Can molecular ferroelectrics challenge pure inorganic ones?

Zhe-Ming Wang and Song Gao*

Molecular materials have attracted much attention due to their advantages of easy modification and fabrication, environmentally friendly and less energy-cost processing, transparent, light weight, mechanical flexibility and possible multi-functionalities, compared to their counter parts of pure inorganic or metallic ones, and many functionalities and properties have been discovered and realized in molecule-based materials [1–4]. Ferroelectrics, as an important class of multifunctional electroactive materials possessing electrically or mechanically switchable, temperature-dependent polarization and/or tunable dielectric responses and nonlinear electro-optic effects, have many applications in temperature sensing, data storage, mechanical actuation, energy harvesting, electromagnetic wave manipulation, and so on [5–8]. The first ferroelectrics, Rochelle salt, which was discovered in 1920–1, is in fact a molecular material, and later a few other molecular systems, such as the well-known potassium dihydrogen phosphate and tri-glycine sulfate, were discovered and developed. However, the rapid development of ferroelectrics took place only after the discovery of pure inorganic ferroelectrics, perovskite barium titanate (BTO) and lead zirconate titanate, because of their large spontaneous polarization ($P_S$), high Curie temperature ($T_C$), large dielectric constant ($\varepsilon'$), and low dielectric loss ($\varepsilon''$ or $\tan\delta$), which are usually unavailable for molecular ferroelectrics [5,6]. These shortcomings for molecular ferroelectrics have been gradually overcome [9–13]; for example, an organic ferroelectrics, croconic acid, has been reported to possess a $P_S$ of 21 $\mu$C cm$^{-2}$ at room temperature, comparable to BTO [9]. Very recently, a research team led by Professor Ren-Gen Xiong in Southeast University, Nanjing, China, has reported [14] that a molecular ferroelectric crystal of diisopropylammonium bromide salt (DIPAB, Figs 1 and 2) showed a $P_S$ of 23 $\mu$C cm$^{-2}$, high $T_C$ of 426 K, large $\varepsilon'$ up to $10^3$, and low $\tan\delta$ of $\sim$0.4%, all close to or beyond the pure inorganic BTO, representing a breakthrough in the research of molecular ferroelectrics.

The DIPAB crystal could be prepared by conventional solution methods under ambient conditions, affording two polymorphs, $\alpha$ and $\gamma$ phases (Fig. 1). At room temperature, the $\alpha$ phase crystallized in the monoclinic chiral space group $P2_1$, which belongs to the polar point group $C_2$. Instead, the $\gamma$ phase is in an orthohombic chiral space group $P2_12_12_1$ within the nonpolar point group $D_2$. So the $\alpha$ phase should be ferroelectrically active, but the $\gamma$ phase is not. Both crystal structures consist of diisopropylammonium cations and Br$^-$ anions, but show different packing patterns with similar N$\cdots$H$\cdots$Br hydrogen bondings, and the two structures are completely ordered.

**Figure 1.** The structures of the three phases of DIPAB, $\alpha$ and $\gamma$ phases at 293 K and the $\beta$ phase at 438 K, and the phase transition routes. Color scheme: C—black, N—cyan, H—white, Br—golden. Green dashed bonds are N$\cdots$H$\cdots$Br hydrogen bonds. Redrawn from the data in [14], by the permission of the authors.

