Electronic Supplementary Information

Highest-T_c organic enantiomeric ferroelectrics obtained by F/H substitution

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Experimental details

Materials. Iodomethane, Fluoromethyl iodide, (*R*)-, (*S*)- and (*Rac*)-(3-fluoropyrrolidinium) hydrochloride (98%), 1-Methylpyrrolidine and pyrrolidinium (98%) are commercially available from sigma-Aldrich.

Synthesis.

DMPI. To a 250 ml beaker containing 10 g pyrrolidinium dissolved in the 50ml THF. 2.5N Methyl iodide was slowly injected into the flask under ice bath. The crude DMPI was obtained as white solid after stirring for 3h at room temperature. Then it was recrystallized in the water. Colorless crystals with yields of 88% was obtained after a few days. ^{1}HNMR. δ_H (400 MHz, D_2O) 3.59 (4 H, s), 3.21 (6 H, s), 2.30 (4 H, s).

***R*- DMFPI.** To a 250 ml beaker containing 10 g *R* - 3-fluoropyrrolidinium hydrochloride was added a sodium hydroxide aqueous solution (3.2 g of sodium hydroxide in 50 ml of deionized water). After 2h, the organic part was extracted by 50ml×3 dichloromethane. The organic layer was collected, dried and concentrated. Fluoropyrrolidinium was then obtained as colorless oil by vacuum distillation. Then it was directly dissolved in the 50ml THF. 2.5N Methyl iodide was slowly injected into

the flask under ice bath. The crude *R* - DMFPI was obtained as white solid after stirring for 3h at room temperature. Then it was recrystallized in the ethanol/water(1:1 in volume). Colorless crystals with yields of 65% was obtained after 7 days. ^{1}HNMR. δ_H (400 MHz, D_2O) 5.63 (1 H, d, *J* 53.2), 4.13 - 3.66 (4 H, m), 3.33 (6 H, d, *J* 19.8), 2.90 - 2.50 (2 H, m).

***S*- DMFPI.** To a 250 ml beaker containing 10 g *S* - 3-fluoropyrrolidinium hydrochloride was added a sodium hydroxide aqueous solution (3.2 g of sodium hydroxide in 50 ml of deionized water). After 2h, the organic part was extracted by 50ml×3 dichloromethane. The organic layer was collected, dried and concentrated. *S*-3- Fluoropyrrolidinium was then obtained as colorless oil by vacuum distillation. Then it was directly dissolved in the 50ml THF. 2.5N Methyl iodide was slowly injected into the flask under ice bath. The crude *S* - DMFPI was obtained as slight yellow solid after stirring for 3h at room temperature. Then it was recrystallized in the ethanol/water(1:1 in volume). Colorless crystals with yields of 60% was obtained after 7 days. ^{1}HNMR. δ_H (400 MHz, D_2O) 5.62 (1 H, dd, *J* 52.9, 3.9), 4.14 - 3.65 (4 H, m), 3.32 (6 H, d, *J* 20.1), 2.71 (2 H, dddd, *J* 33.9, 24.5, 15.9, 7.8).

***Rac*- DMFPI.** To a 250 ml beaker containing 10 g *Rac* - 3-fluoropyrrolidinium hydrochloride was added a sodium hydroxide aqueous solution (3.2 g of sodium hydroxide in 50 ml of deionized water). After 2h, the organic part was extracted by 50ml×3 dichloromethane. The organic layer was collected, dried and concentrated. Fluoropyrrolidinium was then obtained as colorless oil by vacuum distillation. Then it was directly dissolved in the 50ml THF. 2.5N Methyl iodide was slowly injected into the flask under ice bath. The crude *Rac* - DMFPI was obtained as white solid after stirring for 3h at room temperature. Then it was recrystallized in the ethanol/water(1:1 in volume). Colorless crystals with yields of 69% was obtained after 7 days. ^{1}HNMR. δ_H (400 MHz, D_2O) 5.62 (1 H, dd, *J* 53.3, 4.3), 4.17 - 3.66 (4 H, m), 3.32 (6 H, d, *J* 19.7), 2.95 - 2.46 (2 H, m).

