

Electronic Supplementary Information

Enantiomeric perovskite with dual phase transition at high temperature

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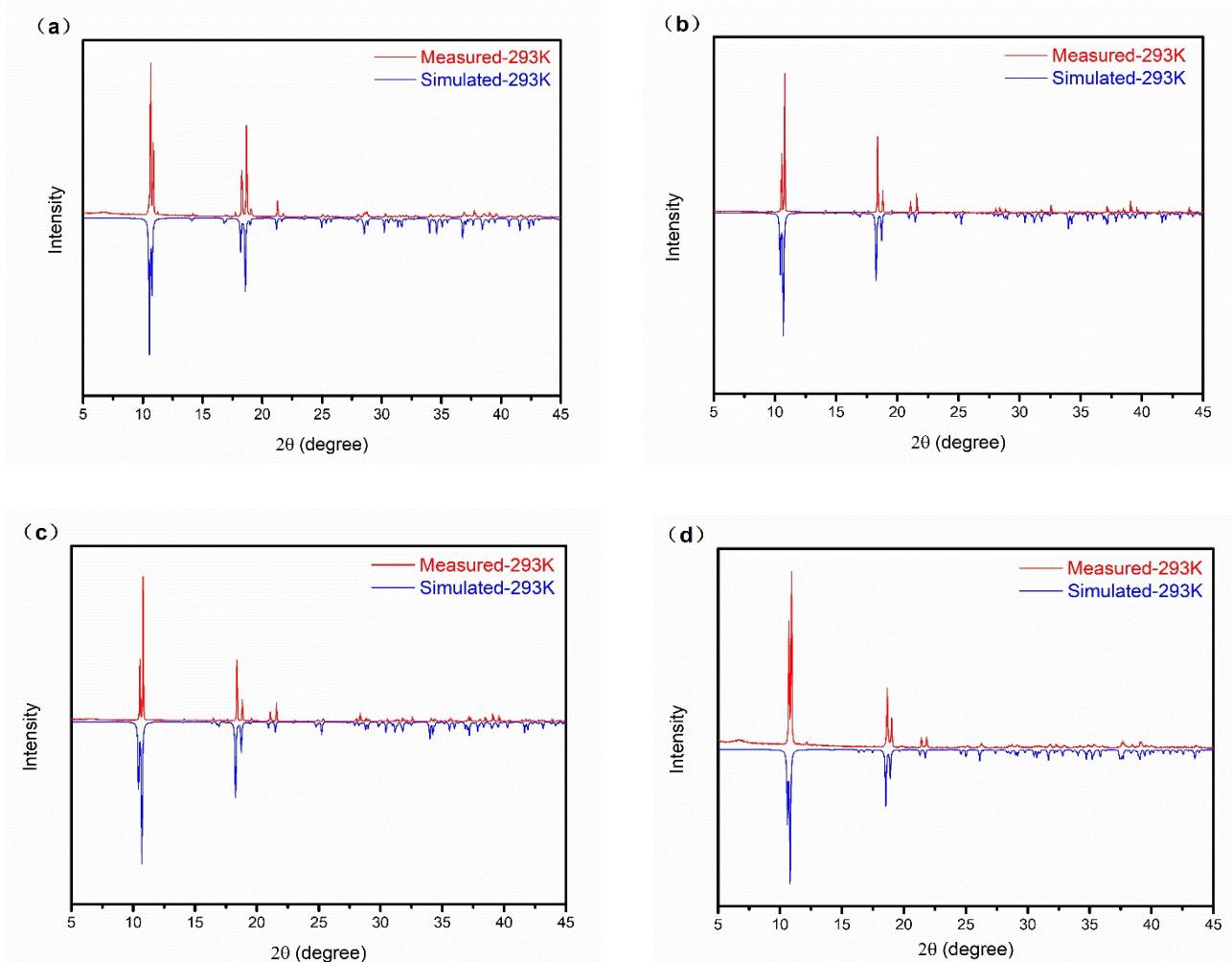


Fig. S1 Measured and simulated powder X-ray diffraction patterns of (a) (N, N-dimethyl pyrrolidinium) CdCl₃, (b) (*R*)- (N, N-dimethyl-3-fluoropyrrolidinium) CdCl₃, (c) (*S*)- (N, N-dimethyl-3-fluoropyrrolidinium) CdCl₃ and (d) (*rac*)- (N, N-dimethyl-3-fluoropyrrolidinium) CdCl₃ at 293 K.

