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Dielectric response of novel one-dimensional hydrogen-bonded molecular crystal [4,6-dmpH][Hca]

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ABSTRACT

The frequency dependent dielectric response due to proton transfer is observed for the novel onedimensional (1D) hydrogen-bonded co-crystal, [4,6-dmpH][Hca] (4,6-dmp=4,6-dimethylpyrimidine, ca=chloranilic acid). This response is only observed for an as-grown crystal in a metastable state with defects of hydrogen bonds. The critical hydrogen-bond length and one-dimensionality might be deeply related to the metstable state.

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1. Introduction

Recently, *proton transfer* phenomena in molecular crystals have attracted much interest in aim for functional materials such as ferroelectrics and anhydrous proton conductors [1]. So far, we have reported the dielectric response by an inter-molecular – N...H...O– proton transfer for $[H_2ca][1,2-da]_2$ ($H_2ca=chloranilic$ acid and 1,2-da=1,2-diazine in Fig. 1) [2]. This response was observed on the way of the migration from N–H...O at 300 K to O–H...N below 90 K, which is proved by the infrared absorption spectra and the temperature dependence of lattice constants. This proton migration induces the small broad peak of dielectric constant because protons transfer only in a molecular unit of $[H_2ca][1,2-da]_2$.

In order to enhance the dielectric response, the molecular crystal with the higher dimensional hydrogen-bonded network is aimed. Then, the molecular pair of 4,6-dmp and H₂ca in Fig. 1 was chosen. The pK_a of 4,6-dmp (=2.7) [3] is a little larger than that of 1,2-da (=2.3) [3], which affords the proton migration crystal. Moreover, the configuration of nitrogen atoms for 4,6-dmp is preferable to construct the 1-D hydrogen-bonded supramolecular structure.

In this report, the preparation, the crystal structure analysis, and the dielectric measurement of the novel hydrogen-bonded co-crystal [4,6-dmpH][Hca] (1) were carried out. As a result, the frequency dependent dielectric responses owing to proton transfer in the metastable state were successfully observed.

2. Experimental detail

The acetonitrile solutions of 4,6-dmp $(3.33 \times 10^{-1} \text{ M}, 2 \text{ mL})$ and H₂ca $(6.19 \times 10^{-3} \text{ M}, 48 \text{ mL})$ were slowly mixed and stored in Pertier cooler at 3 °C. After one night, a high quality of black block crystals of **1** (41.1 mg) were harvested, filtered off, washed with cold acetonitrile and dried in air.

The X-ray single crystal data of **1** were collected at room temperature on a Bruker CCD system (SMART APEX, Mo K α , 21 kW, $2\theta < 60^{\circ}$). The structure was solved by a direct method and refined by the full-matrix least squares technique using Crystal Structure (ver. 3.6.0, Rigaku Co. and Rigaku/MSC). Anisotropic thermal parameters were applied to all non-hydrogen atoms. Crystallographic data of [4,6-dmpH][Hca]: C₁₂H₁₀N₂O₄Cl₂, monoclinic, *P*2₁/c, *a*=13.9361(9)Å, *b*=23.156(2)Å, *c*=8.2051(5)Å, β =97.886(3)°, *V*=2622.8(5)Å³, *Z*=8, *R*=0.0468, *R*_W=0.1112, and GOF=1.009 by using independent 3637 reflections [*I* > 2.0 σ (*I*)].

The measurement of dielectric constant was carried out by quasi-four-probe capacitance method in use of an impedance analyzer (Agilent Technologies 4294A) between 2–100 kHz and 300–360 K. The contacts were made by silver paint.

3. Results and discussions

The crystal structure of **1** was shown in Figs. 2 and 3. The crystallographically independent molecules are two 4,6-dmpH⁺ and two Hca⁻. The positions of proton were determined in consideration of the C–O bond length of chloranilic acid; the C–O bond lengths are reported to be 1.322 Å for neutral chloranilic acid [4], 1.253 and 1.324 Å for monoanion [5], and 1.253 Å for dianion [6], respectively. Since C–O bond lengths of **1** are 1.250(2) and 1.320(2) (α and β in Fig. 2) and 1.249(2) and 1.320(2)



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Fig. 1. Molecular structures of 1,2-da, 4,6-dmp, and H₂ca.



