

## Hydrogen-Bonding Molecular Chains for High-Temperature Ferroelectricity

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### Introduction

Developing organic ferroelectrics with advantages of light-weight, flexible, low-cost, and environmentally benign characteristics is in increasing demand, yet needs elaborate chemical designs of objective functions. Recently, the croconic acid has been found to exhibit high polarization [1], and is the first single-component ferroelectric that is based on the cooperative proton tautomerism. In this study, by the direct observations of the electric polarization - field hysteresis on the molecular crystals with  $\beta$ -diketone enol or carboxylic unit, bistability of the hydrogen-bonding chains has been proved to functionalize the ferroelectricity of high polarization performance at room temperature [2].

### Results and Discussion

At the beginning, we explored the Cambridge Structural Database to seek for the polar crystal structures with the pseudo-symmetry. Among single-component molecules containing the  $\beta$ -diketone enol O=C-C=C-OH moieties, several crystal structures can be taken as the candidates as shown in Fig. 1

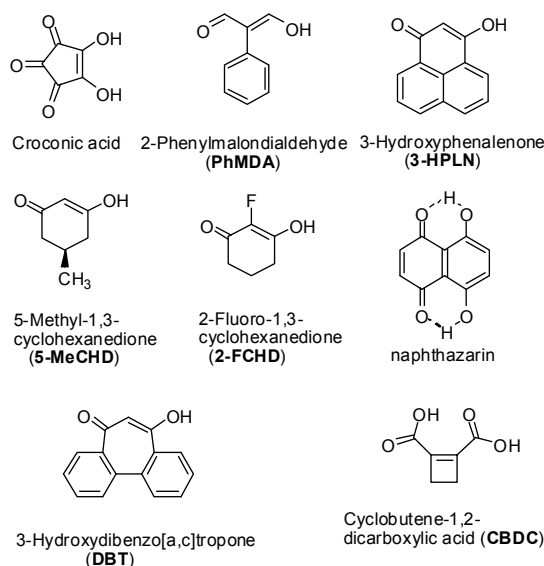


Fig. 1 Single-component organic ferroelectrics and prospective candidates.

We have successfully grown the single crystals and examined the temperature-variation of crystal structures and ferroelectric properties on the PhMDA, 3-HPLN, and CBDC crystals. In these crystals, the uniaxial polarity of the chain satisfies the primary condition of ferroelectricity.

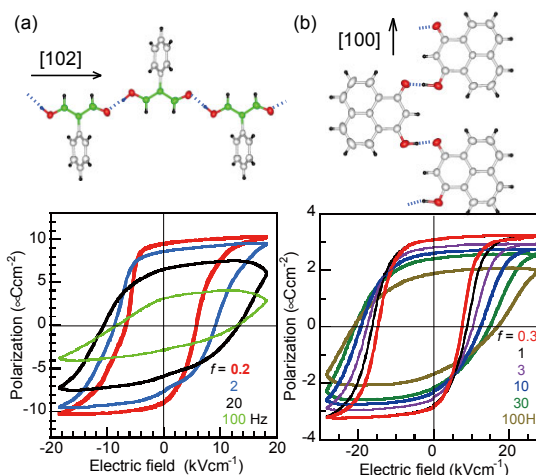


Fig. 2 Hydrogen-bonded chains and polarization hysteresis on (a) PhMDA and (b) 3-HPLN crystals

The infinite sequence of hydrogen bonds (Fig. 2) involving the C=O double bonds (and also C=C bonds in PhMDA and 3-HPLN) are typical of the  $\pi$ -cooperative hydrogen-bonding or the resonance-assisted hydrogen bonding (RAHB), which can effectively strengthen the bonding through the resonance effect. Moreover, each chain can host the bistability necessary for ferroelectricity: all the hydrogen-bonds switch from the O-H $\cdots$ O to O $\cdots$ H-O form at once, and simultaneously also the O=C-C=C-O bond alternation (i.e. the keto-enol transformation) without changing the chemical identity in the PhMDA and 3-HPLN crystals.

This study has disclosed that high-performance ferroelectricity is not specific to only the croconic acid crystal but rather universally existing in many molecular crystals, which can be readily identified by scrutinizing the structural data and the P-E hysteresis (Fig. 2). Beyond the  $\beta$ -diketone enols, carboxylic acid, and the O-H $\cdots$ O bonding-related system focused above, the proton tautomerization represents one of the simplest design principles adaptive to diverse organic compounds including biomolecular system and polymeric ones.

### References

- [1] S. Horiuchi et al., *Nature*, 463, 789 (2010).  
 [2] S.Horiuchi, et. al., *Adv.Mater.* 23, 2098 (2011).

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