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Supporting information

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

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Materials

1, 1′-ethynebenzene-3, 3′, 5, 5′-tetracarboxylate (H_4EBTC) was prepared according the literatures[1]. All commercially available chemicals $[Cu(NO_3)_2]\cdot 3H_2O$ and solvents (DMF, DMSO and CH_3OH) were of reagent grade and used without further purification.

Sample preparation

$[Cu_2(EBTC)(H_2O)_2\cdot G]_\infty$ (**1**) was prepared following the procedure in a published paper.[2] 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 compound $[Cu_2(EBTC)]_\infty$ (**3**) was prepared by heating at 130 ^oC under vacuum overnight.

Physical measurements

Fourier transform infrared (FT-IR) spectra were recorded on an IF66V FT-IR (4000–400 cm^{-1}) spectrophotometer with KBr disc. Power X-ray diffraction (PXRD) data were collected on a Bruker D8 diffractometer with Cu Kα radiation (λ = 1.5418 Å). TGA experiments were performed with a STA449 F3 thermogravimetric analyzer in the 30 – 700 °C range at a warming rate of 10 °C min^{-1} under a nitrogen atmosphere and the polycrystalline samples were placed in an Al_2O_3 crucible. The powered samples of **1** and **3** were pressed into a pellet under the pressure of ca. 10 MPa with a thickness of ca. 0.89 mm, 0.96 mm for **1** and **3**, respectively; the area of **1** and **3** is 7.06 mm^2. Two opposite surfaces of the pellets were covered with a gold film via vacuum coating and the process for the fabrication of films takes several minutes at ambient temperature. The measurements of the temperature and frequency dependent dielectric permittivity and loss were carried out by employing a Concept 80 system (Novocontrol, Germany) in the temperature range -160 - 20 °C (113 - 293 K). The powdered pellets of **1** and **3** were sandwiched by two copper electrodes and the ac frequencies spanned from 1 to 10^7 Hz.

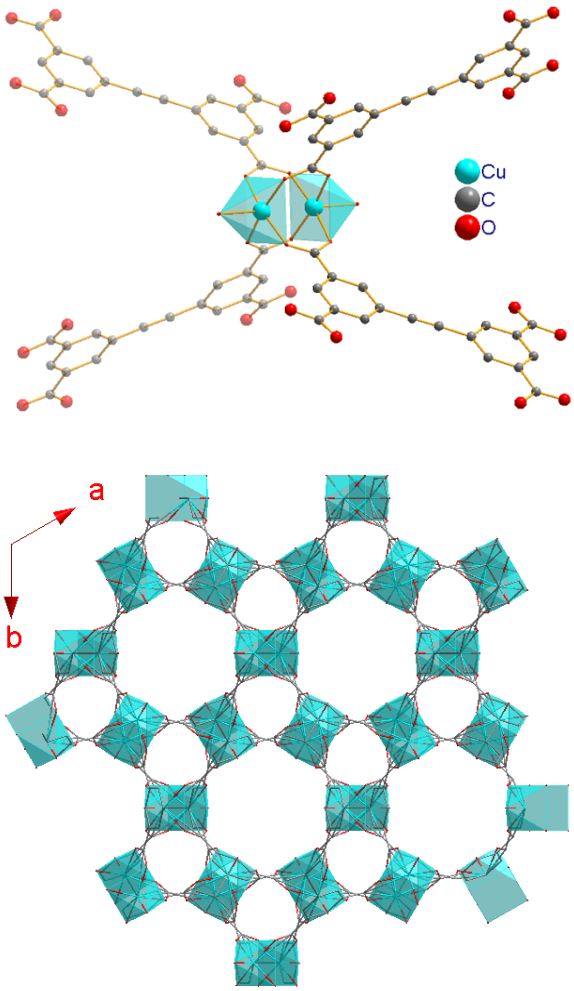


Figure S1 (a) Coordination environments of dicopper paddlewheel (b) packing diagram showing two types of cavities viewed along c-axis direction for **1** and the cif data were taken from the published paper.[2]

