Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Prominent dielectric transitions in organic-inorganic hybrids: (isoamyl-ammonium)$_2$CdX$_4$ (X = Cl and Br)

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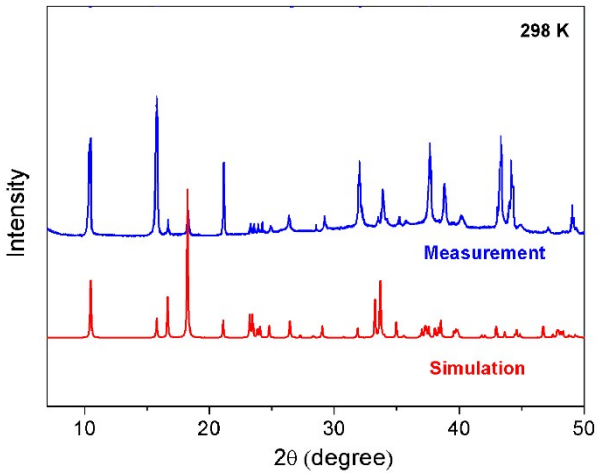

Fig. S1 Experimental powder diffraction (XRPD) patterns of **1** measured at 298 K matching very well with the simulated ones.

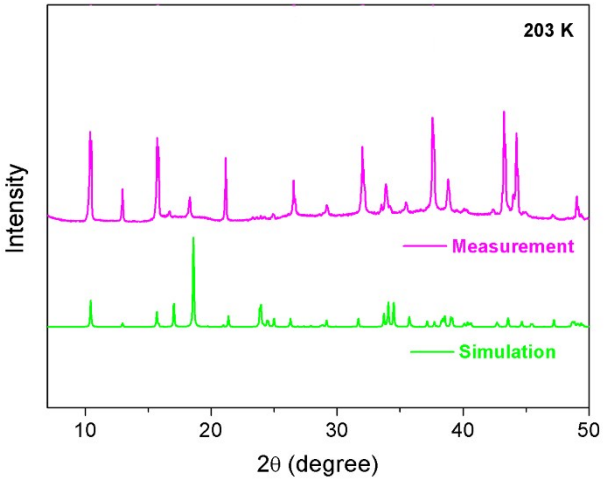

Fig. S2 Experimental powder diffraction (XRPD) patterns of **1** measured at 203 K matching very well with the simulated ones.

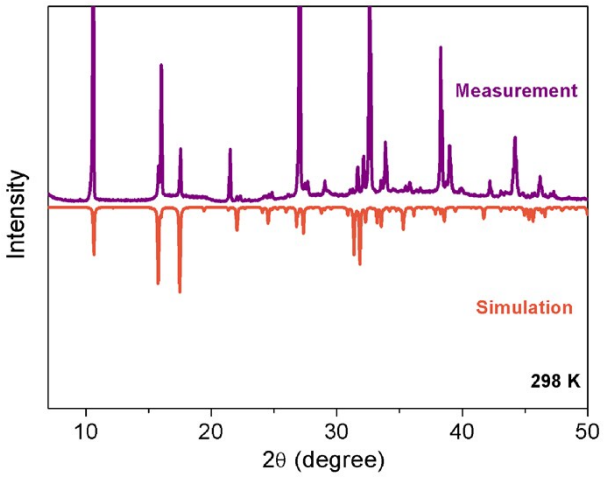

Fig. S3 Experimental powder diffraction (XRPD) patterns of **2** measured at 298 K matching very well with the simulated ones.

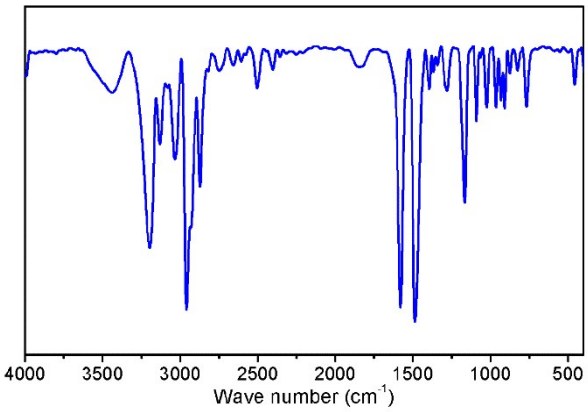

Fig. S4 Infrared (IR) spectra of solid **1** in KBr pellet recorded on a Shimadzu model IR-60 spectrometer at room temperature.

