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Facile Proton Conduction via Ordered Water Molecules in a Phosphonate Metal−Organic Framework

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Abstract: A new phosphonate metal−organic framework (MOF) with a layered motif but not that of the classical hybrid inorganic−organic solid is presented. $Zn_3(L)(H_2O)_2\cdot 2H_2O$ (L = [1,3,5-benzenetriphosphonate]$^{6-}$), henceforth denoted as PCMOF-3, contains a polar interlayer lined with Zn-ligated water molecules and phosphonate oxygen atoms. These groups serve to anchor free water molecules into ordered chains, as observed by X-ray crystallography. The potential for proton conduction via the well-defined interlayer was studied by ^{2}H solid-state NMR spectroscopy and AC impedance spectroscopy. The proton conductivity in H_2 was measured as 3.5×10^{-5} S cm^{-1} at 25 °C and 98% relative humidity. More interestingly, an Arrhenius plot gave a low activation energy of 0.17 eV for proton transfer, corroborating the solid-state NMR data that showed exchange between all deuterium sites in the D_2O analogue of PCMOF-3, even at −20 °C.

Metal−organic frameworks (MOFs) are versatile scaffolding materials because of their modular syntheses, porosity, and crystalline structures. While applications related to gas sorption are prevalent, another energy-relevant domain, ion conduction, has been much less studied. Indeed, only a few ion-conducting coordination polymers have been reported.[1−6] New proton conductors are tremendously relevant for clean energy applications since the cost efficiency of proton exchange membrane fuel cells could be greatly improved by better-performing proton-conducting membranes.[7] At a more fundamental level, the crystallinity of MOFs can provide insight into conduction mechanisms that is often lacking in macromolecular electrolytes because of the lack of long-range order.

Ion conduction occurs in solids via movement of the ion between energetically similar domains. This can occur intrinsically through the material or by some carrier-mediated pathway (e.g., water/hydronium for H^+ ions) in pores of the material. MOFs can enable both forms of conduction, as it has been shown that protons can be passed through the coordination skeleton itself[1a,b,4] or through carriers such as imidazole,[2] 1,2,4-triazole,[5] or water[6] loaded in the pores. Metal phosphonates[8] are appealing candidates for proton conduction. The phosphonate group possesses three oxygen atoms, so ligation of metal ions into multidimensional frameworks is possible while oxygen atoms may still be available to further act as H-bond acceptors.[9] These sites could serve to anchor carrier molecules or directly transfer protons as part of a conduction pathway. However, in the hybrid inorganic−organic motif typically observed for simple layered phosphonates, the phosphonate groups are largely inaccessible because of their coordinative saturation by the metal ions and their sheathing by pendant organic groups. Proton conductors based on sulfonation of such layered materials have been reported.[10]

Herein, we present an approach to proton-conducting phosphonates based on designing ligands that would disfavor the hybrid inorganic−organic motif and form structural domains lined with phosphonate oxygen atoms. The new MOF, $Zn_3(L)(H_2O)_2\cdot 2H_2O$ (L = [1,3,5-benzenetriphosphonate]$^{6-}$), designated as PCMOF-3, has a layered structure in which the phosphonate and Zn^{2+} ions do not saturate each other's coordination spheres. The result is an interlayer region that is rich in phosphonate oxygen atoms and Zn-ligated water molecules. These groups anchor free but ordered water molecules to form a facile proton conduction pathway, as confirmed by the determined activation energies. X-ray diffraction data as well as solid-state $^2H/^{13}C/^{31}P$ NMR studies are reported.

H_6L was prepared by published methods.[11] Single crystals of PCMOF-3 were obtained by diffusion of acetone into $Zn(ClO_4)\cdot 6H_2O$ (0.470 mmol) and H_6L (0.154 mmol) in water (10 mL). X-ray diffraction showed that PCMOF-3 formed an orthorhombic phase (*Cmca*, No. 64; $a = 22.972(5)$ Å, $b = 8.571(2)$ Å, $c = 16.148(3)$ Å). PCMOF-3 was isolated as a pure bulk phase from H_6L and $ZnCO_3\cdot 2Zn(OH)_2\cdot 0.5H_2O$ in refluxing water (Figure S1 in the Supporting Information).

