Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

A homochiral polar molecular piezoelectric material with phase transition and high piezoelectricity precisely designed by cyanomethyl group substitution†

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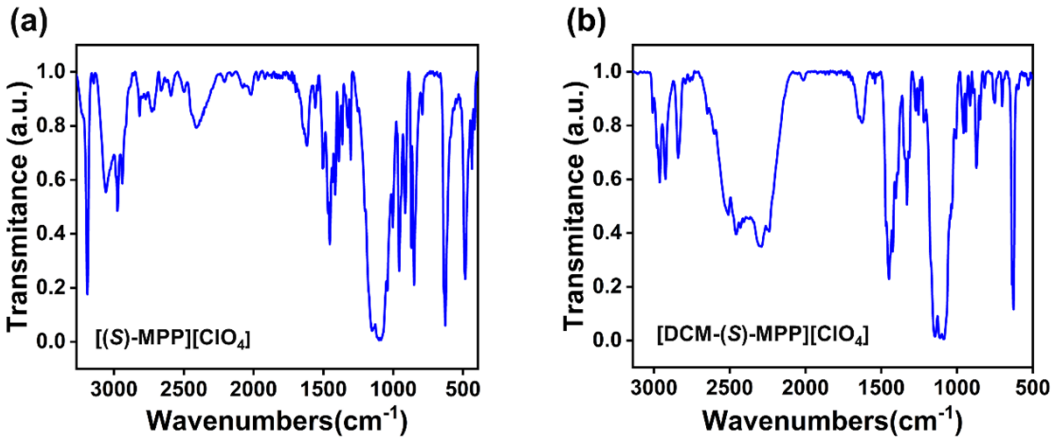

Fig. S1. The infrared absorption spectrums of [(*S*)-MPP][ClO_4] (a)and [DCM-(*S*)-MPP][ClO_4] (b), at room temperature.

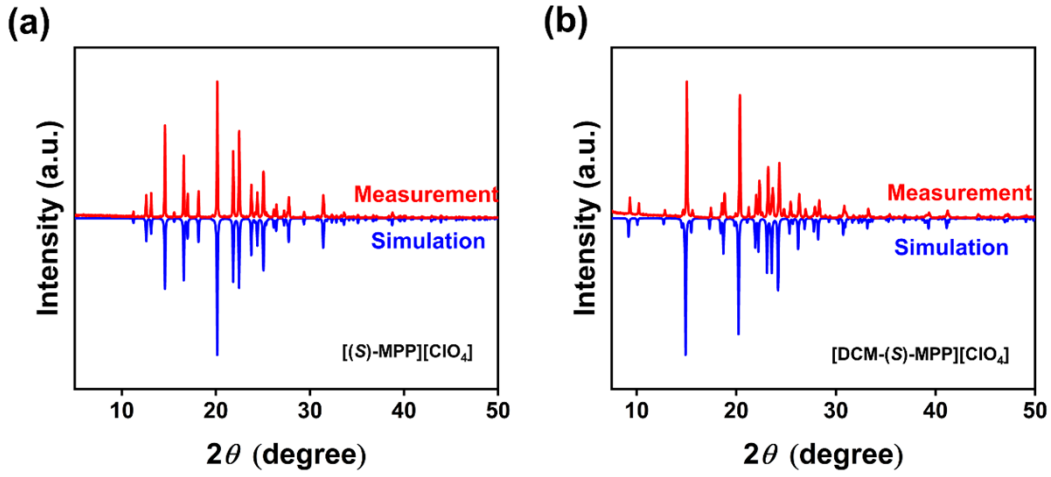

Fig. S2. The PXRD patterns of [(*S*)-MPP][ClO_4] (a) and [DCM-(*S*)-MPP][ClO_4] (b), at room temperature.