Fig. 2. Intermolecular hydrogen bonds for [4,6-dmpH][Hca]. The C–O bonds are denoted as α and β .



Fig. 3. One-dimensional hydrogen-bonded chains indicated by the thick arrows for [4,6-dmpH][Hca].

(α and β), respectively, two chloranilic acids are monoanions. Therefore, one proton transfers from H₂ca to 4,6-dmp, and two kinds of hydrogen bonds coexist: 2.704(2)Å for N⁺-H···O⁻ and 2.875(2)Å for N···H-O, and 2.715(2) and 2.861(2) (Fig. 2). The Hca⁻ and 4,6-dmpH⁺ molecules are arranged alternately to construct 1-D zigzag chains. These 1-D chains are anti-parallelly arranged to each other to afford the 2-D layer (Fig. 3). There are, however, no intermolecular interactions such as π -stacking and hydrogen bonds between 1-D chains.

Fig. 4 shows the temperature dependence of the real part ε' and imaginary part ε'' of the complex dielectric constant of **1**. The frequency-dependent peaks of ε' and ε'' were observed around 352 K only in the initial heating process. This suggests proton transfer between the acid and base might occur. However, both annealed and three-months-aged crystals show no dielectric response [Fig. 4(iv)]. Since the decomposition starts from 364 K with heating the sample by the thermogravimetry (TG), the dielectric response around 352 K is not derived from degrading of a sample. The dielectric responses of freshly prepared samples are reproducible in the initial heating, indicating that the as-grown crystals should be in the metastable state.



Fig. 4. Temperature dependence of the first run of (i) real and (iii) imaginary parts of dielectric constants for [4,6-dmpH][Hca]. (ii) The upper inset is frequency dependence of tan δ . (iv)Temperature dependence of real part of dielectric constant for the annealed sample. (a)2, (b)3, (c)5, (d)10, (e)20, and (f)100 kHz.

As the metastable state, we propose the existence of some defects such as divalent molecules, 4,6-dmpH₂²⁺, along the 1-D hydrogen-bonded chain. The divalent molecules have instability due to coulomb repulsion in 4,6-dmpH₂²⁺, so that protons could move between the oxygen and nitrogen atoms to stabilize the stable state. The Fig. 4 (ii) elucidates that $\tan \delta (=\varepsilon''/\varepsilon')$ extends to low frequencies. The Cole-Cole plot does not show a Debye-arctype, but linear-type. The similar processes have been reported in 1D hydrogen-bonded chains; the dielectric loss in low frequencies was observed in the long alcohol chains such as $(C_{19}H_{40}O)_n$ due to a continuous proton transfer under electric field in 1D hydrogenbonded chain [7]. As for another example of 1D hydrogen-bonded BSQB...4H₂O (BSQB=bisquaricacidbiphenyl), the linear Cole-Cole plot down to low frequencies were also observed. The continuous proton relay is explained as protonic soliton model [8]. Therefore, the dielectric constant and loss of 1 might be also originated from the continuous motion of proton along 1D hydrogen-bonded chains. Once the defects disappear by heating and aging, any dielectric response is no longer observed because hydrogen cannot transfer in the stable state.

Proton transfer is deeply related to the length and the dimensionality of hydrogen bonds. The hydrogen bond length $r(N^+-H\cdots O^-)=$ 2.710Å of **1** is slightly longer than that of 5,5'-DMBP-H₂ca [5,5'-DMBP=5,5'-dimethyl-2,2'-bipyridine, $r(N^+-H\cdots O_-)=$ 2.683Å], which

shows an antiferroelectric phase transition due to the proton transfer [9]. Since the hydrogen bond of **1** is 1-D with critical lengths of hydrogen bonds, the metastable state could appear and demonstrate the dielectric response. The pressure dependence of dielectric constant for **1** is under way to obtain larger and stable dielectric response.

4. Conclusions

In conclusion, a unique 1D hydrogen-bonded dielectric material **1** has been prepared. The frequency-dependent dielectric response due to proton transfer was observed around 352 K only for as-grown crystals in the metastable state with defects of hydrogen bonds. The metastable state is originated from the critical length and one-dimensionality of hydrogen bonds.

Supplementary materials

CCDC 752373 contains the supplementary crystallographic data of **1** for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_re quest@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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