Organic enantiomeric high- T_c ferroelectrics

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For nearly 100 y, homochiral ferroelectrics were basically multi-component simple organic amine salts and metal coordination compounds. Single-component homochiral organic ferroelectric crystals with high-Curie temperature (T_c) phase transition were very rarely reported, although the first ferroelectric Rochelle salt discovered in 1920 is a homochiral metal coordination compound. Here, we report a pair of single-component organic enantiomeric ferroelectrics, (*R*)-3-quinuclidinol and (*S*)-3-quinuclidinol, as well as the racemic mixture (*Rac*)-3-quinuclidinol. The homochiral (*R*)- and (*S*)-3-quinuclidinol crystallize in the enantiomorphic-polar point group 6 (C_6) at room temperature, showing mirror-image relationships in vibrational circular dichroism spectra and crystal structure. Both enantiomers exhibit 622F6-type ferroelectric phase transition with as high as 400 K [above that of BaTiO₃ (T_c = 381 K)], showing very similar ferroelectricity and related properties, including sharp step-like dielectric anomaly from 5 to 17, high saturation polarization (7 $\mu\text{C}/\text{cm}^2$), low coercive field (15 kV/cm), and identical ferroelectric domains. Their racemic mixture (*Rac*)-3-quinuclidinol, however, adopts a centrosymmetric point group 2/*m* (C_{2h}), undergoing a nonferroelectric high-temperature phase transition. This finding reveals the enormous benefits of homochirality in designing high- T_c ferroelectrics, and sheds light on exploring homochiral ferroelectrics with great application.

ferroelectricity | homochirality | enantiomer | ferroelectric domains

Homochirality, manifesting as the lack of mirror symmetry, is deservedly one of the most important and basic attributes of nature (1), and continuously inspires scientific and technological advance in a variety of fields (2–6). Homochiral systems not only have been widely involved in chemical processes such as catalysis, chiral separation, enantioselective sensors, and molecular recognition, but also have played a crucial role in specific physical properties due to the compatibility between the corresponding electronic, optical, magnetic, and structural properties (7–13). The intriguing physical phenomena including chiral magnetic effect, chiral superconductivity, and chiral photonics, offer them a wide range of applications in optoelectronics, information storage, polarization optics, spintronic devices, liquid crystal displays, chiroptical switches, and nanomotors (14–21). As an important subject of ferroelectrics in classical physics, it is of great potential to incorporate the homochirality to ferroelectricity to broaden much more fascinating applications. History has shown such interesting relevance between homochirality and ferroelectrics that the first ferroelectric discovered in 1920, i.e., Rochelle salt [$\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$], is a homochiral metal coordination compound (22), known as the first molecular ferroelectric crystal being optically active, while inorganic ferroelectrics, currently dominating in both academic research and industrial manufacture due to their practical applications in memory elements, capacitors, piezoelectric actuators, and sensors, do not have homochiral centers, leading to significant lagging in the strong correlation between homochirality and ferroelectrics (23, 24).

The symmetry of ferroelectrics makes the inherent relationship between ferroelectricity and homochirality much closer than other physical properties. Specifically, ferroelectric phase must adopt one of 10 polar point groups: 1 (C_1), 2 (C_2), *m* (C_{1h}), *mm*2

(C_{2v}), 4 (C_4), *4mm* (C_{4v}), 3 (C_3), *3m* (C_{3v}), 6 (C_6), and *6mm* (C_{6v}) (25), five of which are chiral including 1 (C_1), 2 (C_2), 4 (C_4), 3 (C_3), and 6 (C_6). Homochiral molecules form enantiomorphic crystals of the corresponding handedness, whereas racemic mixtures that contain equal amounts of molecules of each homochirality may crystallize in nonenantiomorphic or even centrosymmetric point groups. In contrast with the achiral or racemic compounds, homochiral compounds get easier to crystallize in the five chiral-polar point groups and thus the formation of ferroelectricity is enabled. Among these 88 species of potential ferroelectric phase transitions, there are 22 chiral-to-chiral ones (Table 1) (26), providing a rational way to develop ferroelectrics. Recently, the demands of finding simple, flexible, low-cost, and environment-friendly supplements to inorganic ferroelectrics have stimulated a renaissance in molecular ferroelectrics and multiferroics (27–36). The key obstacle of realizing a broad range of application of the emerged molecular ferroelectrics is the diverse material design in ferroelectric systems. Therefore, it is highly desired to combine the homochirality with the high degree of structure-property tunability of molecular ferroelectrics in both experiment and theory.