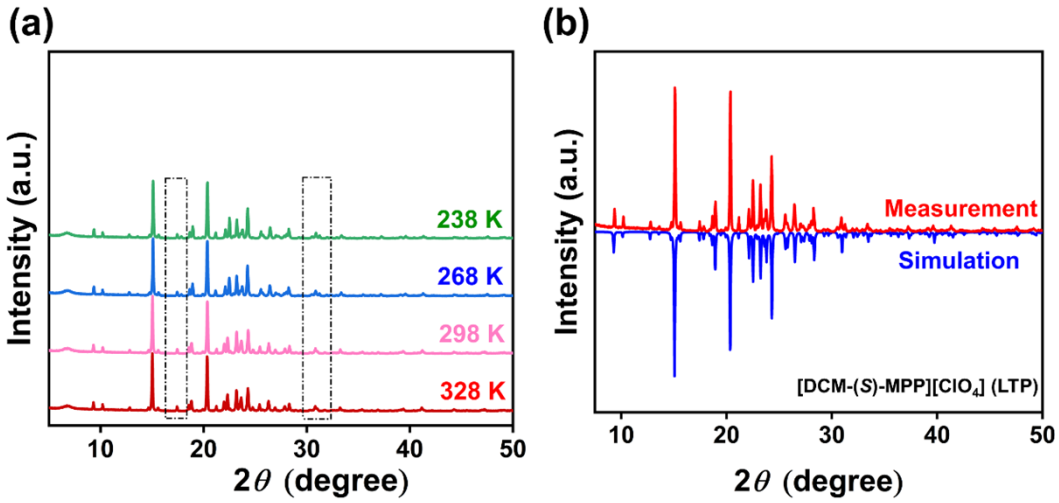

Fig. S3. The Variable-temperature PXRD patterns of [DCM-(*S*)-MPP][ClO_4] (a) and the PXRD patterns of [DCM-(*S*)-MPP][ClO_4] at LTP (b).

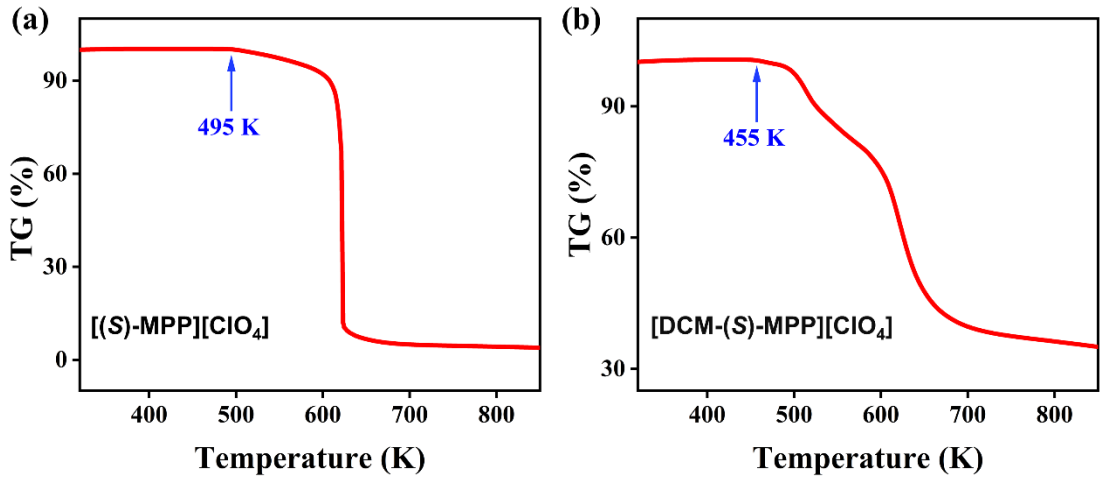

Fig. S4. Thermogravimetric analysis (TGA) curves of [(*S*)-MPP][ClO_4] (a) and [DCM-(*S*)-MPP][ClO_4] (b).

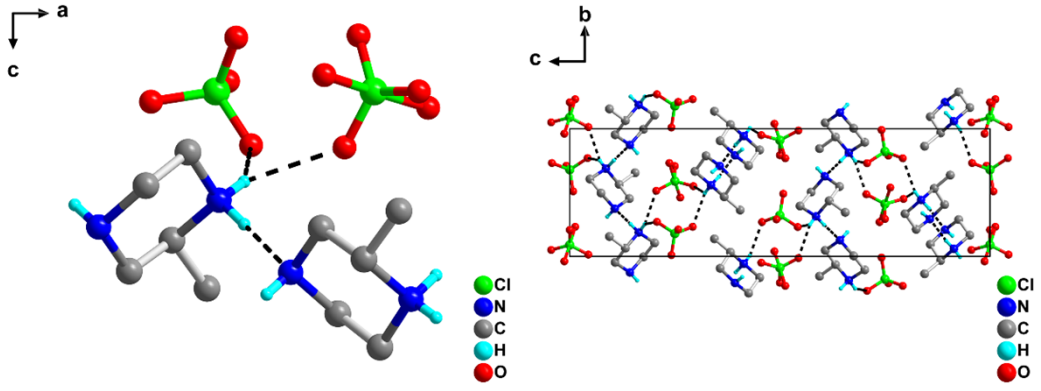

Fig. S5. Hydrogen bond diagram for [(*S*)-MPP][ClO_4]. The black dotted lines represent hydrogen bonds. For clarity, some H atoms are omitted.