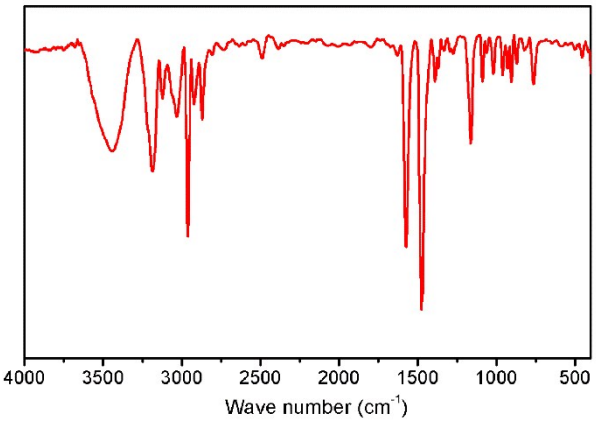

Fig. S5 Infrared (IR) spectra of solid **2** in KBr pellet recorded on a Shimadzu model IR-60 spectrometer at room temperature.

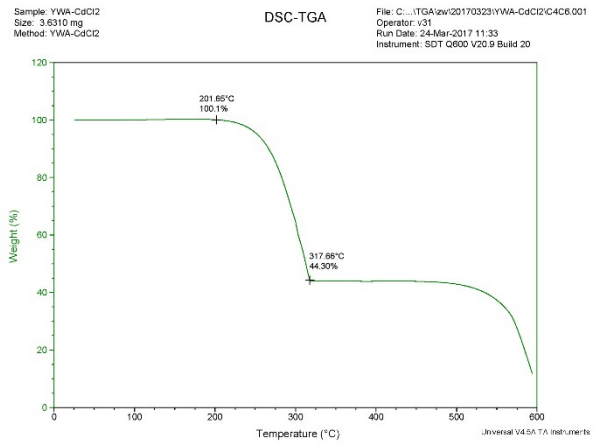

Fig. S6 TGA curve of **1** measured in the temperature range of 25-600 ℃.

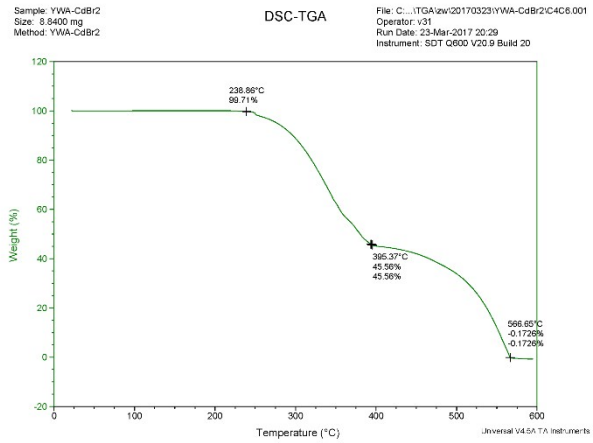

Fig. S7 TGA curve of **2** measured in the temperature range of 25-600 ℃.

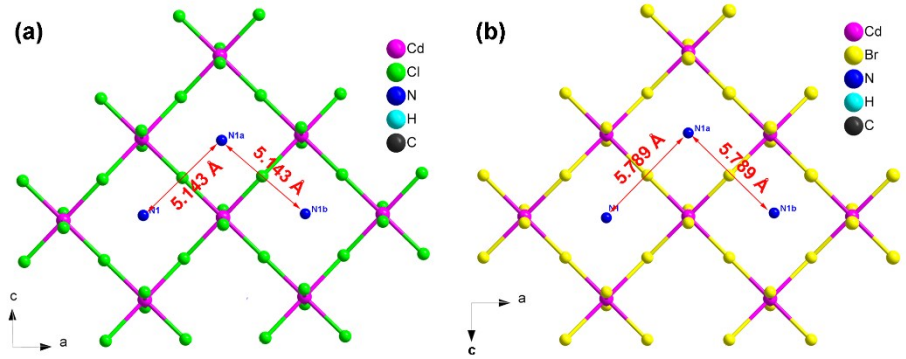

Fig. S8 The distance of adjacent organic cation in **1** (a) and **2** (b). Only N atoms were retained for clarity.

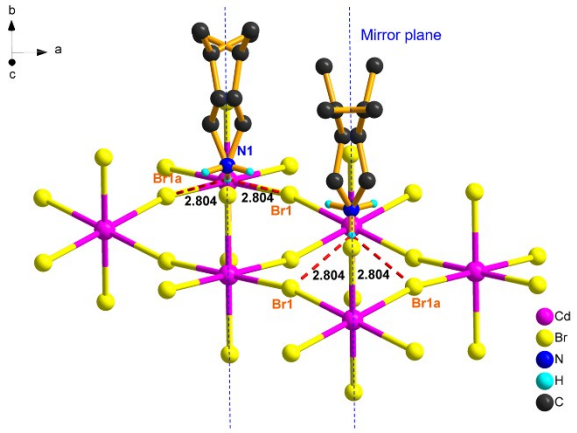

Fig. S9 Hydrogen-bonding interactions (red dashed lines) between the organic and inorganic components in **2** at 298 K. The blue dashed lines stand for the mirror plane. Hydrogen atoms bonded to the C atoms were omitted for clarity.

