Ferroelectric Homochiral Organic Molecular Crystals

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Ferroelectrics based on organic molecular crystals such as thiourea, cyclohexan-1,1'-diacetic acid (CDA), trichloroacetamide (TCAA) and tricyclohexylmethanol (TCHM) or some organic base-inorganic acid salts such as HpyX (Hpy = pyridinium and X=halogen, ClO₄⁻, IO₄⁻, etc.) and HdabcoX (dabco= diazabicyclo[2.2.2]octane; $X = ClO_4^-$, BF_4^- , ReO_4^- , etc.) have been the subject of research for a long time.¹⁻³ However, to explore or develop new ferroelectrics based on unknown pure organic molecular crystals still remains largely unexplored and a great challenge in which the ferroelectric research situation based on homochiral organic compounds and their salts is especially serious and unknown. To our knowledge, there are no examples of homochiral (or optical active) organic compounds reported to be potential ferroelectrics. During our systematical investigation of inorganic-organic hybrid ferroelectrics, we found that pure homochiral compounds (R)-2-methylpiperazine-1,4-diamine (MPADA, 1) and (R)-2-methylpiperazinium bis(dichloroiodate) ((H₂-MPA)(ICl₂)₂, **2**) probably display ferroelectric properties.⁴ Herein we report their crystal structures and possible ferroelectric properties because organic materials are emerging as an alternative to the inorganic counterparts which display efficient molecular nonlinearity, inherent synthetic flexibility, ultrafast response with better processability, higher laser damage threshold, and ease of fabrication and integration into devices.

MPADA was prepared by the reaction of (*R*)-2-methylpiperazine with NaNO₂ and HCl following H₂ reduction, while (H₂-MPA)(ICl₂)₂ can be obtained by the reaction of (*R*)-2-methylpiperazine with HIO₄ and concentrated HCl at room temperature, as shown in Scheme 1.

1 recrystallizes in the solution of water to get $1.6H_2O$ with a chiral space group of $P2_1$ belonging to one of 10 ferroelectric polar point groups, while **2** also directly crystallizes in the chiral space group $P2_1$.⁵ Their powder X-ray diffraction patterns are exactly matched with those fitting by single crystal diffraction patterns. Figure 1 shows that the six-membered ring of piperazine in an asymmetric unit of $1.6H_2O$ has a chair conformation. There are many H-bonds found between NH₂ (amino group) and water, water and the N atom of piperazine ring, and water and water to result in the formation of a three-dimensional (3D) framework through H-bonds (see Supporting Information).

Figure 2 clearly shows that the six-membered ring of piperazine in diprotonated (*R*)-2-methylpiperazine also adopts a chair conformation, while two dichloroiodate anions are almost parallel with a small angle crossing each other. The iodine atom is twocoordinated and not linear ($177.3-178.8^{\circ}$). Also, there are many H-bonds found between Cl and NH₂ (protonated N atom).

Given that the product $1.6H_2O$ and 2 both crystallize in a chiral space group $P2_1$ while it also adopts a polar point group, its piezolelectric properties were investigated. Preliminary studies of single crystal samples indicate that $1.6H_2O$ and 2 are piezo-electricity-active with an approximate d_{33} value of 12.0 and





Figure 1. (left) An asymmetric unit representation of 1 showing that the piperazine ring adopts to the chair conformation. (right) 2D H-bonds net formed through $N \cdots O$ and $O \cdots O$.



Figure 2. (left) An asymmetric unit representation of 2 showing that the piperazine ring adopts to a chair conformation while two dichloroiodate anions are not parallel. (right) 2D H-bonds net formed through $N \cdots O$ and $O \cdots O$.

