NJC

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/njc

NJC RSCPublishing

LETTER

Cite this: DOI: 10.1039/c3nj00000x

Received 00th XXXXX 2013,
Accepted 00th XXXXX 2013

DOI: 10.1039/c3nj00000x

www.rsc.org/njc

A low-κ dielectric metal-organic-framework compound showing novel three-step dielectric relaxations originating from orientation motion of dipolar guest molecules

Ping-Chun Guo, [a,b] Tian-Yu Chen, [a,b] Xiao-Ming Ren,*[a,b] Wei-Hua Ning, [a,b] and Wanqin Jin*[a]

A three-dimensional metal-organic framework compound with a formula $[Cu_2(EBTC)(H_2O)_2{\cdot}8H_2O{\cdot}DMF{\cdot}DMSO]_\infty$ (EBTC = 1, 1′-ethynebenzene-3, 3′, 5, 5′-tetracarboxylate) shows novel three-step dielectric relaxations arising from the orientation motion of dipolar guest molecules and its guest-free framework displays low-κ dielectric permittivity.

Metal-organic-frameworks (MOFs) are highly ordered crystalline coordination polymers with well-defined porous networks[1] and have been widely studied for storage,[2] separations,[3] sensors,[4] catalysis[5] and drug delivery[6] due to their controllable porosity, extremely large specific surface area and structural variety. On the other hand, the host-guest interactions or guest molecules motions under an applied electrical field have recently attracted a growing amount research interests in the porous MOFs since the host-guest interactions or guest molecule motions probably give rise to novel switchable magnetic,[7] solvatochromic,[8] proton conducting,[9] ferroelectric [10] and multiferric[11] properties.

It is worthy to mention that the MOFs-based materials probably show diverse and interesting dielectric features, from the structural viewpoint, this is because (1) the guest molecules in MOFs materials with interconnected nano-sized pores/channels are movable owing to loosely binding to framework although the framework possess highly ordered structure, and the dipole motion of polar guest molecules probably show interesting dielectric response.[12] (2) MOFs compounds are promising low-κ dielectric materials since low-κ dielectrics should be porous where atoms are far apart.[13] The low-κ materials are suitable as an interlayer dielectric material for applications in the semiconducting devices.[14] For instance, a low-κ dielectric is generally used to separate the conducting parts (such as the wire interconnects and transistors) from one another in digital circuits, reduces parasitic capacitance, enable faster switching speeds, decreases cross-talk noise and lowers heat dissipation for a microelectronic device.[15] However, the dielectric properties of MOFs-based compounds have been rarely investigated up to date.

In this study, we present the first example, a MOF compound with a formula $[Cu_2(EBTC)(H_2O)_2{\cdot}G]_\infty$ (compound **1** where $EBTC^{4-}$ = 1, 1′-ethynebenzene-3,3′,5,5′-tetracarboxylate; G = guest molecules and represent DMF, DMSO and H_2O) shows novel three-step dielectric relaxations arising from the reorientation motion of polar guest molecules, while the guest-free framework displays low-κ dielectric permittivity.

The crystal structure and arresting acetylene storage nature of **1** were previously reported by Chen and coworkers.[16] The framework of **1** is comprised of paddle wheel dinuclear Cu_2 units which are connected through $EBTC^{4-}$ ligands to form a three-dimensional (3-D) NbO type crystal structure with two types of nanometer-sized cavities, the small one shows ca. 8.5 Å in diameter and the larger one exhibits irregular elongated cavity of about 8.5×21.5 Å (ref. Figure S1), and the heavily disordered H_2O, DMF and DMSO guest molecules occupy in two types of cavities.[16] We synthesized **1** in this study following the published procedure[16] using solvothermal method at 65 °C and characterized the as-prepared sample by IR spectrum, TG analysis and powder X-ray diffraction (PXRD) measurement (ref. Figure S2-S4). The characteristic vibration bands in IR spectrum are observed for the as-prepared sample of **1** below, the 3419sh, 3311s and 3219s cm^{-1} bands are assigned to ν(O-H) of H_2O molecules. The 2969w, 2948w and 2889w cm^{-1} bands are attributed to the stretching vibrations of C-H from CH_3. The 1706 and 1637 cm^{-1} (two bands overlap) bands are assigned to the ν(C=O) of COO^- and O=C-H (DMF). The 1405s band arises from the bending vibration of C-H of O=C-H (DMF). The 1045s band is attributed to the ν(S=O). The weight loss is ca. 17.5% between 30 and 197 °C, corresponding to losing eight lattice waters (calc. 17.8%); the weight loss is ca. 21.9% between 197 and 307 °C, corresponding to losing one DMF, one DMSO and two coordination waters (calc. 23%). These results are similar to those reported by Chen and coworkers.[16]

