

A Water-Stable Metal–Organic Framework with Highly Acidic Pores for Proton-Conducting Applications

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S Supporting Information

ABSTRACT: Metal–organic framework (MOF) materials are a nontraditional route to ion conductors, but their crystallinity can give insight into molecular-level transport mechanisms. However, some MOFs can be structurally compromised in humid environments. A new 3D metal–organic framework, PCMOF-5, is reported which conducts protons above 10^{-3} S/cm at 60 °C and 98% relative humidity. The MOF contains free phosphonic acid groups, shows high humidity stability, and resists swelling in the presence of hydration. Channels filled with crystallographically located water and acidic groups are also observed.

The development of new materials with targeted properties requires an iterative cycle of design, execution, and assessment. A key aspect of enhancing design is to establish clear structure–activity relationships for the materials under study. With regard to proton conductors, an excellent material should offer an array of proton binding sites of equivalent pK_a with a low activation energy pathway linking them. As many of the best electrolytes are polymeric solids with noncrystalline structures, exact analysis of a structure–activity relationship is often a challenge.¹ Metal–organic frameworks (MOFs) are a structurally diverse platform for a wide range of potential applications.² Relative to the immense effort directed at gas capture and storage applications, ion conduction has received very little attention.³ That said, the hybrid nature of MOFs can be viewed as an opportunity, as they can be perceived as compositionally intermediate to ubiquitous polymeric electrolytes and inorganic solid acids; there has been a recent surge of proton-conducting coordination polymer/MOF materials reported.⁴

Hallmark properties of MOFs are that they have modular synthetic routes, open structures and are crystalline. The crystallinity of MOFs enables direct visualization of structure and enhances design prospects. This includes not just the framework but also guest molecules which are often integral to the proton conduction pathway. Even if not a commercial candidate, a crystalline ion conductor can provide a firm starting point for modeling studies. This point is germane to the value of MOFs as proton electrolytes: even though a particular MOF may not be water stable, it can still provide insight to develop structure–activity relationships. Although some highly robust MOF materials have emerged recently,⁵ the large majority of MOFs are not water stable.⁶ Beyond structural integrity, stability of a MOF proton conductor to hydration

extends to retention of guest proton carriers and resistance to swelling of the material, as macroscopic size deviations would disrupt electrode/electrolyte interfaces.

Here we present a MOF that conducts protons at 4×10^{-3} S/cm (at 98% relative humidity (RH) and 335 K) and shows structural stability to high RH and dilute acidic solutions. The robustness and resistance to swelling of $[\text{La}(\text{H}_5\text{L})(\text{H}_2\text{O})_4]$ (PCMOF-5, L = 1,2,4,5-tetrakisphosphonomethylbenzene) are attributed to a three-dimensionally connected M(III) phosphonate framework. The high proton conductivity is enabled by free phosphonic acid groups lining the pores and crystallographically located intra-pore water molecules. With over 1200 metal phosphonate structures in the Cambridge Structural Database, this represents the first 3D phosphonate with free diprotic acid groups as pendants. Synthetic conditions were employed to give free acid groups and promote “error checking” to yield a crystalline material.

Some recent reports have demonstrated the inclusion of acidic *hydrogen phosphonate protons* within a MOF to create a proton-conducting material.⁷ Also, we have demonstrated that it is possible to produce a proton-conducting material from a crystalline phosphonate with no phosphonic acid protons but with acidic coordinated water.⁸ We sought to design a proton-conducting phosphonate MOF through synthetic controls in order to include *diprotic phosphonic acid groups* within the framework. To achieve this goal, we chose to use a known tetraphosphonic acid ligand, H_8L , to build the MOF. Two previous reports⁹ have shown that this ligand adopts a dense pillared-layered motif with divalent transition metals, with a 2:1 M:L ratio, where a hydrophilic metal phosphonate layer is pillared by a hydrophobic organic layer. We believed that more acidic conditions during synthesis would facilitate the exclusion of some metal centers and replace them with acidic channels.

To synthesize the MOF, pH was reduced during synthesis through the addition of H_2SO_4 ($\text{pH} < 1$), and La(III) was chosen to be able to bind to the phosphonate ligand under the acidic conditions. Upon mixing an aqueous solution of $\text{La}(\text{H}_2\text{SO}_4)_3/\text{H}_2\text{SO}_4$ with an aqueous solution of H_8L , a colorless solution was formed, from which single crystals of PCMOF-5 grew within a day upon standing at room temperature. The addition of acid to the synthesis helps modulate crystal growth, with greater equivalents of acid increasing the time for crystal growth. Addition of a sulfate source to the preparation of a MOF can represent a potentially very stable competing phase. La(III) was chosen, in part,

Received: October 22, 2012

Published: January 10, 2013

because its hydrogen sulfate salt is water soluble. The crystal growth synthesis could be scaled-up to produce PCMOF-5 in bulk, and PXRD measurements on a ground powder matched the simulated pattern from the single-crystal solution (Figure S1).