Significance

For a long time, homochirality in ferroelectrics has been studied rarely, although the first ferroelectric Rochelle salt (potassium sodium L-tartrate tetrahydrate) discovered in 1920 is a homochiral one and the optical activities of organic compounds far outweigh the ferroelectric ceramics. Here, we present a pair of enantiomorphic ferroelectrics, (*R*)-3-quinuclidinol and (*S*)-3-quinuclidinol, and the racemic mixture (*Rac*)-3-quinuclidinol. The two single-component homochiral organic molecules of different handedness form high-Curie temperature (T_c) ferroelectric crystals with similarly outstanding ferroelectricity. They are single-component high- T_c homochiral organic ferroelectrics. Our finding suggests the enormous benefits of homochirality in designing high- T_c ferroelectrics. The incorporation of homochirality will greatly expand the applications beyond the traditional fields of ferroelectrics.

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Table 1. The 22 species of chiral-to-chiral ferroelectric phase transitions

Crystal system	Aizu notation (26)*
Monoclinic	2F1
Orthorhombic	222F1; 222F2
Tetragonal	4F1; 422F1; 422F2 (s); 422F4
Trigonal	3F1; 32F1; 32F2; 32F3
Hexagonal	6F1; 622F1; 622F2 (s); 622F6
Cubic	23F1; 23F2; 23F3; 432F1; 432F2 (s); 432F4; 432F3

*F indicates the paraelectric-to-ferroelectric phase transition.

For nearly 100 y, homochiral ferroelectrics were basically multicomponent simple organic anion salts and metal coordination compounds, such as bis(imidazolium) L-tartrate and (*R*)-(-)-3-hydroxyquinuclidinium halides (37–39), seignette salt ($\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$) (22), (3-ammoniopyrrolidinium) NH_4Br_3 , and (3-ammonioquinuclidinium) NH_4Br_3 in our previous report (29). Single-component homochiral organic ferroelectric crystals are very rarely reported, although some single-component organic ferroelectrics without Curie temperature (T_c) were found (40). Additionally, the optical activities (i.e., polarized properties) of organic compounds far outweigh those of ferroelectric ceramics. Thus, designing single-component organic ferroelectric crystals with high- T_c phase transition remains a great challenge.

Homochirality, as a bridge between polar crystal structure and ferroelectricity, actually represents the interdisciplinary of chemistry, physics, and materials, helping the molecular ferroelectric family get enriched purposely, rather than discovered randomly. Herein, we present the systematic ferroelectric investigation on (*R*)-3-quinuclidinol, (*S*)-3-quinuclidinol, and (*Rac*)-3-quinuclidinol. At room temperature, the former two homochiral organic molecules of different handedness form ferroelectric crystals belonging to the enantiomorphic-polar point group 6 (C_6), whereas their racemic mixture forms a nonferroelectric crystal with the centrosymmetric point group $2/m$ (C_{2h}). The T_c of (*R*)- and (*S*)-3-quinuclidinol is as high as 400 and 398 K, respectively. High- T_c phase transition for these two homochiral organic crystals obey the chiral retention rule and paraelectric phase transition should remain at chiral space group (i.e., $P622$), satisfying the requirement of Kleinman's symmetry transformation and leading to the absence of second-harmonic generation (SHG) signal above T_c , exhibiting one of the most important features for chirality. Piezoresponse force microscopy (PFM) results indicate our homochiral organic crystals are 180° domains in unipolar axis group-to-supergroup obeying Curie symmetry principle. Such success in designing above-room-temperature homochiral organic ferroelectrics indicates the invaluable role of homochirality in generating ferroelectricity. This work offers an effective pathway to further explore high-performance homochiral organic ferroelectrics with tremendous practical value in either memory devices or optoelectronic devices.

Results and Discussion

The chiral features of (*R*)-, (*S*)-, and (*Rac*)-3-quinuclidinol were investigated by vibrational circular dichroism (VCD) measurement. VCD is the extension of CD into the infrared region of the spectrum reflecting vibrational transitions, and has been testified as a powerful technique in the structural analysis of chiral molecules (29). CD signal is the difference in the absorption of left-handed circularly polarized light (L-CPL) and right-handed circularly polarized light (R-CPL) and occurs when a molecule contains one or more chiral chromophores (light-absorbing groups). A CD signal can be positive or negative, depending on whether L-CPL is absorbed to a greater extent than R-CPL (CD signal positive) or to a lower extent (CD signal negative). As