The guest molecules in MOF **1** were exchanged using methanol to give $[Cu_2(EBTC)(H_2O)_2{\cdot}(H_2O)_x(CH_3OH)_y]_\infty$ (**2**) and the guest-free framework compound $[Cu_2(EBTC)]_\infty$ (**3**) was prepared by heating **2** at 130 °C under vacuum. The losing guests procedure does not alter 3-D architecture of **1**, which can be confirmed by powder X-ray diffraction measurements (ref. Figure S2). We also re-determined the single crystal of **1** at 100 K, the cell parameters† are listed in Table S1, which are quite similar to those reported in the literature.[16] Notably, the guest molecules still show highly disordered even if the temperature is down to 100 K.

The dielectric spectra of **1** were investigated in the temperature range of 123-283 K and the frequency range of 1-10^7 Hz. Plots of dielectric permittivity (ε'), dielectric loss [$\tan(\delta)$] *versus* temperature under the selected ac electrical field frequencies are shown in Figure 1(a, b). It is clear, from these figures, that the dielectric permittivity ε' keeps a constant value (5.55-5.63) below 160 K, and then, increases with rising temperature. The dielectric dispersion is observed in the high temperature regime, this phenomenon is especially obvious under the low ac field frequencies ($f < 10^4$ Hz). This behaviour is due to the reorientational motions of polar guest molecules being restricted in low temperature, namely, the polar guest molecules cannot orient themselves with respect to the direction of applied electric field. Then they acquire a weak contribution to the polarization. The guest molecules get enough excitation thermal energy to be able to obey the change under the external electric field more easily in high temperature regime, and the reorientational dynamics of guest molecules is activated. This in return enhances their contribution to the polarization leading to an increase of dielectric permittivity ε’. One or two loss peaks, which maximum positions are dependent on the ac electric field frequency, appear in the tan(δ)-T plots, suggesting the existence of dielectric relaxations.

The ε’ and tan(δ) as a function of frequency are displayed in Figure 1c and 1d for **1** at selected temperatures. At high temperatures, the dielectric permittivity drop rapidly with increasing frequency to 10^4 Hz, This result indicates that the dynamical dipole motion cannot follow the quickly switching of the applied electric field at higher frequencies (when $f > 10^4$ Hz). The dielectric permittivity is almost constant when the frequency of applied ac electrical field is more than 10^6 Hz, the values ε’ = 12.7 at 283 K and ε’ = 5.4 at 123 K. In tan(δ) versus f plots of **1**, the dielectric relaxation process is related to the temperature: the loss peak is absence below 170 K, one loss peak becomes visible between the temperatures of 170 and 200 K, two loss peaks emerge between the temperatures of 200 and 230 K as well as three clear loss peaks are observed above 230 K. The maximums of all loss peaks on the plot of tan(δ) versus f shift toward high frequencies with increasing temperature. This dielectric behaviour is the typical nature of a thermally assisted dielectric relaxation. Different mechanisms of dielectric relaxation show the characteristic of specific ranges of relaxation frequencies. Dielectric relaxation originating from electronic transitions or molecular vibrations has a frequency above 10^{12} Hz, while slow dielectric relaxations from molecule dipole motion or ionic displacement polarization occur in the range 10^2–10^{10} Hz. Thus, the dielectric relaxations in the frequency regime of 1–10^5 Hz observed in MOF **1** arises from dipole motion of polar guest molecules.