PCMOF-5 (Figure 1) crystallizes with a formula of $\text{La}(\text{H}_5\text{L})(\text{H}_2\text{O})_4$ and adopts a modified pillared-layered motif,

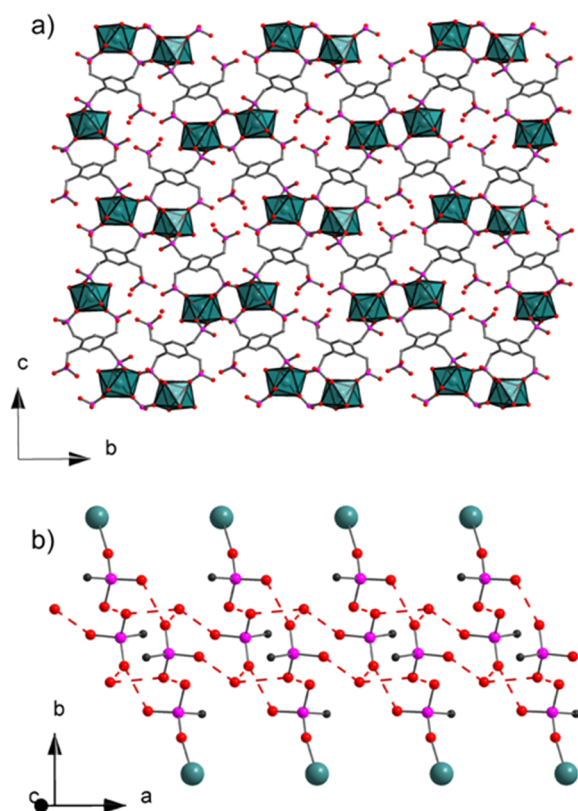


Figure 1. (a) Structure of PCMOF-5 as viewed down the *a*-axis. Free phosphonic acid groups and uncoordinated water molecules are located in each pore. (b) View showing the one-dimensional hydrogen-bonding array formed between phosphonic acid groups and free water molecules in the direction of the *a*-axis.

where a hydrophobic molecule *L* pillars hydrophilic 1D columns of $\text{La}(\text{III})$ phosphonate along the *a*-axis. Alternating between the columns along the *a*-axis are acidic channels housing a single column of water molecules. The 1D $\text{La}(\text{III})$ phosphonate chains are connected into a 3D framework through three of the four phosphonate groups on *L*, leaving the fourth group, a diprotic phosphonic acid, uncoordinated and protruding into the hydrated channel. The hydrated channel is completely lined with phosphonic acid groups, with one coordinated monodentate hydrogen phosphonate per formula unit along the *b*-axis and one uncoordinated phosphonic acid per formula unit along the *c*-axis; three coordinated water molecules do not line the channel and appear to be involved in structural hydrogen bonds with the 1D $\text{La}(\text{III})$ phosphonate columns. Free water molecules fill the channel, alternating between and bridging the phosphonic acid groups through hydrogen bonds. The highly acidic, hydrated nature of the channel, along with the existence of a potential hydrogen bond pathway, suggested this material may be a good proton conductor.

Before proton conductivity was measured for PCMOF-5, structural stability to the highly humid conditions during conductivity testing was assessed. A fresh sample of PCMOF-5 was boiled in water for 7 days without significant loss in crystallinity, or mass loss, indicating the material was insoluble and stable to water (Figure S2). For completeness, although this is an unlikely scenario in a fuel cell where water is omnipresent, the effect of complete dehydration was examined. Full dehydration gives a reversible shift to a structure lacking significant long-range order. Thermogravimetric analysis showed a gradual mass loss of 19.9 wt% in four steps (Figure S3). The first two steps (25–145 °C) are attributed to the loss of pore and coordinated water, respectively (4 H_2O /formula unit: 11.2% obs, 10.9% calc). The next step, up to 300 °C, is attributed to condensation of free phosphonic acid; a formula of $\text{La}_1\text{C}_{10}\text{H}_{10}(\text{P}_2\text{O}_5)(\text{P}_4\text{O}_9)_{0.5}$ is expected, with a loss of 6.5 equiv of water compared to the hydrated structure (17.6 wt% obs, 17.7 wt% calc). Mass loss >300 °C is likely the onset of full decomposition. The amorphization and condensation likely occur with some retention of similar local environment, as a sample heated to release all structural water regained crystallinity by boiling in water (without dissolution) (Figure S4).

