Supporting Information

A novel organic-inorganic hybrid phase transition compound based on 4-Ethylmorpholine with switchable dielectric and luminescent properties

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Experimental section

Materials.

4-Ethylmorpholine (Aladdin, 98%), Manganese Chloride Tetrahydrate (Aladdin, 99%), Cobalt (II) chloride (Aladdin, 99.9%), Cupric chloride dihydrate (Aladdin, 99. 9%), hydrochloric acid and Deionized water were used as received.

Synthesis.

Compound 1 $[4\text{-Ethylmorpholine}]_2MnCl_4$ was obtained by slowly evaporating corresponding aqueous solution (about 30 ml) containing 4-Ethylmorpholine (10 mol), manganese chloride tetrahydrate (10 mmol) and hydrochloric acid (about 3 ml) at room temperature for few days. The synthesis of 2 $[4\text{-Ethylmorpholine}]_2CoCl_4$ and 3 $[4\text{-Ethylmorpholine}]_2CuCl_4$ are similar to the one for $[4\text{-Ethylmorpholine}]_2MnCl_4$. They are obtained after slow evaporation of a stoichiometric mixture of 4-Ethylmorpholine, Cobalt (II) chloride and Cupric chloride dihydrate dilute hydrochloric acid and aqueous solution at room temperature.

Methods.

To record PXRD patterns, we used the Rigaku smartlab X-ray diffraction instrument in the 2θ between 5° and 50° with a step size of 0.02°. Thermogravimetric analyses (TGA) were carried out on a NETZSCH TG209F3 system with a heating rate of 10 K min-1 under a nitrogen atmosphere. Differential scanning calorimetry (DSC) measurements were carried out on a NETZSCH differential scanning calorimeter (polyma) under nitrogen atmosphere in aluminum crucibles with a heating or cooling rate of 15 K min^{-1}. X-ray single crystal diffraction data of three compounds were performed using Mo-Kα radiation (λ = 0.71073) on a Bruker SMART APEX-II CCD diffractometer in the ω scan mode. The structural data were collected at 293 K for three compounds. Data processing with empirical absorption correction was conducted by using the SADABS. Crystal structures were confirmed by direct methods and refined by full-matrix least-squares methods based on F^2 through the SHELXTL and OLEX 2 software package. All non-hydrogen atoms were anisotropically refined via all reflections with $I > 2\sigma(I)$. In addition, the distances and angles between some atoms are calculated by DIAMOND.

CCDC 2112060 – 2112062 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data.request/cif

Table S1 Crystal parameters of compound

Moiety formula	**$[C_6H_{14}NO]_2MnCl_4$**	**$[C_6H_{14}NO]_2CoCl_4$**	**$[C_6H_{14}NO]_2CuCl_4$**
Temperature	293 K	293 K	293 K
Weight	429.10	433.09	437.70
Crystal system	*Triclinic*	*Triclinic*	*Monoclinic*
Space group	*P*-1	*P*-1	$P2_1/c$
a/Å	8.2737(12)	8.2361(4)	17.5510(7)
b/Å	10.4938(15)	10.4179(4)	7.4842(3)
c/Å	12.0521(17)	12.0049(5)	16.2478(7)
α/deg	89.6020(10)	89.486(3)	90
β/deg	79.5170(10)	79.688(3)	114.157(2)
γ/deg	84.3770(10)	84.884(3)	90
Volume/Å^3	1023.9(3)	1009.35(8)	1947.33(14)
Z	2	2	4
R_1 [$I>2\sigma(I)$]	0.0372	0.0374	0.0322
wR_2 [$I>2\sigma(I)$]	0.0808	0.1029	0.0830
GOF	1.010	1.098	1.051

Table S2. Hydrogen bonds under 293 K for compound 1

D—H…A	**D—H**	**H…A**	**D…A**	**＜DHA**
N1—H1…Cl1	0.98(2)	2.31(7)	3.216(2)	154(12)
N2—H2…Cl4	0.98(2)	2.32(7)	3.206(2)	150(13)
C6—H6A…Cl2^{i}	0.97(3)	2.70(8)	3.577(3)	150(16)
C8—H8B…Cl3^{ii}	0.97(3)	2.82(8)	3.732(3)	156(18)
C9—H9B…O2^{iii}	0.97(4)	2.44(19)	3.364(4)	159(2)

