Proton Conducting Materials

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High and Highly Anisotropic Proton Conductivity in Organic Molecular Porous Materials**

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The search for new highly proton-conducting materials has been a subject of intense research because of their potential applications in fuel cells, sensors, and other areas.[1] In recent years, metal–organic frameworks (MOFs) with well-defined pores have been investigated for this purpose because guest molecules, such as water and imidazole in the channels, and/or functional groups lining the channels can provide proton conduction pathways.[2] However, to date, most MOFs do not show high proton conductivity, long-term stability, or durability in moisture. Similar to MOFs, in principle, are organic molecular porous materials,[3] which may serve as good proton conductors, but their proton conduction behavior has never been investigated.

We recently reported an organic molecular porous material based on cucurbit[6]uril (CB[6]), a member of the hollowed-out pumpkin-shaped macrocycle family cucurbit[*n*]uril (CB[*n*], $n = 5–8, 10$) having a hydrophobic cavity accessible through two polar carbonyl-laced portals.[4] The organic molecular porous material has permanent porosity and high thermal and chemical stability, which makes it useful for gas storage and other applications.[5,6] While investigating its crystal structure, we noticed that there is an array of water and acid molecules filling in the channels of the porous material, which prompted us to investigate the proton conductivity of this and related materials. Herein, we present the high and highly anisotropic proton conductivity in cucurbituril-based organic molecular porous materials, which can be modulated by the nature and amount of guest acid molecules present in the channels. Their proton conductivity along the channel direction, which was demonstrated by single-crystal conductivity measurements, is comparable or superior to that of most MOFs[2] or organic proton conductors.[7] To the best of our knowledge, this investigation of the proton conductivity in organic molecular porous materials with permanent porosity is unprecedented.

Recrystallization of CB[6] from 2.4 M HCl and 2.4 M H_2SO_4 solutions produced the isostructural organic molecular porous materials $CB[6]\cdot 1.1\,HCl\cdot 11.3\,H_2O$ (**1**) and $CB[6]\cdot 1.2\,H_2SO_4\cdot 6.4\,H_2O$ (**2**), respectively. Single-crystal X-ray analysis revealed that both **1** and **2** have a honeycomb-like structure with one-dimensional (1D) channels with an average diameter of 7.5 Å and an aperture of about 6 Å along the *c* axis (Figure 1 a),[5] which are filled with water and acid molecules, forming hydrogen-bonded networks (Figure 1 c,d). Similarly, recrystallization of CB[8], a larger member of the CB[*n*] family, produced $CB[8]\cdot 6.8\,HCO_2H\cdot 13\,H_2O$ (**3**), which has a similar honeycomb structure (Figure 1 b).[8] Even though CB[8] is larger than CB[6], the size of the channels in **3** is almost the same as that of **1** or **2**. Similar to **1** and **2**, the channels of **3** were filled with water and formic acid molecules, which form a hydrogen-bonded network (Figure 1 e). Bulk samples of **1**, **2**, and **3** were also characterized by powder X-ray diffraction (PXRD; Supporting Information, Figure S2), TG-DSC (Figure S3), and elemental analysis.

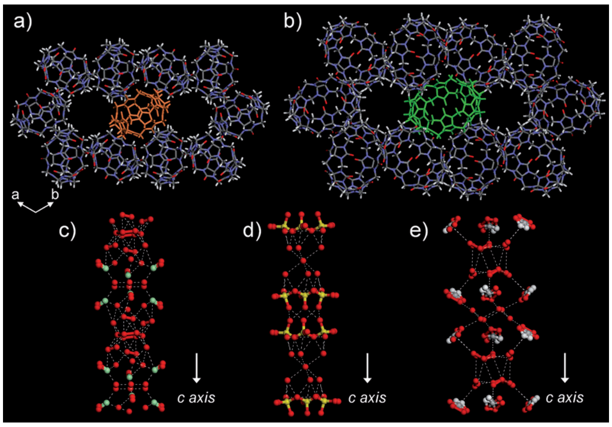

Figure 1. a) X-ray crystal structures of porous CB[6] **1** and **2** viewed down the *c* axis. b) X-ray crystal structure of porous CB[8] **3** viewed down the *c* axis. c) Water–HCl array in the 1D channel of **1**; d) Water–H_2SO_4 array in the 1D channel of **2**; e) Water–HCO_2H array in the 1D channel of CB[8] **3**.