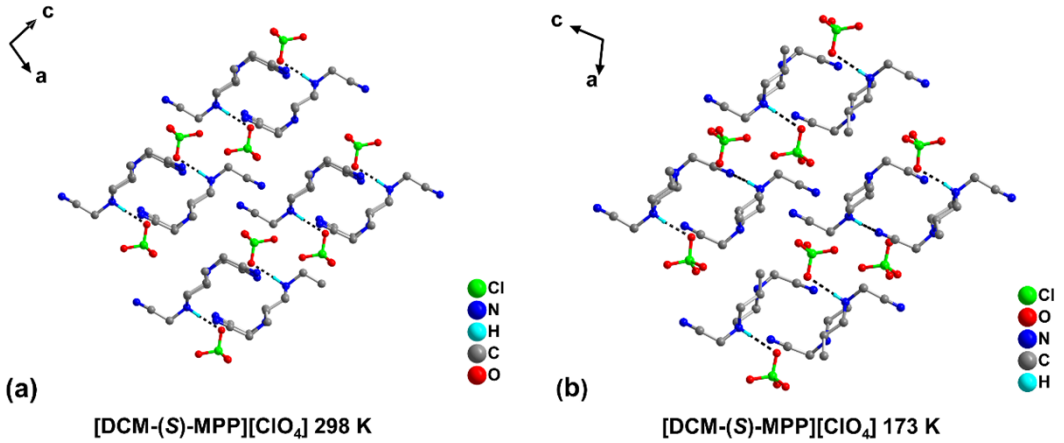

Fig. S6. Diagram of hydrogen bonding for [DCM-(*S*)-MPP][ClO_4] at 298 K (a) and 173 K (b). The black dotted lines represent hydrogen bonds. For clarity, some H atoms are omitted.

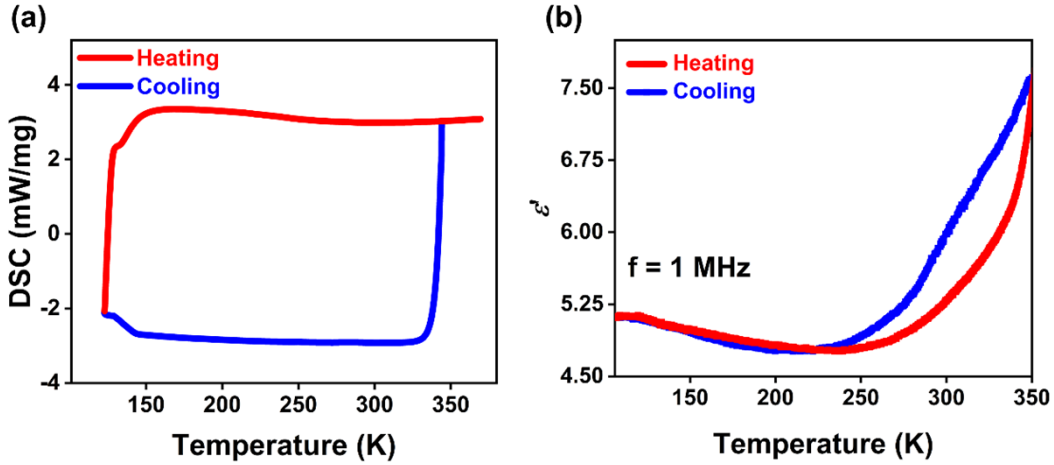

Fig. S7. (a) The DSC curves of [(*S*)-MPP][ClO_4]; (b) temperature dependence of the real part (ε') of [(*S*)-MPP][ClO_4] at 1 MHz.

Fig. S8. The longitudinal piezoelectric coefficient value of [(*S*)-MPP][ClO_4].

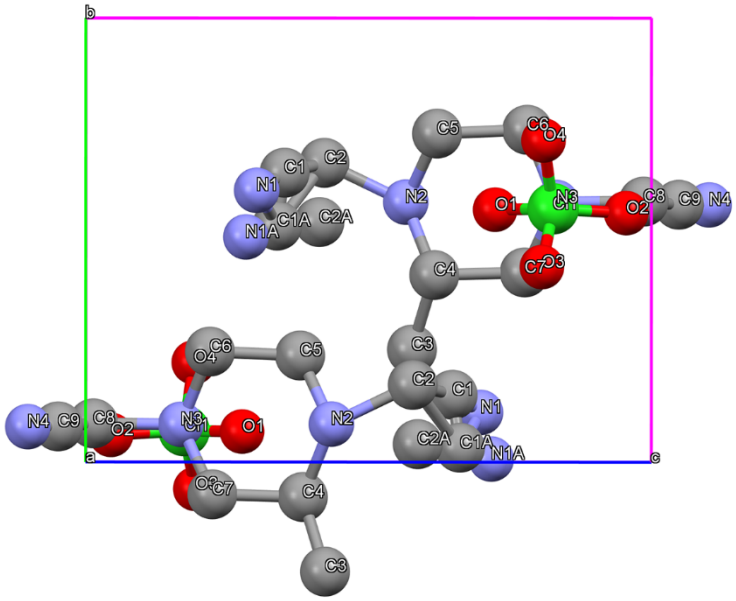

Fig. S9. Distribution of $[DCM\text{-}(S)\text{-}MPP]^+$ cations and $[ClO_4]^-$ anions of $[DCM\text{-}(S)\text{-}MPP][ClO_4]$ at 298 K in a unit cell.

