The low dielectric constant and relaxation dielectric behavior in hydrogen-bonding metal-organic frameworks

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1. Experimental

1.1. Chemicals and reagents

Thee reagents and solvents were purchased from commercial sources and used without further purification. The compound 2-ethyl-4H-imidazole-4,5-dicarbonitrile was synthesized by literature.

1.2. Physical measurements

Elemental analyses (C, H and N) were performed with an Elementar Vario EL III analytical instrument. IR spectra were recorded on a Bruker Vector 22 Fourier Transform Infrared Spectrometer (170SX) (KBr disc). Thermogravimetric (TG) experiment was performed with a TA2000/2960 thermogravimetric analyzer from 40 to 700°C at a warming rate of 10 K/min under a nitrogen atmosphere, and the polycrystalline samples were placed in an aluminum crucible. Temperature and frequency dependent dielectric constant, ε', and dielectric loss, tan(δ), measurements were carried out employing Concept 80 system (Novocontrol, Germany); the powdered pellet, with a thickness of ca. 0.40 mm and 78.5 mm^2 in the area, was coated by gold films on the opposite surfaces and sandwiched by the copper electrodes and the ac frequencies span from 1 Hz to 10^6 Hz. Powder X-ray diffraction (PXRD) data for the as-prepared and the DMF-free samples were collected using Bruker D8 Advance powder diffractometer operating at 40 kV and 40 mA with Cu K radiation λ = 1.5418 Å at ambient temperature.

1.3. Preparations for 1

The preparation of **1** was different from our previous reported work[1]. The main difference is we used 2-ethyl-4H-imidazole-4,5-dicarbonitrile (EIDN) in this paper replaced 2-ethyl-4H-imidazole-4,5-dicarboxylic as the ligand. The synthesis procedure of this compound is in following described: First, the EIDN (4 mmol) and $Zn(NO_3)_2 \cdot 6H_2O$ (1 mmol) in 4:1 mol ratio were dissolved in 20 ml DMF. The mixture were refluxed for 2h, then 6 ml distilled water was added and sealed in Teflon-lined

autoclave and heated to 80℃ for 48h. The reaction product was filled and the solution was slowly evaporated. Colorless block-shape crystals were obtained after 7 days in solution. The crystal was washed with DMF and acetone and dried in air. The yield is ca. 65% based on EIDN, which is higher than our previous reported. The crystal structure of **1** is same as our previous reported. The carboxyl group was produced by hydrolysis of cyano group of EIDN ligand.

[1] S. S. Yu, H. Zhou and H. B. Duan, Synth. React. Inorg. Met.-Org. Chem., 2013, **43,** 1521.

Figure S1 Powder X-ray diffraction patterns for as-prepared sample of **1**, confirming the phase purity of the as-prepared sample (Black lines: experimental patterns; red lines: simulated profiles).

Figure S2 H-bond interactions between O atoms of DMF molecule and H_2EIDA ligand as well as between O atoms of H_2O and N atoms of H_2EIDA ligand.

Figure S3 Crystal structure of **1** illustrating the 3D framework forming by H-bond and O···O interactions.

Figure S4 Complex impedance of **1** at selected temperature