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We thought that **1**, **2**, and **3** would be good proton conducting materials since the water–acid arrays in the channels of **1**, **2**, and **3** can provide a pathway for proton conduction. The proton conductivities of **1**, **2**, and **3** were evaluated by an ac impedance method using a compacted pellet of the powdered samples. The conductivities of **1**, **2**, and **3** obtained from the semicircles in the Nyquist plots (Figure 2a; Supporting Information, Figure S4) increase with increasing relative humidity (RH; Figure 2b; Supporting Information, Figure S5) to reach 1.1×10^{-3}, 1.3×10^{-3}, and 1.3×10^{-4} S cm^{-1}, respectively, at 298 K and 98% relative humidity (RH). These values are comparable to the highest proton conductivity found in MOFs.[2a]

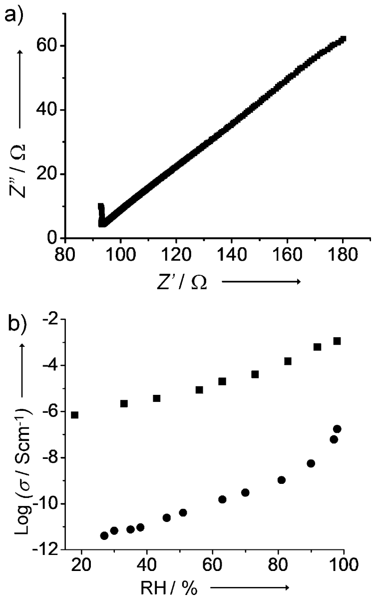

Figure 2. a) Nyquist plot at 298 K and 98% RH of **1**; b) logσ versus RH plot of **1** (■) and **1′** (●).

To study the effect of the water and acid molecules in the channels in **1** and **2** on the proton conductivity, we also prepared guest-removed porous CB[6]. Evacuation of **1** and **2** at 100 °C under vacuum for 24 h produced CB[6]·H_2O (**1′**) and CB[6]·1.1 H_2SO_4·0.7 H_2O (**2′**), respectively, which were characterized by PXRD (Supporting Information, Figure S2), elemental analysis, and TG-DSC (Supporting Information, Figure S3). Note that the evacuation removed almost all the HCl and water molecules from **1**, but eliminated only water molecules from **2**, leaving most H_2SO_4 in the channels. The honeycomb-like structure of the porous CB[6] was maintained, as confirmed by PXRD studies.

We first measured the water vapor adsorption and desorption isotherms of **1′** and **2′** in the RH range 0–95% at 298 K (Figure 3). The drastic increase of adsorbed water in the low vapor pressure range (0–20% RH) suggested that the water molecules are adsorbed in the micropores of the materials. The total amount of adsorbed water molecules calculated from the fully saturated point was 10.7 and 9.8 H_2O per CB[6] for **1′** and **2′**, respectively. While the former was comparable to the initial water content of **1**, the latter is significantly larger than the amount of water found in **2**. The origin of the discrepancy is not clear at the moment. Note that the adsorption and desorption isotherms of **1′** showed a large hysteresis, which may be due to capillary condensation.[9]

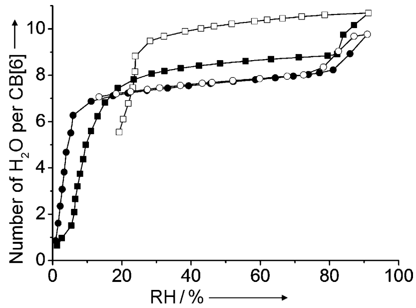

Figure 3. Water vapor adsorption (filled) and desorption (open) isotherms of **1′** (squares)and **2′** (circles)at 298 K.

