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COMMUNICATION

A Proton-conducting Lanthanide Metal-Organic Framework Integrated with Dielectric Anomaly and Second-order Nonlinear Optical Effect

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A multifunctional metal-organic framework generated from chiral tricarboxylate ligand and gadolinium ion has been successfully synthesized and characterized. It shows proton conduction, dielectric anomaly and second-order NLO effect.

Over the past decade, an exponential growth of metal-organic frameworks (MOFs) has been witnessed owing to their widespread application in gas storage, selective separation, catalysis, magnetism, optics, ferroelectrics, and drug delivery.[1] Exceptionally high crystallinity and designability of MOFs provide a unique opportunity to regulate the properties and analyze the structure-activity relationships. Furthermore, the better chemical and thermal stability renders them highly suitable materials to apply in practical processes as functional solid materials. On the other hand, the preparation of solid-state proton conductors, especially polymer, has also been a highly active research area, particularly for fuel-cell applications.[2] However, polymers fail to provide insights into conduction mechanisms and completely recognize the relationships between microstructure and conducting property, owing to the lack of long-range order. Inspired by the above MOFs advantages, considerable efforts have recently been devoted to the design and synthesis of proton conducting MOFs, including water-mediated and anhydrous proton conducting MOFs.[3] Till now, few proton conducting MOFs have been synthesized, using carboxylate, phosphonate and sulfonate groups as organic ligands, via introducing water molecules and loading heterocyclic molecules with proton into the channel and framework, respectively.[4-6] Despite this promising advancement in proton conducting MOFs, there are still some challenges and opportunities to improve the conduction efficiency.

Multifunctional MOFs have recently received growing attention, because fascinating features may be introduced by integrating two or more properties into a single substance. For instance, a number of advanced functional MOFs with intriguing properties have been designed such as chiral magnets,[7] microporous magnets,[8] multiferriocs,[9] porous ferroelectrics,[10] and luminescent sensor.[11] Similarly, proton conducting MOFs have been integrated with magnetism,[12] luminescence,[13] porosity,[14] or chirality.[15] However, to our knowledge, the reports on proton-conducing MOF with dielectric anomalous behaviour have remained scarce.[16] Additionally, second-order nonlinear optical MOFs have achieved

extensive progress due to the potential application of photonics technologies and optoelectronic devices.[17] Therefore, incorporation of both dielectric anomalous and second-order NLO properties into proton-conducting MOFs may give rise to novel multifunctionality in the resulting materials.

Herein, we have presented a chiral three-dimensional lanthanide MOF, $\{[Gd_4(R\text{-}ttpc)_2(R\text{-}Httpc)_2(HCOO)_2(H_2O)_8]\cdot 4H_2O\}_n$, [JUC-125, R-H$_3$ttpc = (3R,3'R,3''R)-1,1',1''-(1,3,5-triazine-2,4,6-triyl)-tripiperidine-3-carboxylic acid], containing hydrophilic channels, the carboxyl oxygen atoms as proton carriers and hydrogen-bonding chains as proton-conducting pathways. The multifunctional properties are found in JUC-125, included proton conduction, dielectric anomaly and second-order NLO response.

Single crystals of JUC-125 were obtained by reacting Gd(NO$_3$)$_3$·6H$_2$O, R-H$_3$ttpc, and dilute HNO$_3$ in H$_2$O/DMF mixed solvents under solvothermal condition. The structure of JUC-125 was solved by single-crystal X-ray diffraction method in chiral monoclinic space group P2$_1$. In the asymmetric unit, there are four Gd(Ⅲ) ions, two completely deprotonated R-H$_3$ttpc ligands (R-ttpc^{3-}), two partially deprotonated R-H$_3$ttpc ligands (R-ttpc^{2-}), two formate ions (HCOO$^-$), eight coordinated aqua molecules, and four lattice water molecules. The fundamental subunit of JUC-125 is composed of two dimers with Gd1-Gd2 distance of 4.131 Å and Gd3-Gd4 distance of 4.117 Å, respectively (Fig. 1a). Each Gd1 atom is nonuple coordinated by two carboxylate oxygen atoms from one R-ttpc^{3-} ligand with chelating bidentate mode, two carboxylate oxygen atoms from one R-ttpc^{3-} ligand with syn-syn bridging bidentate mode, four carboxylate oxygen atoms from two R-ttpc^{3-} ligand with chelating-bridging bidentate mode, and three oxygen atoms from three water molecules (Fig. S1a and S2a). The local coordination environment of Gd2 can be best described as a distorted monocapped square antiprism, being ligated to two carboxylate oxygen atoms from one R-ttpc^{3-} ligand with chelating bidentate mode, two carboxylate oxygen atoms from one R-ttpc^{3-} ligand with syn-syn bridging bidentate mode, two carboxylate oxygen atoms from one R-ttpc^{3-} ligand with chelating-bridging bidentate mode, one carboxyl oxygen atom from one R-ttpc^{2-} ligand, one monodentate formate ion, and one oxygen atom from one water molecule (Fig. S1a and S2b). There is a neutral carboxylic acid in Gd2 coordination environment, owing to the requirement of charge balance and existence of two evidently different C−O distances. The C−O
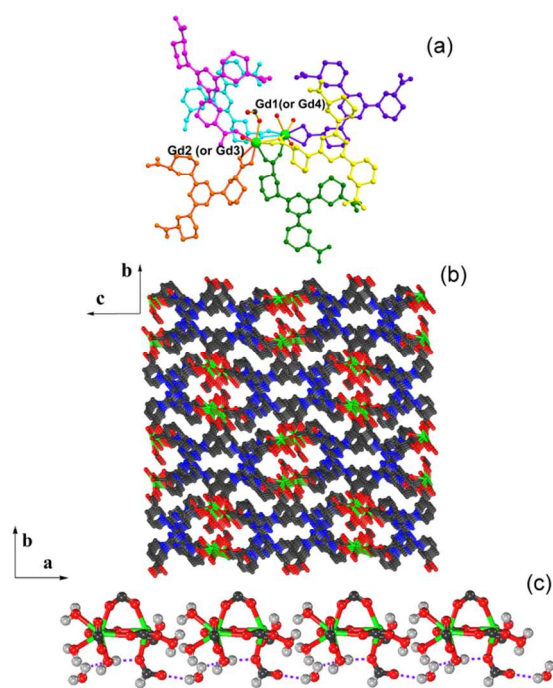
Fig. 1 (a) The fundamental subunit of JUC-125 is composed of two dimers (Gd1-Gd2 or Gd3-Gd4). The bridging ligands are discriminated by colors for clarity. (b) Three dimensional framework of JUC-125. (c) 1D O–H···O hydrogen-bonding chain constructed from the oxygen atoms of lattice water molecules, coordinated aqua molecules and formate ions. The other atoms have been omitted for clarity (Black, C; blue, N; Red, O; Green, Gd; Light Gray, H).

