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Crystal Structure and Switchable Dielectric Properties of Singly Protonated Homopiperazinium Perchlorate

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Singly protonated homopiperazinium perchlorate (**1**) has been synthesized and characterized by single-crystal X-ray diffraction, IR, elemental analysis, DSC and temperature-dependent dielectric analysis. Compound **1** crystallizes in orthorhombic space group Pbca, their homopiperazinium cations are arranged in almost identical orientation by the parallel and nearly ideal linear N-H···N hydrogen bond chains. Very large dielectric change between high and low dielectric states is found at about 400 K due to reversible first-order phase transition. It is the first time that singly protonated homopiperazinium perchlorate is found to be a switchable dielectric material with high phase transition temperature and large dielectric change between high and low dielectric states.

Keywords: Homopiperazine, Organic-inorganic hybrid, Crystal structure, Dielectric property, Molecule-based.

INTRODUCTION

Switchable molecular dielectrics, which undergo transitions between high and low dielectric states at a phase transition temperature (T_c), are promising materials having potential application in data communication, signal processing and sensing and rewriteable optical data storage, *etc*[1,2]. The switching of dielectric constant could principally originate from motional changes of polar molecules or ions between "rotating or hopping" and orientationally ordered states, corresponding to a high-temperature and low-temperature phase, respectively[3]. Based on these principles, a few molecular rotator-stators in crystals have been constructed[4,5], utilizing molecular gyroscopes[6], supramolecular rotators[7,8] and metal-organic frameworks (MOFs)[9]. Meanwhile, some order-disorder molecular-ionic solid have been successfully prepared[10,11]. Though much progress have been achieved in designing sophisticated small molecular analogue machines[12,13], the synthesized switchable molecular dielectrics so far either suffer from lower T_c, or relatively small dielectric change between high and low dielectric states. As a result, practical applications of those materials are limited.

The symmetric diamines for example 1,4-diaza[2.2.2]bicyclooctane (dabco) and piperazine have been widely used to construct compounds containing intermolecular N-H···N hydrogen-bonds, in which the proton transferring inside N-H···N hydrogen bond will bring about interesting dielectric or ferroelectric properties, but for asymmetric diamines such as homopiperzine, there is no report up to now. In this work, we report the crystal structure and switchable dielectric properties of this new organic-inorganic simple salt singly protonated homopiperazinium perchlorate (**1**).

EXPERIMENTAL

All reagents and solvents were purchased from commercial sources and used as received. Elemental analyses for C, H and N were performed on a CHN-O-Rapid analyzer and an Elementar Vario MICRO analyzer. The IR spectra were performed on a Bruker Vector 22 FT-IR spectrometer with KBr discs in the 4000-400 cm^{-1} range. DSC measurements were performed by heating and cooling the samples over the temperature range of 310-412 K on Perkin Elmer Diamond DSC instrument. The measurements were carried out under nitrogen at atmospheric pressure in aluminum crucibles with a heating rate of 5 K min^{-1}. Complex dielectric permittivity was performed using automatic impedance TongHui 2828 Analyzer in the frequency range 10-1000 kHz. The measuring AC voltage was 1 V.

Synthesis of singly protonated homopiperazinium perchlorate: Equal molar ratio of homopiperzine (1 g, 10 mmol) and perchloric acid in 10 mL aqueous solution was stirred, filtered and left to stand undisturbed. Upon slow evaporation at room temperature for several days, single crystals suitable to X-ray analysis were obtained. IR (KBr, ν_{max}, cm^{-1}): 3324(s), 2992 (vs), 2415 (m), 1632 (m), 1573 (w), 1374 (s), 1082 (s). Anal. Calcd. for $C_5H_{13}N_2O_4Cl$: C, 29.93, H, 6.53, N, 13.96. Found: C, 29.30, H, 6.31, N, 14.02 %.

