOF-based proton-conductors, highly humid conditions (commonly near to 100% RH) are usually required.[7e, 9d-f, 15] Because most of these materials have poor hydrophilicity and water retention, water molecules easily desorb from them under low humidity resulting in disconnected proton-conducting pathways. Avoiding this desorption and retaining efficient proton transport under low humidity is of great significance for practical application. To examine the water retention of NENU-3 and HKUST-1, we measured their water adsorption isotherms at 90 ℃. Although the adsorption capacities of them were both lower than those at 25 ℃, NENU-3 can still adsorb ~30 water molecules, whereas the amount for HKUST-1 is less than 9 (Figure 3a), which undoubtedly confirms the improvement of water retention by the incorporation of HPW. In addition, the excellent capacity of water adsorption and retention of NENU-3 reduces the activation barrier for proton hopping among the exterior oxygen atoms of Keggin units which need the assistance of water molecules.[16]

As shown in Figure 3b, the proton conductivities of NENU-3 was 3.1×10^{-6} S cm^{-1} at 25 ℃ and 70% RH, and increased gradually with the increasing temperature up to 4.76×10^{-5} S cm^{-1} at 90 ℃. Similar tendency was observed for HKUST-1 (1.62×10^{-9} S cm^{-1} at 25 ℃ and 1.08×10^{-8} S cm^{-1} at 90 ℃ and 70% RH), which indicated that the proton conductivities strongly depend on temperature. The activation energy of NENU-3 and HKUST-1 were 0.41 eV and 0.69 eV respectively, calculated by the Arrhenius equation. The reduced activation energy and the increased proton conductivity of NENU-3 suggest the presence of continuous H-bonding networks among the HPW units and water molecules (coordinated water and lattice water) in the ordered nano-channels. Grotthuss mechanism is dominant for the proton conduction in NENU-3, which is consistent with the architectural feature that Keggin polyanions are entrapped into pore A without mobility. As for HKUST-1, a vehicular transfer mechanism is predominant, which is reasonable because of the limited number of water molecules in the channels acting as vehicles.

Stability is another restriction for MOFs in practical application. Although some highly robust MOF materials have emerged recently,[17] the large majority of MOFs are not stable,[8] especially in aqueous solution. Water-tolerability of MOF-based proton conducting materials will affect their performance in fuel cells. The crystallinity of HKUST-1 is completely lost after being exposed in water vapor ~2 hours (Figure S3), resulting in no measurable conductivity, which is in agreement with the previous result of Hupp et al.[18] However, strengthened by the bracing function of HPW, the structural integrity of NENU-3 can be maintained even having been soaked in water for more than a week in a broad pH value range from 2 to 8 (Figure S4). Still, there is no structural transformation after the impedance measurement. (Figure S5)

Although the presence of POMs induces a significant enhancement, the proton conductivity for NENU-3 (4.76×10^{-5} S cm^{-1}) is just among the moderate level. Owing to the feasibility of replacing aqua ligands in pore B by other groups, such as acetonitrile, and pyridine,[10, 16] we chose an organic acid with both carboxyl and N-heterocycle, isonicotinic acid (Ina) acting as a proton donor and H-bonding acceptor.

Ina was introduced into NENU-3 by an immersion process (denoted as NENU-3-Ina). Powder X-ray diffraction (PXRD) of NENU-3-Ina suggested that the major structure of NENU-3 was maintained (Figure S6). FTIR demonstrated the existing of Ina in the hybrid material (Figure S7). To make sure that the Ina molecules were accommodated inside the framework, not aggregated on the outer surface, N_2 adsorption of NENU-3-Ina was measured at 77K. The total uptake dramatically decreased compared with NENU-3, which suggested that Ina molecules occupied the residual micropore spaces of NENU-3 (Figure S8). The stability of guest molecules in the pores was checked by rinse the hybrid materials with hot water and ethanol for several times, and the N_2 adsorption curves exhibit no obvious difference (Figure S9). NENU-3-Ina achieved conductivity of 3.79×10^{-4} S cm^{-1} at 40 ℃ and 70% RH, and increased to 1.81 $\times10^{-3}$ S cm^{-1} at 90 ℃ (Figure 3b and S10), which is ~38 times higher than NENU-3. That means a continuous proton transporting highway is built up. Note that the conductivity of bulk Ina is 1.08×10^{-6} S cm^{-1} at 90 ℃ and 70% RH (Figure S11), which is obviously lower than that of NENU-3-Ina. The activation energy of proton hopping of NENU-3-Ina is 0.36 eV (Figure 3b), which belongs to Grotthuss conduction mechanism.

We also investigated the conductivity of NENU-3 with other guest molecules incorporating into the pores, such as imidazole hydrochlorid (NENU-3-ImHCl). This material also yielded an increased proton conductivity of 5.94×10^{-4} S cm^{-1} (at 90 ℃ and 70% RH, Figure S12).

In summary, a class of POM-functionalized MOF materials featuring uniform proton-conducting pathways in three orthogonal directions, good water retention and water stability was prepared by a convenient method. 3-D hydrogen-bonding networks were constructed by arranging POMs and isonicotinic acid alternately, both of which retain acidic protons. POMs were introduced into the framework as multi-functional guests to strengthen the scaffold, fill void space, provide mobile protons, and improve the hydrophilicity and water retetion of the hybrid material. A huge enhancement (more than 4000-fold) in proton conductivity was observed, in NENU-3. These results demonstrated that POMs can be used as excellent modifiers to control conductivity of MOFs besides conventional carboxylic acid species or N-heterocyclic compounds. Isonicotinic acid molecules were purposefully introduced into the framework by post-synthesis modification and led to a further increase (~38-fold) in proton conductivity. This strategy offers promising prospects for adjusting proton conductivity by incorporating two or more guests into MOFs which have pores with different structure and composition.

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