Electronic Supplementary Material (ESI) for CrystEngComm.

Homochiral Hybrid Hexagonal Antiperovskite Crystals [*R* and *S*-3-chloroquinuclidinium]$_3$($CdCl_3$)($CdCl_4$)†

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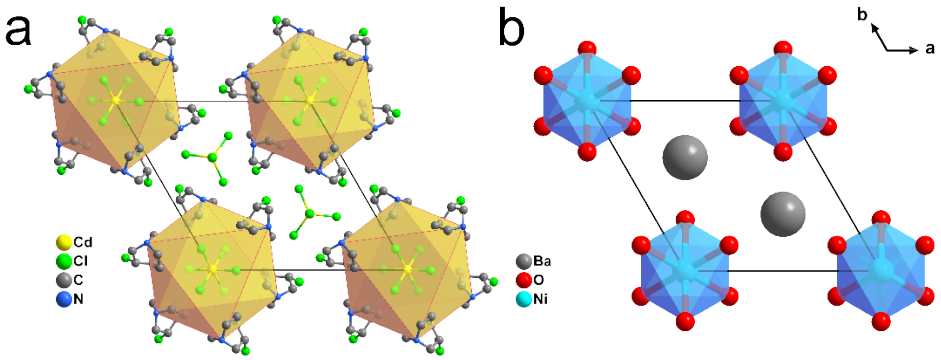

Figure S1. Comparison of the crystal structure of *R*-1 and $BaNiO_3$ along *c*-axis, H atoms were omitted for clarity.

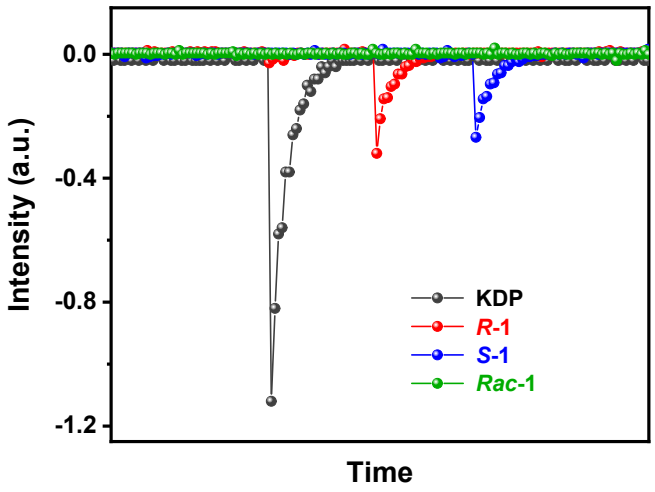

Figure S2. SHG intensity of *R*-1, *S*-1 and *Rac*-1 with the comparison of potassium dihydrogen phosphate (KDP). The measurements were performed using a 5 mg powder sample at room temperature.

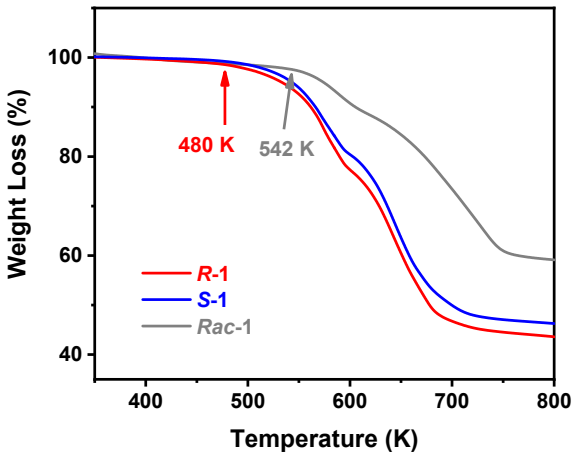

Figure S3. TGA of *R*-1, *S*-1 and *Rac*-1, shows the decomposition points of *R*-1 and *S*-1 are up to 480 K, and the decomposition point of *Rac*-1 is up to 542 K. TGA measurements were carried out in a heating run at the rate of 30 K/min under nitrogen atmosphere. The amount of powder sample used for the TGA is about 3 mg.