The structure of PCMOF-3 (Figure 1), although it is layered, is not that of the classic inorganic−organic hybrid. The structure could be described as columns of L molecules cross-linked by Zn^{2+} ions, both within a single column and between columns, to form neutral layers in the *bc* plane. Within a layer, molecules of L form π-stacked dimers [⊥ distance = 3.718(5) Å] perpendicular to the layer. One phosphonate group lies in the *bc* plane, requiring the other two to be directed away by 60° into the interlayer. The phosphonate oxygens of each dimer coordinate to six tetrahedral zinc centers (four Zn1 and two Zn2). The Zn1 sites are coordinated by four phosphonate O atoms (Zn1−O = 1.917−2.019 Å) that surround the dimer in the *bc* plane. The two Zn2 centers, situated above and below the L dimer, are ligated by two phosphonate O atoms [Zn2−O3 = 1.914(3)] and two disordered water molecules that also point into the interlayer. Along a column, the interdimer distance is 4.138(5) Å. The interlayer distance in PCMOF-3 is 11.486(1) Å, corresponding to half the *a* axis, and the gallery height (treating the structure as rigid to assign metrics) ranges from 5.632(1) Å [2.592(1) Å factoring vdW radii] between aquo ligands on Zn to 8.074 Å (5.034 Å factoring vdW radii) between O10 atoms of phosphonate groups. Phosphonate oxygen atoms from the out-of-layer RPO_3 groups and the Zn2 water molecules serve to make the interlayer highly hydrophilic. In the interlayer, free water molecules are anchored by strong H-bonds [donor−acceptor distances = 2.698(2)−2.895(2) Å] to the RPO_3 groups and

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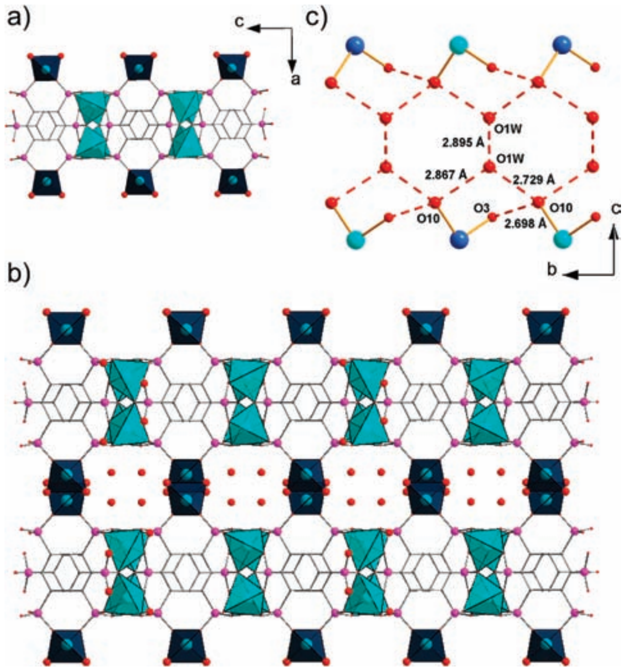

Figure 1. Structure of PCMOF-3 showing (a) a single layer, where light tetrahedra represent fully phosphonate-ligated Zn1 centers and dark tetrahedra represent bis(aquo)-ligated Zn2 centers; (b) two layers stacked to show the channels formed and included water molecules as located in the X-ray difference map; and (c) a cross section of the channel with H-bonds between channel and coordinated water molecules. Cyan and blue represent Zn atoms above and below the plane of the page, respectively.

coordinated water molecules (Figure 1c). The water molecule positions are fully occupied and well-resolved in the X-ray structure, although O10 is disordered, preventing the location of protons. Protons on the free water molecules also were not located.The data above were extracted from a 173 K data collection. Notably, the structure of PCMOF-3 was also collected and solved at 293 K; this solution showed larger thermal parameters but the same atomic positions. This was germane to the ensuing studies.

