



A proton-conducting lanthanide metal–organic framework integrated with a dielectric anomaly and second-order nonlinear optical effect†

Cite this: *Chem. Commun.*, 2014, 50, 6513Received 19th January 2014,
Accepted 26th March 2014

DOI: 10.1039/c4cc00458b

www.rsc.org/chemcommXiaoqiang Liang,^{‡,ab} Feng Zhang,^{‡,a} Haixia Zhao,^c Wei Ye,^b Lasheng Long^c and Guangshan Zhu^{*a}

A multifunctional metal–organic framework generated from chiral tricarboxylate ligands and gadolinium ions has been successfully synthesized and characterized. It shows proton conduction, dielectric anomalous behaviour and a 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 The exceptionally high crystallinity and designability of MOFs provide a unique opportunity to regulate their properties and analyze the structure–activity relationships. Furthermore, their 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 polymers, has also been a highly active research area, particularly for fuel-cell applications.² However, polymers fail to provide insights into the conduction mechanisms and completely recognize the relationships between microstructure and conducting properties, 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 To date, a 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 protons 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 multiferric, porous ferroelectrics,¹⁰ and luminescent sensors.¹¹ Similarly, proton conducting MOFs have been integrated with magnetism,¹² luminescence,¹³ porosity,¹⁴ or chirality.¹⁵ However, to our knowledge, reports on proton-conducting MOFs with dielectric anomalous behaviour have remained scarce.¹⁶ Additionally, second-order nonlinear optical MOFs have achieved extensive progress due to their potential application in 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 present a chiral three-dimensional lanthanide MOF, $\{[\text{Gd}_4(\text{R-ttpe})_2(\text{R-Httpe})_2(\text{HCOO})_2(\text{H}_2\text{O})_8] \cdot 4\text{H}_2\text{O}\}_n$ [JUC-125, R-H₃ttpe = (3R,3'R,3''R)-1,1',1''-(1,3,5-triazine-2,4,6-triyl)-tripiperidine-3-carboxylic acid], containing hydrophilic channels, carboxyl oxygen atoms as proton carriers and hydrogen-bonding chains as proton-conducting pathways. Multifunctional properties are found in JUC-125, including proton conduction, dielectric anomalous behaviour and a second-order NLO response.

Single crystals of JUC-125 were obtained by reacting Gd(NO₃)₃·6H₂O, R-H₃ttpe, and dilute HNO₃ in H₂O–DMF mixed solvent under solvothermal conditions. The structure of JUC-125 was solved by single-crystal X-ray diffraction in the chiral monoclinic space group *P*2₁. In the asymmetric unit, there are four Gd(III) ions, two completely deprotonated R-H₃ttpe ligands (R-ttpe³⁻), two partially deprotonated R-H₃ttpe ligands (R-ttpe²⁻), 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 a Gd1–Gd2 distance of 4.131 Å and a Gd3–Gd4

^a State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, PR China.

E-mail: zhugs@jlu.edu.cn; Fax: +86 431-8516-8331

^b College of Environmental and Chemical Engineering, Xi'an Polytechnic University, Xi'an 710048, PR China

^c State Key Laboratory of Physical Chemistry of Solid Surface and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, PR China

† Electronic supplementary information (ESI) available: Experimental details, additional characterization data and crystallographic data (CIF). CCDC 970128. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc00458b

‡ These authors contributed equally to this work.