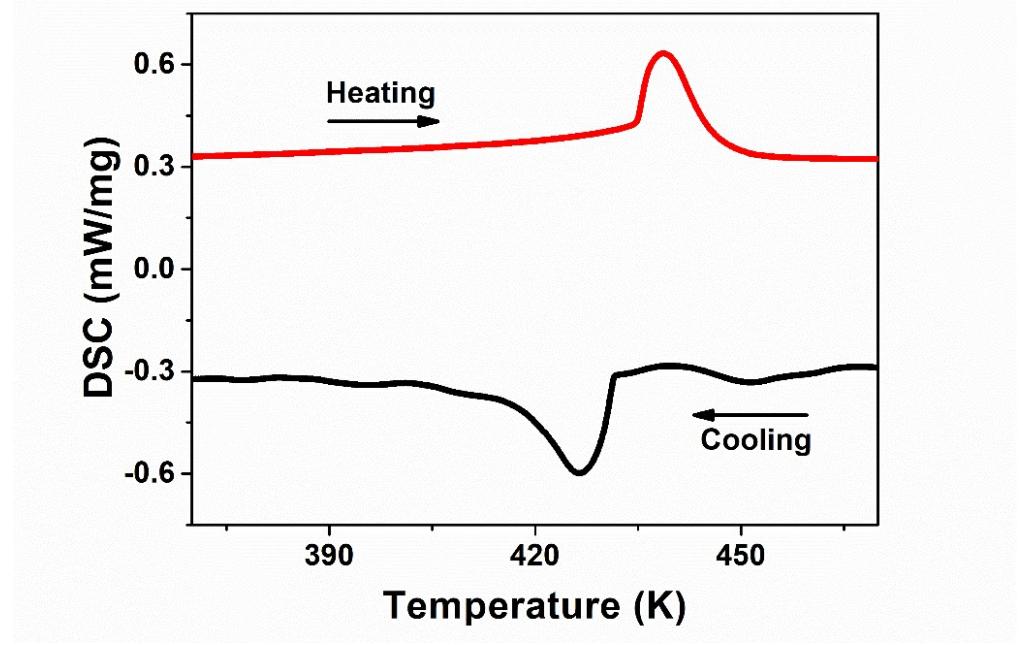


Fig. S2 DSC curves acquired in a heating-cooling cycle of (*rac*) - (N, N-dimethyl-3-fluoropyrrolidinium) CdCl₃.