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

Table S3. Hydrogen bonds under 293 K for compound 2

D—H…A	**D—H**	**H…A**	**D…A**	**＜DHA**
N1—H1…Cl1	0.910(2)	2.3794(18)	3.2237(18)	154.4(2)
N2—H2…Cl4	0.910(2)	2.3810(18)	3.2071(18)	150.88(18)
C1—H1B…Cl2^{i}	0.970(3)	2.715(2)	3.599(2)	151.8(2)
C7—H7A…O1^{ii}	0.969(5)	2.411(4)	3.329(4)	157.7(3)

Symmetry codes：（i）1-x, 1-y, 1-z；（ii）x, -1+y, z.

Table S4. Hydrogen bonds under 293 K for compound 3

D—H…A	D—H	H…A	D…A	＜DHA
N1—H1…Cl2	0.98(15)	2.30(6)	3.2417(16)	162(9)
N2—H2…Cl1	0.98(14)	2.59(7)	3.2936(18)	129(13)
N2—H2…Cl4	0.98(14)	2.53(6)	3.4005(19)	148(13)
C1—H1B…O2^{i}	0.97(14)	2.60(2)	3.402(3)	141(16)

Symmetry codes：（i）1-x, -y, 2-z.

Table S5. Selected bond lengths [Å] and angles [°] for compound 1 at 293 K

(Length/Å)			
Mn1—Cl1	2.3601(7)	N1—C2	1.493(3)
Mn1—Cl4	2.3624(8)	N2—C1	1.493(3)
Mn1—Cl2	2.3474(8)	N2—C12	1.494(3)
Mn1—Cl3	2.3334(8)	N2—C9	1.497(4)
O1—C10	1.418(3)	C1—C10	1.495(4)
O1—C7	1.419(4)	C4—C6	1.493(4)
O2—C3	1.414(3)	C8—C3	1.495(4)
O2—C3	1.406(3)	C12—C7	1.478(4)
N1—C4	1.490(3)	C2—C11	1.490(5)
N1—C8	1.496(3)	C9—C5	1.420(5)

（Angle/°）			
Cl1-Mn1-Cl4	108.04(3)	C1-N2-C9	113.4(2)
Cl2-Mn1-Cl1	106.40(3)	C12-N2-C9	110.1(2)
Cl2-Mn1-Cl4	108.97(3)	N2-C1-C10	110.5(2)
Cl3-Mn1-Cl1	117.44(3)	N1-C4-C6	110.2(2)
Cl3-Mn1-Cl4	107.32(3)	O2-C6-C4	111.7(2)
Cl3-Mn1-Cl2	108.45(3)	C3-C8-N1	110.1(2)
C10-O1-C7	109.1(2)	O1-C10-C1	111.7(2)
C3-O2-C6	108.9(2)	C7-C12-N2	111.2(2)
C4-N1-C8	109.8(2)	O2-C3-C8	111.1(2)
C4-N1-C2	112.9(2)	O1-C7-C12	111.0(2)
C2-N1-C8	111.6(2)	C11-C2-N1	113.3(3)
C1-N2-C12	109.3(2)	C5-C9-N2	114.5(3)

Table S6. Selected bond lengths [Å] and angles [°] for compound 2 at 293 K

（Length/Å）			
Co1—Cl1	2.2787(5)	N1—C9	1.497(3)
Co1—Cl4	2.2805(6)	N2—C6	1.500(2)
Co1—Cl2	2.2643(5)	N2—C12	1.500(3)
Co1—Cl3	2.2559(5)	N2—C7	1.500(3)
O1—C1	1.411(3)	C1—C4	1.500(3)
O1—C3	1.410(3)	C6—C10	1.501(3)
O2—C10	1.421(3)	C8—C3	1.496(4)
O2—C2	1.426(3)	C12—C2	1.475(4)
N1—C4	1.497(3)	C7—C5	1.448(4)
N1—C8	1.506(3)	C9—C11	1.491(5)