Measurements. Single-crystal X-ray diffraction data were performed using Mo-Kα radiation (λ = 0.71073) on a Rigaku Saturn 924 diffractometer in the ω scan mode. We used the CrystalClear software package to process the data. The crystal structures were solved by using the SHELXLTL software package. To record PXRD patterns, we used the Rigaku D/MAX 2000 PC X-ray diffraction instrument. We used the NETZSCH DSC 200F3 instrument under a nitrogen atmosphere to record DSC curves. The dielectric measurements were performed on an automatic impedance Tonghui 2828 analyzer. For SHG experiments, an unexpanded laser beam with low divergence (pulsed Nd:YAG at a wavelength of 1064 nm, 5 ns pulse duration, 1.6 MW peak power, 10 Hz repetition rate) was used. The instrument model is Ins 1210058, INSTEC Instruments, while the laser is Vibrant 355 II, OPOTEK. The double-wave method for recording polarization−electric field hysteresis loops was carried out for thin film sample on a home-built system consisting of programmable waveform generator (Agilent, Model: 33521A), high voltage amplifier (Trek, Model: 623B) and programmable low-current electrometer (Keithley, Model: 6514). PFM visualization of the ferroelectric domain structures was carried out using a commercial atomic force microscope system (MFP-3D, Asylum Research). We used conductive Pt/Ir-coated silicon probes (EFM, Nanoworld) to study domain imaging and polarization switching with a resonant-enhanced PFM mode for enhancing the signal.

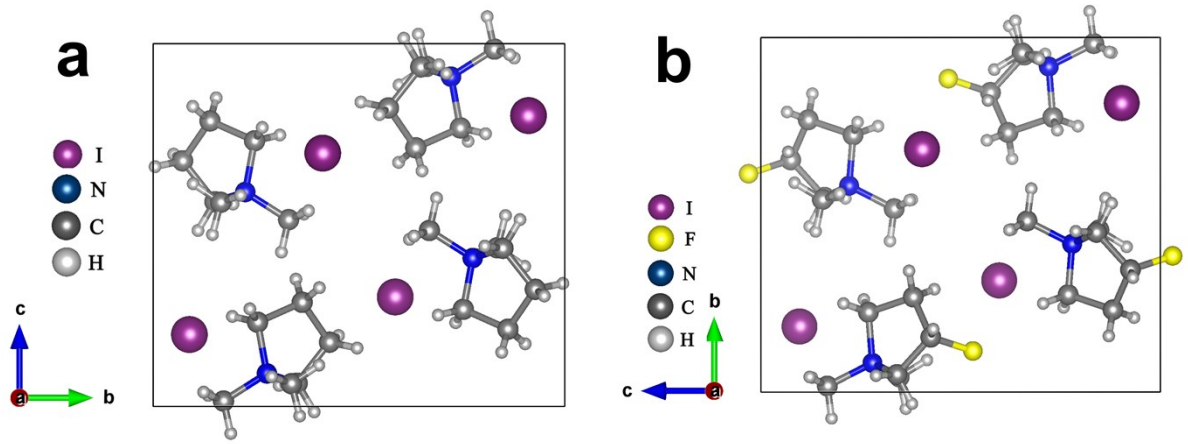

Figure S1. Crystal structures of (a) DMPI and (b) (*Rac*)- DMFPI at 293K.