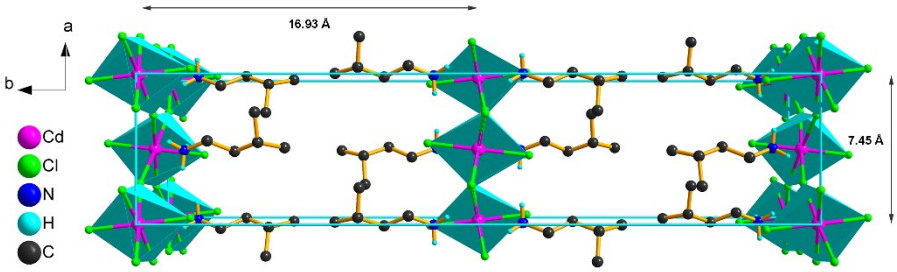

Fig. S10 Perspective view of **1** at 203 K. Hydrogen atoms bonded to the C atoms were omitted for clarity.

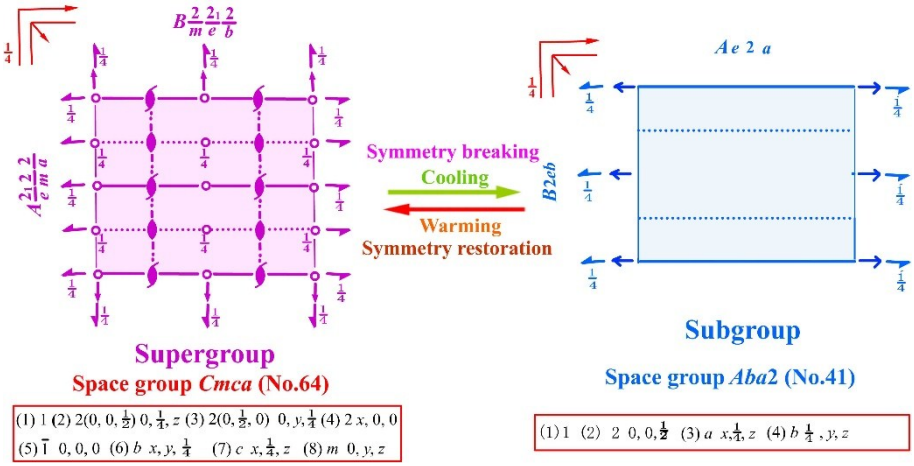

Fig. S11 Spatial symmetry operation changes of **1** from the HTP (*Cmca*) to the LTP (*Aba*2).

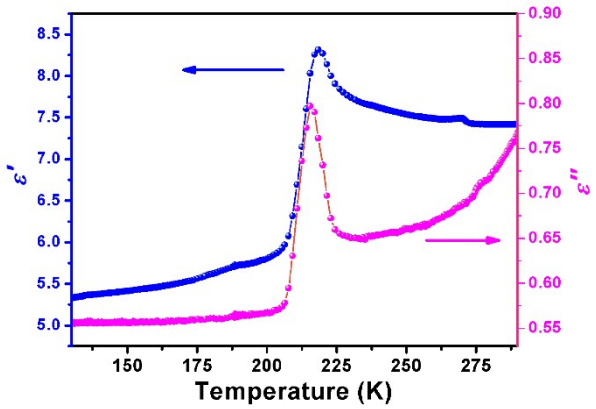

Fig. S12 The temperature-dependence of the real part (ε′) and dielectric imaginary part (ε″) of the polycrystalline sample of **2** at 1000 kHz.

Table S1 Crystal data and structure refinements for **1** and **2**.

Compound	**1**		**2**
T (K)	298	203	298
Formula wt	430.55	430.55	608.35
Space group	*Cmca*	*Aba*2	*Cmca*
a/Å	7.5775(15)	7.45(3)	8.0554(10)
b/Å	33.673(7)	33.85(17)	33.2382(9)
c/Å	7.6500(15)	7.42(4)	8.0623(5)
β (deg)	90	90	90
Volume (Å^3), Z	1952.0(7), 4	1871(16), 4	2158.7(3), 4
F(000)	872	872	1160
Collected rflns	6233	7412	4805
Unique rflns	1175	2054	729
GOF	1.132	1.182	1.127
R_1	0.0480	0.0969	0.1074
wR_2[I>2σ(I)]	0.1262	0.2494	0.3026

Table S2. Selected bond lengths [Å] and angles [°] for **1**[a] at 298 K and 203 K.

