Supporting Information

High-temperature structural phase transition coupled with switchable dielectric properties in an organic-inorganic hybrid crystal: $[NH_3(CH_2)_2Br]_3CdBr_5$

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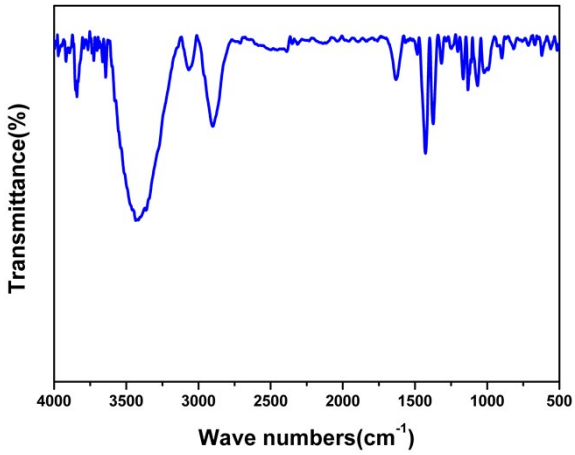

Fig. S1 Infrared (IR) spectra of **1** in KBr pellet recorded on a Shimadzu model IR-60 spectrometer at room temperature.

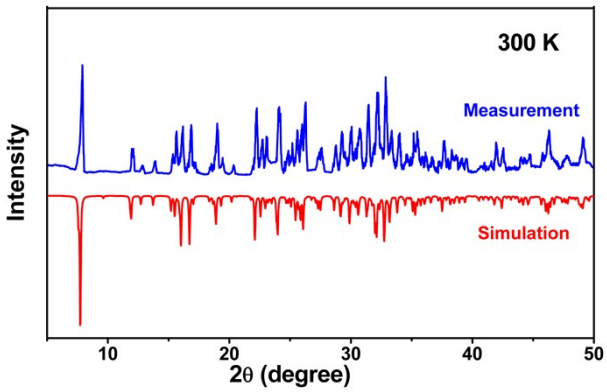

Fig. S2 Experimental powder diffraction (XRPD) patterns match very well with the simulated ones in terms of the crystal structures at 300 K.

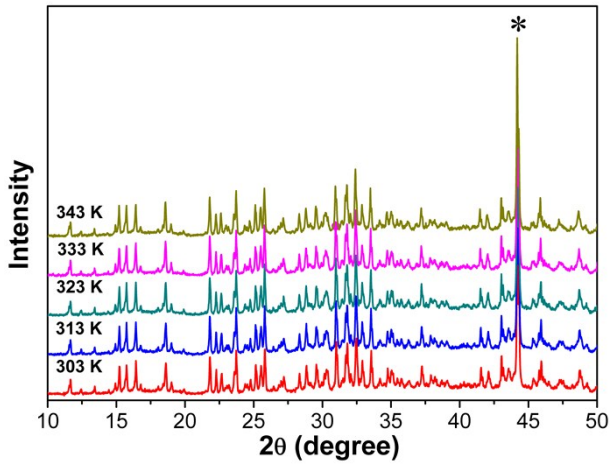

Fig. S3 Experimental powder diffraction (XRPD) patterns were measured in terms of the crystal structures at different temperatures. The strong peaks around 44deg arise from the sample holder.

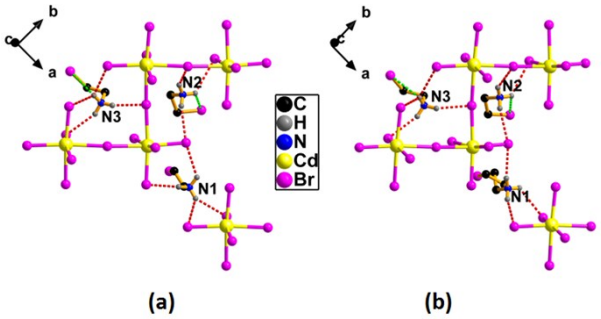

Fig. S4 Hydrogen-bonding interactions (red dashed lines) between the organic and inorganic components in 1 are shown at (a) 293 K and (b) 373 K. The green and red dashed line representative the hydrogen bonds, whose accepter are intramolecular Br atoms and intermolecular Br atoms, respectively. Hydrogen atoms bonded to the C atoms were omitted for clarity.

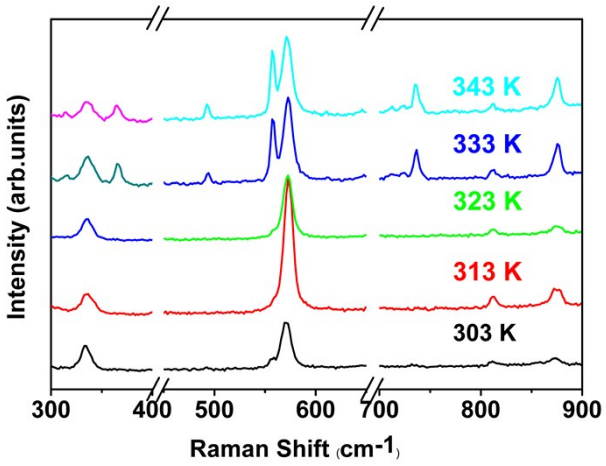

Fig. S5 Raman spectra of **1** in the spectral ranges of 200–3500 cm^{-1} measured at various temperatures.

Table S1. Selected bond lengths [Å] and angles [°] for **1** at 293 K and 373 K.