Importantly, the conductivity measurements in the RH range 25–98% at 298 K revealed that the conductivity of **1′** increased with RH (Figure 2b), with a maximum value of 6.6×10^{-6} S cm^{-1} at 98% RH, which is, however, much lower than that of **1** under the same conditions. In contrast, the conductivity of **2′** was measured to be 4.6×10^{-4} S cm^{-1} at 298 K and 98% RH, which is close to that of **2**. Furthermore, the structures of **1**, **2**, **1′**, **2′**, and **3** were maintained even after impedance measurements, as confirmed by PXRD (Supporting Information, Figure S7). Taken together, these results suggested that although the presence of water molecules filling the channels of the porous CB[6] is important for proton conduction, the presence of an acid–water array in the channels is much more important.

The temperature dependence of proton conductivity over the temperature range 24–40 °C at 98% RH are shown in Figure 4. The activation energies of **1**, **1′**, **2**, **2′**, and **3** were determined from least-squares fits of the slopes (Figure 4) and are summarized in Table 1. These results suggested that Grotthuss hopping mechanism is dominant for the proton conduction in **1**, **2**, and **2′**, whereas a vehicular transfer mechanism predominantly operates for **1′** and **3**.[10]

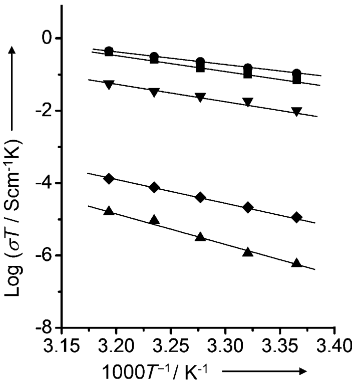

Figure 4. Arrhenius plots of the proton conductivities of **1** (■), **2** (●), **3** (◆), **1′** (▲), and **2′** (▼) under 98% RH conditions.

Table 1: Proton conductivities at 298 K and 98% RH and activation energies for **1**–**3**.

Porous CBs	σ [S cm^{-1}]	E_a [eV]
1	1.1×10^{-3}	0.39
2	1.3×10^{-3}	0.31
3	1.3×10^{-4}	0.56
1′	6.6×10^{-6}	0.76
2′	4.6×10^{-4}	0.35
1, single crystal	2.4×10^{-2},[a] 7.1×10^{-5}[b]	–
2, single crystal	4.3×10^{-2},[a] 5.0×10^{-6}[b]	–

[a] Along the *c* axis. [b] Perpendicular to the *c* axis (see the Supporting Information for details).

Conductivity measurements using compacted pellets of powdered samples often fail to provide intrinsic proton conductivity of a material owing to grain boundaries and sometimes anisotropy of the material. Although there are a number of reports on the proton conductivity of inorganic materials measured using single crystals[11] or grain-boundary-free films,[12] the single-crystal proton conductivity measurement of organic or inorganic–organic hybrid materials, such as MOFs, is still rare.[13] To better understand the proton conduction behavior in the organic molecular porous materials **1** and **2** with a highly anisotropic structure, we decided to measure their proton conductivity using single crystals (see the Supporting Information for details). The conductivities of a single crystal of **1** and **2** along the *c* axis (the channel direction) were measured to be 2.4×10^{-2} S cm^{-1} and 4.3×10^{-2} S cm^{-1}, respectively (Figure 5); these values are at least one order of magnitude higher than those measured with pellets. Similar to the conductivity measurement with pellets, the single-crystal conductivity measurement showed that **2** has slightly higher conductivity than **1**. The single-crystal proton conductivities of **1** and **2** perpendicular to the *c* axis were 7.1×10^{-5} and 5.0×10^{-6} S cm^{-1}, respectively, which are almost 3 or 4 orders of magnitude lower than those along the *c* axis ($\sigma_{\parallel}/\sigma_{\perp} = 340$ and 8600, respectively), and is consistent with the anisotropic channel structure of these materials. The structures of **1** and **2** after the single-crystal impedance measurements were characterized by single-crystal X-ray diffraction. Even though the positions of water and acid molecules are slightly changed (Supporting Information, Figure S8), the overall hydrogen-bonded networks formed by the water and acid molecules in the 1D channels of **1** and **2** remain essentially the same after the impedance measurements.

