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Supporting Information

High temperature structural phase transition and dielectric relaxation in an organic-inorganic hybrid compound: (4-methylpiperidinium)$CdCl_3$†

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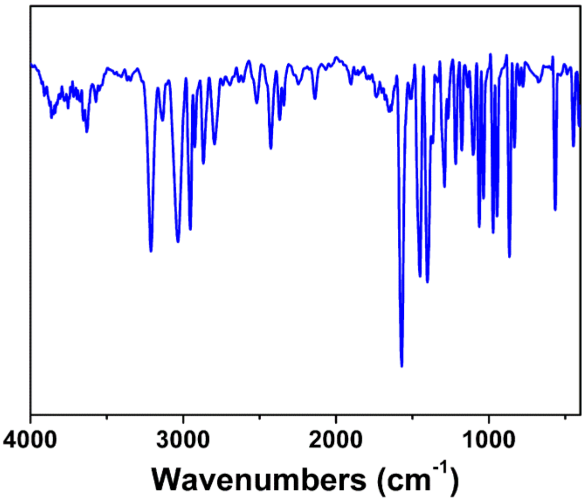

Fig.S1 Infrared (IR) spectra of solid **1** in KBr pellet recorded on a Shimadzu model IR-60 spectrometer at room temperature

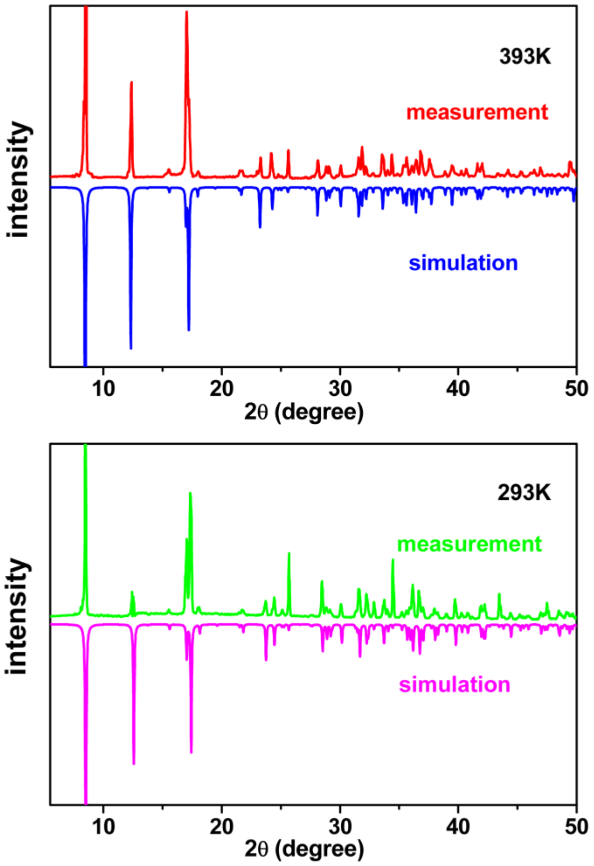

Fig.S2 Experimental powder diffraction (XRPD) patterns matching very well with the simulated ones in terms of the crystal structures for different phases.

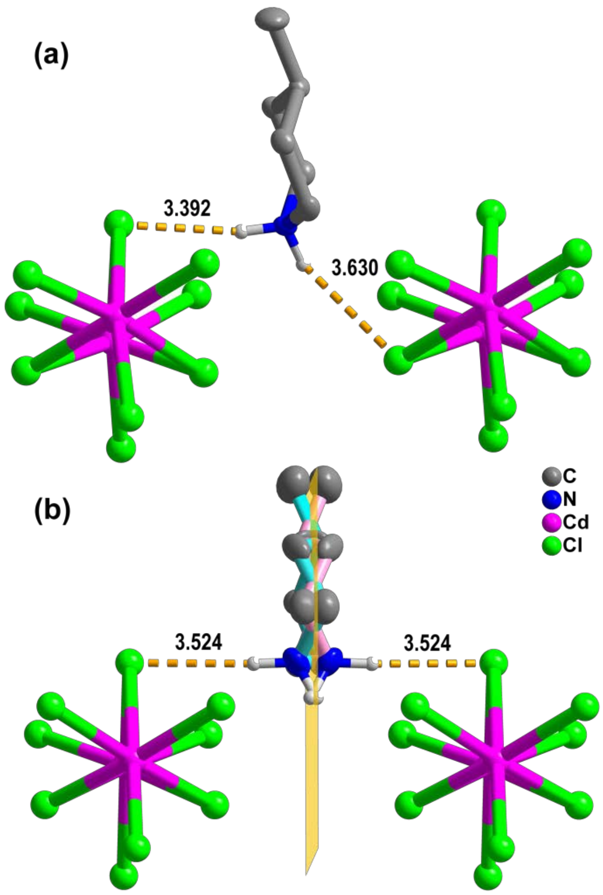

Fig.S3 Perspective views of **1** at (a) 293 K and (b) 393K. Only hydrogen atoms attached to the nitrogen atoms are retained. The hydrogen bonds are indicated by yellow dashed lines. Thermal ellipsoids for the N atoms and C atoms are shown at 30% probability level. A yellow mirror plane (m) passes through the cations.

