High proton conduction in an excellent water-stable gadolinium metal–organic framework†

Xiu-Shuang Xing,‡ Zhi-Hua Fu,*† Ning-Ning Zhang,‡ Xiao-Qing Yu,‡ Ming-Sheng Wang‡ and Guo-Cong Guo‡,*

A new metal–organic framework with excellent water stability, (H[(N(CH₃)₄)₂][Gd₃(NIPA)₆])·3H₂O (1, H₂NIPA = 5-nitroisophthalic acid), displays a proton conductivity of 7.17 × 10⁻² S cm⁻¹ (at 75 °C and 98% relative humidity), which is among the highest values for proton-conducting MOFs.

Proton-conducting materials, as an important component of sensors and hydrogen fuel cells,¹–⁶ have attracted considerable interest. Recently, the studies of proton-conducting materials have been focused on inorganic–organic hybrid porous crystalline materials, such as metal–organic frameworks (MOFs).⁷–¹³ The main advantages of MOFs as proton-conducting materials are their defined structures to provide a useful insight into the proton-conducting pathway and mechanism and functional materials due to its drastic thermal vibration and disorder. The content of water molecules in the channels can further be confirmed by thermogravimetry (TG) analysis (Fig. S3, ESI†) and elemental analysis. The main roles of the tetramethylammonium cations, H⁺ and three water molecules residing in the channel are balancing charges and stabilizing and strengthening the –NO₂ group. It has excellent water stability and shows remarkably high proton conduction at high relative humidity (RH). The maximum single-crystal proton conductivity is 7.17 × 10⁻² S cm⁻¹ at 75 °C and 98% RH, which is among the highest values for proton-conducting MOFs.²¹,²³

Bright yellow prismatic crystals of 1 were synthesized by a solvothermal reaction of gadolinium nitrate hexahydrate and H₂NIPA in DMF at 180 °C for four days. A single-crystal X-ray crystallographic analysis demonstrated that compound 1 crystallizes in cubic space group I₃̅d and features a 3-D anionic framework [Gd₃(NIPA)₆]₃³⁻, and H⁺ and tetramethylammonium cations as counterions existing in the pores. As shown in Fig. 1(a), each Gd(III) is eight-coordinated by two chelating carboxylate groups and four monodentately coordinating carboxylate oxygen atoms of the bridging ligands, forming a distorted cubic configuration. Each ligand bridges three Gd atoms and all O atoms join the coordination. The –NO₂ group, as a strong electron-withdrawing functional group, can promote NIPA ionization to facilitate coordination and hydrophilicity of carboxylate oxygen atoms. The asymmetric and symmetric stretching vibration bands of COO⁻ were observed at 1650 cm⁻¹ and 1459/1387/1344 cm⁻¹, respectively. The absence of the characterized IR absorption band around 2500–2700 cm⁻¹ for a protonated carboxylic group also further implies that the carboxylate groups in 1 are completely deprotonated (Fig. S1, ESI†). Each tetramethylammonium cation connects the framework through weak interactions, C–H···O weak hydrogen bonds, 3.458(9) and 3.844(10) Å (Fig. 1(b)). Fig. 1(c) and Fig. S2 [ESI†] show that O14, O1W and O3W join together through hydrogen bonds, where the distances of O3W–O1W and O1W–O14 are 2.606(30) and 2.941(28) Å, respectively. So, there are abundant hydrogen bonded networks in 1. The structure did not obviously show that O2W participates in the formation of hydrogen bonded networks due to its drastic thermal vibration and disorder. The content of water molecules in the channels can further be confirmed by thermogravimetry (TG) analysis (Fig. S3, ESI†) and elemental analysis. The main roles of the tetramethylammonium cations, H⁺ and three water molecules residing in the channel are balancing charges and stabilizing and strengthening the

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‡ State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China. E-mail: gcguo@fjirsm.ac.cn, mswang@fjirsm.ac.cn, zhihuafu@fjirsm.ac.cn
§ University of Chinese Academy of Sciences, Beijing 100039, P. R. China
† Electronic supplementary information (ESI) available: Experimental section (materials, measurements, and synthesis), and additional tables (Tables S1–S3) and graphics (Fig. S1–S4). CCDC 1874854. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8cc08700h
The thermal stability and the existing experiments of H$_2$O guest stability and water stability experiments were performed first. The thermal stability of three water molecules per molecule (2.85%, calculated) H$^+$ ions are mainly applied to balance the charge of $\text{Gd}_3\text{(NIPA)$_3$}$ and three NIPA ligands (Fig. 1(c)). As depicted in Fig. 1(d), the infinite channels extend along four intersecting directions to generate a framework with 3D pore channels. The crossed infinite channels with hydrophilic frameworks are suitable for water absorption. Moreover, free H$^+$ cations and water molecules in the channel may form complex hydrogen bonded networks and other weak interactions with the framework of $\text{1}$, which are likely to facilitate proton-conducting processes.

To study the proton conduction properties of $\text{1}$, the thermal stability and water stability experiments were performed first. The thermal stability and the existing experiments of H$_2$O guest molecules in the channel of $\text{1}$ were corroborated by TG and differential scanning calorimetry (DSC) analysis data. As shown in Fig. S3 (ESI†), the results also suggest that the weight loss in the range of 30–120 °C is ~2.88%, corresponding to the content of three water molecules per molecule (2.85%, calculated). H$^+$ ions are mainly applied to balance the charge of $\text{1}$ and also give this compound the potential for proton conduction. Then, the water stability experiment of $\text{1}$ was studied by the following three steps: first, being refluxed in water at 75 °C for 2 hours; second, being refluxed in water at 50 °C for 4 hours; and finally, being soaked in water for 24 hours. Notably, no obvious changes in the crystal structure were found in the PXRD patterns of experimental samples, and the peak differences in intensity between the simulated and experimental patterns may result from the preferred orientation of the lattice face (Fig. 2(a)).