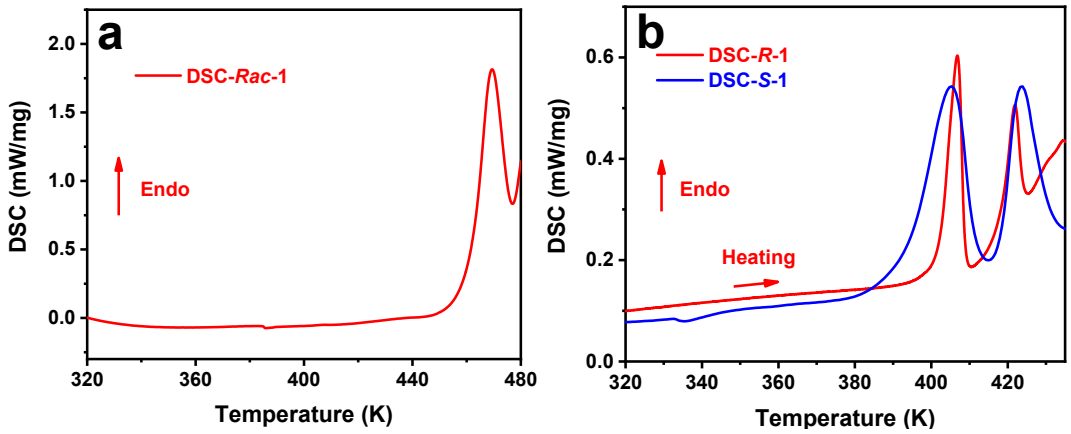

Figure S4. (a) DSC curve of *Rac*-1, showing no thermal anomaly before the melting point 469 K. (b) DSC curve of *R*-1 and S-1, showing the phase transition point around 406 K and melting point around 423 K. DSC measurements were carried out in a heating run at the rate of 20 K/min under nitrogen atmosphere. The amount of powder sample used for the DSC is about 10 mg.

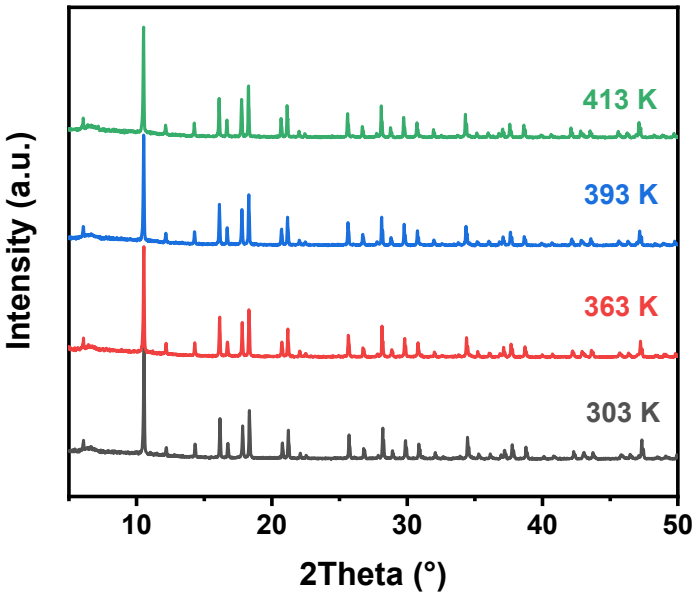

Figure S5. Temperature-dependent PXRD patterns for *R*-1. PXRD measurements were carried out in a heating run at the rate of 10 K/min. The amount of powder sample used is about 20 mg. The measurements are in the angle range from 5 to 50° with a step size of 0.02˚.

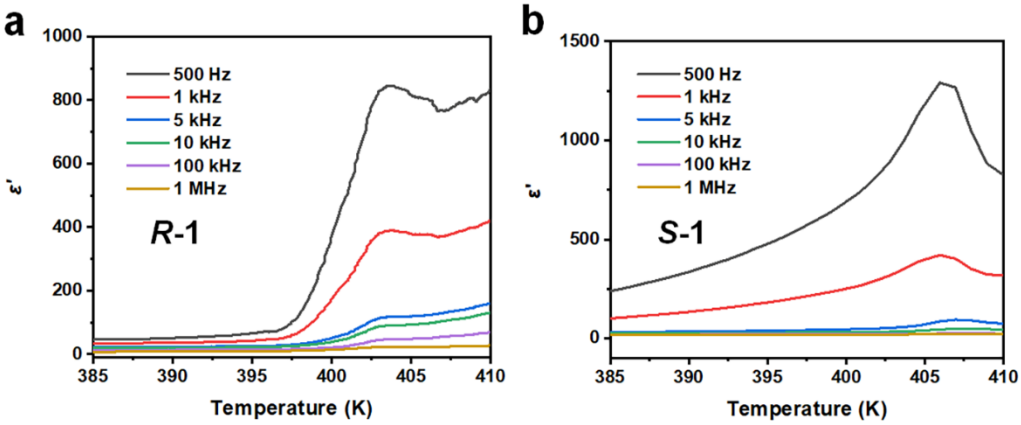

Figure S6. The temperature dependence of the dielectric real part for *R*-1 (a) and *S*-1 (b) at different frequencies (500 Hz – 1 MHz) in a heating run measured at the rate of 20 K/min. For dielectric tests, the powder sample is pressed into sheets of about 0.5mm.