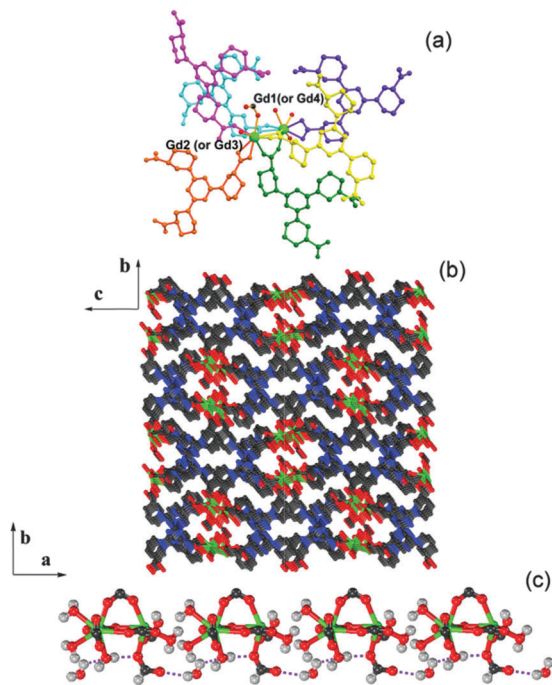


Fig. 1 (a) The fundamental subunit of JUC-125 is composed of two dimers (Gd1–Gd2 or Gd3–Gd4). The bridging ligands are discriminated by color for clarity. (b) The three dimensional framework of JUC-125. (c) The 1D O–H···O hydrogen-bonding chain constructed from the oxygen atoms of the lattice water molecules, 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 4.117 Å, respectively (Fig. 1a). Each Gd1 atom is nonuple coordinated by two carboxylate oxygen atoms from one R-tpc³⁻ ligand with the chelating bidentate mode, two carboxylate oxygen atoms from one R-tpc³⁻ ligand with the *syn-syn* bridging bidentate mode, four carboxylate oxygen atoms from two R-tpc³⁻ ligands with chelating-bridging bidentate modes, and three oxygen atoms from three water molecules (Fig. S1a and S2a, ESI†). 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-tpc³⁻ ligand with the chelating bidentate mode, two carboxylate oxygen atoms from one R-tpc³⁻ ligand with the *syn-syn* bridging bidentate mode, two carboxylate oxygen atoms from one R-tpc³⁻ ligand with the chelating-bridging bidentate mode, one carboxyl oxygen atom from one R-tpc²⁻ ligand, one monodentate formate ion, and one oxygen atom from one water molecule (Fig. S1a and S2b, ESI†). There is a neutral carboxylic acid in the Gd2 coordination environment, owing to the requirement of charge balance and the existence of two evidently different C–O distances. The C–O distance of the oxygen atom bonded to the 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-H₃tpc ligands and each R-H₃tpc ligand bridges three different Gd dinuclear units, thus giving rising to a three-dimensional framework (Fig. 1b). From a topological perspective, if the R-H₃tpc ligand is considered 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 (48²)₂(4⁶8⁷10²) (Fig. S3, ESI†). The 1D rectangular channel with dimensions of *ca.* 5 × 10 Å² along the *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 volume calculated by the PLATON program (Fig. S4, ESI†). Furthermore, there are three interesting features in JUC-125. The first feature is hydrophilic channels formed by carboxylate oxygen atoms, coordinated aqua molecules, and nitrogen atoms from triazine rings (Fig. S5, ESI†). It is possible to accommodate additional water molecules in the hydrophilic channels by an 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 oxygen atoms, and O–H···O interactions between carboxylate oxygen atoms and lattice water molecules (Fig. S6, ESI†). The last striking feature is the presence of a 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 JUC-125 is likely a potential candidate for proton conduction.

Inspired by these structural features, the 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, ESI†) to 3.2 × 10⁻⁷ S cm⁻¹ at ~33% RH (Fig. S11d, ESI†), suggesting that proton conductivity is closely correlated to the number of water molecules encapsulated in the channel.¹⁸ The proton conductivity of JUC-125 was monitored as a function of temperature and 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, ESI†).

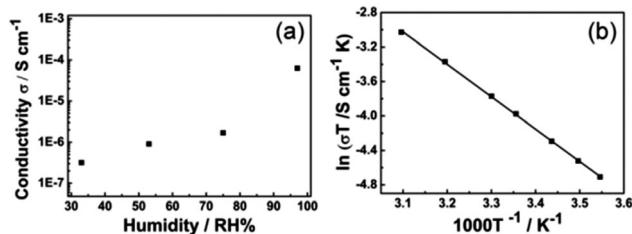


Fig. 2 (a) The RH dependence of the conductivity (σ) for JUC-125 at 298 K. (b) An Arrhenius-type plot of the conductivity of JUC-125 at various temperatures and under ~97% RH conditions.

The Arrhenius plot [$\ln(\sigma T)$ vs. $1000T^{-1}$] with a linear relationship offers an activation energy of 0.32 eV (Fig. 2b), indicating that the proton-conductive behavior may be in accordance with the Grotthuss mechanism (0.1–0.4 eV) of proton transport through hydrogen bonds.¹⁹ JUC-125 has a proton conductivity of $6.3 \times 10^{-5} \text{ S cm}^{-1}$ at 298 K and $\sim 97\%$ RH, comparable to those of the layered phosphonate MOF [$\text{Zn}_3(\text{L})(\text{H}_2\text{O})\cdot 2\text{H}_2\text{O}$, $3.5 \times 10^{-5} \text{ S cm}^{-1}$ at 298 K and 98% RH] and the chiral MOF with helical water chains [$\text{Zn}(\text{L-CI})(\text{Cl})\cdot 2\text{H}_2\text{O}$, $4.45 \times 10^{-5} \text{ S cm}^{-1}$ at 298 K and 98% RH].²⁰