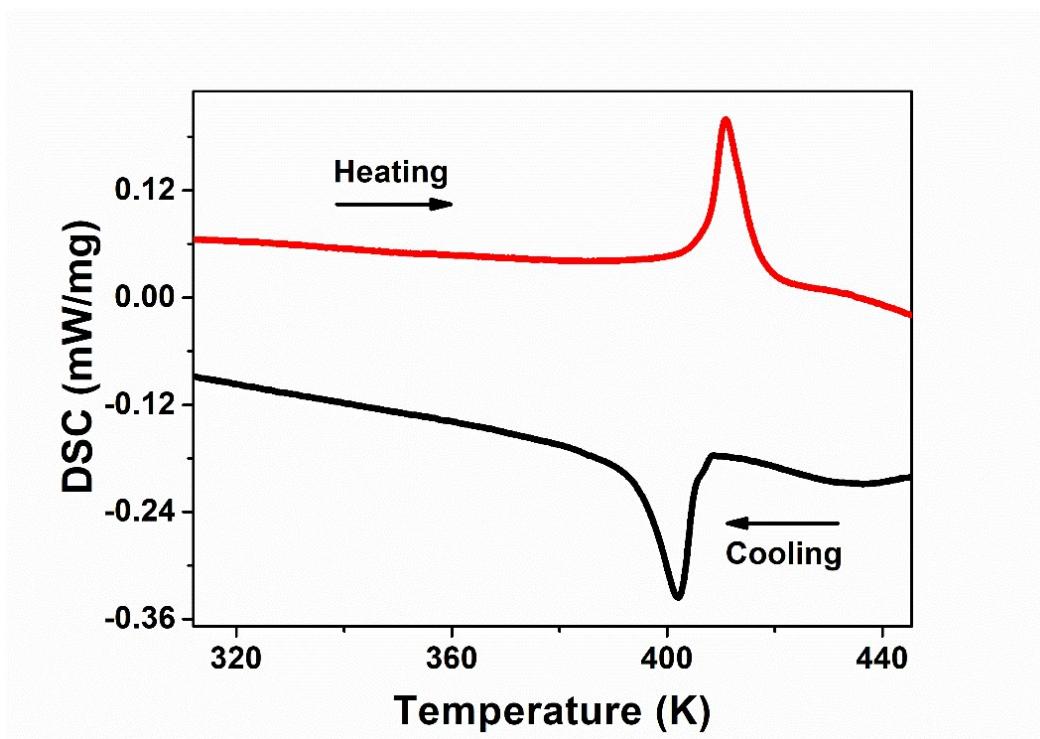


Fig. S3 DSC curves acquired in a heating-cooling cycle of (N, N-dimethyl pyrrolidinium) CdCl₃.

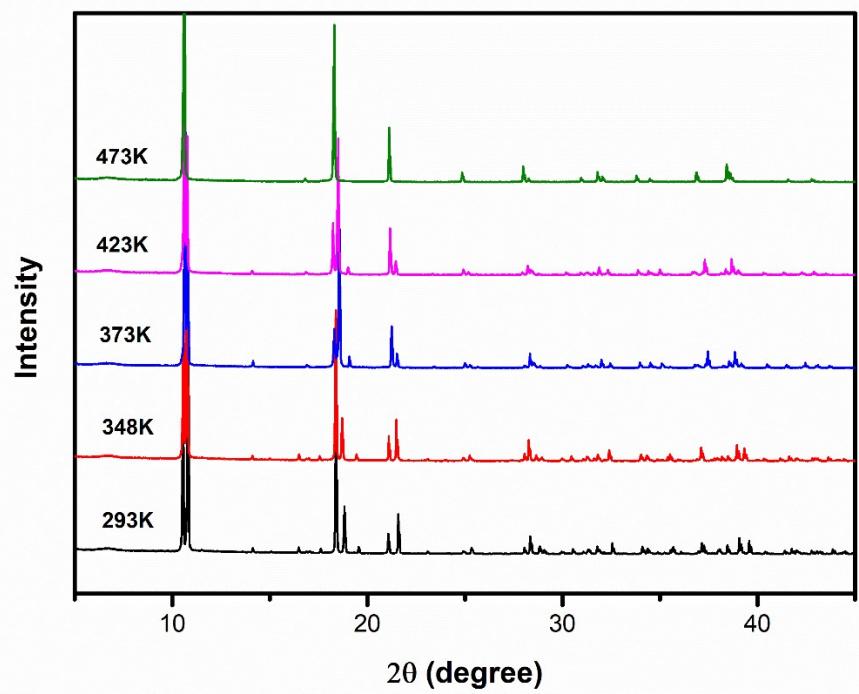


Fig. S4 Variable-temperature PXRD pattern of (*S*)- (N, N-dimethyl-3-fluoropyrrolidinium) CdCl₃ obtained in the temperature range 293-473 K.