expected, the IR spectra of both enantiomorphic crystals are almost the same, while the VCD spectra are nearly mirror images (Fig. 1), providing solid evidence for the enantiomorphic nature of (*R*)- and (*S*)-3-quinuclidinol crystals. In contrast, the (*Rac*)-3-quinuclidinol crystal shows no VCD signal, although similar IR intensity is observed. The VCD spectra of (*R*)- and (*S*)-3-quinuclidinol exhibit five pairs of strong signals ($\Delta\epsilon$) at 1,349; 1,318; 1,309; 1,045; and 816 cm^{-1} , and several relative weak dichroic signals centered at 1,452; 1,342; 1,127; 1,115; 1,079; 1,059; 991; 974; and 939 cm^{-1} , corresponding exactly to the specific IR vibration peaks. From the calculated VCD and IR spectra (*SI Appendix*, Fig. S1), the strongest VCD signal at 1,070 cm^{-1} can be attributed to the C^*-O bond stretch vibration, which also involves the torsional vibrations of the 3-quinuclidinol framework. Note that the calculated IR and VCD spectra show a slight peak shift compared with the measured counterparts. Such a misfit can be attributed to the different molecular configuration under experiment and density-functional theory (DFT) calculation since the calculations of IR and VCD spectra are based on the geometry preoptimization under corresponding B3LYP/6–31G(d) level. The molecular configuration has experienced obvious change after geometry optimization process owing to the structural flexibility.

The single-crystal structure determination reveals that (*R*)-3-quinuclidinol crystallizes in a hexagonal space group $P6_1$ at 298 K (*SI Appendix*, Table S1), belonging to the enantiomorphic-polar point group 6 (C_6). The asymmetric unit contains one 3-quinuclidinol molecule, in which the chiral C3 atom has “*R*” conformation (Fig. 2A), indicating a homochiral molecule. The (*R*)-3-quinuclidinol molecule is ordered with the C–C, C–N, and C–O bond distances in the normal range. One (*R*)-3-quinuclidinol molecule links a neighbor one through O–H...O hydrogen bond, giving rise to an infinite hydrogen-bonded helical chain running along the 6_1 sixfold screw axis in the *c* direction (Fig. 2C and *SI Appendix*, Fig. S2A). The adjacent chains are parallel to each other, and all of the O–H bonds within the chain point to the same direction of the *c* axis. Its enantiomer (*S*)-3-quinuclidinol also adopts a hexagonal space group $P6_5$ at 298 K, in the same 6 (C_6) point group (*SI Appendix*, Table S1). The crystal structure of (*S*)-3-quinuclidinol is enantiomorphic to that of (*R*)-3-quinuclidinol, having a mirror-image relationship (Fig. 2). The chiral C3 atom of the ordered 3-quinuclidinol molecule shows “*S*” conformation (Fig. 2B). The infinite hydrogen-bonded helical chain expands along the 6_5 sixfold screw axis, in the direction of the *c* axis as well, in which the O–H bonds orient along the

Fig. 1. Experimental measured VCD and IR spectra for (*R*)-, (*S*)-, and (*Rac*)-3-quinuclidinol.

Fig. 2. Comparison of the crystal structures of (*R*)- and (*S*)-3-quinuclidinol, showing a mirror-image relationship. The basic unit of (A) (*R*)-3-quinuclidinol and (B) (*S*)-3-quinuclidinol. The infinite hydrogen-bonded helical chains in (C) (*R*)-3-quinuclidinol and (D) (*S*)-3-quinuclidinol. The pink dashed line denotes a mirror plane.

opposite direction of the *c* axis (Fig. 2D and *SI Appendix*, Fig. S2B). Distinct from these two enantiomers, the (*Rac*)-3-quinuclidinol has a monoclinic space group $P2_1/n$ with the centrosymmetric point group $2/m$ (C_{2h}) at 298 K (*SI Appendix*, Table S1). The 3-quinuclidinol molecule is also ordered, while the infinite hydrogen-bonded chain becomes a linear one, and the neighboring chains are antiparallel along the *b* axis (*SI Appendix*, Fig. S3).

Differential scanning calorimetry (DSC) experiments show that each compound undergoes a high- T_c phase transition. A very large endothermic peak upon heating with good reproducibility was observed at $T_{c(R)} = 400$ K for (*R*)-3-quinuclidinol and $T_{c(S)} = 398$ K for (*S*)-3-quinuclidinol, suggesting a first-order phase transition (Fig. 3A and *SI Appendix*, Fig. S4). The T_{cs} of the enantiomers are nearly the same. It is noted that such a high T_c is among the highest ones in molecular ferroelectrics, significantly greater than those for homochiral ones such as Rochelle salt (297 K) (37), bis(imidazolium) L-tartrate (252 K) (34), and (*R*)-3-hydroxyquinuclidinium chloride (340 K) (35), single-component ones including thiourea (169 K) and 2,2,6,6-tetramethylpiperidine 1-oxyl (287 K) (37), as well as even slightly larger than that of the inorganic ferroelectric BaTiO₃ (*SI Appendix*, Table S2). (*Rac*)-3-quinuclidinol also exhibits a first-order phase transition at a lower temperature of $T_{(Rac)} = 365$

