Supporting Information

Two In-Based Organic−Inorganic Hybrid Compounds with Reversible Phase Transition Derived from Order-Disorder Changes of Cations or Anions

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Methods:

Thermal measurements

The thermogravimetric measurement (TG) was performed using a TA SDT650 instrument under a flowing air atmosphere with a heating rate of 5 K/min. Since halogen can cause damage to the instrument, compounds **1** and **2** only test to the decomposition temperature. Differential scanning calorimetry (DSC) measurements were performed on a Netzsch 200F3 instrument with sweeping rates of 10 K/min under a nitrogen atmosphere.

Single crystal X-ray diffraction

The single crystal X-ray diffraction data for compounds **1** and **2** were recorded by a SuperNova Dual Atlas diffractometer equipped with a graphite-monochromated Cu-Ka radiation (λ=1.54184 Å). The crystal structures were solved by the *OLEX2* software package. All non-H atoms were subjected to anisotropic refinement and all H atoms were introduced in calculated positions. The crystal data of compounds **1** and **2** have been deposited in the Cambridge Crystallographic Database Centre as supplementary material, 2083457 (for **1** at 110 K), 2083459 (for **1** at 293K), 2083456 (for **2** at 110 K) and 2076595 (for **2** at 380 K).

Dielectric measurements

The temperature dependence of real electric constant ε ($\varepsilon = \varepsilon' - i\varepsilon''$), where ε' and ε'' are the real and imaginary parts, respectively, was carried out on a TH2828 Precision LCR meter with sweeping rate of approximately 5 K/min at 10 kHz, 50 kHz, 100 kHz, 500 kHz and 1 MHz with an applied voltage of 1.0 V. In the dielectric experiments, the crystals of compounds **1** and **2** were ground and pressed into dense slice, the capacitor was made by painting two faces of the dense slice with silver conducting paste and using gold wires as the electrodes. After being dried by silica gel for two days, the capacitor was detected under a microscope with a Phenix CCD eye and the corresponding software.

Infrared measurements

Fourier transform infrared (FT-IR) spectrum of compounds **1** and **2** were obtained using a Bruker Vertex 70 spectrophotometer within the range of 4000–400 cm^{-1}.

PXRD measurements

The powder X-Ray diffraction (PXRD) pattern was obtained on Rigaku SmatrLab SE advance diffractometer with Cu–Kα radiation (λ = 1.54056 Å) in the range of 5° < 2θ < 50°.

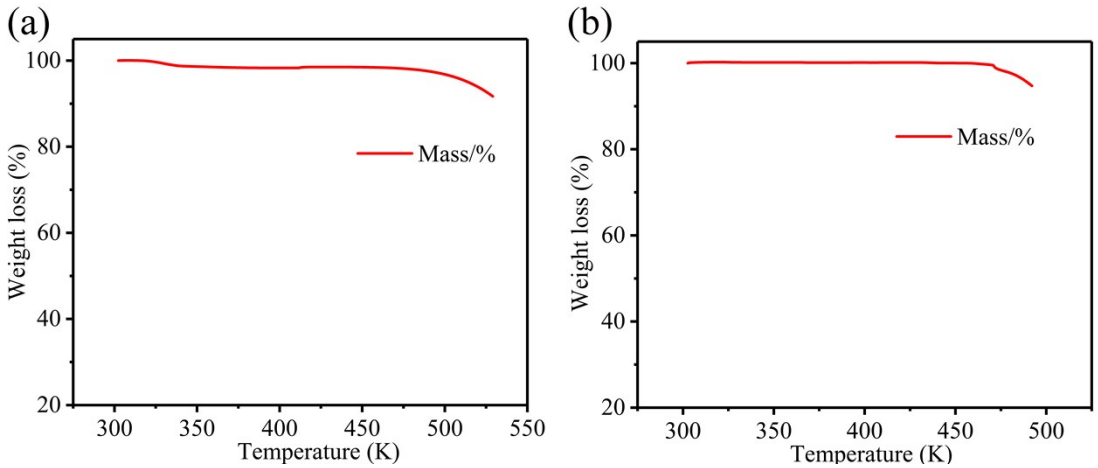

Figure S1. The TG curves of compounds **1** (a) and **2** (b) in flowing air with a heating rate of 5 K/min.