distance of the oxygen atom bonded to Gd2 atom (C36−O10 1.191(14) Å) is markedly shorter than that of the other oxygen atom (C36−O9 1.265(17) Å), suggesting that the O9 atom is most likely protonated. The coordination environments of Gd3 and Gd4 are similar to Gd2 and Gd1, respectively, in which the bond lengths and bond angles of Gd3 and Gd4 are somewhat different from those of Gd2 and Gd1.

Each Gd dinuclear unit is linked by six different R-H$_3$ttpc ligands and each R-H$_3$ttpc ligand bridges three different Gd dinuclear units, thus giving rising to a three-dimensional framework (Fig. 1b). From a topological perspective, if R-H$_3$ttpc ligand is considered as to be a 3-connected node and the Gd dimer a 6-connected node, respectively, the structure of JUC-125 can be simplified as a (3,6)-connected net with a Schläfli symbol of $(4^8 2)_2 (4^6 8^7 10^2)$ (Fig. S3). The 1D rectangular channel with dimensions of ca. 5×10 Å^2 along a axis is occupied by water guest molecules, coordinated formate ions and aqua molecules, which leads to a solvent-accessible void space of 3.1% of the unit-cell volumes calculated by PLATON program (Fig. S4). Furthermore, there are three interesting features in JUC-125. The first feature is hydrophilic channels formed by carboxylate oxygen atoms, coordinated aqua molecules, nitrogen atoms from triazine rings (Fig. S5). It is possible to accommodate the additional water molecules in hydrophilic channels by adsorption method. The second feature is the existence of three types of hydrogen-bonding interactions in the cavity: O–H···O interactions between carboxylate and carboxyl oxygen atoms, O–H···O interactions between coordinated aqua molecules and carboxylate
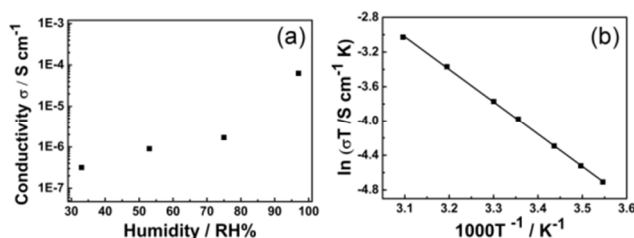

Fig. 2 (a) RH dependence of the conductivity (σ) for JUC-125 at 298 K. (c) Arrhenius-type plot of the conductivity of JUC-125 at various temperatures and under ~97% RH condition.

oxygen atoms, O–H···O interactions between carboxylate oxygen atoms and lattice water molecules (Fig. S6). The last striking feature is the presence of 1D O–H···O hydrogen-bonding chain among the oxygen atoms of lattice water molecules, coordinated aqua molecules and formate ions in the 1D rectangular channel (Fig. 1c). The existence of hydrophilic channels, the carboxyl oxygen atoms as proton carriers and hydrogen-bonding chains as proton-conducting pathways indicates that the JUC-125 is likely a potential candidate for proton conduction.