（Angle/°）			
Cl1-Co1-Cl4	107.69(2)	C1-N2-C9	113.03(17)
Cl2-Co1-Cl1	106.99(2)	C7-N2-C12	110.17(18)
Cl2-Co1-Cl4	109.44(2)	O1-C1-C4	111.44(19)
Cl3-Co1-Cl1	116.07(2)	N1-C4-C1	110.08(16)
Cl3-Co1-Cl4	107.72(2)	N2-C6-C10	110.45(16)
Cl3-Co1-Cl2	108.81(2)	C3-C8-N1	110.44(19)
C3-O1-C1	109.37(16)	O2-C10-C6	111.73(18)
C10-O2-C2	109.28(16)	C2-C12-N2	110.94(18)
C4-N1-C8	109.30(16)	O1-C3-C8	110.6(2)
C9-N1-C4	112.8(2)	C5-C7-N2	113.9(2)
C9-N1-C8	112.0(2)	O2-C2-C12	111.57(18)
C12-N2-C6	109.56(15)	C11-C9-N1	112.9(3)

Table S7. Selected bond lengths [Å] and angles [°] for compound 3 at 293 K

（Length/Å）			
Cu1—Cl1	2.2482(5)	N1—C7	1.488(2)
Cu1—Cl4	2.2532(6)	N2—C8	1.490(3)
Cu1—Cl2	2.2505(6)	N2—C10	1.493(3)
Cu1—Cl3	2.2230(7)	N2—C5	1.506(3)
O1—C12	1.419(3)	C1—C6	1.506(3)
O1—C3	1.416(3)	C4—C9	1.494(3)
O2—C6	1.418(3)	C8—C12	1.510(3)
O2—C2	1.410(3)	C10—C3	1.488(4)
N1—C1	1.494(2)	C7—C2	1.502(4)
N1—C4	1.499(3)	C5—C11	1.471(4)

（Angle/°）			
Cl1-Cu1-Cl4	97.25(2)	C8-N2-C5	114.25(18)
Cl1-Cu1-Cl2	133.61(3)	C10-N2-C5	111.17(18)
Cl2-Cu1-Cl4	99.03(3)	N1-C1-C6	110.07(17)
Cl3-Cu1-Cl1	100.93(3)	C9-C4-N1	112.83(18)
Cl3-Cu1-Cl4	135.16(3)	O2-C6-C1	111.6(2)
Cl3-Cu1-Cl2	97.34(3)	N2-C8-C12	110.47(17)
C3-O1-C12	110.18(16)	C3-C10-N2	109.73(18)
C2-O2-C6	110.18(16)	O1-C12-C8	111.88(19)
C1-N1-C4	113.69(16)	O1-C3-C10	111.4(2)
C7-N1-C1	108.91(16)	N1-C7-C2	109.51 (19)
C7-N1-C4	110.66(17)	O2-C2-C7	112.09(19)
C8-N2-C10	108.71(17)	C11-C5-N2	112.5(2)