20.1 pC/N, respectively, still smaller than that of TGS (~47 pC/N,TGS = triglycine sulfate). The space group P_{2_1} is associated with the point group C_2 , one of the 10 polar point groups (C_1 , C_2 , C_s , $C_{2\nu}$, C_4 , $C_{4\nu}$, C_3 , $C_{3\nu}$, C_6 , $C_{6\nu}$) required for ferroelectric behavior. Experimental results indicate that $1.6H_2O$ and 2 display ferroelectric behaviors, as shown in Figure 3, panels a and b with a good dielectric hysteresis loop, respectively. In Figure 3a, the coercive electric field (E_c) reaches 6 kV/cm, much higher than that of TGS (~0.3 kV/cm), while the remanent polarization (P_r) and spontaneous polarization (P_s) are about 0.75 and $1.0 \mu C/cm^2$, respectively, much smaller than that of TGS ($3.5 \mu C/cm^2$) and

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Figure 3. (a) Polarization versus applied electric field approximately along the *b*-axis in $1.6H_2O$. (b) Polarization versus applied electric field approximately along the *b*-axis in 2, while the inset is the ferroelectric loop of TGS measured at the same conditions as those of $1.6H_2O$ and 2.



Figure 4. (a) The temperature-dependence permittivity of 1 · 6H₂O. (b) Crystal morphology of compound **2** showing a good rhomb.

larger than that of Rochelle salt $(0.25 \,\mu\text{C/cm}^2)$. In Figure 3b, the E_c of **2** reaches about 2 kV/cm, much smaller than that of **1**.6H₂O, while the P_r and P_s are about 0.75 and 1.6 $\mu\text{C/cm}^2$, respectively, much smaller than that of TGS and larger than that of Rochelle salt and **1**.6H₂O. The crystal morphology of compound **2** is depicted in Figure 4b showing a pale-yellow good rhomb while **1**.6H₂O is a colorless block.

The preliminary dielectric constant measurements of $1.6H_2O$ and 2 show that they display a relatively high dielectric constant reaching about more than 10 at room temperature. The temperature-dependence permittivity of $1.6H_2O$ (due to the very low melting point (< 30 °C)) shows that the permittivity changes with temperature remain basically unchanged. However, there is a very small anomaly (or gradual increase) found in the measured temperature ranges (about -20 °C), suggesting that probably there is a phase transition occurring in this ferroelectric system. However, differential scanning calorimetry (DSC) measurements exclude the possibility of phase transition because there is no heat anomaly in the DSC diagram (see Supporting Information) at the same temperature (Figure 4).

Similarly, the temperature-dependence permittivity of 2 shows that there is no anomaly found in low and high temperature ranges (Figure 5). DSC measurements confirm this aspect (see Supporting Information). Most of the organic molecular ferroelectric crystals show that there are phase transitions occurring in their solid-state changes. For example, TCAA (its space group $P2_1$) displays two phase transition steps associated with one small dielectric anomaly along the *b*-axis. However, it only probably displays ferroelectric properties approaching the phase transition temperature (at 353 K), P_s reaching $\sim 0.25 \ \mu C/cm^{\circ}$ much smaller than those found in $1 \cdot 6H_2O$ and 2. A typical molecular ferroelectric crystal thiourea displays four phase steps associated with two measurable crystal structures (Pma21 and Pnma).7 As we are aware, $1.6H_2O$ and 2 are the first examples of ferroelectric organic molecular crystals without phase transition which is similar to that found in an inorganic ferroelectric crystal $LiH_3(SeO_3)_2$ also without phase transition.8



Figure 5. The temperature-dependence permittivity of 2. (a) The low temperature range, (b) high temperature range.



About the ferroelectric origin in the two systems, besides Hbonds, we consider that the orientational disorder of two chair conformations of the six-membered ring of piperazine may be in part responsible for the ferroelectric property because this will cause a reversible change of dipolar moment to result in ferroelectricity in the electric field, as shown in Scheme 2. For compound 2, we still consider that the diprotonated piperazien ring can be treated as a chair-conformation neutral piperazine ring. Thus, according to theoretical calculations, the dipolar moments of state (I) and state (II) are 3.02 D and 3.15 D, respectively. Thus two state energies are 417.88 and 417.87 au, respectively, and the energy difference between two states is approximately $0.012a.u. (\sim 0.3 \text{ eV})$. Similarly, the dipolar moments, state energy, and energy difference in compound 2 are 1.90 D and 1.92 D, 307.25 au and 307.24 au, and 0.0042 au (0.1 eV). Thus, a small energy difference can be easily overcome by a high electric field.

In conclusion, the present work has demonstrated that the homochiral organic small molecule with a six-membered ring will open up an avenue for new organic ferroelectrics exploration.

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Supporting Information Available: X-ray crystallographic cif file and additional measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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