As mentioned above, better proton-conducting electrolytes are a major challenge, and molecular-level insights into such materials are invaluable. However, such information is often not accessible for macromolecular proton conductors because of the lack of long-range structural order and their dynamic nature in environments of varying temperature and humidity. A hallmark property of MOFs is their crystallinity, which allows for direct structural analysis. This is a tremendous asset in understanding function, allowing more meaningful modeling, and enabling rational design of better materials. The ordered chains of water molecules observed crystallographically in PCMOF-3 (Figure 1c) would imply that this material is well-organized to enable Grotthuss proton transfer.[12] Therefore, a study of proton conduction and the possible H-bond transfer pathway was undertaken by impedance spectroscopy and solid-state NMR spectroscopy (SSNMR). Multiple TGA samplings after routine handling of PCMOF-3 showed that the tetrahydrate phase was stable under ambient conditions (Figure S2).

$Zn_3(L)(D_2O)_2\cdot 2D_2O$, which was prepared analogously in D_2O, was studied by variable-temperature ^2H SSNMR (Figure 2) to gain insight into the protonic motion. The broad ^2H NMR spectrum observed at 77 K is characteristic of ^2H in static water molecules. By 240 K, the spectrum consisted of two overlapped line shapes, one the same broad static line shape as at 77 K and the other a narrower line shape indicating dynamic averaging. The broad line disappeared by 250 K, and the remaining line shape, which can be defined by a single quadrupole coupling constant and asymmetry parameter, showed that all of the ^2H atoms were dynamically equivalent. This is consistent with rapid exchange of ^2H between all possible site types within the orthorhombic structure, which must involve a combination of reorientation and exchange via translation within the two-dimensional layers. It should be noted that this experiment did not determine whether just ^2H or entire water molecules moved (Grotthuss vs vehicular proton transfer). The featureless line shape that then grew to become the only line shape by room temperature indicates a further exchange process, which we suspect arises from ^2H exchange among crystallites via excess nonstructural surface water, thus allowing isotropic orientational averaging. ^{13}C and ^{31}P SSNMR analyses of PCMOF-3 were also carried out (Figures S3−S5) and found to be in excellent agreement with the crystallographic data.

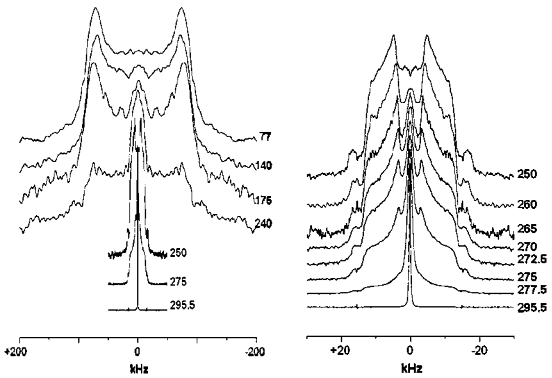

Figure 2. ^2H SSNMR of $Zn_3(L)(D_2O)_2\cdot 2D_2O$ (isostructural to PCMOF-3) with the chemical shift scale expanded on the right, showing rapid exchange of deuterium atoms by 250 K.

For impedance analyses, powdered PCMOF-3 was pressed between porous C electrodes (Sigracet, GDL 10 BB, no Pt) in a circular die. The proton conductivity in H_2 was measured as 3.5×10^{-5} S cm^{-1} at 25 °C and 98% relative humidity. The aquo ligands on Zn serve as the chief source of protons. This value was highly humidity-dependent and dropped to 4.5×10^{-8} S cm^{-1} at 25 °C and 44% relative humidity (Figure S7). Impedance studies on the deuterated sample in a H_2 atmosphere humidified (98%) with D_2O gave a conductivity of 1.0×10^{-5} S cm^{-1}, the lower value being expected for the heavier isotope. The absolute values of these conductivity data are modest, likely as a result of the two-dimensional nature of PCMOF-3, which would constrain intergrain proton transfer; however, with the SSNMR and crystallographic data in hand, the opportunity existed to establish a precise structure−activity relationship because of the ordered MOF material and the crystallographically located water molecules. Rather than at higher temperature, which would cause partial dehydration even by 40 °C, PCMOF-3 was studied below ambient temperature, as the ^2H SSNMR data had indicated mobile protons/deuterons even at −20 °C. Such a variable-temperature impedance study would allow the activation energy of the proton transfer to be extracted on the basis of an Arrhenius relationship.

