Supporting Information

A room temperature reversible phase transition containing dielectric switch of a host-guest supramolecular metal-halide compound †

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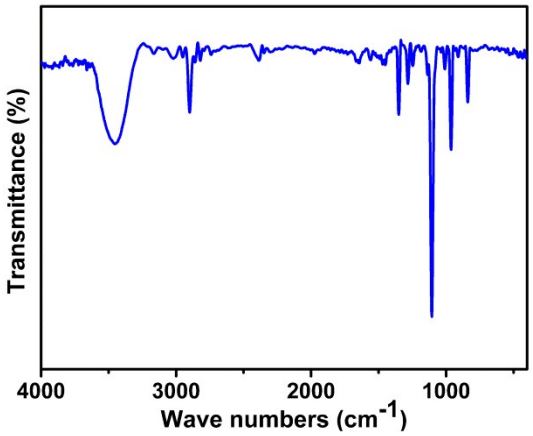

Fig. S1 Infrared (IR) spectra of solid **1** in KBr pellet recorded on a Shimadzu model IR-60 spectrometer at room temperature.

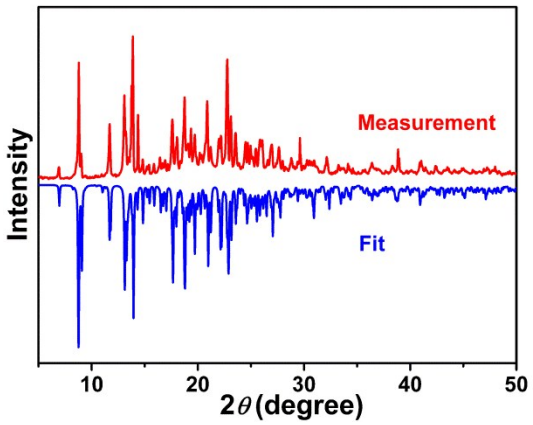

Fig. S2 Experimental powder diffraction (XRPD) patterns matching very well with the simulated ones in terms of the crystal structures of **1**.

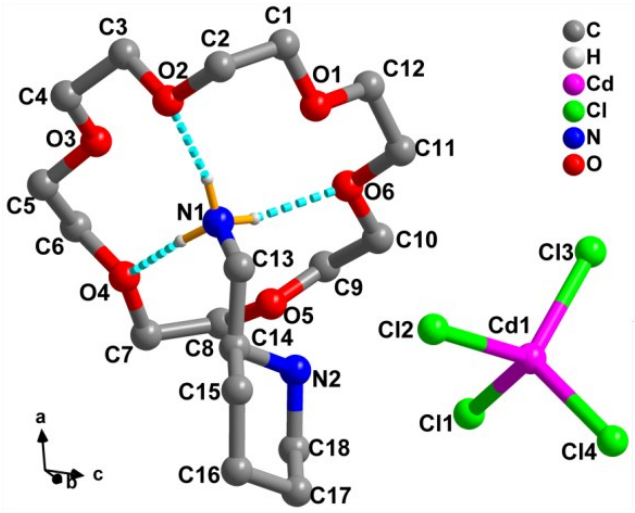

Fig. **S3** The asymmetric units of [(2-AMPD)(18-crown-6)]$CdCl_4$ **(2)** at 293 K. H atoms bonded to the C atoms are omitted for clarity.