According to the crystal structure data collected at 298 K, we select a unit cell and assume that the centers of the positive charges of the $[DCM\text{-}(S)\text{-}MPP]^+$ cations and the negative charges of the $[ClO_4]^-$ anions are located on the N atoms and Cl atoms, respectively, based on the point-charge model. The spontaneous polarization P_s has been estimated to be 0.54 μC cm^{-2}.

Atoms	Atom coordinate	Coordinate of charge center
Cl	Cl1^1(0.28735, 0.5706, 0.82607)	(0.5, 0.3206, 0.5)
	Cl1^2(0.71265, 0.0706, 0.17393)	
N	N3^1(0.7027, 0.5849, 0.8318)	(0.5, 0.3349, 0.5)
	N3^2(0.2973, 0.0849, 0.1682)	

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

=[(-e×0.3206)+(e×0.3349)]×2×b/V

=(0.0143×2×7.5471×10^{-10}×1.602×10^{-19} C m)/(642.596×10^{-30} m^3)

=5.4×10^{-3} C m^{-2}

=0.54 μC cm^{-2}

Table S1. Crystal data and structure refinements for [(*S*)-MPP][ClO_4] at 173 K and [DCM-(*S*)-MPP][ClO_4] at 173 K and 298 K.

	[(*S*)-MPP][ClO_4]	**[DCM-(*S*)-MPP][ClO_4]**	
Temperature	**173 K**	**173 K**	**298 K**
Empirical formula	$C_5H_{13}ClN_2O_4$	$C_9H_{15}ClN_4O_4$	$C_9H_{15}ClN_4O_4$
Weight	200.62	278.70	278.70
Crystal system	tetragonal	monoclinic	monoclinic
Space group	$P4_32_12$	$P2_1$	$P2_1$
a/Å	8.1484(2)	13.9407(7)	8.8528(6)
b/Å	8.1484(2)	7.4715(4)	7.5471(7)
c/Å	26.8449(11)	18.8287(9)	9.7043(8)
α/°	90	90	90
β/°	90	106.620(5)	97.654(7)
γ/°	90	90	90
Volume/Å^3	1782.41(11)	1879.23(17)	642.60(9)
Z	8	6	2
*R*1 [I>2σ(I)]	0.0407	0.0547	0.0754
w*R*2 [I>2σ(I)]	0.1015	0.1406	0.2139
GOF	1.043	0.920	1.051

Table S2. Selected bond lengths and angles of hydrogen bonding for [(*S*)-MPP][ClO_4] at 173 K.

D—H···A	**D—H (Å)**	**H···A (Å)**	**D···A (Å)**	**D—H···A (°)**
N1—H1A···O1	0.84(4)	2.29(4)	2.985(4)	141(3)
N1—H1A···O5^1	0.84(4)	2.30(4)	2.890(4)	128(3)
N1—H1B···N2^2	0.92(4)	1.97(4)	2.875(3)	172(3)

Table S3. Selected bond lengths and angles of hydrogen bonding for [DCM-(*S*)-MPP][ClO_4] at 173 K and 298 K.

	D—H···A	**D—H (Å)**	**H···A (Å)**	**D···A (Å)**	**D—H···A (°)**
173 K	N7—H7···N4	1.00	2.25	3.001(5)	130.7
	N10—H10···O9	1.00	1.98	2.893(4)	151.3
	N2—H2···O4	1.00	1.81	2.791(4)	166.1
298 K	N3—H3···O1	0.98	1.87	2.847(5)	176.2

Table S4. Selected bond angles [°] for compound [DCM-(*S*)-MPP][ClO_4] at 173 K and 298 K.

173 K		**298 K**	
C4—N2—C2	112.6(3)	C4—N2—C2	131.3(3)
C2—N2—C3	112.6(3)	C4—N2—C2A	99.7(4)
C8—N3—C5	112.1(4)	C5—N2—C2	88.69(19)
C8—N3—C6	113.0(4)	C5—N2—C2A	124.9(4)
C11—N6—C12	110.6(3)	C7—N3—C8	113.0(6)
C11—N6—C13	113.0(3)	C6—N3—C8	110.1(6)
C17—N7—C16	111.8(3)		
C17—N7—C15	113.7(3)		
C21—N10—C20	113.7(3)		
C22—N10—C20	111.2(3)		
C24—N11—C26	114.2(4)		
C26—N11—C23	110.5(4)		