Inspired by the structural feature, proton conductivity of JUC-125 was measured by AC impedance spectroscopy using a quasi-four-probe method. The humidity-dependent proton conductivity of JUC-125 was determined at 298 K in the RH range of ~97% to ~33% (Fig. 2a). The measurement results show that the conductivity lowers by two orders of magnitude from 6.3×10^{-5} S cm^{-1} at ~97% RH (Fig. S11a) to 3.2×10^{-7} S cm^{-1} at ~33% RH (Fig. S11d), suggesting that proton conductivity is closely correlated to the number of water molecules encapsulated in channel.[18] The proton conductivity of JUC-125 was monitored as a function of temperature varied from 282 K to 323 K at ~97% RH. There is a gradual increase in the conductivity as the temperature is raised, reaching a maximum value of 1.5×10^{-4} S cm^{-1} at 323 K (Fig. S12f). Arrhenius plot [ln(σT) vs 1000T^{-1}] with a linear relationship offers an activation energy of 0.32 eV (Fig. 2b), indicating that proton-conductive behavior may be in accordance with Grotthuss mechanism (0.1 − 0.4 eV) of proton transport through hydrogen bond.[19] JUC-125 has proton conductivity of 6.3×10^{-5} S cm^{-1} at 298 K and ~97% RH, comparable to those of the layered phosphonate MOF [Zn$_3$(L)(H$_2$O)·2H$_2$O, 3.5×10^{-5} S cm^{-1} at 298 K and 98% RH] and the chiral MOF with helical water chain [Zn(l-L$_{Cl}$)(Cl)·2H$_2$O, 4.45×10^{-5} S cm^{-1} at 298 K and 98% RH].[20]

We also evaluated the dielectric property of JUC-125. The temperature dependences of ac dielectric constant and dielectric loss of JUC-125 at various frequencies $10^2 − 10^7$ Hz and $10^4 − 10^7$ Hz, respectively, are shown in Figure 3. As illustrated in Figure 3a, the dielectric permittivity at 100 Hz first remains approximately constant between 200 K and 255 K, then increases sharply with a maximum of 78 at 288 K, finally decreases rapidly with the further increase in temperature. Meanwhile, the dielectric constant peak gradually shifts toward lower temperature and the height decreases with increasing frequency. The noticeable dielectric response in the low-frequency region may be attributed to orientational polarization and proton displacement of water molecules with large dipole moment.[21] The dielectric loss peak of about 2.7 is observed at 10^4 Hz and 288 K (Fig. 3b), implying energy dissipation from ionic movement and polarization. The large dielectric loss (tan δ > 1) in the high-frequency region is presumably linked to disproportionation defects and polar nanodomain, generated from proton transfer along the hydrogen-bonding chain at applied field.[22] While the endothermic peak of JUC-125 was not detected by DSC measurement, which illustrates the nonexistence of phase transition. The lager leakage current density of the order of $10^{-3} – 10^{-5}$ A cm^{-2} under the employed
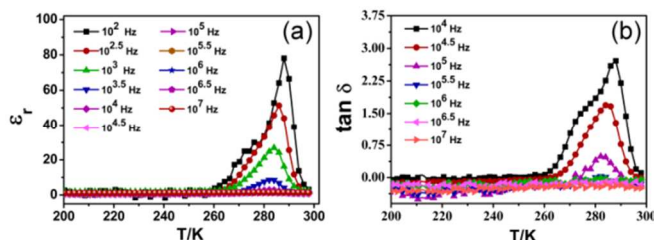
Fig.3 The dielectric constant (a) and the dielectric loss (b) for JUC-125 measured as a function of temperature at various frequencies.

condition in JUC-125 is also investigated (Fig. S10), which demonstrates that the ferroelectric effect is possibly due to leakage current. These results reveal that the anomalous dielectric behavior was not arisen from the ferroelectric-paraelectric phase transition, but from water molecules.[23]

JUC-125 theoretically exhibits the second-order NLO effect, because it crystallizes in the chiral space group $P2_1$. On the basis of the principle proposed by Kurtz and Perry,[24] the second harmonic generation (SHG) intensity of JUC-125 has been estimated by using the microcrystalline sample. Preliminary experimental result indicates that JUC-125 indeed displays SHG activity with a value of approximately 0.5 times that of urea. The notable SHG efficiency of JUC-125 is likely to result from the strength and numbers of intermolecular hydrogen bondings constructed from water molecules.[25]

In conclusion, we have successfully fabricated a multifunctional lanthanide-based MOF material with proton conduction, dielectric anomalous and second-order NLO behaviours. JUC-125 shows a proton conductivity of 6.3×10^{-5} S cm^{-1} at 298 K and ~97% RH, anomalous dielectric constant and loss peaks at 288 K, as well as SHG activity with a value of approximately 0.5 times that of urea. These interesting properties may be associated with water molecules, hydrogen-bonding chains and chiral structure. The versatile water molecules encapsulated in chiral MOF, which turn stones into gold, create hydrogen-bonding interaction and proton transport pathway and further contribute to proton transfer along hydrogen bond to achieve proton conduction, dielectric anomaly and SHG activity. The study reveals that some intriguing properties could be obtained by introducing water molecules or water clusters into MOF channels[26], and provides a novel insight into the design and synthesis of multifunctional MOFs.

Notes and references

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