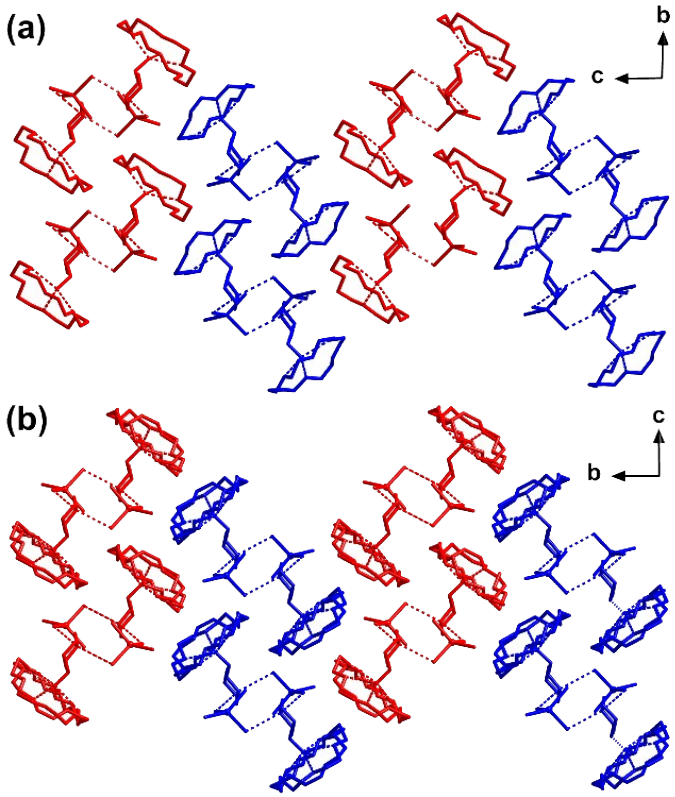

Fig. S4 Packing diagrams of **1** at (a) 273 K and (b) 323 K. The red and blue represent two different structural arrangements. All the H atoms were omitted for clarity.

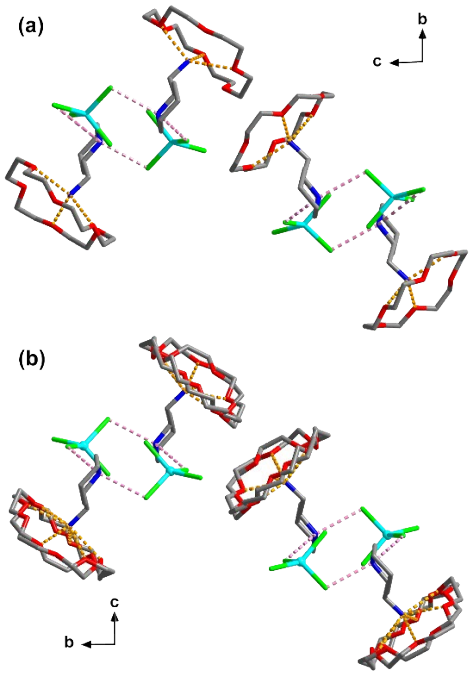

Fig. S5 The hydrogen-bonding diagrams of **1** (a) at 273 K (b) at 323 K. The yellow/ pink dash lines stand for the N-H···O/Cl hydrogen bonds.

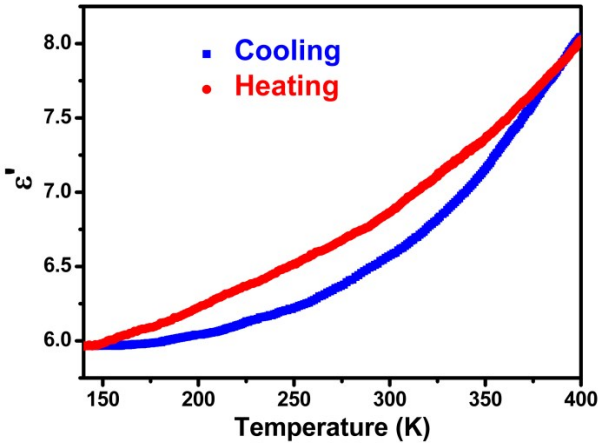

Fig. **S6** Temperature-dependent dielectric constants (ε') of [(2-AMPD)(18-crown-6)]$CdCl_4$ **(2)** was measured at 1000 kHz upon heating and cooling.

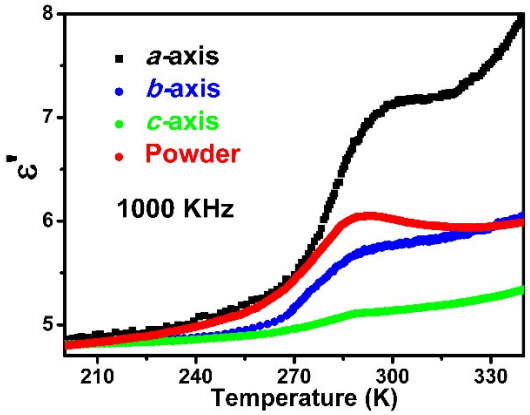

Fig. S7 Temperature-dependent dielectric permittivity of **1** measured on single-crystal samples along

a, b, and c axes and the powder samples at 1000 KHz upon cooling.

Table S1. Crystallographic data and structure refinements of [(2-AMPD)(18-crown-6)]$CdCl_4$ **(2).**

Formula sum	$C_{18}H_{40}O_6N_2Cl_4Cd$
Formula weight	634.73
Crystal system	Monoclinic
Space group	$P2_1/c$
Temperature / K	293
a / Å	15.653 (3)
b / Å	9.780 (2)
c / Å	19.737 (4)
α / deg	90.00
β / deg	109.68 (3)
γ / deg	90.00
Volume (Å^3)	2845.0 (11)
Z	4
Reflns measured	18572
Independent reflections	6413
Reflns used	5134
GOF	1.10
R_1 [$I > 2\sigma(I)$]	0.046
wR_2 [$I > 2\sigma(I)$]	0.113

Table S2. Selected bond lengths [Å] and angles [°] for **1**[a] at 273 K and 323 K.