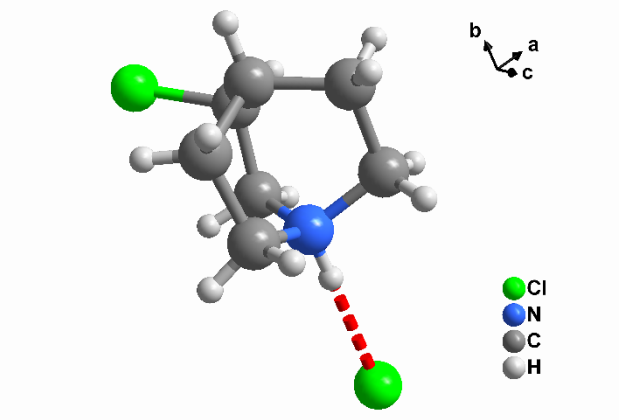

Figure S7. Crystal structure of *R*-3-chloroquinuclidinium chloride. The red dash stands for the hydrogen bond interactions.

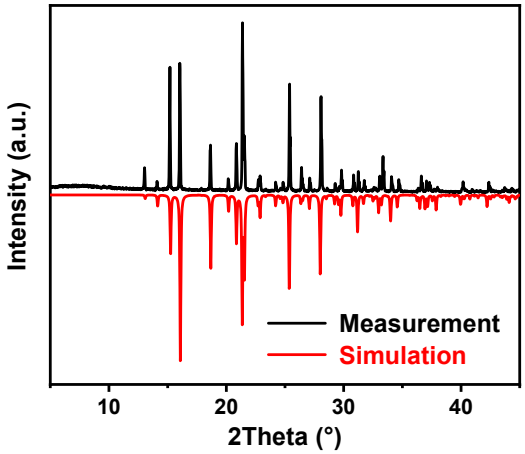

Figure S8. Comparison of measured and simulated PXRD patterns of *R*-3-chloroquinuclidinium chloride at room temperature. PXRD measurements were carried out in a heating run at the rate of 10 K/min. The amount of powder sample used is about 20 mg. The measurements are in the angle range from 5 to 45° with a step size of 0.02˚. The simulated PXRD patterns are from the simulation of the crystal CIF file by Mercury software.

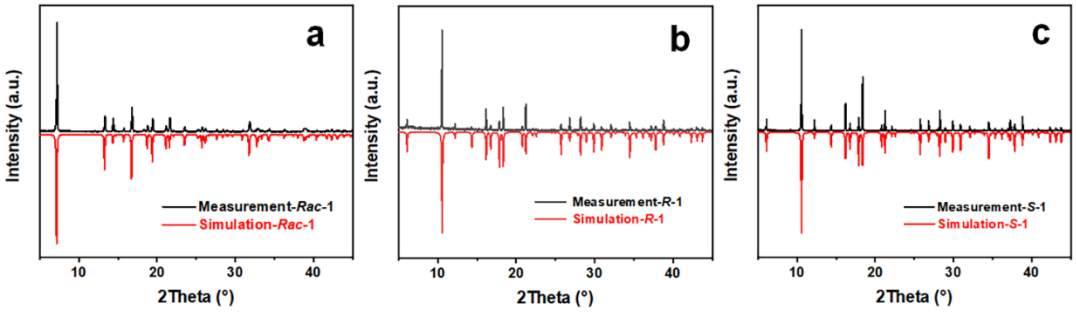

Figure S9. Comparison of measured and simulated PXRD patterns of *Rac*-1 (a), *R*-1 (b), and *S*-1 (c) at room temperature. PXRD measurements were carried out in a heating run at the rate of 10 K/min. The amount of powder sample used is about 20 mg. The measurements are in the angle range from 5 to 45° with a step size of 0.02˚. The simulated PXRD patterns are from the simulation of the crystal CIF files by Mercury software.

Table S1. Crystal data and structure refinements for *Rac*-1, *R*-1, *S*-1 and *R*-3-chloroquinuclidinium chloride.