We also evaluated the dielectric properties of JUC-125. The temperature dependencies of the ac dielectric constant and dielectric loss of JUC-125 at various frequencies from 10^2 – 10^7 Hz and 10^4 – 10^7 Hz, respectively, are shown in Fig. 3. As illustrated in Fig. 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, and finally decreases rapidly with further increase in temperature. Meanwhile, the dielectric constant peak gradually shifts toward lower temperatures 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 a large dipole moment.²¹ A 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 ($\tan \delta > 1$) in the high-frequency region is presumably linked to disproportionation defects and polar nanodomains, generated from proton transfer along the hydrogen-bonding chain at the applied field.²² Meanwhile, the endothermic peak of JUC-125 was not detected by DSC measurement, which illustrates the nonexistence of phase transition. The larger leakage current density on the order of 10^{-3} – $10^{-5} \text{ A cm}^{-2}$ under the employed conditions in JUC-125 was also investigated (Fig. S10, ESI†), and demonstrates that the ferroelectric effect is possibly due to leakage current. These results reveal that the anomalous dielectric behavior did not arise 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 was estimated by using a microcrystalline sample. The 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 number of intermolecular hydrogen bonds constructed from water molecules.²⁵

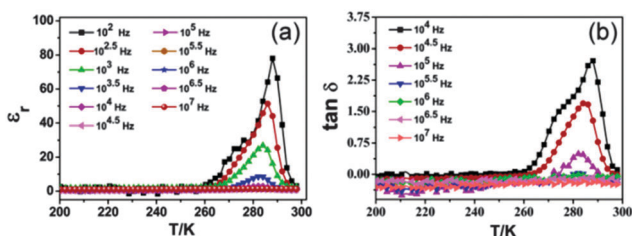


Fig. 3 The dielectric constant (a) and the dielectric loss (b) for JUC-125 measured as a function of temperature at various frequencies.

In conclusion, we have successfully fabricated a multifunctional lanthanide-based MOF material with proton conduction, and dielectric anomalous and second-order NLO behaviours. JUC-125 shows a proton conductivity of $6.3 \times 10^{-5} \text{ S cm}^{-1}$ at 298 K and $\sim 97\%$ 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 the chiral structure. The versatile water molecules encapsulated in the chiral MOF, which turn stones into gold, create hydrogen-bonding interactions and proton transport pathways and further contribute to proton transfer along the hydrogen bonds to achieve proton conduction, dielectric anomalous behaviour 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.

We are grateful for the financial support of the National Basic Research Program of China (973 Program 2012CB821700), the National Natural Science Foundation of China (20831002; 20502024), the China Postdoctoral Science Foundation (20100481049), the Scientific Research Program from the Education Department of Shaanxi Provincial Government (2013JK0654), the Priming Scientific Research Foundation for Doctors (BS1115) and the Provincial Innovation Training Project (1399) for College Students of Xi'an Polytechnic University. We also thank Prof. Yi-Zhi Li for crystal refinement and Dr Tao Wu for Vibrational Circular Dichroism measurements.