K (*SI Appendix*, Fig. S5A). The entropy change (ΔS) accompanying the phase transition is about $34.68 \text{ Jmol}^{-1}\cdot\text{K}^{-1}$ for (*R*)-3-quinuclidinol, $34.57 \text{ Jmol}^{-1}\cdot\text{K}^{-1}$ for (*S*)-3-quinuclidinol, $25.82 \text{ Jmol}^{-1}\cdot\text{K}^{-1}$ for (*Rac*)-3-quinuclidinol, which is significantly larger than those of most of the molecular phase transition compounds (25), and comparable to those of plastic ones (41). The ΔS in the phase transition process is even larger than that in the melting process (*SI Appendix*, Fig. S6), confirming a crystal-to-plastic transition feature. Based on the Boltzmann equation, $\Delta S = R \ln N$, (where R is the gas constant and N is the ratio of the numbers of respective geometrically distinguishable orientations), the $N_{(R)}$, $N_{(S)}$, and $N_{(Rac)}$ are calculated to be 64.8, 63.9, and 22.3, respectively, which suggests an ordered–disordered phase transition with highly disordered component in the structure of high-temperature plastic phase. The phase transitions were then further verified by the temperature dependence of the real part (ϵ') of the complex permittivity ϵ ($\epsilon = \epsilon' + i\epsilon''$, where ϵ'' is the imaginary part of the permittivity). Each compound shows sharp step-like dielectric anomaly around the T_c (Fig. 3B and *SI Appendix*, Fig. S5B) and large thermal hysteresis, similar to those observed in (*R*)-3-hydroxyquinuclidinium halides which undergo plastic transitions (38).

Fig. 3. Phase transitions of (*R*)- and (*S*)-3-quinuclidinol. (A) DSC curves in a heating–cooling mode. (B) Temperature-dependent ϵ' at 1 MHz in the heating–cooling cycles.

Because of the plastic characteristics, it is difficult to determine the single-crystal structure of the high-temperature phase (HTP) above T_c . Variable-temperature powder X-ray diffraction (PXRD) measurements were then performed. In each compound, the PXRD patterns recorded at 298 K are in good accordance with those simulated from single-crystal structure (Fig. 4 A–C), verifying the phase purity. The number of patterns in the HTP is very few in each compound, which is much less than that in the room-temperature phase (RTP), indicating a higher symmetry. The PXRD patterns of (*R*)-3-quinuclidinol and (*S*)-3-quinuclidinol are almost the same in both RTP and HTP phases (Fig. 4 A and B). The Pawley refinements of the PXRD data in HTP reveal that both enantiomers have hexagonal lattices with the most possible space groups of $P6_122$ for (*R*)-3-quinuclidinol and $P6_522$ for (*S*)-3-quinuclidinol (SI Appendix, Fig. S7 A and B), suggesting a ferroelectric phase transition in them.

According to the 22 species of chiral-to-chiral ferroelectric phase transitions summarized in Table 1, only the 622F6 one is suitable for the ferroelectric phase with point group 6 (C_6). In addition, based on the Curie symmetry principle, there is a group-to-supergroup relationship between the ferroelectric and paraelectric space group. The minimal nonisomorphic supergroup of $P6_1$ in (*R*)-3-quinuclidinol and $P6_5$ in (*S*)-3-quinuclidinol is $P6_122$ and $P6_522$, respectively, both belonging to the point group 622. Therefore, the high-temperature paraelectric space group is $P6_122$ for (*R*)-3-quinuclidinol and $P6_522$ for (*S*)-3-quinuclidinol.

For (*Rac*)-3-quinuclidinol, although its PXRD patterns in RTP are different from those of the enantiomers, their PXRD patterns in the HTP are very similar (Fig. 4 A–C). The Pawley refinements also suggest a hexagonal lattice in the HTP, and one of

the most possible space groups is $P6_3/mmc$ (SI Appendix, Fig. S7C), which indicates that the phase transition in (*Rac*)-3-quinuclidinol should be a ferroelastic one. It is known that, in molecular phase transition compounds, the small and flexible organic components such as quinuclidinium, 1,4-diazabicyclo[2.2.2]octanium, and trimethylchloromethylammonium cations usually become disordered in the HTP with a high symmetry (25, 28). In this case, the 3-quinuclidinol should exhibit severe disorder in the HTP of all of the three compounds, which is consistent with the large entropy change observed in the DSC results.