To characterize the proton conductivity of PCMOF-5, AC impedance analysis was performed on multiple samples with varying % RH in air. The narrow 1D channels in PCMOF-5 necessitated multiple heating and cooling cycles for samples to equilibrate; equilibrium was faster at higher RH (Figure S5). Representative Nyquist plots are shown in Figure 2. Bulk and

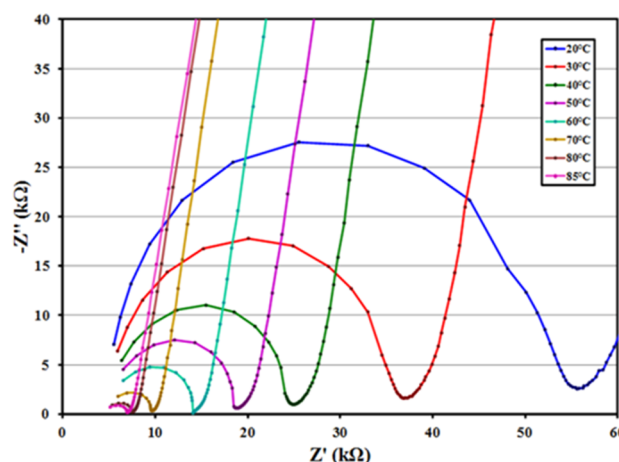


Figure 2. Nyquist plots for PCMOF-5 at 90% RH and various temperatures.

grain boundary contributions to the resistivity are not resolved into separate semicircles, consistent with an ion-conductive interfacial region. This is to be expected as the particle peripheries would contain phosphonic acid groups and hydrated metal ions. The low-frequency tail is consistent with blocking effects at the electrode, as would be expected for ionic conduction. Analysis on PCMOF-5 at 98% RH gave very good conductivity of $1.3 \times 10^{-3} \text{ S/cm}$ at 21.5 °C that rose to $2.5 \times 10^{-3} \text{ S/cm}$ at 60.1 °C (Figure 3). The activation energy measured was 0.16 eV, a very low value on par with solid acids (cf. $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 29\text{H}_2\text{O}$ (0.15 eV),^{10a} $\text{Sb}_2\text{O}_5 \cdot 5.4\text{H}_2\text{O}$ (0.17 eV),^{10b} and $\beta\text{-Al}_{10.34}\text{Mg}_{0.66}\text{O}_{17}(\text{H}_3\text{O})_{1.66}$ (0.17 eV)^{10c}), indicating a highly efficient Grotthuss mechanism. Indeed, this is the lowest activation energy for total conduction (both bulk and grain

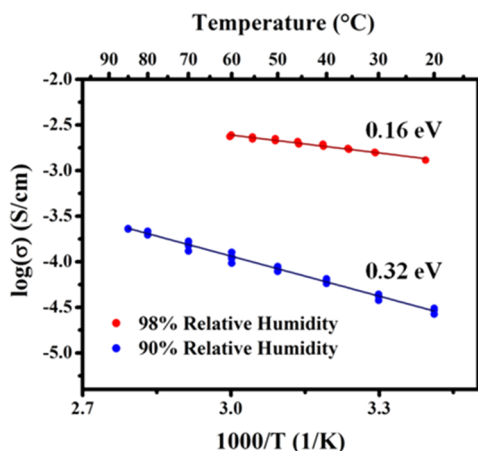


Figure 3. Log of conductivity as a function of inverse temperature for PCMOF-5 as measured at 90% and 98% RH.

boundary effects) observed in any proton-conducting MOF material. Costantino et al. have reported a lower value, but this was derived from only the bulk resistivity.¹¹ Reducing the humidity to 90% gave conductivity values between 2×10^{-5} and 2×10^{-4} S/cm from 20 to 85 °C, with an activation energy calculated at 0.32 eV (Figure 3). This is still within the range of Grotthuss behavior but indicating a less organized pathway. To ensure that conductivity was not due to residual H_2SO_4 from the synthesis, a second sample was washed with water multiple times and then boiled in water for 1 day prior to measurement. This sample also gave conductivity values in the same range as the untreated sample with the same activation energy of 0.32 eV (Figure S6). Lowering the humidity gave an exponential loss in conductivity due to the loss of water within the framework, but conductivity could be recovered after dehydration, as a sample which was heated to 105 °C fully regained conductivity upon exposure to high RH (Figures S7 and S8). Phase integrity was confirmed by PXRD after impedance analysis and corroborated by the linearity of the temperature dependence (Figure S9).