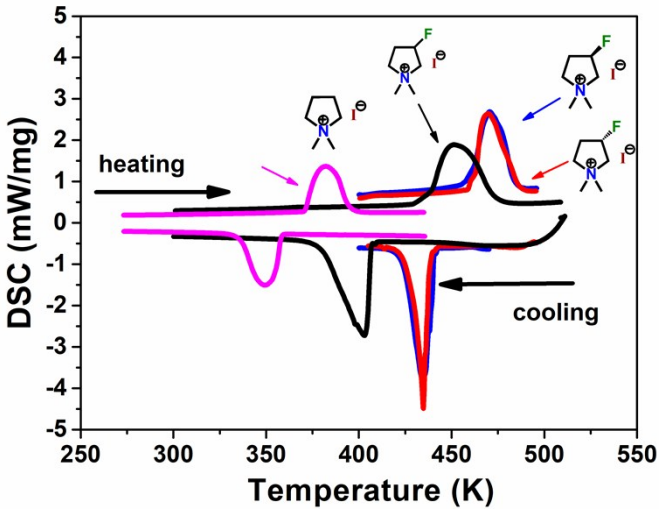

Figure S2. DSC curves for DMPI, and (*R*)-, (*S*)-, (*Rac*)-DMFPI.

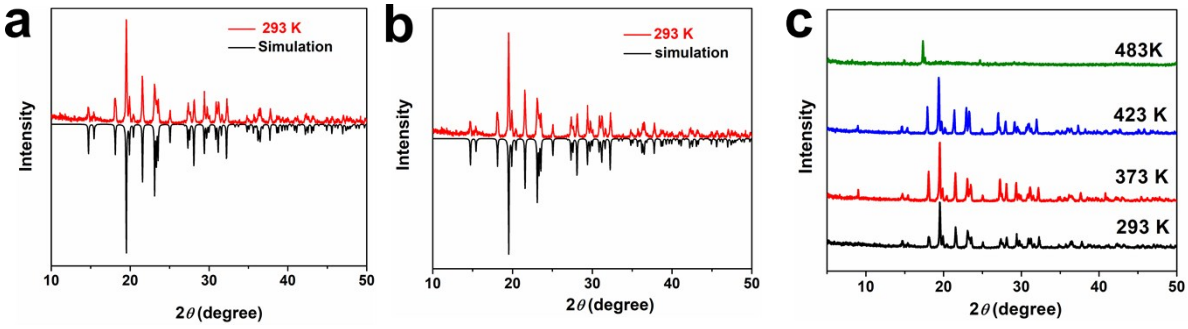

Figure S3. Patterns of the powder X-rays diffraction (PXRD) of (a) (*R*)-DMFPI and (b) (*S*)-DMFPI at 293 K match well with the simulated ones, verifying the purity of the bulk phase. (c) The variable-temperature PXRD data of (*R*)-DMFPI.

