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Wide Control of Proton Conductivity in Porous Coordination Polymers

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Supporting Information

ABSTRACT: The proton conductivities of the porous coordination polymers M(OH)(bdc−R) [H_2bdc = 1,4-benzenedicarboxylic acid; M = Al, Fe; R = H, NH_2, OH, $(COOH)_2$] were investigated under humid conditions. Good correlations among pK_a, proton conductivity, and activation energy were observed. Fe(OH)(bdc−$(COOH)_2$), having carboxy group and the lowest pK_a, showed the highest proton conductivity and the lowest activation energy in this system. This is the first example in which proton conductivity has been widely controlled by substitution of ligand functional groups in an isostructural series.

Proton conductivities of inorganic or organic compounds, such as zirconium phosphate, metal oxides, and Nafion, have been studied for applications of these compounds in fuel cells and sensors.[1] They require acidic groups as proton-carrier sources and/or hydrogen-bonded networks as proton-conduction pathways.[2] However, within a series of the same organic or inorganic compounds, the proton-carrier concentration, hydrogen-bonded network, or pK_a of the acidic group has not been widely controlled.

Recently, porous coordination polymers (PCPs) or metal−organic frameworks (MOFs) have attracted much attention because of their unique features such as gas storage, selective separation, catalytic properties, and electron[3] and proton[4] conductivities. In comparison with other porous materials such as activated carbon and zeolites, one of the main advantages of PCPs is their highly designable nature: we are able to select various types of metal ions and organic ligands.[5] This highly designable nature enables us to control the physical properties by selecting suitable metal ions and ligands in addition to controlling the size and shape of the pores.[6] It is particularly the inner surface characteristics of PCPs, such as hydrophilicity and acidity, that are expected to affect the concentration and mobility of proton carriers; hence, proton conductivity can be widely controlled by substituting functional groups. In this paper, we report on the wide control of proton conductivity in an isostructural PCP framework through the substitution of carboxylic, hydroxyl, and amino groups.

We focused on porous frameworks of MIL-53(M) (MIL = Materials of Institut Lavoisier; M = trivalent metal ion), also designated as M(OH)(bdc) (H_2bdc = 1,4-benzenedicarboxylic acid).[7] They consist of infinite chains of corner-sharing $MO_4(OH)_2$ octahedra interconnected by dicarboxylate groups and have one-dimensional diamond-shaped channels (Figure 1). MIL-53 has unique properties, such as large flexibility of the framework (called breathing), CO_2 adsorption accompanied by the breathing, drug delivery, and Li-insertion reactions.[8] Because of its large flexibility, MIL-53 does not tend to show polymorphism; the framework is retained when functional groups are introduced on the ligands.[9] In general, structural polymorphism often occurs in PCPs, especially when coordinating functional groups are introduced. Therefore, MIL-53 provides us with an ideal target system for widely controlling the physical properties in an isostructural series. Here we used the series Al(OH)(bdc)(H_2O) [MIL-53(Al)] (**1**), Al(OH)(bdc−NH_2)(H_2O) [MIL-53(Al)−NH_2] (**2**), Al(OH)(bdc−OH)$(H_2O)_{1.5}$ [MIL-53(Al)−OH] (**3**), and Fe(OH)(bdc−$(COOH)_2$)(H_2O) [MIL-53(Fe)−$(COOH)_2$] (**4**). **1**−**4** were synthesized using previously reported methods[10] and characterized by powder X-ray diffraction (PXRD) and elemental analysis (Figure S1 in the Supporting Information).