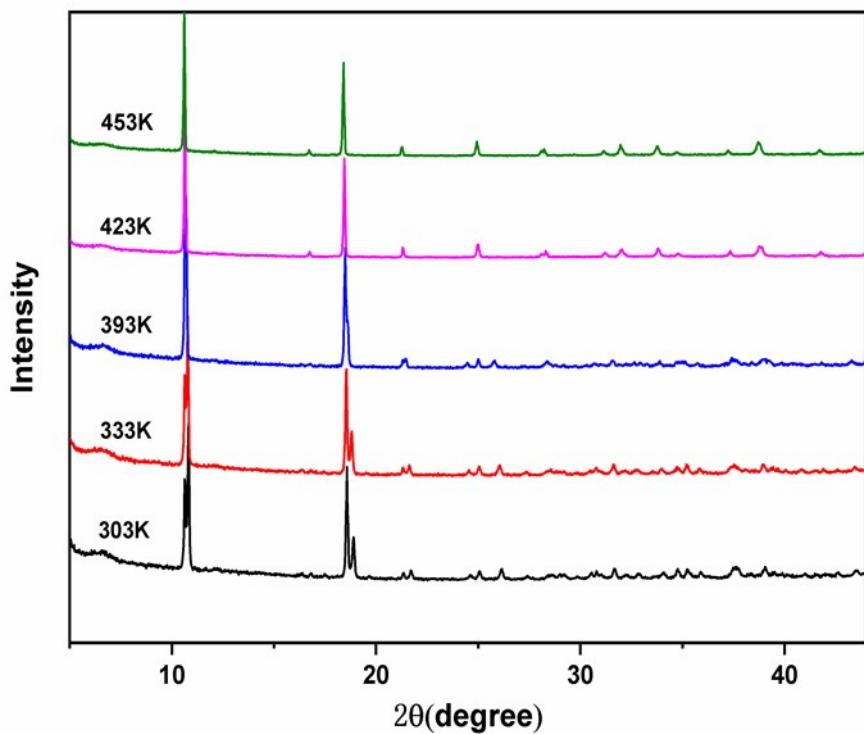


Fig. S5 Variable-temperature PXRD pattern of (*rac*)- (N, N-dimethyl-3-fluoropyrrolidinium) CdCl₃ obtained in the temperature range 303-453 K.