298 K	Cd1-Cl1	2.7062(4)	Cd1-Cl2	2.554(2)
	Cl2^{i}-Cd1-Cl1^{i}	90.31(5)	Cl2-Cd1-Cl1^{i}	89.69(5)
	Cl2^{i}-Cd1-Cl1^{ii}	90.31(5)	Cl2-Cd1-Cl1^{ii}	89.69(5)
	Cl1^{i}-Cd1-Cl1^{ii}	88.856(18)	Cl2^{i}-Cd1-Cl1	89.69(5)
	Cl2-Cd1-Cl1	90.31(5)	Cl1^{ii}-Cd1-Cl1	91.144(18)
	Cl2^{i}-Cd1-Cl1^{iii}	89.69(5)	Cl2-Cd1-Cl1^{iii}	90.31(5)
	Cl1^{i}-Cd1-Cl1^{iii}	91.144(18)	Cl1-Cd1-Cl1^{iii}	88.856(18)
203 K	Cd1-Cl1	2.627(14)	Cd1-Cl2	2.563(13)
	Cl2-Cd1-Cl1^{iv}	91.4(2)	Cl2^{iv}-Cd1-Cl1^{iv}	97.0(2)
	Cl2-Cd1-Cl1	97.0(2)	Cl2^{iv}-Cd1-Cl1	91.4(2)

	$Cl1^{iv}$-Cd1-Cl1	84.6(8)	Cl2-Cd1-$Cl1^{v}$	88.3(2)
	$Cl2^{iv}$-Cd1-$Cl1^{v}$	84.1(2)	Cl1-Cd1-$Cl1^{v}$	88.9(4)
	Cl2-Cd1-$Cl1^{vi}$	84.1(2)	$Cl2^{iv}$-Cd1-$Cl1^{vi}$	88.3(2)
	$Cl1^{iv}$-Cd1-$Cl1^{vi}$	88.9(4)	$Cl1^{v}$-Cd1-$Cl1^{vi}$	97.5(8)

[a] Symmetry codes: (i) -x+1,-y+1,-z (ii) -x+3/2,-y+1,z-1/2 (iii) x-1/2,y,-z+1/2 (iv) -x+1,-y+2,z (v) -x+1/2,y,z-1/2 (vi) x+1/2,-y+2,z-1/2

Table S3. Selected bond lengths [Å] and angles [°] for **2**[a] at 298 K.

298 K	Cd1-Br1	2.8670(6)	Cd1-Br2	2.695(3)
	$Br2^{i}$-Cd1- $Br1^{i}$	91.56(12)	Br2-Cd1- $Br1^{i}$	88.44(12)
	$Br2^{i}$-Cd1- $Br1^{ii}$	88.44(12)	Br2-Cd1- $Br1^{ii}$	91.56(12)
	$Br1^{i}$-Cd1- $Br1^{ii}$	90.76(3)	$Br2^{i}$-Cd1- $Br1^{iii}$	91.56(12)
	Br2-Cd1- $Br1^{iii}$	88.44(12)	$Br1^{i}$-Cd1- $Br1^{iii}$	89.24(2)
	$Br2^{i}$-Cd1- Br1	88.44(12)	Br2-Cd1- Br1	91.56(12)
	$Br1^{ii}$-Cd1- Br1	89.24(3)	$Br1^{iii}$-Cd1- Br1	90.76(3)

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

Table S4. Hydrogen-Bond Geometry (Å, deg) for N-H···Cl interactions at 298 K and 203 K in **1**[a].

	D–H···A	H···A	D···A	D–H···A
298 K	N1-H1A···$Cl1^{i}$	2.94	3.406(5)	114.6
	N1-H1A···$Cl1^{ii}$	2.56	3.406(5)	158.1
	N1-H1B···$Cl1^{iii}$	2.91	3.565(6)	132.1
	N1-H1C···$Cl2^{iii}$	2.68	3.320(7)	129.4
203 K	N1-H1A···$Cl1^{iv}$	2.54	3.04(3)	116.5
	N1-H1B···$Cl1^{v}$	2.67	3.52(3)	159.0
	N1-H1C···$Cl1^{vi}$	2.52	3.39(3)	163.7

[a] Symmetry codes: (i) x-1,y,z (ii) x-1/2,y,-z+1/2 (iii) -x+1/2,-y+1,z-1/2 (iv) -x+1,-y+2,z (v) x+1/2,-y+2,z+1/2 (vi) -x+1/2,y,z+1/2

Table S5. Hydrogen-Bond Geometry (Å, deg) for N-H···Br interactions at 298 K in **2**[a].

	D–H···A	H···A	D···A	D–H···A
298 K	N1-H1A···Br1	2.80	3.47(7)	132.5
	N1-H1A···$Br1^{i}$	2.80	3.47(7)	132.5

[a] Symmetry codes: (i) x+1/2,y,-z+1/2