Solid-state NMR analysis was also performed to study the phase transition process. Fig. 4D shows the ^{13}C cross-polarization spectra under magic-angle spinning of the three compounds before and after phase transition. A tentative assignment for the signals has been made (see the cartoon picture in Fig. 4D). It is considered that the signals between 40 and 50 ppm are from site 3 and 6 and the signals between 15 and 28 ppm from site 4 and 7. However, the exact assignment of these signals requires further study. Before transition, the main difference in the spectra of the three compounds lies in the signals of site 3 and 6. For (*Rac*)-3-quinuclidinol, the carbons at site 3 and 6 show the clear difference in the chemical shift, whereas for the enantiomers such chemical shift difference is much smaller. A close look at the signals shows that the signals of site 3 and 6 of (*S*)-3-quinuclidinol have a 50-Hz difference and those of (*R*)-3-quinuclidinol almost merge together. From the chemical structure, the carbons at site 3 and 6 are chemical equivalent and thus anticipated to have the same chemical shift. Thus, the difference in the chemical shifts of the signals of site 3 and 6 can be likely attributed to the different environments caused by the local packing. In this context, the different signals of site 3 and 6 indicate that the carbons

Fig. 4. PXRD patterns and ^{13}C NMR spectra variations in the phase transition process. Temperature-dependent PXRD patterns of (A) (*R*)-3-quinuclidinol, (B) (*S*)-3-quinuclidinol, and (C) (*Rac*)-3-quinuclidinol. (D) Solid-state ^{13}C NMR spectra of (*R*)-, (*S*)-, and (*Rac*)-3-quinuclidinol before and after phase transition. (Inset) Cartoon picture of 3-quinuclidinol.

Fig. 6. Ferroelectric domains and polarization switching for the thin films of (R)-3-quinuclidinol (A–H) and (S)-3-quinuclidinol (I–P) by PFM measurements. (A and I) Vertical and (C and K) lateral PFM phase images. (B and J) Vertical and (D and L) lateral PFM amplitude images. (E and M) Vertical PFM phase and (F and N) amplitude signals as functions of the tip voltage for the selected points, showing local PFM hysteresis and butterfly loops. Vertical phase (G and O) and amplitude (H and P) images recorded after polarization switching with dc bias +130 and +78 V in the thin films of (R)-3-quinuclidinol (G and H) and (S)-3-quinuclidinol (O and P), respectively.

phase and amplitude images, confirming the polarization switching of the ferroelectric domains (*SI Appendix, Figs. S8B and S9B*). Meanwhile, the emerging domains both exhibit hexagonal shape, which indicates that the growth of domains abides by the point-group symmetry of hexagonal crystals. Finally, when the opposite tip biases of −150 and −120 V are applied to the center, the polarization directions of central regions can be switched back, as shown in the box-in-box patterns (*SI Appendix, Figs. S8C and S9C*). Moreover, the amplitude signals in both lateral and vertical components do not change obviously, suggesting that the switching should be 180° ferroelectric one. Overall, the PFM results unambiguously establish the existence of stable and switchable polarization in the thin films of (R)-3-quinuclidinol and (S)-3-quinuclidinol.

Taking the symmetry variation of ferroelectric transition of (R)- and (S)-3-quinuclidinol into account, the Aizu notation 622F6 can be explained by losing six symmetry elements (*SI Appendix, Fig. S10*). For a given ferroelectric structure, the corresponding paraelectric phase structure can be restored by applying the lost twin symmetry to the existing ferroelectric counterpart. Therefore, in the (R)- and (S)-3-quinuclidinol crystal, the structure of paraelectric phase can be imaged through applying the lost symmetry

operations to the ferroelectric $P6_1$ and $P6_5$ structures, respectively. As shown in Fig. 7 B and E, the structure of paraelectric phase can be regarded as twofold disorder in each electroneutral (R)- and (S)-3-quinuclidinol molecule along different twofold rotation axes. These twofold rotation axes strictly obey the symmetry requirement of space group $P6_122$ and $P6_522$.