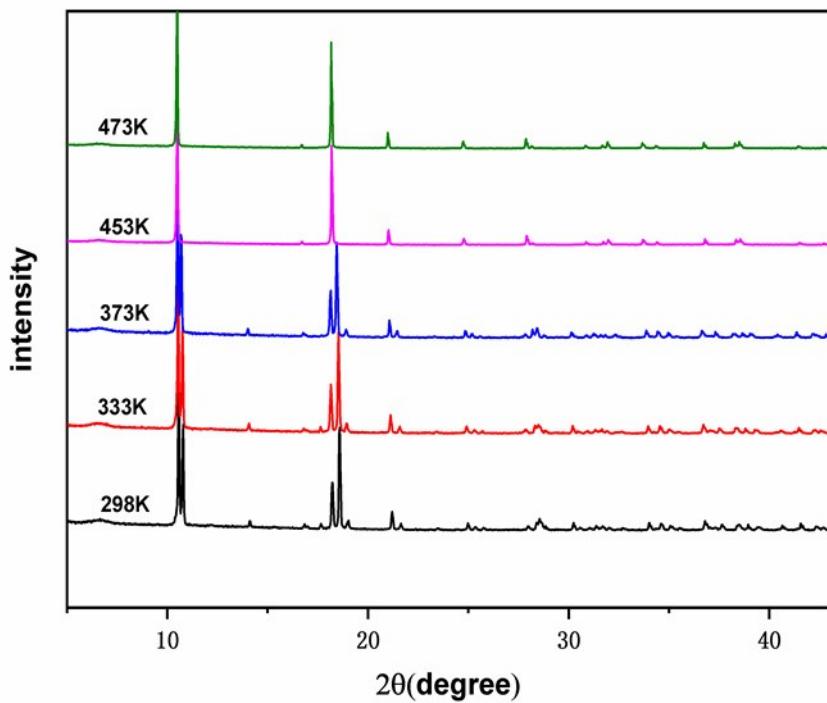


Fig. S6 Variable-temperature PXRD pattern of (N, N-dimethyl pyrrolidinium) CdCl₃ obtained in the temperature range 298-473 K.

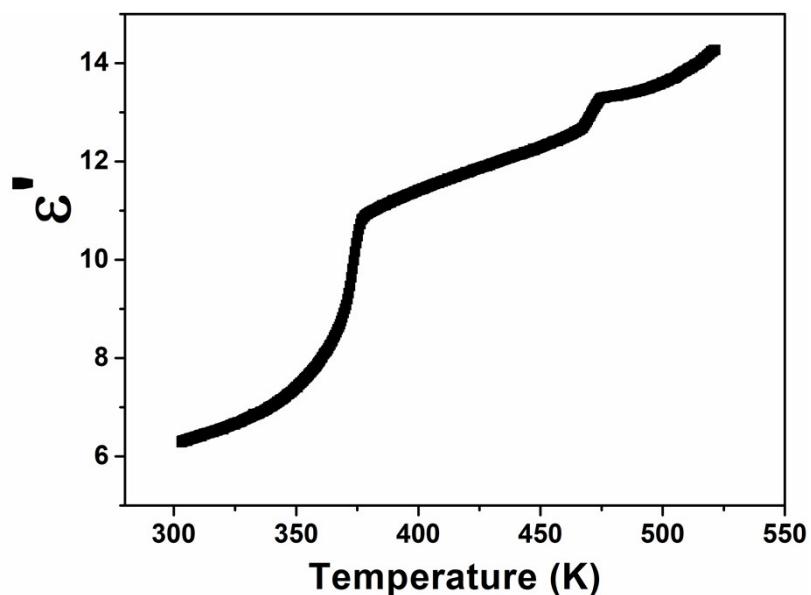


Fig. S7 Temperature dependence of the real part (ϵ') of the dielectric constant of (S)- (N, N-dimethyl-3-fluoropyrrolidinium) CdCl₃ at 1 MHz in the heating-cooling cycle.