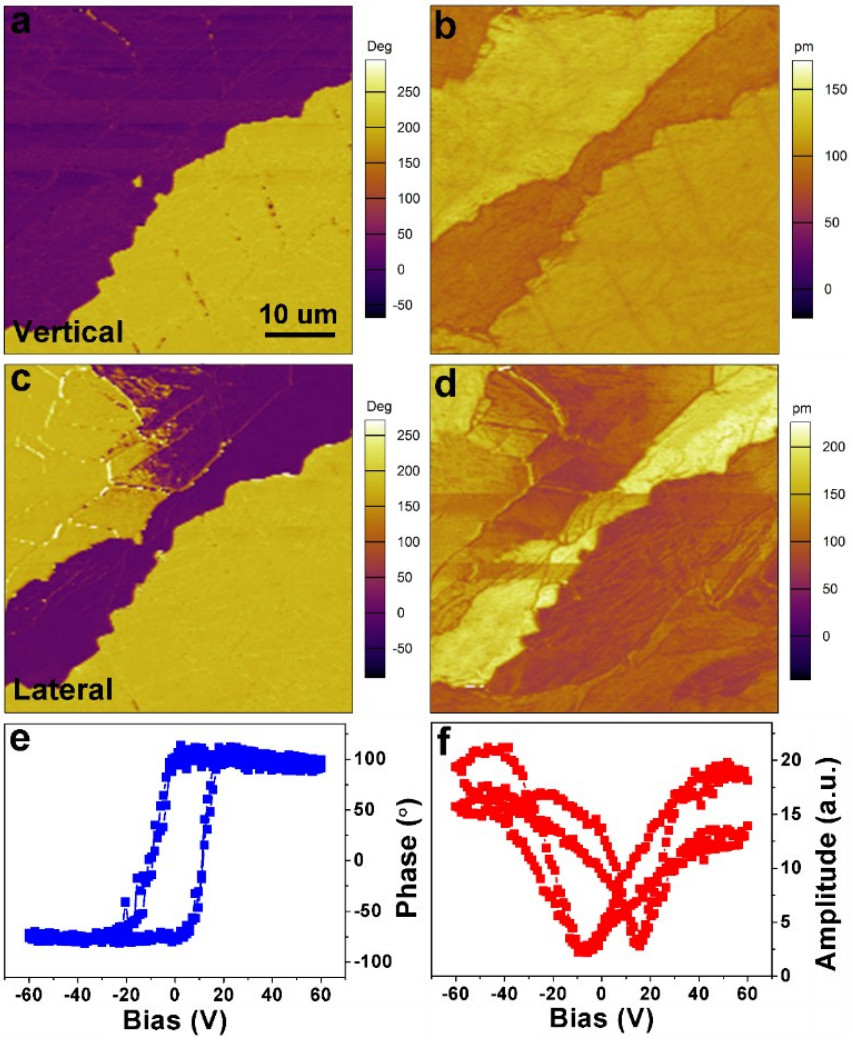

Figure S4. Vertical phase (a) and amplitude (b) images and lateral phase (c) and amplitude (d) images of the PFM for the thin film of (*S*)-DMFPI. (e) Phase and (f) amplitude signals as functions of the tip voltage for a selected point, showing local PFM hysteresis loops.

Calculation of polarization of (*R*) and (*S*)-DMFPI according to a point charge model

According to the crystal structure data collected at 293 K, we select a unit cell and assume that the centers of the positive charges of the (*R*)-DMFPI cations and the negative charges of iodine ions are located on the N atoms and I atoms, respectively.

Atoms	Atom coordinate		Coordinate of charge center
I	I1 (0.03752, 0.6215, 0.32607)	I5 (-0.03752, 0.1215, 0.67393)	(0.5, 0.1215, 0.25)
	I2 (1.03752, 0.6215, 0.32607)	I6 (0.96248, 0.1215, 0.67393)	
	I3 (-0.03752, 0.1215, -0.32607)	I7 (0.03752, -0.3785, 0.32607)	
	I4 (0.96248, 0.1215, -0.32607)	I8 (1.03752, -0.3785, 0.32607)	
N	N1 (0.4048, 0.1314, 0.2792)		(0.4048, 0.1314, 0.2792)

$P_s = \lim \frac{1}{V} \sum q_i r_i$

$= (q_I r_I + q_N r_N) / V$

$= [(-e \times 0.1215) + (e \times 0.1314)] \times 2 \times b/V$

$= [-0.0099 \times 2 \times 1.6 \times 10^{-19} \times 7.6228 \times 10^{-10}\ \text{C m}] / (444.75 \times 10^{-30}\ \text{m}^3)$

$= -0.543 \times 10^{-2}\ \text{C m}^{-2}$

$|Ps| = 0.543 \times 10^{-2}\ \text{C m}^{-2} = 0.543\ \mu\text{C cm}^{-2}$

Atoms	Atom coordinate		Coordinate of charge center
I	I1 (1.0375, 0.7177, 0.32607)	I5 (0.9625, 0. 2177, 0.67393)	(0.5, 0.2177, 0.25)
	I2 (0.0375, 0.7177, 0.32607)	I6 (-0.0375, 0. 2177, 0.67393)	
	I3 (0.9625, 0.2177, -0.32607)	I7 (1.0375, -0.2823, 0.32607)	
	I4 (-0.0375, 0. 2177, -0.32607)	I8 (0.0375, -0.2823, 0.32607)	
N	N1 (0.4047, 0.2067, 0.2794)		(0.4047, 0.2067, 0.2794)