293 K	Cd1—Br1	2.717 (3)	Cd1—Br2	2.802 (4)
	Cd1—Br3	2.900 (4)	Cd1—Br3^{i}	2.952 (3)
	Cd1—Br4	2.700 (3)	Cd1—Br5	2.696 (4)
	Br3—Cd1^{ii}	2.952 (3)		
	Br1—Cd1—Br2	90.27 (7)	Br1—Cd1—Br3	89.43 (13)
	Br1—Cd1—Br3^{i}	172.32 (5)	Br2—Cd1—Br3	84.02 (6)
	Br2—Cd1—Br3^{i}	83.31 (7)	Br3—Cd1—Br3^{i}	85.71 (13)
	Br4—Cd1—Br1	95.91 (14)	Br4—Cd1—Br2	92.18 (6)
	Br4—Cd1—Br3	173.47 (5)	Br4—Cd1—Br3^{i}	88.58 (13)
	Br5—Cd1—Br1	98.66 (8)	Br5—Cd1—Br2	167.15 (5)
	Br5—Cd1—Br3	86.83 (8)	Br5—Cd1—Br3^{i}	87.03 (9)
	Br5—Cd1—Br4	96.05 (8)	Cd1—Br3—Cd1^{ii}	168.56 (5)
373 K	Cd1—Br1	2.7181	Cd1—Br2	2.8051
	Cd1—Br3	2.9188	Cd1—Br3^{iii}	2.9714
	Cd1—Br4	2.7049	Cd1—Br5	2.6989
	Br3—Cd1^{iv}	2.8051		
	Br1—Cd1—Br2	90.3	Br1—Cd1—Br3	89.5
	Br1—Cd1—Br3^{iii}	172.5	Br2—Cd1—Br3	84.2
	Br2—Cd1—Br3^{iii}	83.5	Br3—Cd1—Br3^{iii}	85.7
	Br4—Cd1—Br1	96.0	Br4—Cd1—Br2	92.3
	Br4—Cd1—Br3	173.5	Br4—Cd1—Br3^{iii}	88.5
	Br5—Cd1—Br1	98.6	Br5—Cd1—Br2	167.3
	Br5—Cd1—Br3	86.8	Br5—Cd1—Br3^{iii}	86.9
	Br5—Cd1—Br4	95.8	Cd1—Br3—Cd1^{iv}	168.8

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

Table S2. Hydrogen-Bond Geometry (Å, deg) for N-H···Br interactions at 293 K and 373 K in **1**.

	D–H···A	H···A	D···A	D–H···A
293 K	N1—H1C • • • Br^{4v}	2.84	3.483 (11)	129.7
	N1—H1C • • • Br^{2v}	2.63	3.352 (12)	137.5
	N1—H1D • • • Br1	2.73	3.357 (11)	127.6
	N1—H1D • • • $Br8^{iv}$	3.13	3.876 (13)	141.7
	N1—H1E • • • Br4	2.51	3.400 (11)	172.7
	N2— H2C • • • $Br3^{viii}$	2.78	3.545 (10)	143.6
	N2— H2C • • • $Br2^{viii}$	3.07	3.762(13)	135.1
	N2—H2D • • • $Br5^{vii}$	2.76	3.379 (11)	127.1
	N2—H2D • • • Br7	2.78	3.199 (10)	109.6
	N2—H2D • • • $Br4^{vii}$	3.13	3.634 (11)	117.5
	N2—H2E • • • $Br1^{vi}$	2.70	3.571 (12)	163.7
	N2—H2E • • • $Br3^{vi}$	3.05	3.455 (11)	109.5
	N3—H3C • • • $Br3^{iii}$	2.50	3.375 (10)	164.4
	N3—H3D • • • $Br2^{ii}$	2.54	3.384 (10)	156.1
	N3—H3D • • • $Br3^{ii}$	3.06	3.492 (10)	111.4
	N3—H3E • • • Br8	2.78	3.221 (11)	111.3
	N3—H3E • • • $Br1^{ii}$	2.88	3.519 (11)	129.2
	N3—H3C • • • $Br4^{i}$	2.91	3.524 (11)	126.4
373 K	N1— H1A • • • $Br4^{xiv}$	2.64	3.512	164.6
	N1—H1B • • • $Br2^{xiv}$	2.77	3.393	127.9
	N1—H1C • • • Br1	2.50	3.341	156.7
	N2—H2A • • • $Br3^{ix}$	2.81	3.581 (12)	144.3
	N2—H2A • • • $Br2^{ix}$	3.11	3.806 (15)	135.2
	N2— H2B • • • $Br1^{xiii}$	2.71	3.580 (13)	163.1
	N2—H2C • • • Br4	3.11	3.647 (13)	119.9
	N2—H2C • • • Br5	2.82	3.432 (12)	126.5
	N3—H3A • • • $Br3^{x}$	2.52	3.383 (12)	161.9
	N3—H3B • • • $Br4^{xi}$	2.90	3.557 (12)	131.2
	N3—H3B • • • $Br1^{xii}$	2.94	3.570 (12)	128.0
	N3—H3C • • • $Br2^{xii}$	2.57	3.426 (11)	159.8

[b] Symmetry codes: (i)−*x*+1, −*y*+1, −*z*+1; (ii) −*x*+1, −*y*+2, −*z*+1; (iii) *x*−1/2, −*y*+3/2, *z*−1/2; (iv) *x*+1, −*y*+2, *z*+1/2; (v) −*x*+2, *y*, −*z*+3/2; (vi) *x*, −*y*+2, *z*−1/2;(vii) *x*, −*y*+1, *z*−1/2; (viii) −*x*+3/2, −*y*+3/2, −*z*+1;(ix) −x+1/2, y−1/2, −z+3/2;

(x) x+1/2, y−1/2, z; (xi) −x+1, y, −z+3/2; (xii) −x+1, y−1, −z+3/2;(xiii) x, y−1, z; (xiv) −x, y, −z+3/