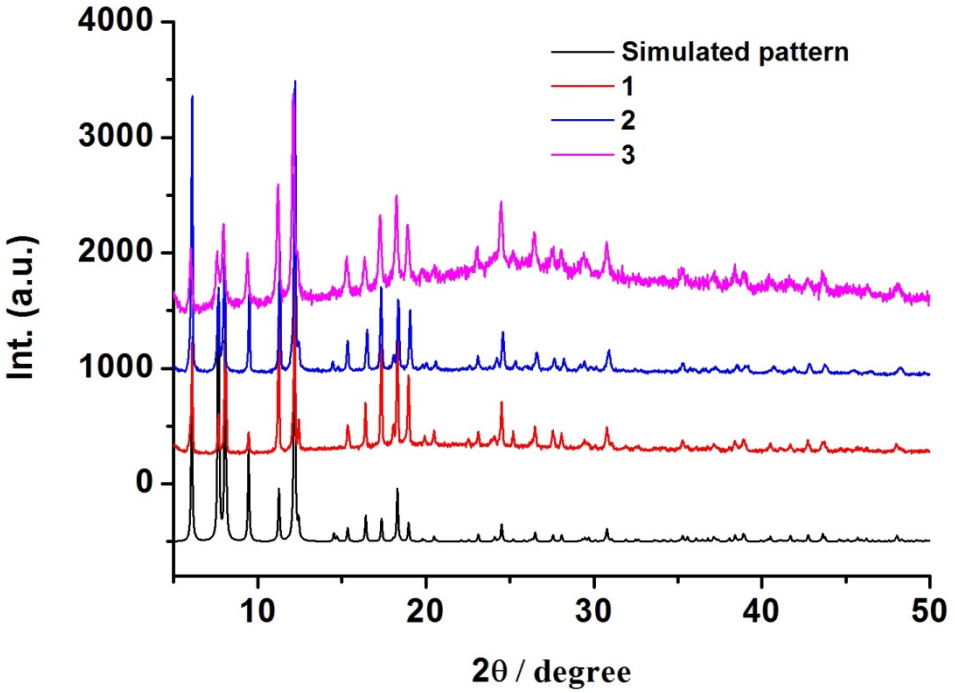


Figure S2 PXRD patterns of **1**, **2** and **3**, respectively (the simulated pattern of **1** was obtained from the single crystal data in reported paper[2]).

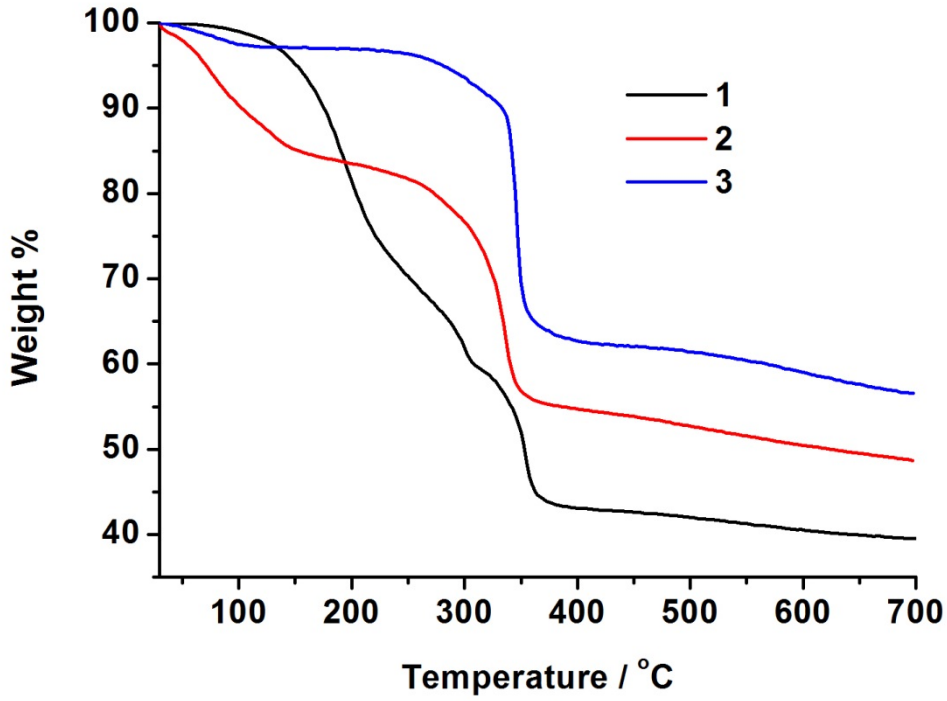
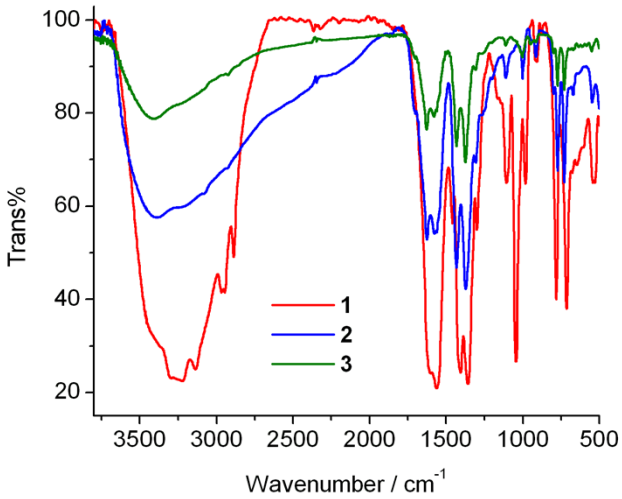