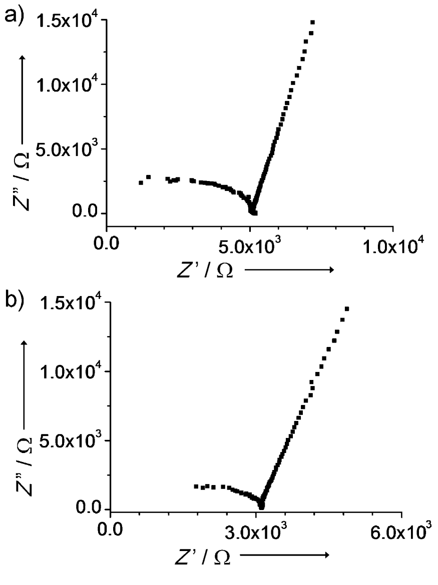

Figure 5. Nyquist plots of single crystals along *c*-axis a) **1** at 295 K and b) **2** at 293 K.

In conclusion, we have demonstrated high and highly anisotropic proton conductivity for cucurbituril-based organic molecular porous materials. The isostructural organic porous materials showed different proton conductivity depending on the nature and amount of acid molecules present in the channels. Porous CB[6] **2** containing sulfuric acid in the channels showed the highest conductivity and the lowest activation energy among the series. This is the first example to demonstrate that proton conductivity can be controlled by changing guest acid molecules filling in the channels of isostructural porous materials. Furthermore, the highly anisotropic conduction behavior of the materials was studied by single-crystal conductivity measurements. Much higher conductivity was observed along the channel direction than that perpendicular to the channel direction. To the best of our knowledge, **2** showed the highest anisotropic proton conductivity ($\sigma_{\parallel}/\sigma_{\perp} = 8600$) among the known proton conducting materials to date.[13b,14] Taken together, these results suggest that the acid–water arrays in the 1D channels of the molecular porous materials serve as a major proton conduction pathway. Although the proton conductivity of these materials is somewhat lower than that of the well-established proton conducting materials, such as Nafion, their highly anisotropic proton conductivity compared to that of polymeric materials[14] suggests their potential utility in device applications in which highly directional proton conduction is desired. Finally, this study demonstrating a new way to control the proton conductivity of porous materials provides a new insight into the design of proton conducting materials, which are likely to be useful for developing solid electrolytes, acid catalysts, and proton sensors.

Experimental Section

Organic porous materials **1** and **2** were obtained by recrystallization of CB[6]·3H_2O from 2.4 M aqueous HCl and H_2SO_4 solutions, respectively. Similarly, recrystallization of CB[8]·12H_2O from 60% formic acid produced **3**.

Crystal data for **2**: $C_{36}H_{36}N_{24}O_{12}\cdot6.1H_2O\cdot1.1H_2SO_4$, $M_r = 1196.43$, Trigonal, $R\bar{3}$ (No. 148), $a = 32.028(2)$ Å, $c = 12.380(1)$ Å, $V = 10998(1)$ Å^3, $Z = 9$, $T = 100$ K, $\mu = 0.180$ mm^{-1}, $\rho_{calcd} = 1.626$ g cm^{-3}, $2\theta_{max} = 59.9°$, 7029 reflections measured, 5112 unique ($R_{int} = 0.0745$), $R_1 = 0.1954$ (4358 reflections with $I > 2\sigma(I)$), $wR_2 = 0.3968$ (all data), GOF = 1.062, 458 parameters and 165 restraints. Crystal data for **3**: $C_{48}H_{48}N_{32}O_{16}\cdot9.6H_2O\cdot7.7HCO_2H$, $M_r = 1828.43$, Trigonal, $R\bar{3}$ (No. 148), $a = 38.789(2)$ Å, $c = 13.748(1)$ Å, $V = 17914(1)$ Å^3, $Z = 9$, $T = 100$ K, $\mu = 0.132$ mm^{-1}, $\rho_{calcd} = 1.525$ g cm^{-3}, $2\theta_{max} = 51.6°$, 7659 reflections measured, 5471 unique ($R_{int} = 0.0422$), $R_1 = 0.089$ (5471 reflections with $I > 2\sigma(I)$), $wR_2 = 0.2847$ (all data), GOF = 1.053, 713 parameters and 216 restraints. CCDC 816917 (**2**) and CCDC 816916

(**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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