$P_s = \lim \frac{1}{V} \sum q_i r_i$

$= (q_I r_I + q_N r_N) / V$

$= [(-e \times 0.2177) + (e \times 0.2067)] \times 2 \times b/V$

$= [-0.011 \times 2 \times 1.6 \times 10^{-19} \times 7.6205 \times 10^{-10}\ \text{C m}] / (444.22 \times 10^{-30}\ \text{m}^3)$

$= -0.604 \times 10^{-2}\ \text{C m}^{-2}$

$|Ps| = 0.604 \times 10^{-2}\ \text{C m}^{-2} = 0.604\ \mu\text{C cm}^{-2}$

Table S1. Crystal data and structure refinements for (*R*) and (*S*)-DMFPI.

Compound	**(*R*)-DMFPI**		**(*S*)-DMFPI**	
Temperature (K)	**293**	**473**	**293**	**473**
Formula	**C6 H13 F N, I**	**---**	**C6 H13 F N, I**	**---**
Formula weight	**245.07**	**---**	**245.07**	**---**
Crystal system	**Monoclinic**	**Cubic**	**Monoclinic**	**Cubic**
Space group	***P* 2_1**	**---**	***P* 2_1**	**---**
***a*, *b*, *c* (Å)**	**5.9613(3)** **7.6228(3)** **10.1630(4)**	**10.123(13)** **10.123(13)** **10.123(13)**	**5.9585(2)** **7.6205(3)** **10.1558(4)**	**10.119(3)** **10.119(3)** **10.119(3)**
***α*, *β*, *γ* (°)**	**90** **105.627(4)** **90**	**90** **90** **90**	**90** **105.571(4)** **90**	**90** **90** **90**
Volume /Å^3	**444.75(3)**	**1037(4)**	**444.22(3)**	**1036.1(9)**
Z	**2**	**---**	**2**	**---**
Density/g cm^{-3}	**1.830**	**---**	**1.832**	**---**
***R*1**	**0.0185**	**---**	**0.0184**	**---**
***wR*2**	**0.0477**	**---**	**0.0474**	**---**
GOF	**1.004**	**---**	**1.002**	**---**

Table S2. Crystal data and structure refinements for (*Rac*)-DMFPI and DMPI.

Compound	**(*Rac*)-DMFPI**		**DMPI**	
Temperature (K)	**293**	**473**	**293**	**423**
Formula	**C6 H13 F N, I**	**---**	**C6 H14 N, I**	**---**
Formula weight	**245.07**	**---**	**227.08**	**---**
Crystal system	**Monoclinic**	**Cubic**	**Monoclinic**	**Hexagonal**
Space group	***P*** 2_1***/c***	**---**	***P*** 2_1***/n***	**---**
***a*, *b*, *c* (Å)**	**7.2723(1)** **10.4559(2)** **11.9429(3)**	**10.120(3)** **10.120(3)** **10.120(3)**	**7.2325(2)** **11.9157(3)** **10.4951(3)**	**6.9558(18)** **6.9558(18)** **5.829(3)**
***α*, *β*, *γ* (°)**	**90** **97.868(2)** **90**	**90** **90** **90**	**90** **94.932(2)** **90**	**90** **90** **120**
Volume /Å^3	**899.57(3)**	**1036.4(10)**	**901.12(4)**	**244.22(19)**
Z	**4**	**---**	**4**	**---**
Density/g cm^{-3}	**1.810**	**---**	**1.674**	**---**
***R*1**	**0.0170**	**---**	**0.0199**	**---**
***wR*2**	**0.0458**	**---**	**0.0510**	**---**
GOF	**1.002**	**---**	**1.003**	**---**