The excellent structural feature of hydrogen bonded networks, water tolerance and thermal stability of $\text{1}$ give us a chance to explore its single-crystal proton conduction properties. Until now, proton conductivity measurements of proton-conducting MOFs have been almost exclusively performed on pelleted samples and there are only seven reported MOFs with proton conductivities being measured using single-crystal samples. Although measurements on pellets are beneficial to offer macroscopic proton conductivity of one material, it is difficult to reveal intrinsic proton conduction mechanisms, and the effect of the grain boundary sometimes cannot be ignored. Proton conductivity measurements in this work were performed on single crystal samples. Single-crystal proton conductivity of $\text{1}$ was evaluated by an AC impedance/gain-phase analyzer using a single-crystal sample (cross section size: 0.024/0.024/0.04 cm, length: 0.117 cm). The conductivities of the samples were derived from the impedance values by employing the equation:

$$\sigma = \frac{d}{\text{Z}}$$

where $\sigma$ is the conductivity ($\text{S cm}^{-1}$), $d$ is the thickness (cm) of the measured sample, $S$ is the electrode area (cm$^2$), and $Z$ represents the impedance (Ω) calculated by fitting the arc at selected temperatures using the ZView program, where the total resistance includes two parts, i.e., $R_s$ and $R$, representing the resistance from the bulk phase and charge transfer, respectively (Fig. S4, ESI†). Generally, the proton-conducting property of MOFs is influenced by two main factors: RH and temperature. For $\text{1}$, similar to the previously reported MOFs, RH may play an important role in the proton conduction process mainly due to the adsorption of water molecules. Fig. 2(b) shows the excellent water-adsorption ability of $\text{1}$ at high RH. The conductivities of $\text{1}$...
increase by about two orders of magnitude as humidity increases coinciding with moisture sensitivity (Fig. 3), indicating that more water molecules absorbed can form more abundant hydrogen bonded networks to build proton-conducting pathways. To elucidate the proton-conducting mechanism of 1, we studied proton conductivities in the form of Nyquist plots (Z’ versus Z”) at different temperatures under 98% RH. As shown in Fig. 2(c), compound 1 also shows temperature-dependent proton conductivity at 98% RH. The conductivity increased with elevated temperature established by the construction of an Arrhenius plot. For 1, the σ values are $4.07 \times 10^{-2}$, $4.76 \times 10^{-2}$, $5.69 \times 10^{-2}$, $6.49 \times 10^{-2}$, $6.92 \times 10^{-2}$ and $7.17 \times 10^{-2}$ S cm$^{-1}$ at 25, 35, 45, 55, 65 and 75 °C, respectively. The maximum single-crystal proton conductivity of 1 is among the highest values for proton-conducting MOFs, which mainly rank from $10^{-5}$ to $10^{-2}$ S cm$^{-1}$ (Table S3, ESI†). The calculated activation energy ($E_a$) was found to be around $0.13$ eV (Fig. 2[d]) indicating that proton conduction adopts the Grothuss mechanism, i.e., protons “hop” through a hydrogen-bonded network.\textsuperscript{33}

In this work, in order to demonstrate the mechanism possibly responsible for the high and intrinsic proton conductivities of 1, we studied the relationship of RH and capacity for inclusion of water molecules of 1 through its water vapor adsorption/desorption isotherms at 25 °C (Fig. 2[b]). Compound 1 shows relatively rapid adsorption of water molecules at low humidity and adsorbs about 6 molecules per formula unit at 94% RH. As shown in Fig. 3, the proton conductivities also increase sharply as the free water molecule number of 1 increases. These results reveal that it possesses high moisture sensitivity and forms more abundant hydrogen bonded networks after adsorbing additional water molecules at high RH. An obvious hysteresis is observed in the adsorption/desorption process at low humidity (Fig. 2[b]), which further confirms the flexible framework of 1. In addition, elevating temperature may have three effects on enhancing the proton conductivity: (1) enhancing hydrophilicity of the framework to adsorb and stabilize more water molecules in a humid environment, which forms more abundant hydrogen bonded networks; (2) increasing the acidity of free water molecules facilitating proton transfer; (3) the more drastic thermal vibration and disorder of O2W to accelerate the proton mobility. As a result, compound 1 obtains maximum proton conductivity at 75 °C and 98% RH. Although compound 1 shows finite hydrogen bonded chains due to the drastic thermal vibration and disorder of O2W (Fig. 1[a]), the calculated $E_a$ proves that the outstanding conductive property of 1 is mainly on account of abundant hydrogen bonded networks formed by free H+, H2O and the framework (Fig. 1[c] and Fig. S2, ESI†).

In conclusion, we found that the new Gd-MOF, [H[(N(CH$_3$)$_2$)$_2$]-[Gd$_3$(NIPA)$_6$]-3H$_2$O], shows excellent water stability and high proton-conductive properties. Single crystal proton conductivity measurements demonstrate that compound 1 has a maximum proton conductivity $\sigma = 7.17 \times 10^{-2}$ S cm$^{-1}$ at 75 °C and 98% RH, which is among the highest values for proton conducting MOFs. This work expands the system of MOFs with single-crystal proton conduction.

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Conflicts of interest

There are no conflicts to declare.

Notes and references