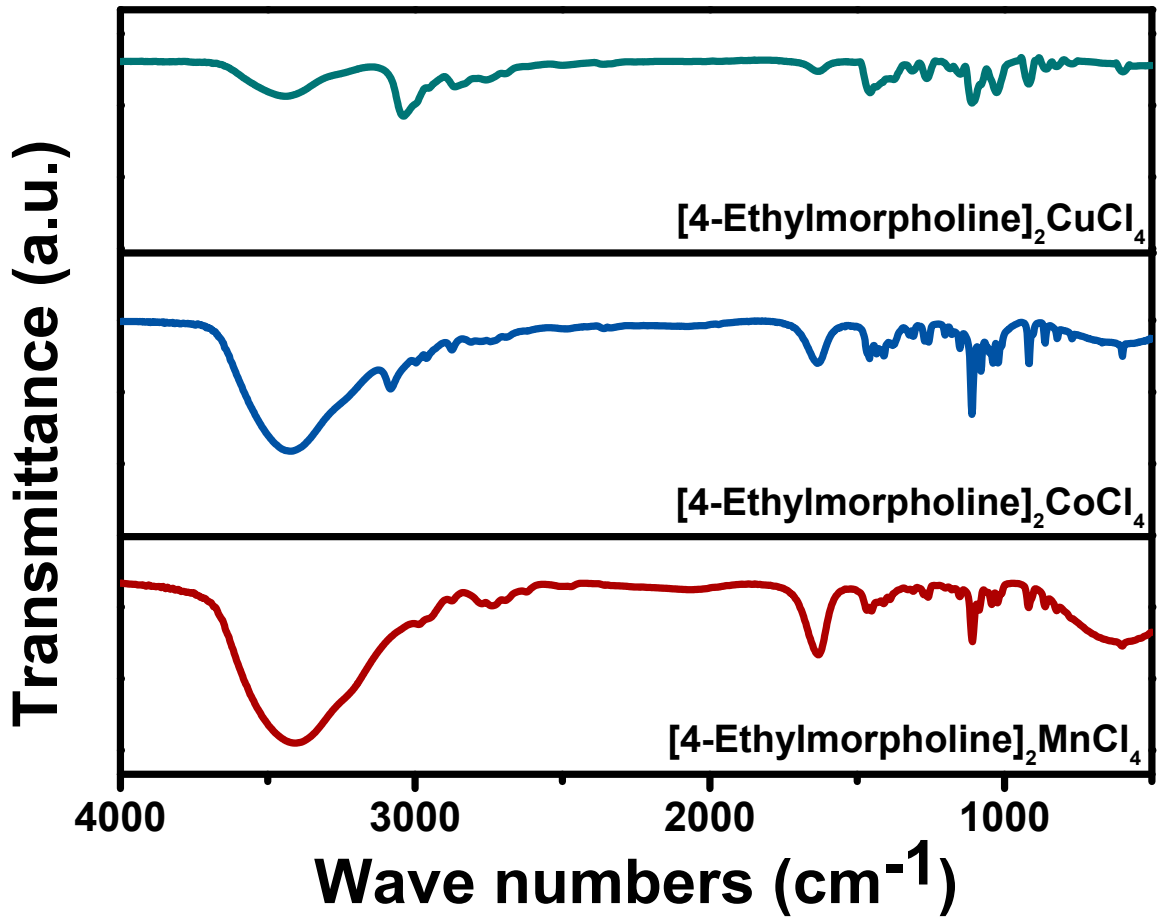

Figure S1. IR of the compound 1, compound 2 and compound 3.

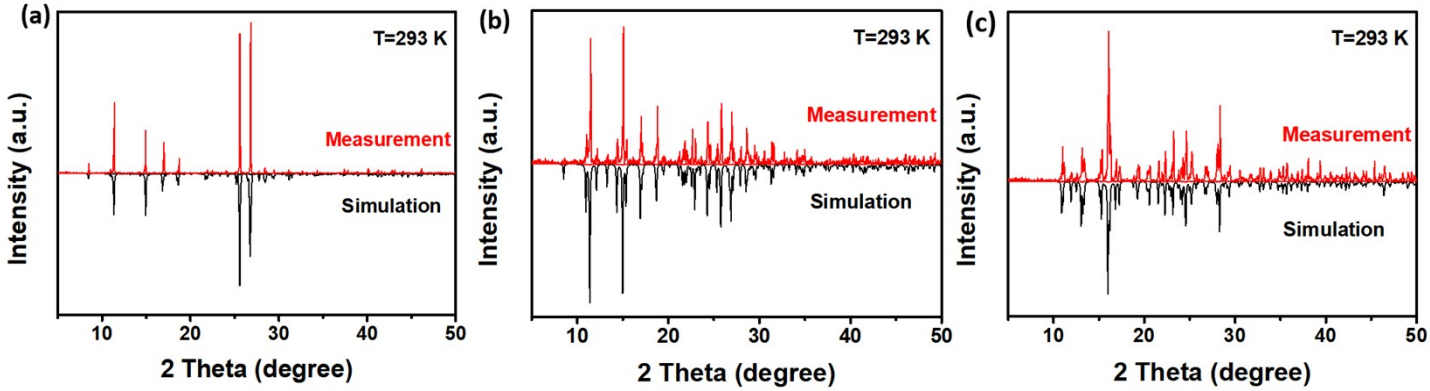

Figure S2. XRD measurement of compound 1 (a), compound 2 (b) and compound 3 (c).