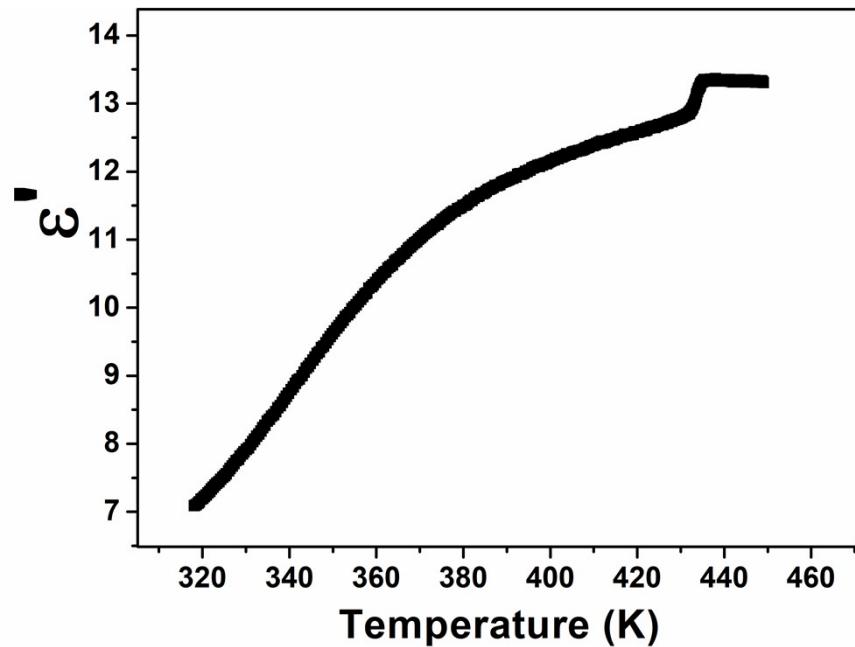


Fig. S8 Temperature dependence of the real part (ϵ') of the dielectric constant of (rac)- (N, N-dimethyl-3-fluoropyrrolidinium) CdCl_3 at 1 MHz in the heating-cooling cycle.

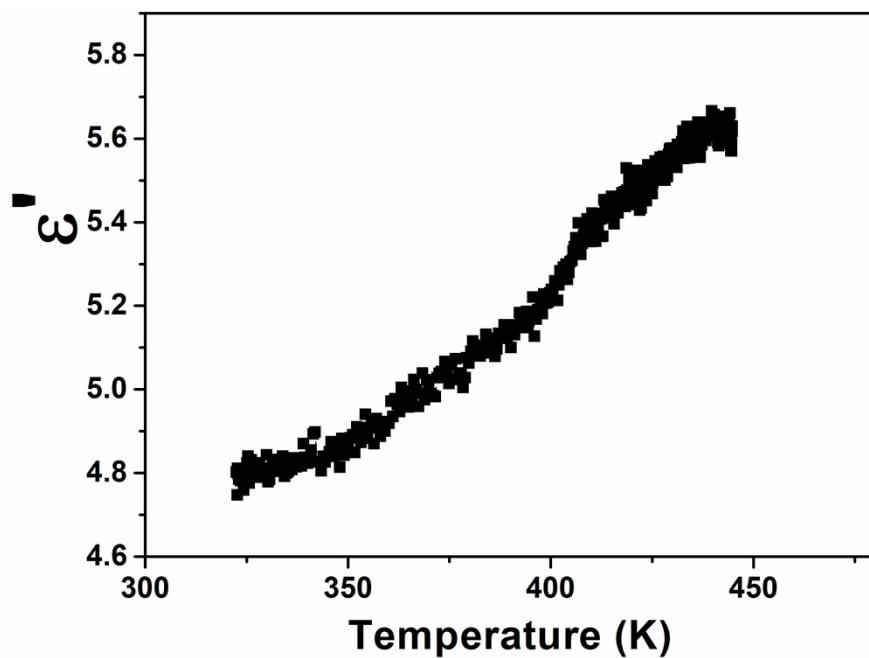


Fig. S9 Temperature dependence of the real part (ϵ') of the dielectric constant of (N, N-dimethylpyrrolidinium) CdCl_3 at 1 MHz in the heating-cooling cycle.

