

Rational Designs for Highly Proton-Conductive Metal–Organic Frameworks

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Metal–organic frameworks (MOFs) have attracted much interest because of the variety of architectures with significant porosity and thus high surface area as well as guest arrangements that can be controlled on a nanoscale by a self-assembly process.¹ These materials have been reported to provide many functionalities such as gas sorption,² catalysis,³ magnetism,⁴ and electrical conductivity.⁵

Proton conductivity in solid-state materials has interested us from the point of view of transport dynamics^{6,7a} and its applications in fuel cells.⁷ In particular, organic polymers,⁸ metal oxides,⁹ and other inorganic or organic compounds¹⁰ have been studied and applied to electrochemical devices. In general, these materials need proton carriers such as H₃O⁺ or H⁺ given by acid or OH groups. They also require proton-conducting pathways composed of hydrogen-bond networks.

We have focused on the proton conductivity of MOFs. For example, copper rubeanate and its derivatives were found to show proton conductivity that is dependent on the uptake of water molecules and additional protons derived from the reduction of copper ions.¹¹ In this work, we propose three types of rational design to introduce proton carriers into MOFs. The simplest method is to introduce them directly as counterions such as NH₄⁺, H₃O⁺, and HSO₄[−] into the pores of frameworks (type I). The second is to put acid groups on frameworks, the protons being provided from them (type II). The third is to incorporate acidic molecules into voids (type III).

We have succeeded in constructing a highly proton-conductive MOF by introducing protons together with water molecules as conducting media in the gallery of a layered oxalate-bridged anionic layer framework [Zn₂(ox)₃]^{2−}∞ (ox = oxalate), (NH₄)₂(adp)·[Zn₂(ox)₃]·3H₂O (adp = adipic acid). We adopted a combination of two of the concepts by introducing NH₄⁺ ions using the anionic framework (type I) and putting carboxyl end groups of adipic acid in a honeycomb-shaped void (type III). This MOF showed a superprotonic conductivity of 10^{−2} S cm^{−1} at ambient temperature, comparable to organic polymers such as Nafion, which is in practical use in fuel cells.¹² Here, we report its synthesis, crystal structure, and proton conductivity as a function of temperature.

(NH₄)₂(adp)[Zn₂(ox)₃]·3H₂O (**1**) was prepared by a hydrothermal method with zinc oxide, adipamide, and H₂(ox)·2H₂O in water using an autoclave at 130 °C. The crystal structure of **1** was determined by single-crystal X-ray diffraction (SCXRD) at 113 K (Figure 1).¹³ It forms typical oxalate-bridged two-dimensional (2-D) honeycomb sheets of [Zn₂(ox)₃]^{2−}∞,^{4b,14} in which each zinc ion is octahedrally coordinated by three oxalate ligands. Alternate conformations of Δ− and Λ− in metal sites result in the 2-D layer

structure of the framework. The adp molecules penetrate the hexagonal voids of these layers (Figure 1a). From the SCXRD, it was found that adipamide is converted into adipic acid under hydrothermal conditions. In the IR spectrum of **1**, the stretching mode of the carboxylic acid group was observed at 1736 cm^{−1}, while that of the amide group was absent (see Supporting Information (SI)), confirming the existence of adipic acid in this compound.

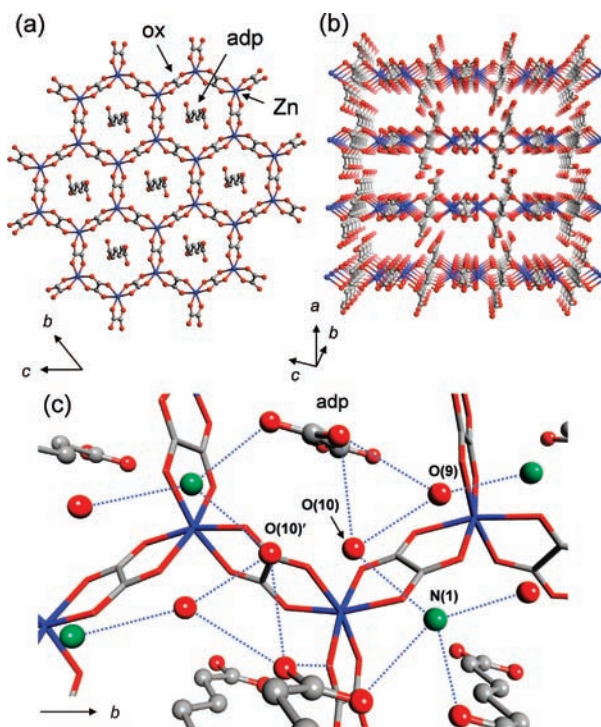


Figure 1. (a) Honeycomb layer structure of **1**. (b) Perspective view along the *b*-axis. Guest molecules are omitted. (c) Hydrogen-bond arrangements of −COOH, H₂O, and NH₄⁺ in the interlayer. Hydrogen bonds are shown as blue dotted lines. The colors of red, green, gray, and blue correspond to oxygen, nitrogen, carbon, and zinc atoms, respectively.