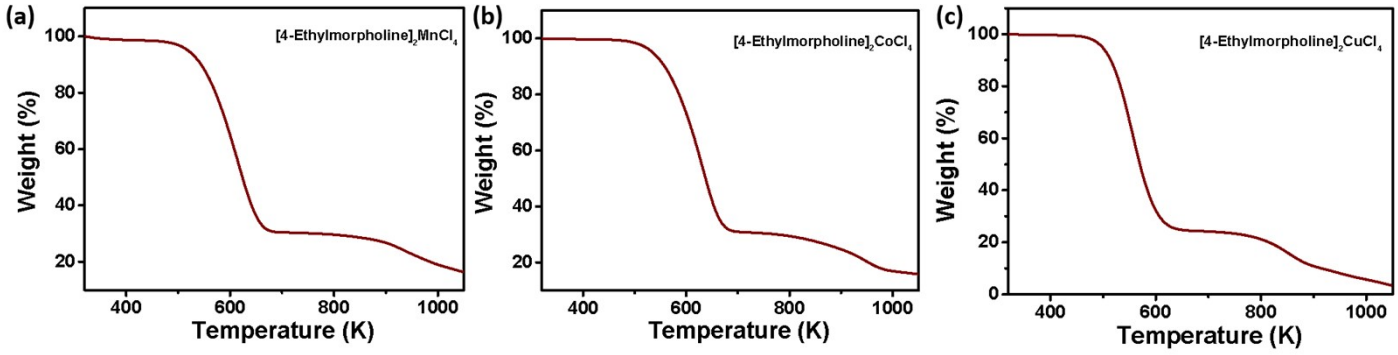

Figure S3. TGA of the compound 1 (a), compound 2 (b) and compound 3 (c).