Notes and references

- 1 Some special issues on MOFs: (a) *Chem. Rev.*, 2012, **112**, 673–1278; (b) *Chem. Soc. Rev.*, 2009, **38**, 1201–1508.
- 2 H. Zhang and P. Shen, *Chem. Rev.*, 2012, **112**, 2780.
- 3 (a) S. L. Li and Q. Xu, *Energy Environ. Sci.*, 2013, **6**, 1656; (b) M. Yoon, K. Suh, S. Natarajan and K. Kim, *Angew. Chem., Int. Ed.*, 2013, **52**, 2688; (c) G. K. H. Shimizu, J. M. Taylor and S. Kim, *Science*, 2013, **341**, 354.
- 4 S. Horike, Y. Kamitsubo, M. Inukai, T. Fukushima, D. Umeyama, T. Itakura and S. Kitagawa, *J. Am. Chem. Soc.*, 2013, **135**, 4612.
- 5 C. Dey, T. Kundu and R. Banerjee, *Chem. Commun.*, 2012, **48**, 266.
- 6 (a) J. A. Hurd, R. Vaidyanathan, V. Thangadurai, C. I. Ratcliffe, I. M. Moudrakovski and G. K. H. Shimizu, *Nat. Chem.*, 2009, **1**, 705; (b) S. Bureekaew, S. Horike, M. Higuchi, M. Mizuno, T. Kawamura, D. Tanaka, N. Yanai and S. Kitagawa, *Nat. Mater.*, 2009, **8**, 831.
- 7 C. Train, M. Gruselle and M. Verdager, *Chem. Soc. Rev.*, 2011, **40**, 3297.
- 8 P. Dechambenoit and J. R. Long, *Chem. Soc. Rev.*, 2011, **40**, 3249.
- 9 G. C. Xu, W. Zhang, X. M. Ma, Y. H. Chen, L. Zhang, H. L. Cai, Z. M. Wang, R. G. Xiong and S. Gao, *J. Am. Chem. Soc.*, 2011, **133**, 14948.
- 10 Z. G. Guo, R. Cao, X. Wang, H. F. Li, W. B. Yuan, G. J. Wang, H. H. Wu and J. Li, *J. Am. Chem. Soc.*, 2009, **131**, 6894.
- 11 B. L. Chen, S. C. Xiang and G. D. Qian, *Acc. Chem. Res.*, 2010, **43**, 1115.
- 12 H. Okawa, M. Sadakiyo, T. Yamada, M. Maesato, M. Ohba and H. Kitagawa, *J. Am. Chem. Soc.*, 2013, **135**, 2256.
- 13 R. M. P. Colodrero, K. E. Paphanasiou, N. Stavgianoudaki, P. Olivera-Pastor, E. R. Losilla, M. A. G. Aranda, L. León-Reina, J. Sanz, I. Sobrados, D. Choquesillo-Lazarte, J. M. García-Ruiz, P. Atienzar, F. Rey, K. D. Demadis and A. Cabeza, *Chem. Mater.*, 2012, **24**, 3780.
- 14 D. Umeyama, S. Horike, M. Inukai and S. Kitagawa, *J. Am. Chem. Soc.*, 2013, **135**, 11345.

- 15 X. Liang, F. Zhang, W. Feng, X. Zou, C. Zhao, H. Na, C. Liu, F. Sun and G. Zhu, *Chem. Sci.*, 2013, **4**, 983.
- 16 W. X. Chen, H. R. Xu, G. L. Zhuang, L. S. Long, R. B. Huang and L. S. Zheng, *Chem. Commun.*, 2011, **47**, 11933.
- 17 O. R. Evans and W. B. Lin, *Acc. Chem. Res.*, 2002, **35**, 511.
- 18 J. J. Sumner, S. E. Creager, J. J. Ma and D. D. Desmarteau, *J. Electrochem. Soc.*, 1998, **145**, 107.
- 19 "Proton Conductors: Solids, Membranes and Gels-Materials and Devices", P. Colomban, *Chemistry of Solid State Materials*, Cambridge University Press, Cambridge, UK, 1992, vol. 2.
- 20 (a) J. M. Taylor, R. K. Mah, I. L. Moudrakovski, C. I. Ratcliffe, R. Vaidhyanathan and G. K. H. Shimizu, *J. Am. Chem. Soc.*, 2010, **132**, 14055; (b) S. C. Sahoo, T. Kundu and R. Banerjee, *J. Am. Chem. Soc.*, 2011, **133**, 17950.
- 21 Q. Ye, Y. M. Song, G. X. Wang, K. Chen, W. D. Fu, P. W. H. Chan, J. S. Zhu, S. D. Huang and R. G. Xiong, *J. Am. Chem. Soc.*, 2006, **128**, 6554.
- 22 M. Szafranski and A. Katrusiak, *J. Phys. Chem. B*, 2008, **112**, 6779.
- 23 M. Sánchez-Andújar, S. Yáñez-Vilar, B. Pato-Doldá, C. Gómez-Aguirre, S. Castro-García and M. A. Señaris-Rodríguez, *J. Phys. Chem. C*, 2012, **116**, 13026.
- 24 S. K. Kurtz and T. T. Perry, *J. Appl. Phys.*, 1968, **39**, 3798.
- 25 Y. R. Xie, R. G. Xiong, X. Xue, X. T. Chen, Z. L. Xue and X. Z. You, *Inorg. Chem.*, 2002, **41**, 3323.
- 26 (a) H. X. Zhao, X. J. Kong, H. Li, Y. C. Jin, L. S. Long, X. C. Zeng, R. B. Huang and L. S. Zheng, *Proc. Natl. Acad. Sci. U. S. A.*, 2011, **108**, 3481; (b) B. Zhou, A. Kobayashi, H. Cui, L. S. Long, H. Fujimori and H. Kobayashi, *J. Am. Chem. Soc.*, 2011, **133**, 5736.