Carboxylic acid groups of adp are situated in the interlayer space of [Zn₂(ox)₃]^{2−}∞ sheets (Figure 1b). Water molecules and ammonium ions are located next to carboxylic acid groups as shown in Figure 1c. As seen in the description of the interlayer, type I and type III modes are both present. Several short hydrogen bonds exist between adp and ox ions (2.688(4) Å), O(10) and O(9) atoms of water molecules (2.638(12) Å), and N(1) atoms of ammonium ions and O(10) atoms of water molecules (2.789(7) Å). Other molecules are also closely located within a distance of 3.037(5) Å between neighbor atoms, indicating the formation of 2-D hydrogen-

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bond networks among adp molecules, ammonium ions, water molecules, and ox ions of the framework. The presence of an extended hydrogen-bonded network and the additional protons from the carboxylic acid and ammonium ions forming this network indicate that **1** can potentially be a high proton-conducting material. It should be noted that the occupancy of O(10) atoms with the remarkably short distance of 2.189(13) Å between O(10) and O(10)' was determined to be 50%. Thus, each oxygen atom was found to be located on one side of the O(10) or O(10)' site.

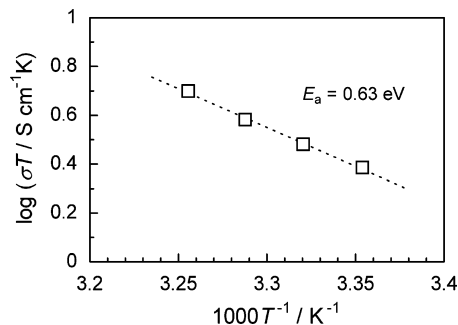


Figure 2. Arrhenius plots of the proton conductivity of **1** under 98% RH conditions. Least-squares fitting is shown as a dotted line.

The proton conductivity of **1** was therefore evaluated by the ac impedance method using a compacted pellet of the powdered sample with two gold electrodes attached to the surface. The proton conductivity of **1** was found to be $8 \times 10^{-3} \text{ S cm}^{-1}$ at 25 °C under 98% relative humidity (RH) conditions, estimated from the Nyquist plot shown in the SI. This proton conductivity is comparable to Nafion, which is in practical use in fuel cells. However, the trihydrate **1** is transformed to the dihydrate below 85% RH, which was confirmed by thermal gravimetric analysis and X-ray structure analysis. The dihydrate showed a much lower proton conductivity of $6 \times 10^{-6} \text{ S cm}^{-1}$ at 70% RH, suggesting that water molecules play an important role in creating the proton-conducting pathways.

The temperature dependence of the proton conductivity was also measured under 98% RH conditions. Figure 2 shows the Arrhenius plots of the proton conductivity of **1**. The activation energy (E_a) of **1** was found to be 0.63 eV. The mechanism of proton conduction of **1** is, therefore, expected to be similar to that of the Grotthuss mechanism, that is, proton transport of additional protons such as H_3O^+ by reforming hydrogen bonds between H_3O^+ and water molecules.¹⁵ Compared with typical hydrated proton conductors having this mechanism, such as Nafion ($E_a = 0.22 \text{ eV}$)^{7a,12} and $\text{HUO}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$ ($E_a = 0.32 \text{ eV}$),¹⁶ the E_a value of **1** is very high. This suggests that proton conduction in **1** includes some other process such as direct diffusion of additional protons with water molecules or ammonia molecules (vehicle mechanism).¹⁷ The existence of half-occupied oxygen sites of O(10) may be derived from direct-jump diffusion. The fact that **1** exhibits a high proton conductivity despite the large E_a is indicative of a high carrier concentration, originating from the combination of counterions NH_4^+ and included adp.

In summary, we propose rational designs for highly proton-conductive MOFs and have demonstrated a highly proton-conductive MOF based on the concepts, introducing protons into the pores as counteranions by using the anionic frameworks (type I) and including acid molecules to provide additional protons by partial dissociation of these acid groups (type III). This is the first example of an MOF to exhibit a superprotonic conductivity of $10^{-2} \text{ S cm}^{-1}$ at ambient temperature.

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Supporting Information Available: Synthetic procedure, IR spectra, ac impedance measurements, X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (13) Single-crystal X-ray data for **1**, $\text{C}_{12}\text{H}_{24}\text{N}_2\text{Zn}_2\text{O}_{19}$, FW = 631.08, triclinic, $P1$ (No. 2), $a = 7.9858(1) \text{ \AA}$, $b = 9.1574(4) \text{ \AA}$, $c = 9.4523 \text{ \AA}$, $\alpha = 62.025(6)^\circ$, $\beta = 82.335(7)^\circ$, $\gamma = 72.873(7)^\circ$, $V = 583.39(4) \text{ \AA}^3$, $Z = 1$, $T = 113 \text{ K}$, $D_c = 1.796 \text{ g/cm}^3$, $\mu = 21.48 \text{ cm}^{-1}$, 4330 reflections collected, 2497 unique reflections ($R_{\text{int}} = 0.025$), $R_1 = 0.0429$ (for $I > 2\sigma(I)$), $wR_2 = 0.1779$ (unique reflections), GOF = 1.337.
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