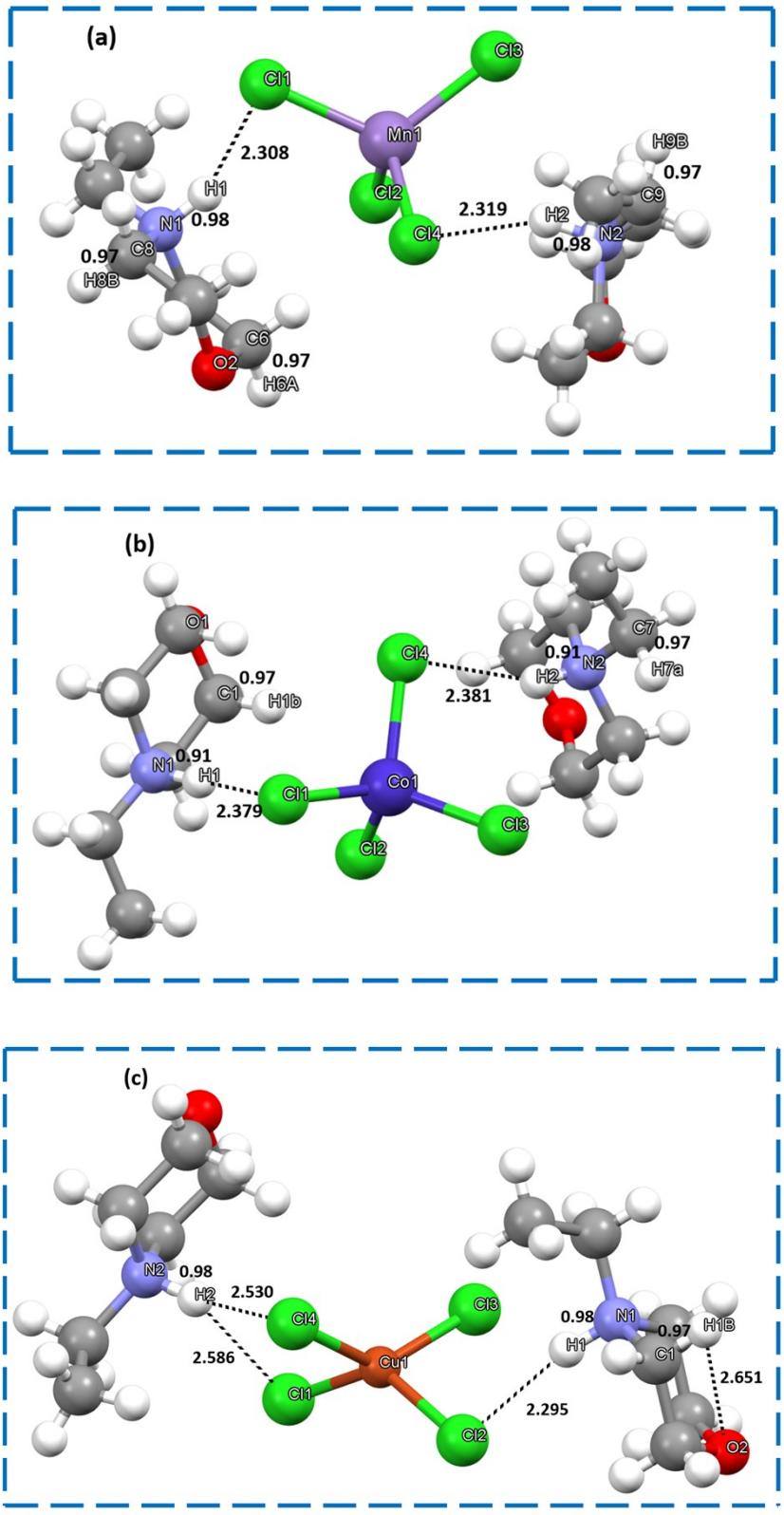

Figure S4. Compound structures of compound 1 (a), compound 2 (b) and compound 3 (c).

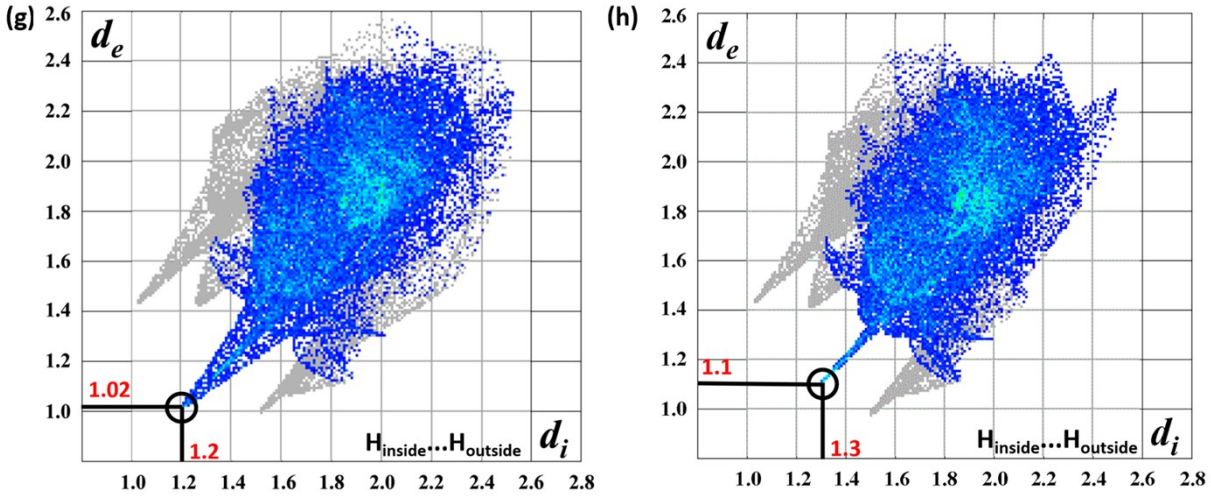

Figure S5. Two-dimensional fingerprint plots of compound 1 (g) and compound 2 (h).