The high conductivity, with corresponding low activation energy at 98% RH, is likely due to complete occupancy of the intra-channel water sites within PCMOF-5 under the highly humid conditions. As the uncoordinated water molecules are integral to the proton transfer pathway, any loss in these molecules leads to an increase in activation energy due to a longer average distance for the proton to hop between sites. Especially given that the pathway is 1D, this should have a significant effect on conductivity. This hypothesis is supported qualitatively by the observation that the activation energy doubles to 0.32 eV, and the conductivity drops 1 order of magnitude at 90% RH. Below 50% RH, conductivity was negligible, likely representing loss of the hydrogen bond pathway in PCMOF-5. The uncoordinated phosphonic acid groups make the structure reminiscent of phosphonic acid containing proton-conducting polymers.¹² The crystallographic location of the atoms within the structure offers a useful handle for further design or modeling of the conductivity of better proton-conducting materials.

Owing to the excellent ligating ability of organophosphonates, the incorporation of free phosphonic acid groups into a coordination polymer is a significant challenge. In a search of the Cambridge Structural Database, only six metal organophosphonate compounds were found (of 1258 polymeric metal

phosphonates) that possessed free phosphonic acid groups, and all of these were either 1D or 2D coordination networks.¹³ Although these materials were not studied as electrolytes, even if the backbone of the material was water stable, the solid would likely experience swelling with hydration and present issues for interfacial stability of a membrane electrode assembly. PCMOF-5 represents the first coordination polymer with a 3D structure to have uncoordinated phosphonic acid groups. For proton conduction via a Grotthuss mechanism, beyond acidity, the fact that these groups are uncoordinated and able to reorient is notable.

The realization of the free phosphonic acid groups in a water-stable network was a direct result of a synthetic strategy employing highly acidic conditions and minimizing competing phases. Kitagawa recently reported HPO_4^{2-} - and H_2PO_4^- -containing Zn azole coordination polymers that conduct in the range 1.2×10^{-4} – 2.6×10^{-4} S/cm at 130 °C.^{40,p} These compounds are 1D and 2D networks, so they may be susceptible to swelling/dissolution, but these authors were targeting anhydrous conduction. Demadis and Cabeza also recently reported Gd 2-hydroxyphosphonoacetic acid and La tetramethylenediamine- N,N,N',N' -tetrakis(methylenephosphonic acid) MOFs with coordinated hydrogen phosphonate where acidic conditions were employed to mediate protic state and obtained conductivities of 3.2×10^{-4} and 8.0×10^{-3} S/cm at 98% RH and ambient temperature.^{7a,b} The value of 2.5×10^{-3} S/cm at 60 °C and 98% RH for PCMOF-5 is among the highest conductivities reported for a MOF material, with the highest reported values being 8×10^{-3} S/cm at ~ 20 °C for the La material above and for $(\text{NH}_4)_2(\text{adipic acid})\cdot[\text{Zn}_2(\text{oxalate})_3]\cdot 3\text{H}_2\text{O}$ by Kitagawa,^{4e} 1×10^{-2} S/cm at 150 °C and low RH for H_2SO_4 loaded in MIL-101,^{4q} and finally 2.1×10^{-2} S/cm at ~ 85 °C and 90% RH in PCMOF2^{1/2}.^{4r}

Better proton-conducting materials are needed that can operate both at higher temperatures and in humid environments. Humidity commonly augments conduction, provided the integrity of the electrolyte and the interfacial contacts with electrodes can be retained. Compositionally robust electrolytes should also be resistant to swelling. Water stability is a challenge for MOF materials in general, but this is a critical factor for proton electrolyte applications. Here we have presented PCMOF-5, a 3D MOF with pores lined with uncoordinated acid groups. PCMOF-5 shows proton conductivity on the order of the best MOF materials with the lowest activation energy for proton transfer in any MOF. Moreover, it is stable to water in terms of both the framework connectivity but also with regard to swelling. The ordered structure provides direct visualization of the proton transfer pathway and opportunities for material improvements.

■ ASSOCIATED CONTENT

⑤ Supporting Information

Details of synthesis, powder XRD, gas sorption, impedance analysis, and CIF file for PCMOF-5. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the Natural Sciences and Engineering Research Council (NSERC) of Canada for support of this research. J.M.T. and K.W.D. acknowledge scholarship support from the Alberta Ingenuity Fund.

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