Compound	*Rac*-1	*R*-1	*S*-1	*R*-3-chloroquinuclidinium chloride
Formula weight	364.38	912.85	912.85	182.08
Temperature/K	293(2)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Hexagonal	Hexagonal	Orthorhombic
Space group	$P2_1/n$	$P6_3$	$P6_3$	$P2_12_12_1$
a/Å	7.1351(3)	16.8561(13)	16.71020(10)	8.3125(9)
b/Å	24.6782(7)	16.8561(13)	16.71020(10)	9.4931(9)
c/Å	7.2386(3)	6.8554(5)	6.81010(10)	11.6083(11)
α/deg	90	90	90	90
β/deg	107.239(4)	90	90	90
γ/deg	90	120	120	90
Volume/Å^3	1217.32(8)	1686.9(3)	1646.82(3)	916.03(16)
Z	4	2	2	4
Density/(g.cm^{-3})	1.988	1.797	1.841	1.32
R_1 [$I>=2\sigma(I)$]	0.1025	0.0447	0.1135	0.0487
wR_2 [$I>=2\sigma(I)$]	0.2507	0.0953	0.2707	0.1255
GOF	1.029	0.998	1.191	1.032

Table S2. Selected N-H…Cl hydrogen bond parameters for *Rac*-1.

D-H…A	**d(D-H)/Å**	**d(H-A)/Å**	**d(D-A)/Å**	**D-H-A/deg**
N(1)-H(1)…Cl(3)$^{\#1}$	0.98	2.52	3.274(5)	133.3
N(1)-H(1)…Cl(3)	0.98	2.83	3.433(5)	120.3
N(1)-H(1)…Cl(1)$^{\#1}$	0.98	2.95	3.656(5)	129.4

Symmetry Code: #1 2-X, -Y, 1-Z

Table S3. Selected Cd-Cl bond lengths [Å] and Cl-Cd-Cl angles [deg] for *Rac*-1.

Atom-Atom	Length/Å	Atom-Atom-Atom	Angle/deg
Cd(1)-Cl(3)	2.5519(12)	Cl(1)-Cd(1)-Cl(3)#1	157.29(4)
Cd(1)-Cl(3)#1	2.6797(15)	Cl(1)#2-Cd(1)-Cl(3)#1	89.01(5)
Cd(1)-Cl(1)	2.6527(17)	Cl(1)#2-Cd(1)-Cl(3)	133.99(4)
Cd(1)-Cl(1)#2	2.5132(14)	Cl(1)#2-Cd(1)-Cl(1)	84.00(5)
Cd(1)-Cl(2)	2.4386(13)	Cl(2)-Cd(1)-Cl(3)	108.67(4)
Cd(1)-Cd(1)#1	3.9105(6)	Cl(2)-Cd(1)-Cl(3)#1	98.33(5)
Cd(1)-Cd(1)#2	3.8402(6)	Cl(2)-Cd(1)-Cl(1)	104.09(6)
Atom-Atom-Atom	**Angle/deg**	Cl(2)-Cd(1)-Cl(1)#2	117.33(5)
Cl(3)-Cd(1)-Cl(3)#1	83.29(4)	Cl(3)-Cd(1)-Cl(1)	86.11(5)

Symmetry Code: #1 2-X,-Y,2-Z;#2 3-X,-Y,2-Z

Table S4. Selected bond lengths [Å] and Cl-Cd-Cl angles [deg] for *R*-1.

Atom-Atom	Length/Å	Atom-Atom-Atom	Angle/°
Cd(2)-Cl(3)	2.467(5)	Cl(3)-Cd(2)-Cl(2)	109.82(7)
Cd(2)-Cl(2)#1	2.486(2)	Cl(3)-Cd(2)-Cl(2)#1	109.82(7)
Cd(2)-Cl(2)#2	2.486(2)	Cl(3)-Cd(2)-Cl(2)#2	109.82(7)
Cd(2)-Cl(2)	2.486(2)	Cl(2)-Cd(2)-Cl(2)#2	109.12(7)
Cd(1)-Cd(1)#3	3.4277(3)	Cl(2)-Cd(2)-Cl(2)#1	109.12(7)
Cd(1)-Cd(1)#4	3.4277(3)	Cl(2)#1-Cd(2)-Cl(2)#2	109.12(7)
Cd(1)-Cl(1)	2.6790(19)	Cl(1)#8-Cd(1)-Cl(1)#4	83.46(7)
Cd(1)-Cl(1)#5	2.6793(19)	Cl(1)-Cd(1)-Cl(1)#8	96.54(3)
Cd(1)-Cl(1)#6	2.6789(19)	Cl(1)#6-Cd(1)-Cl(1)#4	96.54(3)
Cd(1)-Cl(1)#3	2.6793(19)	Cl(1)#7-Cd(1)-Cl(1)#5	96.54(3)
Cd(1)-Cl(1)#7	2.6789(19)	Cl(1)#6-Cd(1)-Cl(1)#5	96.54(3)
Cd(1)-Cl(1)#8	2.6793(19)	Cl(1)#7-Cd(1)-Cl(1)	83.47(7)
Atom-Atom-Atom	**Angle/°**	Cl(1)#6-Cd(1)-Cl(1)	83.47(7)
Cl(1)#5-Cd(1)-Cl(1)#4	83.46(7)	Cl(1)-Cd(1)-Cl(1)#4	96.54(3)
Cl(1)#7-Cd(1)-Cl(1)#8	96.54(3)	Cl(1)#8-Cd(1)-Cl(1)#5	83.46(7)
Cl(1)#6-Cd(1)-Cl(1)#7	83.47(7)		