Keeping the paraelectric structure in mind, we further illustrate the ferroelectric switching process in a quantitative way through DFT calculation. In particular, unlike displacive ferroelectrics, the intermediate structure states during the ferroelectric reversal are typically difficult to develop in order-disorder molecular ferroelectrics. In this case, the symmetry variation of ferroelectric transition 622F6 only has twofold rotation, which provides the possibility to construct the full reversal path between two ferroelectric states. First, the rotation center is set at the centroid of the molecule, which is defined as the weighted average position of constituent atoms. Second, the orientation of the rotation axis is based on the symmetry of paraelectric $P6_122$ space group, rather than arbitrary distribution. Specifically, the direction of the rotation axis of six independent (R)-3-quinuclidinol molecules is along [210], [120], [110], $[\bar{2}10]$, $[\bar{1}20]$, and

Fig. 7. Structural evolution from ferroelectric to paraelectric phase of the enantiomers. Initial structures in ferroelectric phase of (A) (*R*)-3-quinuclidinol and (D) (*S*)-3-quinuclidinol. Simulated structures in paraelectric phase of (B) (*R*)-3-quinuclidinol and (E) (*S*)-3-quinuclidinol. Switched structures in another ferroelectric phase of (C) (*R*)-3-quinuclidinol and (F) (*S*)-3-quinuclidinol. Pink ball stands for rotation center.

[$\bar{1}\bar{1}0$] (Fig. 7A). Herein, the sense of rotation is defined as a pair to artificially keep the polarization along the c axis during the ferroelectric reversal (canceling each other perpendicular to the c axis, including a and b axes). Through sophisticated coordinate transformation and matrix calculation, the structure of each intermediate state during the ferroelectric flipping process can be obtained. Based on these continuous rotating structures, Berry phase method is employed to calculate the microscopic ferroelectric polarization. As shown in Fig. 8A, the calculated value of ferroelectric polarization of (*R*)-3-quinuclidinol crystal shows a continuous change along with the structure parameter λ , which represents different structural states during the ferroelectric switching from $+P$ ($\lambda = +1$) to $-P$ ($\lambda = -1$) polarization state. When $\lambda = \pm 1$, the absolute value of the calculated polarization is about $7.1 \mu\text{C}/\text{cm}^2$, consistent with the experimental one obtained from P - E loops, and the polarization direction is opposite along the crystallographic c axis. During the ferroelectric switching process ($-1 < \lambda < 1$), the polarization value changes monotonously, and turns to zero at $\lambda = 0$, which indicates a reference phase with zero polarization. On the other hand, the energies of two ferroelectric states with different polarizations are equivalent ($\lambda = \pm 1$) and symmetric (Fig. 8B), and the energy barrier for the polarization reversal reaches the maximum at $\lambda = 0$ state. The variation of the energy path shows a typical ferroelectric double-well potential with two opposite polarization states located at two symmetric energy minimums. In addition, similar symmetry breaking and polarization reversal process are also revealed in (*S*)-3-quinuclidinol, where the values of ferroelectric polarizations are exactly the same, but in opposite directions. In the specific operation, due to the mirror symmetry between (*R*)- and (*S*)-3-quinuclidinol crystal, the direction of the rotation axis of six independent (*S*)-3-quinuclidinol molecules is along [$\bar{1}\bar{1}0$], [$1\bar{2}0$], [$2\bar{1}0$], [$1\bar{1}0$], [$1\bar{2}0$], and [$2\bar{1}0$] (Fig. 7D). The energy of ferroelectric phase in (*S*)-3-quinuclidinol crystal and the energy barrier are

exactly the same as its enantiomer (*R*)-3-quinuclidinol, indicating that they are intrinsically equivalent except for chirality.

Conclusions

In conclusion, we have demonstrated a pair of organic enantiomorphic ferroelectrics, (*R*)-3-quinuclidinol and (*S*)-3-quinuclidinol, as well as their racemic mixture (*Rac*)-3-quinuclidinol. Both homochiral (*R*)- and (*S*)-3-quinuclidinol adopt the enantiomorphic-polar

Fig. 8. Ferroelectric switching process of (*R*)- and (*S*)-3-quinuclidinol by DFT calculation. (A) Ferroelectric polarization evolution and (B) energy variation as a function of structure parameter λ .

point group 6 (C_6) at 298 K, and undergo a high- T_c 622 F_6 -type ferroelectric phase transition with a close transition temperature as high as 400 K. The two enantiomorphic ferroelectrics also show similar ferroelectricity and ferroelectric-related properties. The (*Rac*)-3-quinuclidinol has the centrosymmetric point group 2/ m (C_{2h}) at 298 K, exhibiting a nonferroelectric high-temperature phase transition. The homochirality in molecular crystal is quite favorable to crystallize in polar point group, facilitating the precise design of high- T_c ferroelectrics. Considering the abundant existing homochirality, one can expect more homochiral molecular ferroelectrics to be discovered with high performance. The introduction of homochirality in molecular ferroelectrics will greatly broaden the applications beyond the traditional fields of ferroelectrics.