273 K	N1—C1	1.484(7)	N4—C19	1.489(7)
	C1—C2	1.503(9)	C19—C20	1.487(9)
	C2—C3	1.506(9)	C20—C21	1.509(9)
	C3—C4	1.533(8)	C21—C22	1.519(8)
	C4—C5	1.518(7)	C22—C23	1.504(7)
	C5—N1	1.480(6)	C23—N4	1.491(6)
	C5—C6	1.516(7)	C23—C24	1.513(7)
	C6—N2	1.484(6)	C24—N3	1.477(6)
	Cu1—Cl1	2.288(17)	Cu2—Cl5	2.259(17)
	Cu1—Cl2	2.207(19)	Cu2—Cl6	2.288(18)
	Cu1—Cl3	2.239(17)	Cu2—Cl7	2.241(18)
	Cu1—Cl4	2.243(19)	Cu2—Cl8	2.208(18)
	Cl1—Cu1—Cl2	98.89(7)	Cl5—Cu2—Cl6	96.45(6)
	Cl1—Cu1—Cl3	129.32(7)	Cl5—Cu2—Cl7	97.60(7)
	Cl1—Cu1—Cl4	99.42(6)	Cl5—Cu2—Cl8	137.96(8)
	Cl2—Cu1—Cl3	99.30(8)	Cl6—Cu2—Cl7	131.96(7)
	Cl2—Cu1—Cl4	137.02(9)	Cl6—Cu2—Cl8	101.00(7)
	Cl3—Cu1—Cl4	98.48(7)	Cl7—Cu2—Cl8	98.48(7)
323 K	N1—C1	1.509(9)	C5—C6	1.509(9)

C1—C2	1.476(11)	C6—N2	1.490(8)
C2—C3	1.516(12)	Cu1—Cl1	2.257(3)
C3—C4	1.558(11)	Cu1—Cl2	2.310(2)
C4—C5	1.495(9)	Cu1—Cl3	2.263(3)
C5—N1	1.508(8).	Cu1—Cl4	2.214(3)
Cl1—Cu1—Cl2	127.75(10)	Cl2—Cu1—Cl3	98.75(10)
Cl1—Cu1—Cl3	98.87(9)	Cl2—Cu1—Cl4	100.34(10)
Cl1—Cu1—Cl4	100.28(11)	Cl3—Cu1—Cl4	135.67(11)

Table S3. Hydrogen-bond geometry (Å) at 273 K and 323 K.

	D—H···A	H···A	D···A	D—H···A
273 K	N1—H1A···Cl6i	2.33	3.194(5)	165
	N1—H1B···Cl7ii	2.47	3.150(5)	134
	N2—H2A···O1	1.88	2.766(5)	172
	N2—H2B···O3	2.05	2.931(7)	170
	N2—H2C···O5	2.02	2.873(6)	160
	N3—H3C···O8	2.00	2.855(7)	160
	N3—H3D···O10	2.08	2.907(7)	155
	N3—H3E···O12	1.98	2.835(7)	161
	N4—H4C···Cl3	2.36	3.084(5)	139
	N4—H4D···Cl1iii	2.27	3.154(5)	170
323 K	N1—H1A···Cl1iv	2.44	3.151(5)	136
	N1—H1B···Cl2v	2.29	3.184(5)	170
	N2—H2A···O3’	2.25	2.845(5)	123
	N2—H2A···O4’	1.96	2.783(7)	152
	N2—H2B···O1’	2.21	2.865(6)	129
	N2—H2B···O2’	2.16	2.958(7)	147
	N2—H2C···O5’	2.19	2.832(7)	128
	N2—H2C···O6’	2.10	2.918(7)	150
	N2—H2C···O5	1.99	2.833(5)	155
	N2—H2C···O6	2.37	2.969(7)	124
	N2—H2B···O1	2.00	2.844(7)	155
	N2—H2B···O2	2.51	3.017(7)	116
	N2—H2A···O3	2.07	2.908(6)	154
	N2—H2A···O4	2.40	2.993(7)	124

Symmetry codes: (i) −x+1, −y+1, −z+1; (ii) x, y+1, z; (iii) −x+1, −y+1, −z; (iv) x, y, 1+z; (v) 1−x, −y, 1−z.