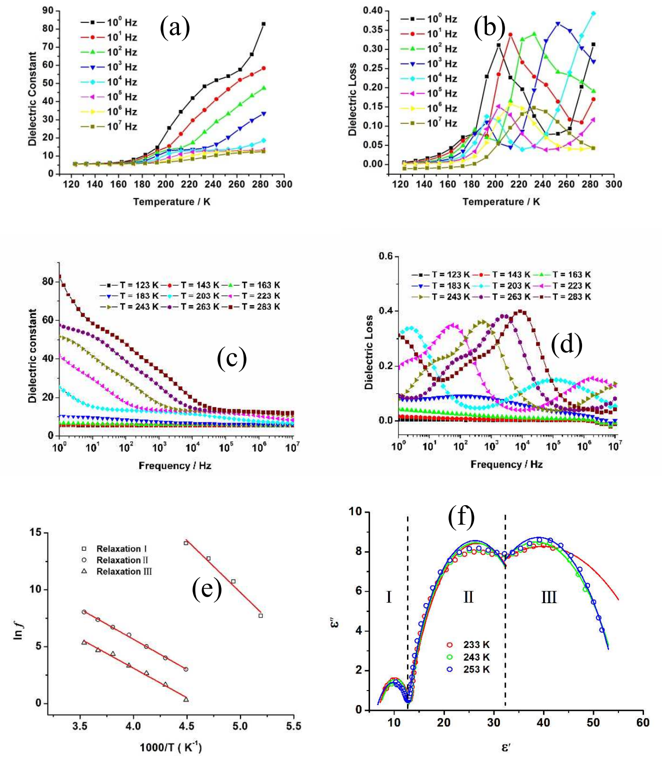


Figure 1 (a, b) Temperature dependencies of ε' and $\tan(\delta)$ of **1** in the 1–10^7 Hz frequency range. (c, d) Frequency dependencies of the ε' and $\tan(\delta)$ of **1** in the 123-283 K temperature range. (e) Plots of lnf versus 1/T for three dielectric relaxation processes and (f) Cole-Cole plots of **1** at 233, 243 and 253 K (open circles: experimental data; solid lines: theoretically reproduced data).

We analyse the macroscopic relaxation time and potential barrier according to the following empirical Arrhenius relationship:

$$\tau = \tau_0 \exp(\frac{E_a}{k_B T}) \qquad (1)$$

Where $\tau = 1/f_{max}$ and f_{max} is the frequency at maximum in the tan(δ) versus f plot at a selected temperature, τ_0 represents the characteristic macroscopic relaxation time, and E_a is so-called the activation energy or potential barrier. The best fits were undertaken for the data of three relaxation regimes to Eq.(1) to give the following parameters (see Figure 1e and Table S1): the activation energy E_a = 76.0 kJ·mol^{-1}, 44.2 kJ·mol^{-1} and 43.1 kJ·mol^{-1} with corresponding macroscopic relaxation time (τ_0) of 1.22×10^{-25} s, 3.22×10^{-13} s and 6.96×10^{-12} s. The orientation change of molecules involves the processes of intermolecular bonds breaking and forming. The activation energy E_a values obtained from fits fall within the regime of intermolecular H-bond energy,[17] indicating that the orientation change of molecules is probably related to the breaking and forming process of intermolecular H-bonds, and there probably exist H-bond interactions between guest molecules as well as between guest molecules and the framework in MOF **1**.

Most dielectric materials behave differently than the Debye response. Thus, it is necessary to modify the empirical expression representing the Cole-Cole plot. One such a modification was proposed by Cole and Cole[18] and is given by:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}} \qquad (2)$$

Where ε_0 is the static dielectric permittivity, ε_∞ is the dielectric permittivity at theoretically infinitely high frequencies, τ is the relaxation time, and α is related to the dispersion of the relaxation processes ($0 \le \alpha \le 1$). Figure 1f shows the Cole-Cole plots of the relaxation process for **1** at selected temperatures, where three semicircles occur to indicate the existence of three different dielectric relaxation processes. The best fits were performed for the plots of imaginary part (ε") versus real part (ε') of dielectric permittivity to yield the parameters ε_0, ε_∞, and α for three relaxation processes below, α_1 values of 0.45–0.50, α_2 values of 0.28–0.30 and α3 values of 0.39–0.61, respectively, at the selected temperatures (ref. Table S1). The relatively large α values suggest that three dielectric relaxation processes show the moderate distribution of the relaxation time and depart from the Debye dielectric response model.