Single crystal X-ray crystallography: X-ray diffraction experiment was carried out on compound **1** using a Rigaku Saturn 924 diffractometer with MoK_α radiation ($\lambda = 0.71073$). Data processing including empirical absorption correction was performed using the crystalclear software package (Rigaku, 2005). The structure was solved using direct methods and successive fourier difference synthesis (SHELXS-97) and refined using the full-matrix least-squares method on F^2 using the SHELXLTL software package (Sheldrick, 2008). Non-H atoms were refined anisotropically using all reflections with $I > 2s(I)$. H atoms on C atoms were placed in calculated positions and refined using 'riding' model and ammonium H atoms were picked out from the Q peaks in difference Fourier maps. The packing views were drawn with DIAMOND (Brandenburg and Putz, 2005) Visual Crystal Structure Information System Software.

RESULTS AND DISCUSSION

Crystal structure: Compound **1** crystallizes in orthorhombic space group Pbca. The homopiperazine ring adopts chair-like conformation (Fig. 1a). The protonation influences its ring geometry for the C-N distances of $C-NH_2^+$ are longer than those of $C-NH^+$. Neighboring homopiperazinium cations are hold together *via* strong N-H···N hydrogen bond chains expanding along [010] direction (Fig. 1b). The hydrogen bonds are spatially arranged in almost identical orientation along the chain. Then if it is driven by external stimuli such as electric field, the proton can be transferred within bistable N-H···N hydrogen bonds, which will be helpful to produce spontaneous polarization just like ferroelectric compound $dabcoHReO_4$[14]. The parallel and nearly ideal linear hydrogen bonds aggregates are unique among crystals in general. In $dabcoHClO_4$[15] and $dabcoHBF_4$[16] the consecutive chains of N-H···N hydrogen-bonded $dabcoH^+$ cations are arranged antiparallel and the cations in piperazinium tetrafluoroborate ($[NH_2(CH_2)_4NH][BF_4]$)[17] and lithium hydrazinium sulfate ($LiN_2H_5SO_4$)[18] are linked into zigzag chains.

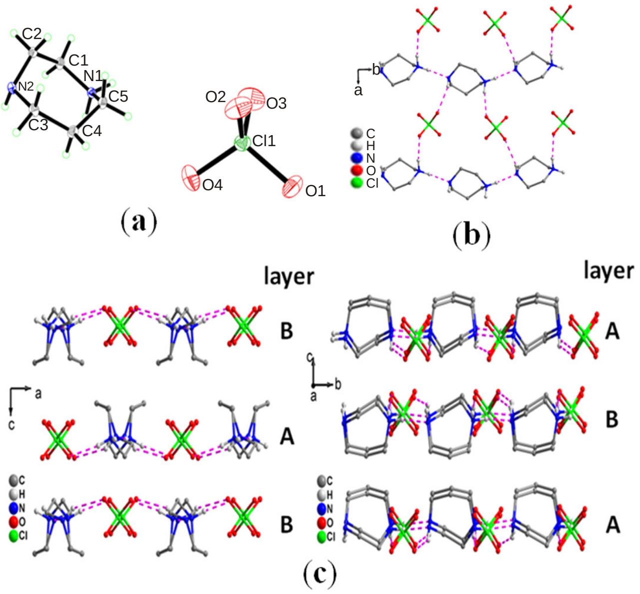

Fig. 1. (a) ORTEP diagram of compound **1**; (b) Single layer structure of compound **1**; (c) Packing diagram viewed along b axis (left) and along a axis (right)

In addition to N-H···N hydrogen bond interaction, there exists N-H···O hydrogen bond interactions, linking molecules into two-dimensional layer structure. Fig. 1c presents the packing mode of compound **1** viewed along the b axis (left) and a axis (right) of the unit cell. This figure also shows that A and B layers in the ab plane are arranged in an alternating ABABAB fashion along the c axis.

Thermal analysis: The DSC measurement for compound **1** in the temperature region of 310-412 K showed one pair of reversible peaks, an exothermic peak at 396.1 K and an endothermic peak at 400.3 K (Fig. 2a). The observed peaks represented one reversible phase transition with a thermal hysteresis of about 4 K. The sharp peaks revealed the discontinuous character of the phase transition, being indicative of a first-order phase transition[19]. Thus, for warming process, $\Delta H = 9.46$ J/g; for cooling process, $\Delta H = 10.08$ J/g, the averaged ΔH is estimated to be 9.77 J/g. For the warming process, $T_C = 400.3$ K, $\Delta S = (9.46/400.3)\ Jg^{-1}K^{-1} = 2.363 \times 10^{-2}\ Jg^{-1}K^{-1}$ while for the cooling process, $T_C = 396.1$ K, $\Delta S = (10.08/396.1)\ Jg^{-1}K^{-1} = 2.545 \times 10^{-2}\ Jg^{-1}K^{-1}$.