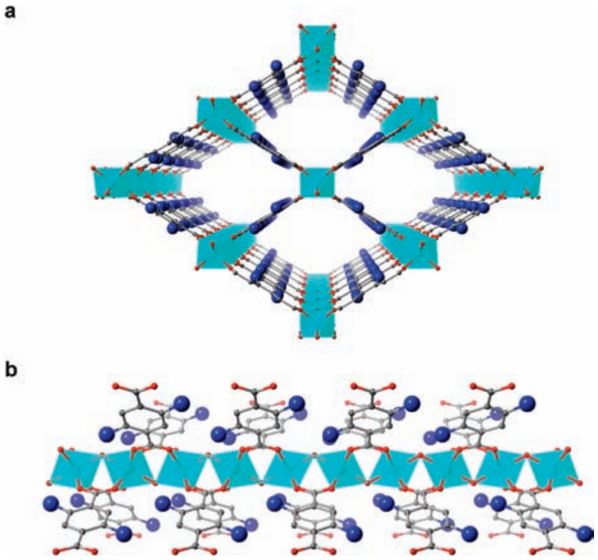

Figure 1. Views of the structure of MIL-53(M). (a) Chains of corner-sharing $MO_4(OH)_2$. (b) The structure along the channel axis. Al or Fe, C, O, and H are represented as light-blue, gray, red, and blue, respectively. The blue atoms show functional groups (−NH_2, −OH, or −COOH).[10]

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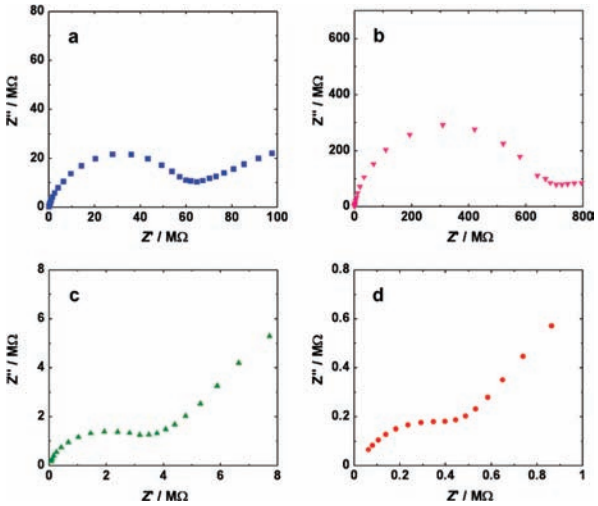

Figure 2. Nyquist plots of (a) **1** (blue ■), (b) **2** (pink ▼), (c) **3** (green ▲), and (d) **4** (red ●) at 298 K and 95% RH.

Table 1. Proton Conductivities at 298 and 353 K under 95% RH and Activation Energies for 1−4

	σ (S cm^{-1})		
M(OH)(bdc−R)	298 K	353 K	E_a (eV)
1, R = H	2.3×10^{-8}	3.6×10^{-7}	0.47
2, R = NH_2	2.3×10^{-9}	4.1×10^{-8}	0.45
3, R = OH	4.2×10^{-7}	1.9×10^{-6}	0.27
4, R = $(COOH)_2$	2.0×10^{-6}	0.7×10^{-5}	0.21

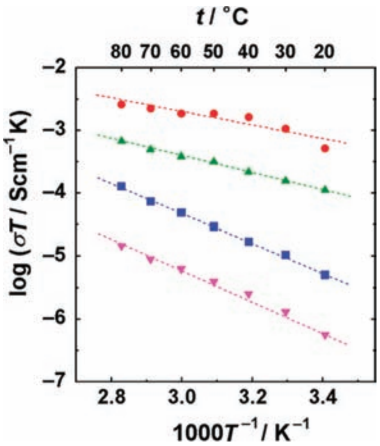

Figure 3. Arrhenius plots of the proton conductivities of **1** (blue ■), **2** (pink ▼), **3** (green ▲), and **4** (red ●) under 95% RH conditions. Least-squares fits are shown as dotted lines.

The proton conductivities of **1**−**4** were measured by a quasi-four-probe method, using gold wires and gold paste, with a Solartron SI 1260 impedance/gain-phase analyzer and a 1296 dielectric interface. The conductivities were determined from the semicircles in the Nyquist plots, as shown in Figure 2. The proton conductivities of **1**−**4** were 2.3×10^{-8}, 2.3×10^{-9}, 4.2×10^{-7}, and 2.0×10^{-6} S cm^{-1}, respectively, at 298 K and 95% relative humidity (RH) (Table 1).