The dielectric properties have not been investigated for **2** because the methanol/water molecules located in the cavities of **2** start to release at ambient temperature and more easily escape under a N_2 flow (the dielectric measurement was carried out using N_2 flow to control the temperature of the sample), and this situation is hard to give the intrinsic dielectric feature of **2**. The dielectric spectra of **3** in the forms of ε'-T and tan(δ)-T as well as ε'-f and tan(δ)-f are shown in Figure 2, which are extremely distinct from those of **1**. The dielectric properties of guest-free MOF **3** exhibit two typical natures (1) the dielectric permittivity values fall within the range of 4.9-6.2 and associated with quite low dielectric loss value (tan(δ) < 0.018) in the temperature range of 113-293 K and under the ac frequency of 1-10^7 Hz. These results demonstrate that the guest-free MOF **3** is a low-κ dielectric material. (2) No clear dielectric relaxation was observed when f > 100 Hz, further suggesting that the three-step dielectric relaxations observed in **1** originate from the reorientation motion of disordered polar lattice solvents.

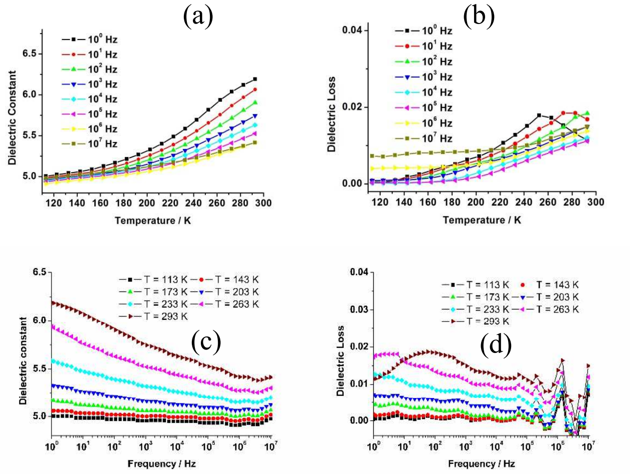


Figure 2 (a, b) Temperature and (c, d) frequency dependences of the dielectric permittivity, ε′, and dielectric loss, tan(δ), of **3**.

Hunger and coworkers investigated the relative permittivity of dimethylsulfoxide (DMSO) and N, N-dimethylformamide (DMF) at temperatures from 278 to 328 K and pressures from 0.1 to 5 MPa, the results disclosed that the relative permittivity value is 37.2±0.1 for DMF and 46.0±0.1 for DMSO at 298.15 K and 0.1 MPa, and decreases a little with increasing temperature.[19] Malmberg and Maryott studied the dielectric constant of water from 273 to 373 K, and found that the dielectric constant of water has the value 78.30 at 298 K, and the temperature dependent dielectric constant follows the equation $\varepsilon_r = 87.740 - 0.40008t + 9.398(10^{-4})t^2 - 1.410(10^{-6})t^3$, where *t* represents temperature and its unit is degree centigrade (°C). The *ε'* value of MOF **1** is 82.78 at 283 K under 1 Hz, this value is significant different from that of DMF or DMSO at ambient temperature, while close to that of water.

In summary, we comparatively studied the dielectric spectra of a 3-D NbO type crystal structure MOF (**1**) and its guest-free framework (**3**). MOF **1** possesses two types of nanometer-sized cavities which are occupied by the polar solvents H_2O, DMF and DMSO and shows novel three-step dielectric relaxations. These relaxation processes are related to the reorientation motion of polar guest molecules under an ac electrical field since the guest molecules located in nano-sized cavities are loosely bound to the framework. The guest-free metal-organic-framework compound **3** shows quite low dielectric permittivity and loss. This study suggested the possibility of interesting dielectric property and rather useful low-κ dielectric materials in semiconductor devices via the rational designed MOFs with pores or channels.