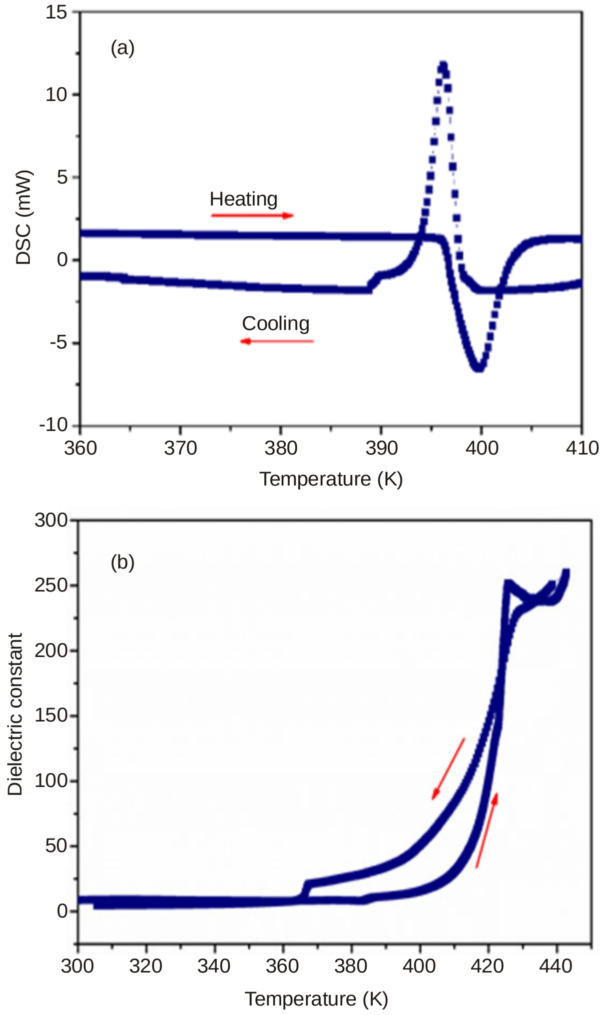

Fig. 2. (a) DSC measurement result of compound **1**; (b) dielectric constants of compound **1** as a function of temperature

Dielectric properties: A phase transition is usually accompanied by the anomaly of dielectric constant near the structural phase transition temperature. Fig. 2b showed the temperature-dependent dielectric constant of compound 1 in powder pressed pellet at the frequency of 1 MHz. Upon heating process, the dielectric constant remained almost unchanged till 410 K and then it sharply increased from about 7 to 250. Upon the following cooling process, reversible dielectric anomaly was observed, suggesting that there is a phase transition. The little temperature difference between DSC peaks and dielectric anomaly may be related to the heating rate and response time.

It is worth noting that the dielectric constant change before and after phase transition in compound **1** is significantly larger than that previously reported in $(Him)_2[KFe(CN)_6]$[20], $[Mn_3(HCOO)_6](H_2O)(CH_3OH)$[21], 4-methylanilinium perchlorate[22] and symmetric diammonium[14] $dabcoHReO_4$. The phase transition temperature is also very high. Based on the structural similarity of compound **1** and its analogies, the order-disorder motions of N-H···N hydrogen bonds and perchlorate may play a crucial role in its phase transition mechanism and the deformation of homopiperazine ring may also be one of the contributors. Unfortunately, the crystal structure of compound **1** at high temperature can not be obtained. The phase transition mechanism should be further studied, but the exhibited switchable dielectric properties of compound **1** will lead homopiperazine to be widely studied in searching for new dielectric materials.

Conclusion

In summary, compound **1** is a new type of switchable dielectric materials with large dielectric change between high and low dielectric states corresponding to the reversible first-order phase transition occurred at ca. 400 K. Homopiperazine may be a good candidate to prepare new dielectric materials.

Supplementary data

CCDC No. 992441 contains the supplementary crystallographic data for this paper. It can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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