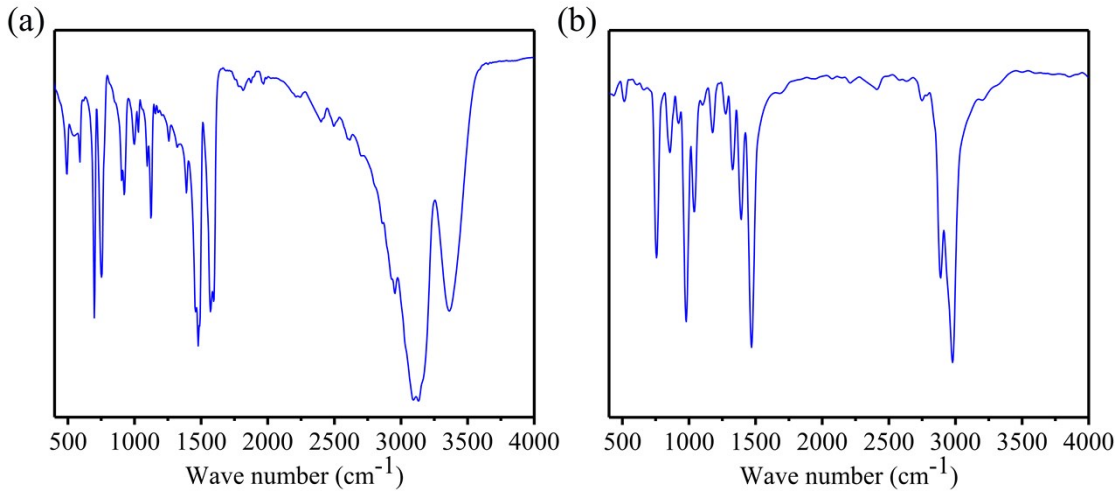

Figure S2. IR spectrum of compounds **1** and **2**.

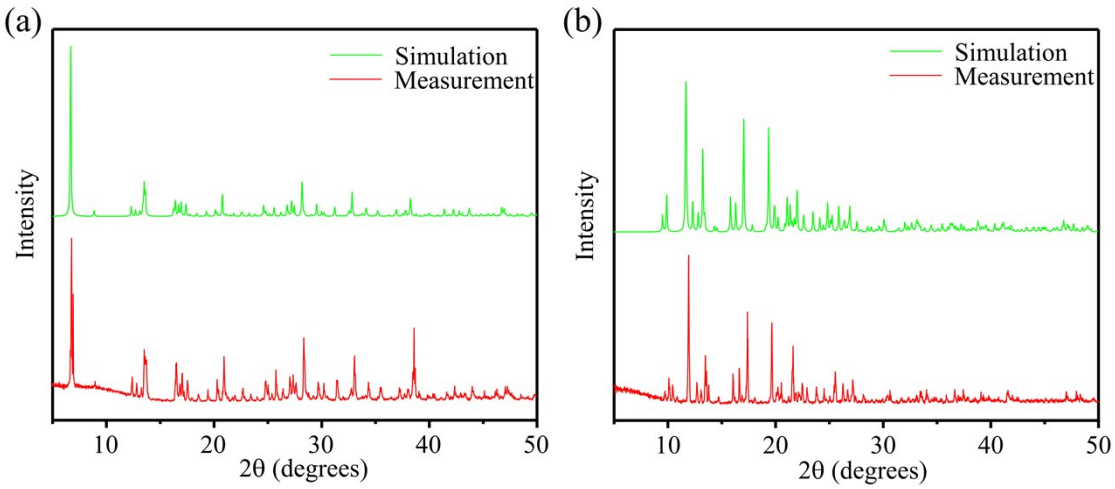

Figure S3. PXRD of compounds **1** and **2**.

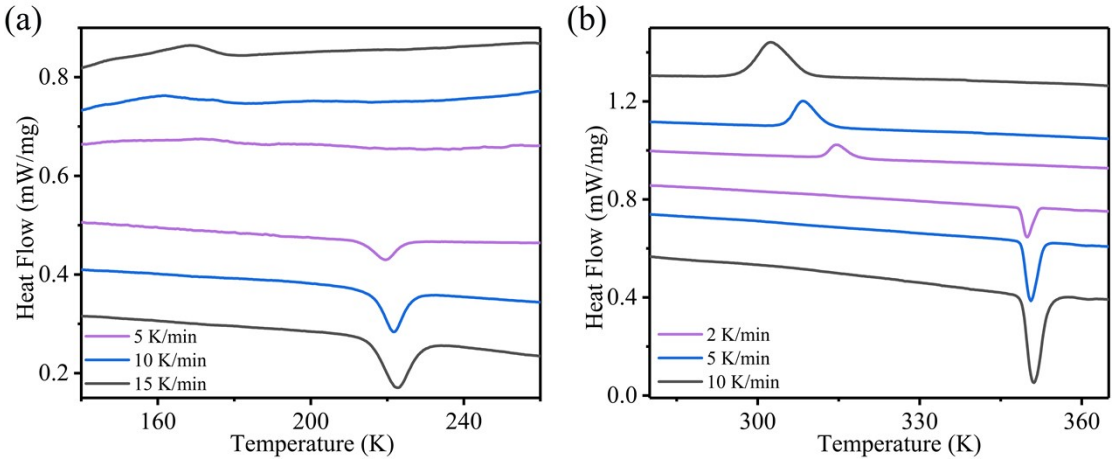

Figure S4. DSC curves of **1** (a) and **2** (b) at different sweeping rates.