Authors thank the Priority Academic Program Development of Jiangsu Higher Education Institutions and the National Nature Science Foundation of China (Grant no. 91122011, 21271103 and 21176115) for financial support.

Experimental

$[Cu_2(EBTC)(H_2O)_2{\cdot}G]_\infty$ (**1**) was prepared following the procedure in a published paper.[16] The sample exchanged by methanol, $[Cu_2(EBTC)(H_2O)_2{\cdot}(H_2O)_x(CH_3OH)_y]_\infty$ (**2**), was obtained by soaking **1** in methanol for 24 h and then refreshing for three times. The activated solvent-free framework compound $[Cu_2(EBTC)]_\infty$ (**3**) was prepared by heating **2** at 130 °C under vacuum overnight.

Notes and references

[a] *State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing University of Technology, Nanjing 210009, P.R. China. E-mail: xmren@njut.edu.cn; wqjin@njut.edu.cn*

[b] *College of Science, Nanjing University of Technology, Nanjing 211816, P. R. China.; Fax: +86 25 58139481; Tel: +86 25 58139476; E-mail: xmren@njut.edu.cn*

† Crystallographic data: Trigonal system, space group R-3m, a = b = 18.6844(11) Å, c = 32.862(4) Å, α = β = 90.00°, γ = 120.00°, V = 9935.3(14) Å^3, Z = 9, T = 293(2) K in literature.[16] Trigonal system, space group R-3m, a = b = 18.7095(16) Å, c = 32.610(6) Å, α = β = 90.00°, γ = 120.00°, V = 9886(2) Å^3, Z = 9, T = 100(2) K in this work.

Electronic Supplementary Information (ESI) available: [ESI includes physical measurements; PXRD patterns, IR spectra, TG plots of **1-3**, the coordination sphere and packing diagram of $[Cu_2(EBTC)]_\infty$ framework; Tables of crystal structure data of **1** at 100 K, the parameters fitted by Arrhenius equation and the parameters of the Cole-Cole plots fitted by the general Debye models]. See DOI: 10.1039/c000000x/

1 O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature* 2003, **423**, 705; S. Kitagawa; R. Kitaura and S. Noro, *Angew. Chem., Int. Ed.* 2004, **43**, 2334; G. Férey, *Chem. Soc. Rev.* 2008, **37**, 191.

2 M. Dincă, A. F. Yu and J. R. Long, *J. Am. Chem. Soc.* 2006, **128**, 8904.

3 D. N. Dybtsev, H. Chun, S. H. Yoon, D. Kim and K. Kim, *J. Am. Chem. Soc.* 2004, **126**, 32; G. Li, W. Yu, Y. Cui, *J. Am. Chem. Soc.* 2008, **130**, 4582; C. Zhu, G. Yuan, X. Chen, Z. Yang, Y. Cui, *J. Am. Chem. Soc.* 2012, **134**, 8058.

4 H. L. Jiang, Y. Tatsu, Z. H. Lu and Q. Xu, *J. Am. Chem. Soc.* 2010, **132**, 5586.

5 D. B. Dang, P. Y. Wu, C. He, Z. Xie and C. Y. Duan, *J. Am. Chem. Soc.* 2010, **132**, 14321; M. Yoon, R. Srirambalaji and K. Kim, *Chem. Rev.* 2012, **112**, 1196.

6 P. Horcajada, R. Gref, T. Baati, P. K. Allan, G. Maurin, P. Couvreur, G. Férey, R. E. Morris and C. Serre, *Chem. Rev.* 2012, **112**, 1232; J. D. Rocca, D. Liu, W. B. Lin, *Acc. Chem. Res.* 2011, **44**, 957.