Materials and Methods

Materials. (*R*)-3-quinuclidinol, (*S*)-3-quinuclidinol, and (*Rac*)-3-quinuclidinol are commercially available, purchased from Shanghai Boka-chem Tech Inc. Colorless block crystals were obtained by recrystallization of the purchased product in distilled water.

Thin-Film Preparation. The precursor solutions of (*R*)- and (*S*)-3-quinuclidinol were prepared by dissolving 400 mg of the as-grown crystals in 1 mL methanol. Thin films of (*R*)- and (*S*)-3-quinuclidinol were deposited by spin-

coating the precursor solution onto the cleaned indium-tin-oxide-coated glass at $179 \times g$ for 60 s and then dried at 35 °C for 30 min.

Physical Properties Measurement. Methods of XRD, DSC, dielectric, SHG, P - E hysteresis loop, pyroelectric, and PFM measurements were described previously (28, 29). For the measurement of P - E hysteresis loops, the thickness of the single crystals are 0.38 and 0.32 mm for (*R*)- and (*S*)-3-quinuclidinol crystal, respectively. For single-crystal XRD experiments, Cu- $K\alpha$ -type radiation was used.

Calculation Condition. The spontaneous polarization was evaluated by the Berry phase method developed by King-Smith and Vanderbilt (45). The first-principles calculations were performed within the framework of DFT implemented in the Vienna Ab initio Simulation Package (VASP) (46, 47). The exchange–correlation interactions were treated within the generalized gradient approximation of the Perdew–Burke–Ernzerhof type (48). The energy cutoff for the expansion of the wave functions was fixed to 550 eV. For the integrations over the k space we used a $5 \times 5 \times 2$ k -point mesh. The experimental crystal structure at 298 K was used as the ground state for evaluating the ferroelectric polarization.