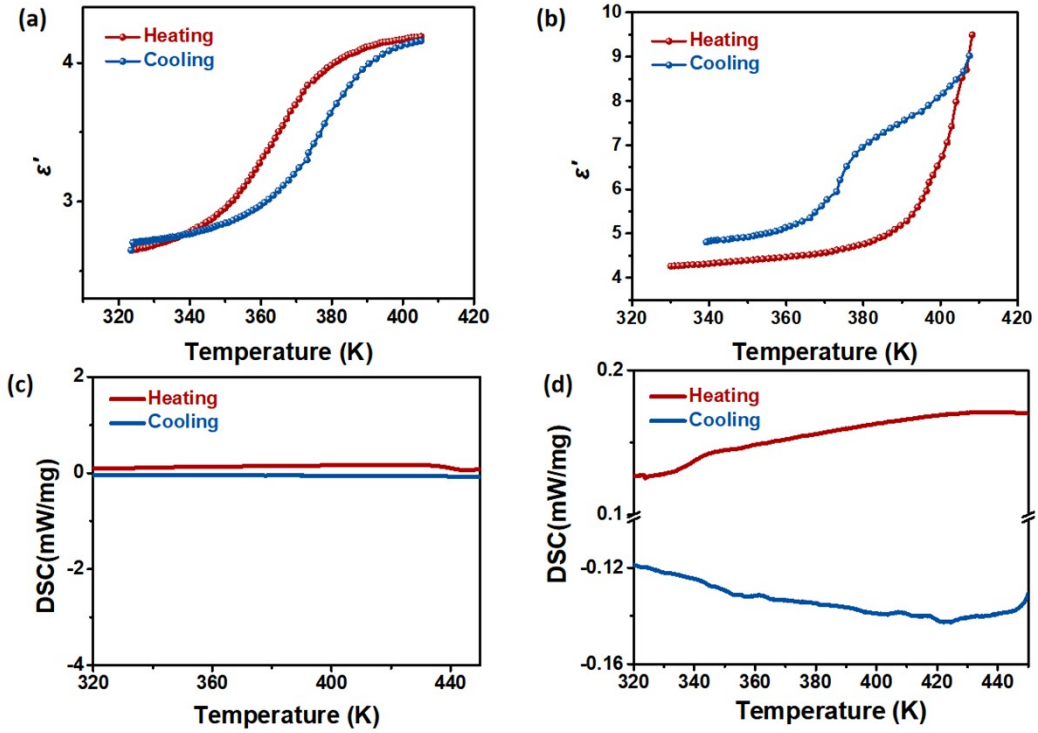

Figure S6. Temperature-dependent real part (ε') of the dielectric constant for 2 (a) and 3 (b). DSC curves of 2 (c) and 3 (d).

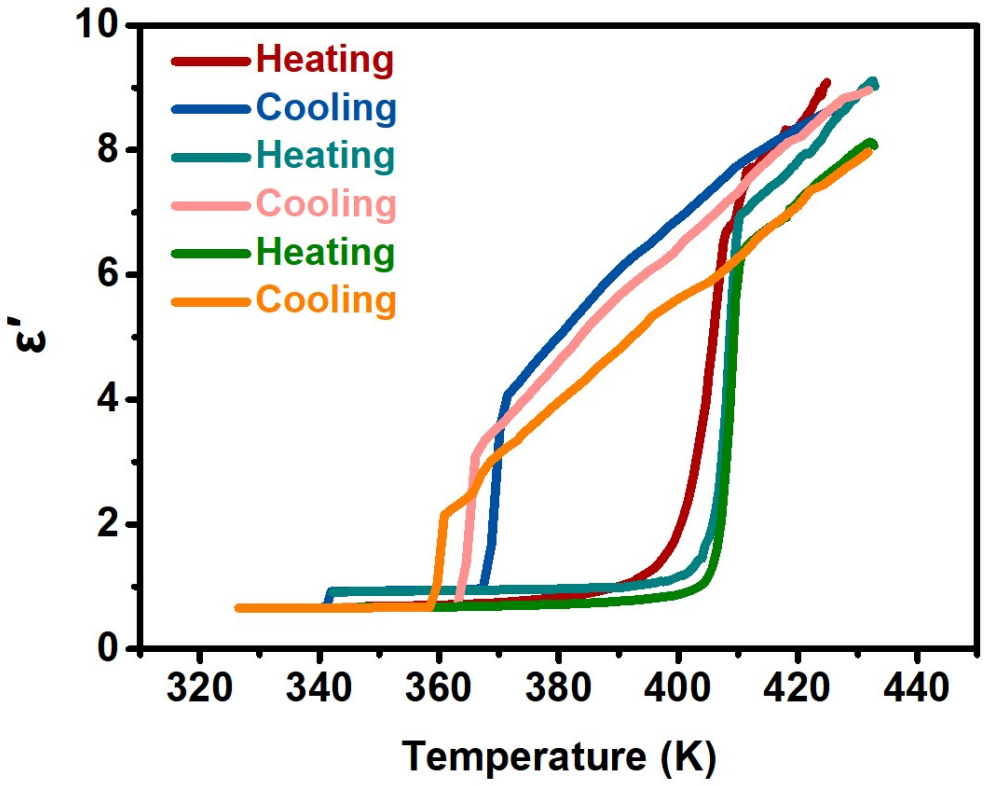

Figure S7. Dielectric cycle measurement of compound 1 at 1MHz.

The calculation processes of entropy and N

(1) $\Delta S = \Delta H \times Mr$ / K

= 9.995×429/425

= 10.089 J (K mol)-1

(2) $\Delta S = R\ln N$ (R=8.314 J/(mol·K))

$N = 3.36$