

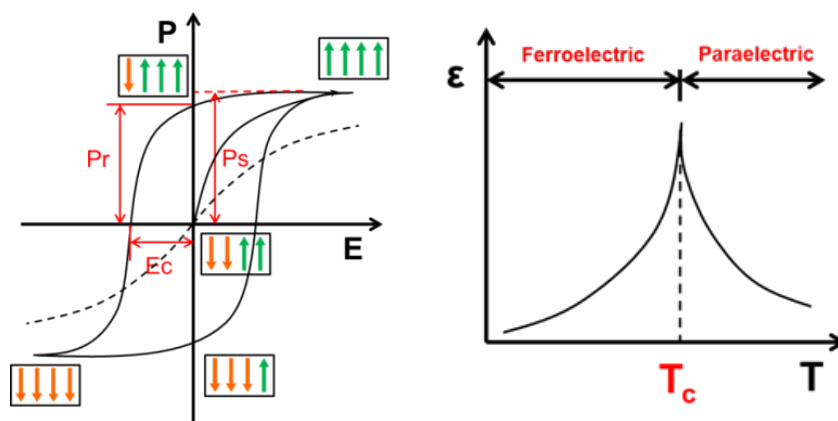
# Molecular Ferroelectrics

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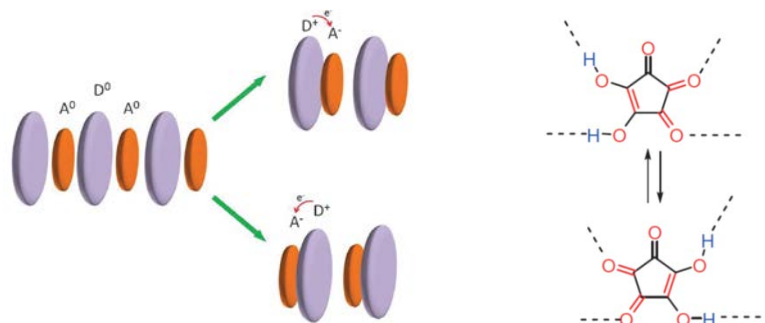
Ferroelectrics are certain materials in which spontaneous electric polarization can be reversed by applying an external electric field. Consequently, the polarization ( $P$ ) as a function of applied field strength ( $E$ ) draws a hysteresis loop under alternating field. Due to this switchable nature, ferroelectric can be used in non-volatile memory elements.<sup>1-2</sup> Moreover, the ferroelectric compounds usually have a Curie temperature  $T_c$  for a paraelectric-to-ferroelectric phase transition. When the temperature approaches  $T_c$ , a sharp increase in dielectric constant ( $\epsilon$ ) is observed as dictated by Curie-Weiss law, which can be exploited for developing high- $\epsilon$  capacitors.<sup>3</sup> (Fig. 1)



**Figure 1:** Hysteresis loop and phase transition in ferroelectrics

The most prevalent ferroelectric materials are perovskites, specifically barium titanate (BTO) and lead zirconate titanate (PZT). However, they are rigid and heavyweight, and require high temperature processing, which limits their application in certain field. Also, high lead content in PZT is a major environmental concern. In this regard, molecular ferroelectrics are drawing attention recently in light of their lightness, flexibility and non-toxicity.<sup>4</sup>

Much of the current literature on molecular ferroelectrics falls into one of three strategies. The first is to utilize the collective electron transfer from donors to acceptors in mixed-stack charge-transfer (CT) complexes. These complexes can undergo a neutral-to-ionic transition and dimerize into electron donor (D)-acceptor (A) pairs, which breaks the center of symmetry in the lattice and leads to polarization, as shown in Fig. One successful example<sup>5</sup> is the tetrathiafulvalene-chloranil (TTF-CA) complex, which shows a hysteresis loop with a large remnant polarization of  $6.3 \mu\text{m}/\text{cm}^2$ . It was noted that the ferroelectricity is mainly attributed to electronic polarization rather than ionic displacement. In addition, Tayi and coworkers<sup>6</sup> reported room-temperature ferroelectricity in supramolecular networks of charge-transfer complexes between a pyromellitic diimide-based acceptor and three donors that are derivatives of naphthalene, pyrene and TTF. Hysteresis loop was observed in all three complexes at 300K with remnant polarization exceeding  $1 \mu\text{m}/\text{cm}^2$ .



**Figure 2:** Polarization switching in CT complexes and proton-transfer compounds

Some organic compounds allow collective site-to-site proton transfer in hydrogen bonds, which switches the polarization. This strategy was demonstrated in some single-component ferroelectrics. In these compounds, additional hidden pseudo-centricity are generated when protons are ignored, facilitating polarization reversal. Tokura group reported a room temperature polarization of  $20 \mu\text{m}/\text{cm}^2$  in croconic acid<sup>7</sup>. In the crystal structure, molecules are arranged in two-dimensional sheets, and each one can transfer two hydroxyl protons to adjacent molecules during the polarization switching. In their follow-up work<sup>8</sup>, room-temperature ferroelectricity and antiferroelectricity was revealed in benzimidazole derivatives with polarization of 5 to  $10 \mu\text{m}/\text{cm}^2$  at room temperature.

Another approach is to utilize the disorder-order transition of ammonium ions in crystal. A metal-organic complex compound  $[\text{C}_2\text{H}_5\text{NH}_3]_2[\text{CuCl}_4]$  possesses a perovskite-type structure<sup>9</sup>, with layers of ethyl-ammonium groups attaching distorted  $\text{CuCl}_6$  octahedra. The ordering of  $[\text{C}_2\text{H}_5\text{NH}_3]^+$  at 247 K results in a paraelectric-ferroelectric phase transition. Notably, at 77 K the remnant polarization reaches  $37 \mu\text{m}/\text{cm}^2$ . Ferroelectricity has been discovered recently in two simple diisopropylammonium (DIPA) salts, DIPA chloride<sup>10</sup> and DIPA bromide<sup>11-12</sup>. DIPA chloride shows a spontaneous polarization of  $8.9 \mu\text{m}/\text{cm}^2$  and a  $T_c$  of 440 K, and DIPA bromide has a large polarization of  $23 \mu\text{m}/\text{cm}^2$ , comparable to that of barium titanate. Their ferroelectricity is believed to arise from the order-disorder behavior of the N atoms.

Despite the progress that has been made in recent years, the field of molecular ferroelectrics is still in its infancy. Further efforts are needed to better understand molecular mechanism, to facilitate crystal engineering by design, and to improve the performance of molecular ferroelectrics.

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