**Figure 2.** (a) The temperature dependence of the dielectric constant of the $\alpha$ DIPAB crystal under several frequencies. (b) The $P_s$ versus $T$ plots measured by a pyroelectric technique, and inset, the ferroelectric hysteresis loops under several temperatures below $T_C$. Redrawn from the data in [14], by the permission of the authors.
When heating the crystals to temperatures above $T_C$ of 426 K, both polymorphs entered a disordered state in which the NH$_2$ group of the diisopropylammonium cation flipped between two positions to add a mirror in the structures, thus resulting in the high temperature $\beta$ phase of a centrosymmetric structure belonging to the monoclinic space group $P2_1/m$ in the nonpolar point group $C_{2h}$. The $\alpha$ to $\beta$ transition is reversible, while $\gamma$ to $\beta$ transition, probably via the $\alpha$ phase, is irreversible (Fig. 1). The transitions are characterized and confirmed by differential scanning calorimetry and second harmonic generation measurements. Accompanied by the phase transition, the $\alpha$ crystal displayed a prominent dielectric anomaly at $T_C = 426$ K, with the peak $\varepsilon'$, as high as $1.6 \times 10^3$ at the lowest frequency of 400 Hz (Fig. 2a). Below $T_C$, the material still possesses rather high $\varepsilon'$ values of several tens and small $\tan\delta$ values of $\sim$0.4%. The polar $\alpha$ crystal displayed typical ferroelectric hysteresis loops (Fig. 2b, inset). Just below the $T_C$, the coercive field is estimated to be 5.0 kV cm$^{-1}$ and the $P_S$ of $\sim$10 $\mu$C cm$^{-2}$, and both increased on further cooling. The $P_S$ value measured using a pyroelectric technique is $23 \mu$C cm$^{-2}$ (Fig. 2b) and further confirmed by the first-principle density functional theory calculations, resulted from the nearly parallel arrangement of the dipoles from the anion to cation in the structure. The $P_S$ of 23 $\mu$C cm$^{-2}$ is close to 26 $\mu$C cm$^{-2}$ of BTO, and the $T_C$ of 426 K higher than 393 K of BTO [5,6], and these data are beyond most known molecular ferroelectrics. The stripes of ferroelectric domains were revealed by the study of piezoresponse force microscopy.

The works [13,14] by Professor Xiong’s team have demonstrated that molecular ferroelectrics with ferroelectric properties of large $P_S$, high $T_C$, large $\varepsilon'$ and low $\varepsilon''$ or $\tan\delta$, comparable to the pure inorganic ferroelectric oxides, are now possible to be obtained, and those disadvantages and limits, such as small $P_S$ and low $T_C$, of molecular ferroelectrics for their practical applications, could be paved. This has opened a new avenue to the applications of those molecular ferroelectrics which are much more environmentally friendly, easy fabrication and less energy-cost processing, lighter weight, and so on, than the pure inorganic oxide counters.

Zhe-Ming Wang and Song Gao
Beijing National Laboratory for Molecular Sciences, College of Chemistry and Molecular Engineering, Peking University, China
*Corresponding author.
E-mail: gaosong@pku.edu.cn

REFERENCES
1. Zhou, H-C, Long, JR and Yaghi, OM. Chem Rev 2012; 112: 673–4.
2. Long, JR and Yaghi, OM. Chem Soc Rev 2009; 38: 1213–4.
3. Cheetham, AK and Rao, CNR. Science 2007; 318: 58–9.
4. Rao, CNR, Cheetham, AK and Thirumurugan, A. J Phys: Condens Matter 2008; 20: 083202.
5. Lines, ME and Glass, AM. Principles and applications of ferroelectrics and related materials. Oxford: Clarendon, 1977.
6. Jona, F and Shirane, G. Ferroelectric crystals. Oxford: Pergamon, 1962.
7. Zhang, W and Xiong, R-G. Chem Rev 2012; 112: 1163–95.
8. Hang, T, Zhang, W and Ye, H-Y et al. Chem Soc Rev 2011; 40: 3577–98.
9. Horiuchi, S, Tokunaga, Y and Giovannetti, G et al. Nature 2010; 463: 789–93.
10. Horiuchi, S and Tokura, Y. Nat Mater 2008; 7: 357–66.
11. Horiuchi, S, Kumai, R and Tokura, Y. Chem Commun 2007; 2321–29.
12. Horiuchi, S, Kagawa, F and Hatahara, K et al. Nat Commun 2012; 3: 1308.
13. Fu, D-W, Zhang, W and Cai, H-L et al. Adv Mater 2011; 23: 5658–62.
14. Fu, D-W, Cai, H-L and Liu, Y et al. Science 2013; 339: 425–8.