A second set of impedance analyses was performed in anhydrous H_2 gas using Pt−C gas-diffusion electrodes (5 mg of Pt/m^2, ELAT, BASF fuel cell) at 98% relative humidity over the temperature range 5−25 °C. Under these conditions, protons were generated at the anode. As mentioned, a 293 K X-ray data solution confirmed that the structural description above is valid over this temperature range. Nyquist plots clearly showed bulk and grain boundary contributions to the impedance, as demonstrated by two distinct semicircles (Figure S8, expanded in Figure S9). Figure 3 shows the logarithm

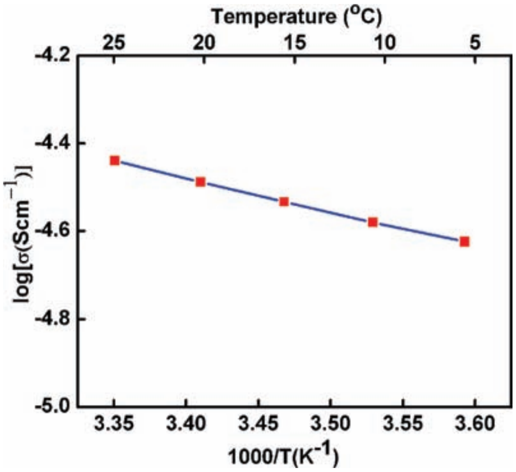

Figure 3. Plot of log(σ) as a function of 1000/T over the temperature range 5−25 °C at 98% relative humidity for the grain interior conductivity of PCMOF-3.

of the absolute conductivity σ of bulk PCMOF-3 as a function of 1000/T. Arrhenius plots [ln(σT) vs 1000/T] gave linear relationships (Figures S10 and S11), from which the activation energy was extracted. The activation energy for the proton transfer derived from the bulk conductivity of PCMOF-3 was 0.17 eV. This very low value indicates that the ordered water molecules observed crystallographically function to transport protons via a Grotthuss hopping mechanism as opposed to the more energy intensive vehicular transfer mechanism. Activation energy values typically attributed to Grotthuss transfer via water molecules are in the range of 0.1−0.4 eV.[13] The activation energy for PCMOF-3 is among the lowest observed. As a comparison, the activation energy for 1 M HCl has been reported as 0.11 eV[14] and that of Nafion as 0.22 eV.[15] The activation energy for proton transfer in PCMOF-3 is similar to those reported for highly acidic, hydrated metal oxide proton conductors such as $H_3PMo_{12}O_{40}\cdot 29H_2O$ (0.15 eV),[16] $Sb_2O_5\cdot 5.4H_2O$ (0.17 eV),[17] and β-$Al_{10.34}Mg_{0.66}O_{17}(H_3O)_{1.66}$ (0.17 eV).[18]

Ion conduction in a MOF has been reported in only a handful of cases.[1−6] In addition to representing an intriguing new class of ionomers, ordered MOF structures provide valuable anchor points for establishing structure−activity relationships in proton-conducting solids, essentially a firm handhold for modeling. PCMOF-3 represents a proton-conducting metal phosphonate in which the conductivity does not require secondary sulfonic acid sites. The structure allows both phosphonate O atoms and Zn aquo ligands to participate in proton transfer. The polar interlayer serves as a scaffold for highly ordered water molecules that form a Grotthuss proton transfer pathway, as evidenced by the very low activation energy and the proton mobility at −20 °C. The design rationale of PCMOF-3 offers options for altering the spatial orientation of H-bonding groups by altering the ligand core as well as for changing the acidity of the aquo ligands by changing the metal ion. The layered motif would also be amenable to intercalation of less volatile proton carriers such as N-heterocycles, and work on these possibilities is ongoing in our research group.