Figure S3 The TG plots of **1-3** at a heating rate of 10°C/min, respectively.


100
80
60
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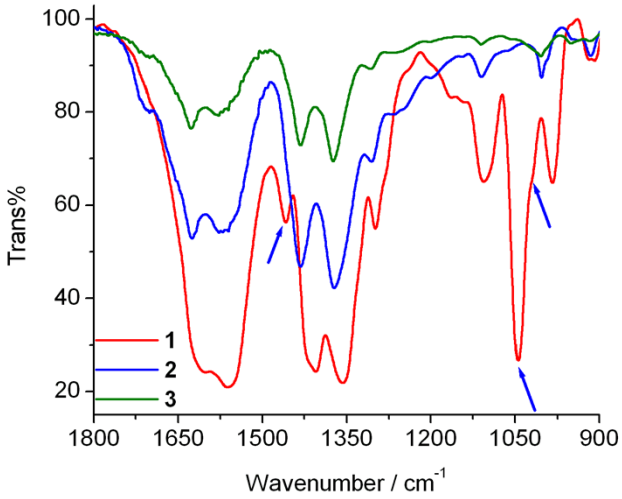
20
Trans%
1
2
3
3500
3000
2500
2000
1500
1000
500
Wavenumber / cm-1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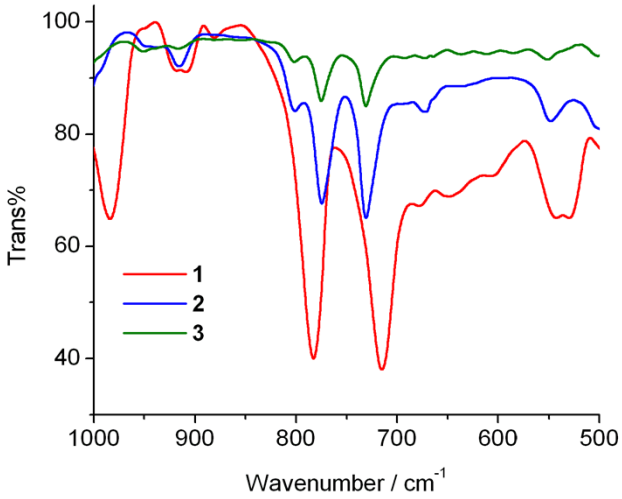
Wavenumber / cm-1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700
600
500
Wavenumber / cm-1

Figure S4 IR spectra of **1-3** (KBr pellet) in the region 3800-500 cm^{-1}. In the IR spectrum of **1**: 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).

Thus, three components H_2O, DMF and DMSO can be confirmed in the as-prepared MOF **1** sample from the IR spectrum of as-synthesized sample. In addition, the TGA disclosed that the experimental results are in agreement with the calculated one if the as-prepared sample of MOF 1 has the formula $Cu_2(BETC)(H_2O)_2{\cdot}8H_2O{\cdot}DMF{\cdot}DMSO$.