Symmetry Code: #1 1+Y-X,1-X,+Z;#2 1-Y,+X-Y,+Z;#3 -Y+X,-1+X,-1/2+Z;#4 -Y+X,-1+X,1/2+Z;#5 2-X,-Y,1/2+Z;#6 1-Y,-1+X-Y,+Z;#7 2+Y-X,1-X,+Z;#8 1+Y,1-X+Y,1/2+Z.

Table S5. Selected bond lengths [Å] and Cl-Cd-Cl angles [deg] for *S*-1.

Atom-Atom	Length/Å	Atom-Atom-Atom	Angle/°
Cl(3)-Cd(2)	2.4720(18)	Cl(1)$^{\#5}$-Cd(1)-Cl(1)$^{\#4}$	83.26(6)
Cd(2)-Cl(2)	2.437(4)	Cl(1)-Cd(1)-Cl(1)$^{\#8}$	83.45(6)
Cd(1)-Cd(1)$^{\#4}$	3.40506(4)	Cl(1)$^{\#7}$-Cd(1)-Cl(1)$^{\#6}$	96.64(2)
Cd(1)-Cd(1)$^{\#3}$	3.40504(5)	Cl(1)$^{\#7}$-Cd(1)-Cl(1)$^{\#4}$	96.64(2)
Cd(1)-Cl(1)$^{\#4}$	2.6599(18)	Cl(1)$^{\#6}$-Cd(1)-Cl(1)$^{\#5}$	83.26(6)
Cd(1)-Cl(1)$^{\#6}$	2.6599(18)	Cl(1)-Cd(1)-Cl(1)$^{\#7}$	83.45(6)
Cd(1)-Cl(1)$^{\#7}$	2.6550(18)	Cl(1)$^{\#8}$-Cd(1)-Cl(1)$^{\#4}$	96.64(2)
Cd(1)-Cl(1)$^{\#9}$	2.6599(18)	Cl(1)$^{\#6}$-Cd(1)-Cl(1)$^{\#4}$	83.26(6)
Cd(1)-Cl(1)	2.6550(18)	Cl(1)$^{\#8}$-Cd(1)-Cl(1)$^{\#7}$	83.45(6)
Cd(1)-Cl(1)$^{\#8}$	2.6550(18)	Cl(1)-Cd(1)-Cl(1)$^{\#5}$	96.64(2)
Atom-Atom-Atom	**Angle/°**	Cl(1)$^{\#8}$-Cd(1)-Cl(1)$^{\#5}$	96.64(2)
Cl(3)-Cd(2)-Cl(3)$^{\#2}$	109.11(7)	Cl(1)-Cd(1)-Cl(1)$^{\#6}$	96.64(2)
Cl(2)-Cd(2)-Cl(3)	109.83(7)	Cl(3)$^{\#1}$-Cd(2)-Cl(3)	109.11(7)
Cl(2)-Cd(2)-Cl(3)$^{\#2}$	109.83(7)	Cl(3)$^{\#1}$-Cd(2)-Cl(3)$^{\#2}$	109.11(7)
Cl(2)-Cd(2)-Cl(3)$^{\#1}$	109.83(7)		

Symmetry Code: $^{\#1}$1-Y,+X-Y,+Z;$^{\#2}$1+Y-X,1-X,+Z;$^{\#3}$-X,-Y,-1/2+Z;$^{\#4}$-X,-Y,1/2+Z;$^{\#5}$+Y,-X+Y,1/2+Z;$^{\#6}$-Y+X,+X,1/2+Z;$^{\#7}$-Y,+X-Y,+Z;$^{\#8}$+Y-X,-X,+Z;$^{\#9}$+Y,-X+Y,1/2+Z

Table S6. The information of optical rotations.

Optical Rotation $[\alpha]_D^{25}$/°	*R*	*S*
Hexagonal antiperovskites	+9.085	-9.072
3-chloroquinuclidinium chloride	+30.23	-30.15