Supporting Information

Toward the Targeted Design of Molecular Ferroelectrics: Modifying Molecular Symmetries and Homochirality

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Supplementary Text

"Parent-child relationship" and "grandparent-grandchild relationship":

In the light of the Curie symmetry principle, the symmetry group of the lowtemperature ferroelectric phase should be a non-isomorphic subgroup of the hightemperature paraelectric symmetry group along the direction of the P_s . Such group-tosubgroup relationship can be divided into two types: "parent-child relationship" and "grandparent-grandchild relationship". If the ferroelectric space group is a maximal non-isomorphic subgroup of the paraelectric one along the direction of the P_s , the paraelectric and ferroelectric phases follow a "parent-child" relationship and this ferroelectric should be uniaxial. On the contrary, if the ferroelectric space group is a subgroup but not a maximal non-isomorphic subgroup of the paraelectric one, they follow a "grandparent-grandchild" relationship and this ferroelectric should be multiaxial. As the names imply, there is one generation between "parent-child" and more than one generation between "grandparent-grandchild", where the ferroelectric group is a non-isomorphic subgroup of a maximal non-isomorphic subgroup of the paraelectric one. Through simple analogy, it is easier to distinguish between multiaxial and uniaxial ferroelectrics.

"Momentum matching theory":

With regard to the "momentum matching theory", the momentum here involves various molecular motions, such as translational motion, rotational motion, vibrational motion. The momentums of these motions mainly depend on molecular sizes, weights, and particularly intermolecular interactions between cations and anions, which are like ropes connecting them. To develop multiaxial molecular ferroelectrics, cations and anions are best to exhibit severely orientational disorder and are thus capable of inducing a high symmetry in the paraelectric phase. Meanwhile, they should become totally or partially ordered with specific orientations in the ferroelectric phase, which generally causes a lower symmetry and the consequent striking symmetry breaking. The matching degree between cation and anion plays a crucial role in modulating multiaxial ferroelectricity, so the "momentum matching theory" is put forward reasonably.

For instance, we compare a cation and an anion to the same size of feather and iron, respectively, and then compare the intermolecular interaction to a rope connecting them. As the same force is applied, the movement of the feather is more intense than that of the iron, and it is also difficult for the feather to move the iron through the rope. When the feather is totally disordered, the iron is still ordered. And when the force is strong enough for the iron to become disordered, the rope had already broken, i.e. the compound has melted or decomposed. Moreover, before melted or decomposed, its coercive field is much larger than the dielectric breakdown field, which should be a pyroelectric but not a ferroelectric, since the pyroelectrics will break down electrically (short) before the coercive field is reached.

Take another example, we compare the cation and anion to the same size of feathers, and then compare the intermolecular interactions to various ropes with different elasticity connecting them. The feathers tend to become disordered when external forces are small. If the elasticity of rope is very strong, the rope is difficult to make the feathers become ordered, which means that the phase transition temperature would be very low or there is no phase transition. In contrast, if the rope is very hard, it would limit the movement of the feathers, i.e. the strong intermolecular interaction could decelerate the molecular rotations and makes the cations and anions become ordered. The phase transition temperature would increase and the crystal symmetry

would be lower at room temperature, where the consequent striking symmetry breaking is favorable for multiaxial ferroelectricity.