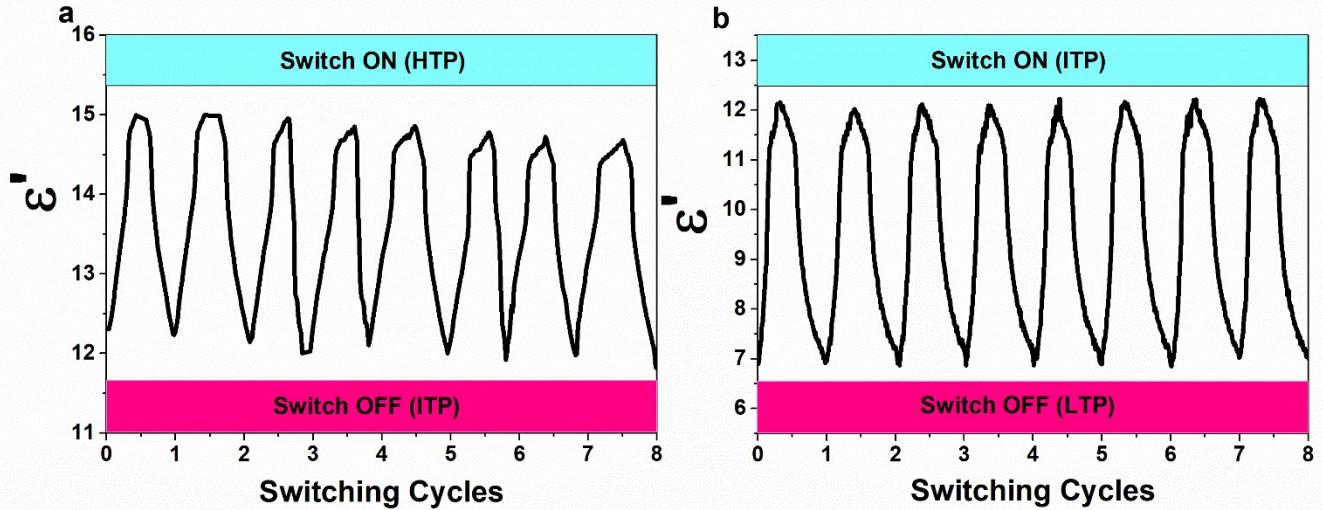


Fig. S10 The switching of the dielectric measurement for the (S)- DMFP CdCl₃. Switching (a) between HTP and ITP (b) between ITP and LTP.

Table. S1 Crystal data and structure refinements for (*R*)- and (*S*)- (N, N-dimethyl-3-fluoropyrrolidinium) CdCl₃ at 293K.

Compound	(<i>R</i>)-(N, N-dimethyl-3-fluoropyrrolidinium) CdCl ₃	(<i>S</i>)-(N, N-dimethyl-3-fluoropyrrolidinium) CdCl ₃
Temperature	293 K	293 K
Formula	[C ₁₂ H ₂₆ F ₂ N ₂][Cd ₂ Cl ₆]	[C ₁₂ H ₂₆ F ₂ N ₂][Cd ₂ Cl ₆]
Formula weight	673.87	673.87
Crystal system	Orthorhombic	Orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a, b, c</i> (Å)	6.7569(2) 16.9429(4) 18.9468(5)	6.7593(3) 16.9501(6) 18.9218(8)
α, β, γ (°)	90 90 90	90 90 90
Volume /Å ³	2169.06(10)	2167.89(15)
<i>Z</i>	4	4
Density/g cm ⁻³	2.064	2.065
<i>R</i> ₁	0.0233	0.0156
<i>wR</i> ₂	0.0596	0.0396
GOF	1.138	1.046

Table. S2 Crystal data and structure refinements for (*rac*) - (N, N-dimethyl-3-fluoropyrrolidinium) CdCl₃ and (N, N-dimethyl pyrrolidinium) CdCl₃ at 293K.

Compound	(<i>rac</i>)-(N, N-dimethyl-3-fluoropyrrolidinium) CdCl ₃	(N, N-dimethyl pyrrolidinium) CdCl ₃
Temperature	293 K	293 K
Formula	[C ₆ H ₁₃ FN][CdCl ₃]	[C ₆ H ₁₄ N][CdCl ₃]
Formula weight	336.93	318.95
Crystal system	Orthorhombic	Monoclinic
Space group	<i>Pbca</i>	<i>P2₁/C</i>
<i>a, b, c</i> (Å)	16.4212(12) 6.7765(4) 19.4918(15)	9.4120(4) 16.6860(7) 6.8357(2)
<i>α, β, γ</i> (°)	90 90 90	90 94.382(4) 90
Volume /Å ³	2169.0(3)	1070.40(7)
<i>Z</i>	8	4
Density/g cm ⁻³	2.064	1.980
<i>R</i> ₁	0.0709	0.0311
<i>wR</i> ₂	0.2144	0.0930
GOF	1.077	1.091