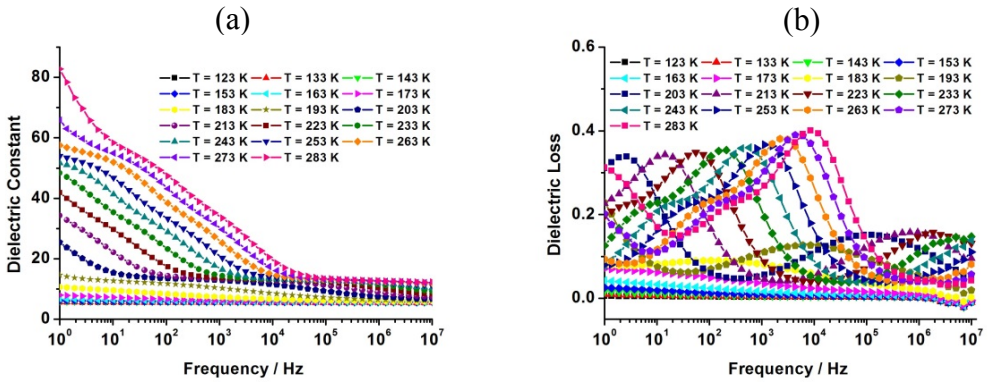

Figure S5 (a, b) Frequency dependencies of the ε′ and tan(δ) of **1** in the 123-283 K temperature range.

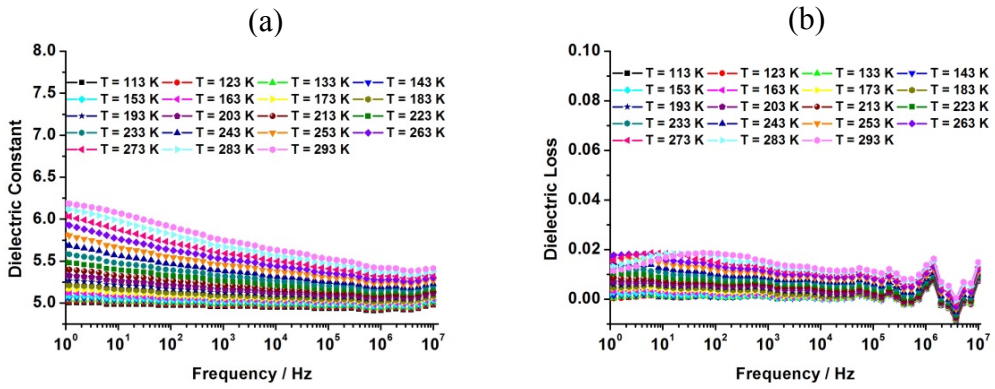

Figure S6 (a, b) Frequency dependences of the dielectric permittivity, ε′, and

dielectric loss, tan(δ), of **3**.

Table S1 Lattice parameters in **1** from the literature and this work

Compound	**1**	**1**[2]
Temp./K	100(2)	296(2)
Wavelength / Å	0.71073	0.71073
Space group	*R-3m*	*R-3m*
a (Å)	18.7095(16)	18.6844(11)
b (Å)	18.7095(16)	18.6844(11)
c (Å)	32.610(6)	32.862(4)
α (°)	90	90
β (°)	90	90
γ (°)	120	120
V (Å^3)/Z	9886(2)/9	9935.3(14)/9

$^aR_1 = \sum||F_o| - |F_c||/|F_o|$, $^awR_2 = [\sum w(\sum F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table S2 The parameters fitted by Arrhenius equation.

Parameters	Relaxation I	Relaxation II	Relaxation III
H (kJ.mol^{-1})	76.0	44.2	43.1
τ_o (s)	1.22×10^{-25}	3.22×10^{-13}	6.96×10^{-12}

Table S3 The parameters of the Cole-Cole plots fitted by the general Debye models.

T/K	Relaxation I			Relaxation II			Relaxation III		
	ε_∞	ε_s	α	ε_∞	ε_s	α	ε_∞	ε_s	α
233	13.44	6.81	0.46	40.48	12.82	0.30	65.63	13.95	0.61
243	13.26	7.05	0.45	39.83	12.71	0.29	56.26	20.69	0.43
253	13.23	6.38	0.50	39.81	12.60	0.28	55.62	22.30	0.39

References:

(1) H. Zhou, H. Dang, J. H. Yi, A. Nanci, A. Rochefort and J. D. Wuest, *J. Am. Chem. Soc.*, 2007, **129**, 13774.

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