7 G. J. Halder, C. J. Kepert, B. Moubaraki, K. S. Murray, J. D. Cashion, *Science* 2002, **298**, 1762; Z. M. Wang, B. Zhang, H. Fujiwara, H. Kobayashi and M. Kurmoo, *Chem. Commun.* 2004, 416; X. Bao, H. J. Shepherd, L. Salmon, G. Molnár, M. L. Tong, A. Bousseksou, *Angew. Chem., Int. Ed.* 2012, **51**, 1236.

8 Z. Z. Lu, R. Zhang, Y. Z. Li, Z. J. Guo, H. G. Zheng, *J. Am. Chem. Soc.* 2011, **133**, 4172.

9 D. Umeyama, S. Horike, M. Inukai, S. Kitagawa, *J. Am. Chem. Soc.* 2013, **135**, 11345.

10 X. Y. Dong, B. Li, B. B. Ma, S. J. Li, M. M. Dong, Y. Y. Zhu, S. Q. Zang, Y. Song, H. W. Hou, T. C. W. Mak, *J. Am. Chem. Soc.* 2013, **135**, 10214; H. X. Zhao, X. J. Kong, H. Li, Y. C. Jin, L. S. Long, X. C. Zeng, R. B. Huang, L. S. Zheng, *PNAS* 2011, **108**, 3481; P. Jain, V. Ramachandran, R. J. Clark, H. D. Zhou, B. H. Toby, N. S. Dalal, H. W. Kroto, A. K. Cheetham, *J. Am. Chem. Soc.* 2009, **131**, 13625.

11 G. Rogez, N. Viart and M. Drillon, *Angew. Chem., Int. Ed.* 2010, **49**, 1921.

12 X. Y. Dong, B. Li, B. B. Ma, S. J. Li, M. M. Dong, Y. Y. Zhu, S. Q. Zang, Y. Song, H. W. Hou, T. C. W. Mak, *J. Am. Chem. Soc.* 2013, **135**, 10214; H. Cui, B. Zhou, L. S. Long, Y. Okano, H. Kobayashi and A. Kobayashi, *Angew. Chem., Int. Ed.* 2008, **47**, 3376.

13 A. Jain, S. Rogojevic, S. Ponoth, N. Agarwal, I. Matthew, W.N. Gill, P. Persans, M. Tomozawa, J.L. Plawsky, E. Simonyi, *Thin Solid Films* 2001, **398-399**, 513.

14 K. Zagorodniy, G. Seifert, and H. Hermann, *Appl. Phys. Lett.* 2010, **97**, 251905.

15 J. P. Reynard, C. Verove, E. Sabouret, P. Motte, B. Descouts, C. Chaton, J. Michailos, K. Barla, *Microelectron. Eng.* 2002, **60**, 113.

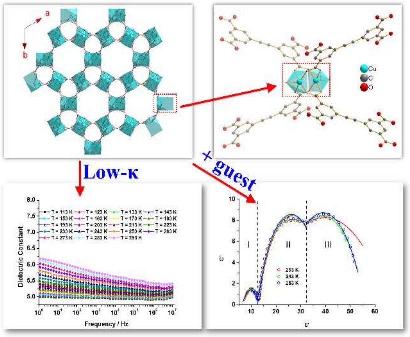
16 Y. X. Hu, S. C. Xiang, W. W. Zhang, Z. X. Zhang, L. Wang, J. F. Bai, B. L. Chen, *Chem. Commun.* 2009, 7551.

17 T. Steiner, *Angew. Chem. Int. Ed.* 2002, **41**, 48.

18 K. S. Cole, R. H. Cole, *J. Chem. Phys.* 1941, **9**, 341.

19 J. Hunger, R. Buchner, M. E. Kandil, E. F. May, K. N. Marsh, G. Hefter, *J. Chem. Eng. Data* 2010, **55**, 2055.

20 C. G. Malmberg and A. A. Maryott, *J . Research NBS* 1956, **56**, RP2641.



A metal-organic-framework compound shows novel three-step dielectric relaxations arising from reorientation motion of polar guest molecules and its guest-free framework is low-κ dielectric material.