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- Wagnière GH (2007) *On Chirality and the Universal Asymmetry* (Wiley-VCH, Weinheim, Germany).
- Siegel JS (2001) Biochemistry. Single-handed cooperation. *Nature* 409:777–778.
- Ellis J (2003) Particle physics: Antimatter matters. *Nature* 424:631–634.
- Kumar A, et al. (2017) Chirality-induced spin polarization places symmetry constraints on biomolecular interactions. *Proc Natl Acad Sci USA* 114:2474–2478.
- Rai R, Krishnan BP, Sureshan KM (2018) Chirality-controlled spontaneous twisting of crystals due to thermal topochemical reaction. *Proc Natl Acad Sci USA* 115:2896–2901.
- Lodahl P, et al. (2017) Chiral quantum optics. *Nature* 541:473–480.
- Fireman-Shoresh S, Popov I, Avnir D, Marx S (2005) Enantioselective, chirally templated sol-gel thin films. *J Am Chem Soc* 127:2650–2655.
- Hodgkinson I, Wu QH (2001) Inorganic chiral optical materials. *Adv Mater* 13:889–897.
- Wang Y, Xu J, Wang Y, Chen H (2013) Emerging chirality in nanoscience. *Chem Soc Rev* 42:2930–2962.
- Torsi L, et al. (2008) A sensitivity-enhanced field-effect chiral sensor. *Nat Mater* 7:412–417.
- Liu M, Zhang L, Wang T (2015) Supramolecular chirality in self-assembled systems. *Chem Rev* 115:7304–7397.
- Ohkoshi S, et al. (2014) 90-degree optical switching of output second harmonic light in chiral photomagnet. *Nat Photonics* 8:65–71.
- Yang Y, da Costa RC, Fuchter MJ, Campbell AJ (2013) Circularly polarized light detection by a chiral organic semiconductor transistor. *Nat Photonics* 7:634–638.
- Bode M, et al. (2007) Chiral magnetic order at surfaces driven by inversion asymmetry. *Nature* 447:190–193.
- Li Q, et al. (2016) Chiral magnetic effect in ZrTe₅. *Nat Phys* 12:550–554.
- Zhang S, et al. (2018) Reciprocal space tomography of 3D skyrmion lattice order in a chiral magnet. *Proc Natl Acad Sci USA* 115:6386–6391.
- Nandkishore R, Levitov LS, Chubukov AV (2012) Chiral superconductivity from repulsive interactions in doped graphene. *Nat Phys* 8:158–163.
- Zhu H, et al. (2018) Observation of chiral phonons. *Science* 359:579–582.
- Chen Q, et al. (2010) Structure and structural transition of chiral domains in oligo(p-phenylenevinylene) assembly investigated by scanning tunneling microscopy. *Proc Natl Acad Sci USA* 107:2769–2774.
- Shopsowitz KE, Qi H, Hamad WY, MacLachlan MJ (2010) Free-standing mesoporous silica films with tunable chiral nematic structures. *Nature* 468:422–425.
- Yeom J, et al. (2015) Chiral templating of self-assembling nanostructures by circularly polarized light. *Nat Mater* 14:66–72.
- Valasek J (1921) Piezo-electric and allied phenomena in Rochelle salt. *Phys Rev* 17:475–481.
- Scott JF (2007) Applications of modern ferroelectrics. *Science* 315:954–959.
- Kim D, et al. (2018) Electron-hole separation in ferroelectric oxides for efficient photovoltaic responses. *Proc Natl Acad Sci USA* 115:6566–6571.
- Shi PP, et al. (2016) Symmetry breaking in molecular ferroelectrics. *Chem Soc Rev* 45:3811–3827.
- Aizu K (1969) Possible species of ferroelastic crystals and of simultaneously ferroelectric and ferroelastic crystals. *J Phys Soc Jpn* 27:387–396.
- Fu DW, et al. (2013) Diisopropylammonium bromide is a high-temperature molecular ferroelectric crystal. *Science* 339:425–428.
- You YM, et al. (2017) An organic-inorganic perovskite ferroelectric with large piezoelectric response. *Science* 357:306–309.
- Ye HY, et al. (2018) Metal-free three-dimensional perovskite ferroelectrics. *Science* 361:151–155.
- Tang YY, et al. (2018) Multiaxial molecular ferroelectric thin films bring light to practical applications. *J Am Chem Soc* 140:8051–8059.
- Liu Y, et al. (2014) Ferroelectric switching of elastin. *Proc Natl Acad Sci USA* 111:E2780–E2786.
- Besara T, et al. (2011) Mechanism of the order–disorder phase transition, and glassy behavior in the metal-organic framework [(CH₃)₂NH₂]₂Zn(HCOO)₃. *Proc Natl Acad Sci USA* 108:6828–6832.
- Jain P, Dalal NS, Toby BH, Kroto HW, Cheetham AK (2008) Order-disorder antiferroelectric phase transition in a hybrid inorganic-organic framework with the perovskite architecture. *J Am Chem Soc* 130:10450–10451.
- Jain P, et al. (2009) Multiferroic behavior associated with an order-disorder hydrogen bonding transition in metal-organic frameworks (MOFs) with the perovskite ABX₃ architecture. *J Am Chem Soc* 131:13625–13627.
- Abhyankar N, et al. (2017) Understanding ferroelectricity in the Pb-free perovskite-like metal-organic framework [(CH₃)₂NH₂]₂Zn(HCOO)₃: Dielectric, 2D NMR, and theoretical studies. *J Phys Chem C* 121:6314–6322.
- Zhao HX, et al. (2011) Transition from one-dimensional water to ferroelectric ice within a supramolecular architecture. *Proc Natl Acad Sci USA* 108:3481–3486.
- Sun Z, Chen T, Luo J, Hong M (2012) Bis(imidazolium) L-tartrate: A hydrogen-bonded displacive-type molecular ferroelectric material. *Angew Chem Int Ed Engl* 51:3871–3876.
- Li PF, et al. (2016) Anomalous rotary polarization discovered in homochiral organic ferroelectrics. *Nat Commun* 7:13635.
- Ye HY, et al. (2013) Molecule-displacive ferroelectricity in organic supramolecular solids. *Sci Rep* 3:2249.
- Horiuchi S, Tokura Y (2008) Organic ferroelectrics. *Nat Mater* 7:357–366.
- Pan Q, et al. (2017) A three-dimensional molecular perovskite ferroelectric: (3-aminopyrrolidinium)RbBr₃. *J Am Chem Soc* 139:3954–3957.
- Kleinmann DA (1962) Nonlinear dielectric polarization in optical media. *Phys Rev* 126:1977–1979.
- Lee D, et al. (2015) Emergence of room-temperature ferroelectricity at reduced dimensions. *Science* 349:1314–1317.
- Bonnel DA, Kalinin SV, Kholkin A, Gruverman A (2009) Piezoresponse force microscopy: A window into electromechanical behavior at the nanoscale. *MRS Bull* 34:648–657.
- King-Smith RD, Vanderbilt D (1993) Theory of polarization of crystalline solids. *Phys Rev B Condens Matter* 47:1651–1654.
- Kresse G, Furthmüller J (1996) Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput Mater Sci* 6:15–50.
- Kresse G, Furthmüller J (1996) Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys Rev B Condens Matter* 54:11169–11186.
- Perdew JP, Burke K, Ernzerhof M (1996) Generalized gradient approximation made simple. *Phys Rev Lett* 77:3865–3868.