The temperature dependence of the proton conductivities of **1**−**4** at 95% RH are shown in Figure 3. The proton conductivities of all four compounds increased with increasing temperature. The activation energies were 0.47, 0.45, 0.27, and 0.21 eV, respectively, as determined from least-squares fits of the slopes (Table 1).

In the MIL-53 system, proton carriers are expected to originate from μ_2-OH groups between metal ions, coordinating carboxylate groups, and/or functional groups in the channels. The acidity of μ_2-OH is supposed to be almost the same in these MIL-53 derivatives because the energies of their μ_2-OH stretching vibrations are almost equal (3630 cm^{-1}) and independent of functional groups in the channels (Figure S2). The acidity of the coordinating carboxylate groups is also independent of the functional group, because the C=O stretching vibration peaks are almost the same (1560 cm^{-1}). The largest contribution to the proton conductivity in this system is thought to be proton carriers from the acidity of the functional group. The acidities of the functional groups are given by the Hammett relation and were estimated from the pK_a values of the substituted benzoic acids.[11] The pK_a values of meta-substituted benzoic acids (R = $-NH_2$, −H, −OH, and −COOH) are 4.74, 4.19, 4.08, and 3.62, respectively.[12] The order of these values correlates well with the order of proton conductivities observed for the substituted MIL-53 derivatives: $-NH_2$ < −H < −OH < −COOH. There is also a good correlation with the activation energies: $-NH_2$, −H > −OH > −COOH. Thus, the proton conductivity and activation energy in the MIL-53 system can be widely controlled by substituting the functional groups on the ligands.

The Grotthuss and vehicle mechanisms have been proposed to interpret the proton conduction in solid compounds.[2] The reported activation energies for the Grotthuss and vehicle mechanisms are in the ranges 0.1−0.4 and 0.5−0.9 eV, respectively. Therefore, proton conduction in **1**−**4** could be classified mainly as the Grotthuss mechanism. In addition, from structural analyses,[10] the water molecules have been found to be trapped by strong hydrogen bonds to μ_2-OH in MIL-53 compounds, so it seems difficult for the vehicle mechanism to be applied in this system.

The water adsorption and desorption isotherms of **1**−**4** were measured at 298 K and 95% RH. The water uptakes were 1, 1, 5, and 1.5 per metal unit, respectively, as shown in Figure S3. **3** exhibits breathing in going from $\mathbf{3}\cdot 2H_2O$ to $\mathbf{3}\cdot 5H_2O$, which was confirmed by the PXRD patterns (Table S1).[13] It changes from a narrow-pore (NP) phase (size of the diamond-shaped channels: 19.344 Å × 7.627 Å) for $2H_2O$ to a large-pore (LP) phase (17.47 Å × 12.179 Å) for $5H_2O$. Despite the high uptake for **3**, **4** shows higher proton conductivity than **3**. Therefore, the acidity of the functional groups is the dominant contributing factor to the proton conduction, and excess water amounts seem to make little contribution to the enhancement of the proton conductivity in this system. This agrees with the observation that the proton conductivity of **3** showed little change in going from the NP to LP phase. Hydrogen-bonded networks are formed along one-dimensional channels with μ_2-OH, water molecules, coordinating carboxylate sites, and functional groups.[10] Therefore, in this system, proton-conduction pathways are considered to be along these one-dimensional channels.

In conclusion, the proton conductivities in a series of MIL-53(M) compounds **1**−**4** have been investigated. Good correlations among pK_a, proton conductivity, and activation energy were observed. MIL-53(Fe)−$(COOH)_2$ showed the highest proton conductivity and the lowest activation energy because it has the lowest pK_a value (i.e., the highest proton carrier concentration) in this system. This is the first example in which proton conductivity has been widely controlled by substitution of ligand functional groups in an isostructural series of PCPs. These results will provide good tuning and precise control of the proton conductivity and subsequently enable us to develop useful solid electrolytes and acid catalysts.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Synthetic methods, PXRD patterns, IR spectra, water adsorption and desorption isotherms, and conductivity measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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