Crystal System	Aizu Notation							
Triclinic	$1F1(1)^{a}$							
Monoclinic	2F1 (2/2); mF1 (2/2); 2/mF1 (2); 2/mFm (1); 2/mF2 (1)							
Orthorhombic	222F1 (4/2); 222F2 (1); mm2F1 (4/2); mm2Fm (2/2); mmmF1 (4); mmmFm (2); mmmFmm2 (1)							
Tetragonal	$4F1 (4/2); \ \overline{4}F1 (4/2); \ \overline{4}F2 (1); 4/mF1 (4); 4/mFm (2); 4/mF4 (1); 422F1 (8/2); 422F2(s) (2); 422F4 (1); 4mmF1 (8/2); 4mmFm (4/2); \ \overline{4}2mF1 (8/2); \ \overline{4}2mF2(s) (2); \ \overline{4}2mFm (4/2); \ \overline{4}2mFmm2 (1); 4/mmmF1 (8); 4/mmmFm(s) (4); 4/mmmFm(p) (4); 4/mmmFmm2(s) (2); \ 4/mmmF4mm (1)$							
Trigonal	$3F1 (3/2); \ \overline{3}F1 (3); \ \overline{3}F3 (1); 32F1 (6/2); 32F2 (3/2); 32F3 (1); 3mF1 (6/2); 3mFm (3/2); \overline{3}mF1 (6); \ \overline{3}mF2 (3); \ \overline{3}mFm (3); \ \overline{3}mF3m (1)$							
Hexagonal	6F1 (6/2); $\overline{6}F1$ (6/2); $\overline{6}Fm$ (3/2); $\overline{6}F3$ (1); 6/mF1 (6); 6/mFm (3); 6/mF6 (1); 622F1 (12/2); 622F2(s) (3); 622F6 (1); 6mmF1 (12/2); 6mmFm (6/2); $\overline{6}m2F1$ (12/2); $\overline{6}m2Fm(s)$ (6/2); $\overline{6}m2Fm(p)$ (6/2); $\overline{6}m2Fmm2$ (3/2); $\overline{6}m2F3m$ (1); 6/mmmF1 (12); 6/mmmFm(s) (6); 6/mmmFm(p) (6); 6/mmmFmm2(s) (3); 6/mmmF6mm (1)							
Cubic	23F1 (12/2); 23F2 (3); 23F3 (4/2); $m\overline{3}F1$ (12); $m\overline{3}Fm$ (6); $m\overline{3}Fmm2$ (3); $m\overline{3}F3$ (4); 432F1 (24/2); 432F2(s) (6); 432F4 (3); 432F3 (4); $\overline{4}3mF1$ (24/2); $\overline{4}3mFm$ (12/2); $\overline{4}$ $3mFmm2$ (3); $\overline{4}3mF3m$ (4/2); $m\overline{3}mF1$ (24); $m\overline{3}mFm(s)$ (12); $m\overline{3}mFm(p)$ (12); $m\overline{3}mFmm2$ (6); $m\overline{3}mF4mm$ (3); $m\overline{3}mF3m$ (4)							

 Table S1. 88 species of potential paraelectric-to-ferroelectric phase transitions.

^a F indicates the paraelectric-to-ferroelectric phase transition, while p and s indicate that the symmetry elements of the ferroelectric phase correspond to the principal and side symmetric axes in the paraelectric phase, respectively. State numbers are included in the round brackets, while the simple numbers represent reversible ferroelectrics. The number 1 belongs to 18 types of uniaxial ferroelectrics, and numbers greater than 1 are the sums of equivalent polar directions of multiaxial ferroelectrics. Besides, for complex state numbers such as "3/2", "4/2" and so on, the common number 2 on the right of the forward slash indicates reorientable ferroelectrics, whereas the numbers on the left of it denote the sums of equivalent polar directions.

Compound	Quinuclidine		Quinuclidinum hydrochloride		Quinuclidinum hydrobromide		Quinuclidinum hydroiodine		
Temperature	93 K	293 K	293 K	363 K	223 K	323 K	223 K	353 K	443 K
Crystal system Space group	Trigonal P3	Cubic Pm3m	Monoclinic $P2_1/m$	Tetragonal P4/nmm	Orthorhombic Pmn2 ₁	Tetragonal P4/n	Tetragonal -	Cubic $P\overline{4}3m$	Cubic Fm3m
a	6.0552	8.8622	6.2373	6.6022	7.162	6.7555	9.834	9.9331	9.9928
b	6.0552	8.8622	6.7993	6.6022	9.4848	6.7555	9.834	9.9331	9.9928
С	9.978	8.8622	9.4836	9.4601	6.0882	9.622	9.796	9.9331	9.9928
α	90	90	90	90	90	90	90	90	90
β	90	90	90.580	90	90	90	90	90	90
γ	90	90	90	90	90	90	90	90	90
V	316.8	696.02	402.17	412.36	413.57	439.13	947.3	980.06	997.8

Table S2. Lattice parameters of quinuclidine and quinuclidinum halides.





Figure S1. The crystal structure of quinuclidinum at 93 K.

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Figure S2. The crystal structure of quinuclidinum at 293 K.





Figure S3. The crystal structure of quinuclidinum hydrochloride at 293 K.



Figure S4. The crystal structure of quinuclidinum hydrochloride at 363 K.

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Datablock p21 - ellipsoid plot



Figure S5. The crystal structure of quinuclidinum hydrobromide at 223 K.



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Figure S6. The crystal structure of quinuclidinum hydrobromide at 323 K.

Datablock P-43M - ellipsoid plot



Figure S7. The crystal structure of quinuclidinum hydroiodine at 353 K.

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Figure S8. The crystal structure of quinuclidinum hydroiodine at 443 K.