Table S1. Selected bond lengths [Å] and angles [°] for **1**^{a} at 293 and 393 K

293K			
Cd1—Cl1	2.676(18)	Cl1—Cd1—Cl2	98.67(9)
Cd1—Cl2	2.610(3)	Cl1—Cd1—Cl3	105.34(9)
Cd1—Cl3	2.616(3)	Cl1—Cd1—Cl1$^{\mathrm{ii}}$	172.69(12)
Cd1—Cl2$^{\mathrm{i}}$	2.627(3)	Cl1—Cd1—Cl2$^{\mathrm{i}}$	81.27(9)
Cd1—Cl1$^{\mathrm{ii}}$	2.744(19)	Cl1—Cd1—Cl3$^{\mathrm{i}}$	83.24(9)
Cd1—Cl3$^{\mathrm{i}}$	2.613(3)	Cl2—Cd1—Cl3	86.12(6)
		Cl2—Cd1—Cl1$^{\mathrm{ii}}$	80.29(10)
		Cl2—Cd1—Cl2$^{\mathrm{i}}$	95.85(13)
		Cl2—Cd1—Cl3$^{\mathrm{i}}$	177.60(9)
		Cl3—Cd1—Cl1$^{\mathrm{ii}}$	81.86(9)
		Cl3—Cd1—Cl2$^{\mathrm{i}}$	172.78(13)
		Cl3—Cd1—Cl3$^{\mathrm{i}}$	91.98(12)
		Cl1$^{\mathrm{ii}}$—Cd1—Cl2$^{\mathrm{i}}$	91.61(8)
		Cl1$^{\mathrm{ii}}$—Cd1—Cl3$^{\mathrm{i}}$	127.84(7)
		Cl2$^{\mathrm{i}}$—Cd1—Cl3$^{\mathrm{i}}$	85.85(6)
393K			
Cd1—Cl1	2.660(6)	Cl1—Cd1—Cl2	81.23 (13)
Cd1—Cl2	2.614(4)	Cl1—Cd1—Cl2$^{\mathrm{iii}}$	81.23 (13)
Cd1—Cl2 $^{\mathrm{iii}}$	2.614(4)	Cl1—Cd1—Cl2$^{\mathrm{iv}}$	95.01(14)
Cd1—Cl2$^{\mathrm{iv}}$	2.626(4)	Cl1—Cd1—Cl2$^{\mathrm{v}}$	95.01(14)
Cd1—Cl2$^{\mathrm{v}}$	2.626(4)	Cl1—Cd1—Cl1$^{\mathrm{iv}}$	176.6(2)
Cd1—Cl1$^{\mathrm{iv}}$	2.660 (6)	Cl2—Cd1—Cl2$^{\mathrm{iii}}$	86.15(18)
		Cl2—Cd1—Cl2$^{\mathrm{iv}}$	93.98(15)
		Cl2—Cd1—Cl2$^{\mathrm{v}}$	176.18(10)
		Cl2—Cd1—Cl1$^{\mathrm{iv}}$	101.25(14)
		Cl1$^{\mathrm{iv}}$—Cd1—Cl2$^{\mathrm{iii}}$	101.25(14)
		Cl1$^{\mathrm{iv}}$—Cd1—Cl2$^{\mathrm{iv}}$	82.47(13)
		Cl1$^{\mathrm{iv}}$—Cd1—Cl2$^{\mathrm{v}}$	82.47(13)
		Cl2$^{\mathrm{iii}}$—Cd1—Cl2$^{\mathrm{iv}}$	176.18(10)
		Cl2$^{\mathrm{iii}}$—Cd1—Cl2$^{\mathrm{v}}$	93.98(15)
		Cl2$^{\mathrm{iv}}$—Cd1—Cl2$^{\mathrm{v}}$	85.64(19)

^{a}Symmetry codes:

(i) *x*+1/2, −*y*+3/2, *z*; (ii) *x*-1/2, −*y+3/2*, *z*; (iii) *x*, −*y+3/2*, −*z*; (iv) *x*−1/2, −*y*, −*z*+1/2; (v) *x*−1/2, −*y*+3/2, −*z*+1/2.

Table S2. Hydrogen-bond geometry (**Å**, °) for N–H···Cl interactions at 293 and 393 K in **1**[b]

	D—H···A	D—H	H···A	D···A	D—H···A
293K	N1—H1C···Cl1^{ii}	0.89	2.53	3.392 (8)	164.6
	N1—H1D···Cl3^{i}	0.89	2.91	3.630 (8)	139.0
393K	N1—H1C···Cl2^{iii}	0.90	2.63	3.523 (3)	170.5

[b] Symmetry codes:
(i) *x*-1/2, -*y*+3/2, *z*; (ii) *x*-1, *y*, *z*+1; (iii) *x*, *y*-1, *z*.

Table S3. Temperature dependence of the dielectric parameters: relaxation time (s), distribution parameter (α), and dielectric increment (ε_0-ε_∞) for **1**.

T(K)	370	375	380	385
ε_∞	6.17	6.32	6.45	6.48
ε_0	16.06	14.85	13.83	13.29
$\tau \times 10^7$s	15.91	7.96	5.30	3.18
α	0.0978	0.1046	0.0722	0.0813