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Supporting Information Available: Detailed preparation, characterization, CIF files (173 and 293 K), ^{31}P and ^{13}C SSNMR data, and additional impedance plots for PCMOF-3. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Nagao, Y.; Fujishima, M.; Ikeda, R.; Kanda, S.; Kitagawa, H. *Synth. Met.* **2003**, *133*, 431. (b) Nagao, Y.; Kubo, T.; Nakasuji, K.; Ikeda, R.; Kojima, T.; Kitagawa, H. *Synth. Met.* **2005**, *154*, 89. (c) Okawa, H.; Shigematsu, A.; Sadakiyo, M.; Miyagawa, T.; Yoneda, K.; Ohba, M.; Kitagawa, H. *J. Am. Chem. Soc.* **2009**, *131*, 13516. (d) Sadakiyo, M.; Yamada, T.; Kitagawa, H. *J. Am. Chem. Soc.* **2009**, *131*, 9906. (e) Yamada, T.; Morikawa, S.; Kitagawa, H. *Bull. Chem. Soc. Jpn.* **2010**, *83*, 42.
(2) Bureekaew, S.; Horike, S.; Higuchi, M.; Mizuno, M.; Kawamura, T.; Tanaka, D.; Yanai, N.; Kitagawa, S. *Nat. Mater.* **2009**, *8*, 831.
(3) (a) de Combarieu, G.; Morcrette, M.; Millange, F.; Guillou, N.; Cabana, J.; Grey, C. P.; Margiolaki, I.; Férey, G.; Tarascon, J. M. *Chem. Mater.* **2009**, *21*, 1602. (b) Férey, G.; Millange, F.; Morcrette, M.; Serre, C.; Doublet, M. L.; Greneche, J. M.; Tarascon, J. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 3259. (c) de Combarieu, G.; Hamelet, S.; Millange, F.; Morcrette, M.; Tarascon, J. M.; Férey, G.; Walton, R. I. *Electrochem. Commun.* **2009**, *11*, 1881.
(4) Ohkoshi, S.; Nakagawa, K.; Tomono, K.; Imoto, K.; Tsunobuchi, Y.; Tokoro, H. *J. Am. Chem. Soc.* **2010**, *132*, 6620.
(5) Hurd, J. A.; Vaidhyanathan, R.; Thangadurai, V.; Ratcliffe, C. I.; Moudrakovski, I. M.; Shimizu, G. K. H. *Nat. Chem.* **2009**, *1*, 705.
(6) Duan, C. Y.; Wei, M. L.; Guo, D.; He, C.; Meng, Q. J. *J. Am. Chem. Soc.* **2010**, *132*, 3321.
(7) (a) Kreuer, K. D.; Paddison, S. J.; Spohr, E.; Schuster, M. *Chem. Rev.* **2004**, *104*, 4637. (b) Hamrock, S. J.; Yandrasits, M. A. *Polym. Rev.* **2006**, *46*, 219.
(8) (a) Clearfield, A. *Dalton Trans.* **2008**, 6089. (b) Maeda, K. *Microporous Mesoporous Mater.* **2004**, *73*, 47. (c) Shimizu, G. K. H.; Vaidhyanathan, R.; Taylor, J. M. *Chem. Soc. Rev.* **2009**, *38*, 1430.
(9) (a) Kong, D. Y.; Clearfield, A. *Cryst. Growth Des.* **2005**, *5*, 1263. (b) Mao, J. G.; Wang, Z. K.; Clearfield, A. *J. Chem. Soc., Dalton Trans.* **2002**, 4541.
(10) (a) Alberti, G.; Boccali, L.; Casciola, M.; Massinelli, L.; Montoneri, E. *Solid State Ionics* **1996**, *84*, 97. (b) Stein, E. W.; Clearfield, A.; Subramanian, M. A. *Solid State Ionics* **1996**, *83*, 113. (c) Jang, M. Y.; Park, Y. S.; Yamazaki, Y. *Electrochemistry* **2003**, *71*, 691.
(11) Kong, D.; Clearfield, A.; Zoń, J. *Cryst. Growth Des.* **2005**, *5*, 1767.
(12) Agmon, N. *Chem. Phys. Lett.* **1995**, *244*, 456.
(13) Colomban, P.; Novak, A. *J. Mol. Struct.* **1988**, *177*, 277.
(14) Bockris, J. O. M.; Reddy, A. K. N. *Modern Electrochemistry*; MacDonald Press: London, 1970; Vol. 1, Chapter 5.
(15) Slade, R. C. T.; Hardwick, A.; Dickens, P. G. *Solid State Ionics* **1983**, *9−10*, 1093.
(16) Nakamura, O.; Kodama, T.; Ogino, J.; Migake, Y. *Chem. Lett.* **1979**, 17.
(17) England, W. A.; Cross, M. G.; Hamnett, A.; Wiseman, P. J.; Goodenough, J. B. *Solid State Ionics* **1980**, *1*, 231.
(18) Baffier, N.; Badot, J. C.; Colomban, P. *Solid State Ionics* **1984**, *13*, 233.

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