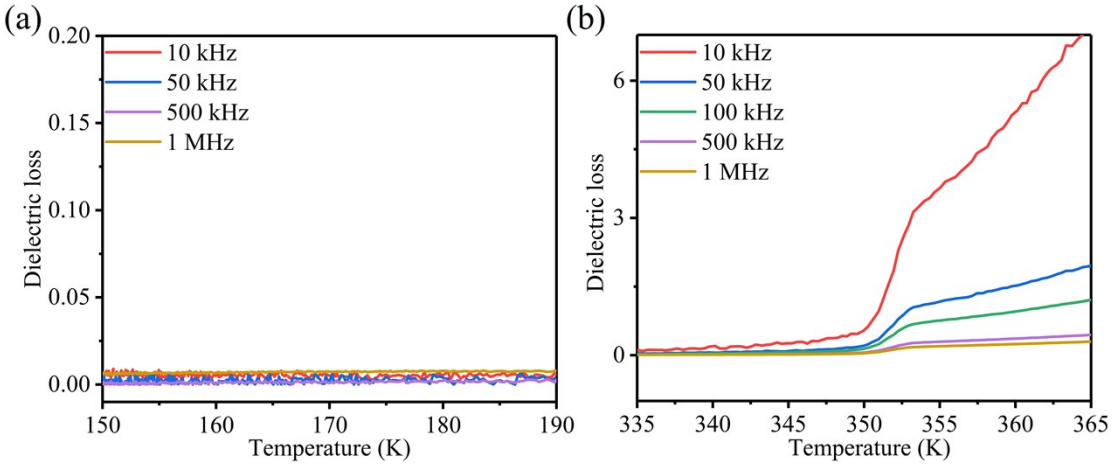

Figure S5. Temperature-dependence of imaginary part (ε″) of dielectric permittivity of compounds **1** and **2** measured at selected frequencies.

Table S1. Selected crystallographic data for compounds **1** and **2**.

compounds	**1**		**2**	
Temperature/K	110	293	110	380
Moiety formula	$C_{16}H_{26}Br_5InN_2O$		$C_{12}H_{28}Cl_4InN$	
Formula weight	776.76		442.97	
Crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic
Space group	$P2_1/n$	$P2_1/m$	*Pbca*	*Pbca*
a/Å	14.264(19)	10.912(8)	13.6589(10)	14.299(4)
b/Å	8.874(12)	8.556(7)	16.4433(12)	16.580(5)
c/Å	19.71(3)	14.164(11)	17.4222(12)	17.771(5)
α/°	90	90	90	90
β/°	109.673(18)	110.910(14)	90	90
γ/°	90	90	90	90
V (Å^3)	2349(5)	1235.3(17)	3913.0(5)	4213(2)
Z	4	2	8	8
ρ_{calc} (g/cm^{-3})	2.196	2.083	1.504	1.397
F(000)	1472.0	732.0	1792.0	1792.0
GOF on F^2	1.005	1.009	1.055	0.941
R_1, wR_2 [$I >$ $2\sigma(I)$]	$R_1 = 0.0333$, $wR_2 = 0.0624$	$R_1 = 0.0921$, $wR_2 = 0.2229$	$R_1 = 0.0294$, $wR_2 = 0.0678$	$R_1 = 0.0611$, $wR_2 = 0.1339$
R indices (all data)	$R_1 = 0.0608$, $wR_2 = 0.0710$	$R_1 = 0.1548$, $wR_2 = 0.2602$	$R_1 = 0.0386$, $wR_2 = 0.0737$	$R_1 = 0.2182$, $wR_2 = 0.1970$
Reflections collected	19349	5950	32563	13781
$\Delta\rho^a$ (e Å^{-3})	1.06/-0.82	3.02/-2.16	0.45/-0.37	0.44/-0.34

Table S2. Selected bond lengths (Å) and angles (°) for compounds **1** and **2**.

1 (110 K)			
In1–Br1	2.666(3)	C4–C5	1.400(7)
In1–Br2	2.683(3)	C5–C6	1.377(8)
In1–Br3	2.603(4)	C6–C7	1.372(8)
In1–Br4	2.620(3)	C7–C8	1.408(7)
In1–Br5	2.691(3)	C9–C10	1.516(7)
In1–O1	2.277(4)	C10–C11	1.511(7)
N1–C1	1.502(6)	C11–C12	1.376(7)
N2–C9	1.501(6)	C11–C16	1.385(7)
C1–C2	1.495(6)	C12–C13	1.393(8)
C2–C3	1.516(7)	C13–C14	1.383(8)
C3–C4	1.387(6)	C14–C15	1.370(8)
C3–C8	1.389(7)	C15–C16	1.392(8)
Br1–In1–Br2	89.99(1)	C4–C3–C8	118.1(5)
Br1–In1–Br5	88.70(1)	C8–C3–C2	120.7(4)
Br3–In1–Br1	92.45(3)	C3–C4–C5	120.7(5)
Br3–In1–Br2	92.62(2)	C6–C5–C4	120.1(5)
Br3–In1–Br4	97.24(2)	C7–C6–C5	120.6(5)
Br3–In1–Br5	94.44(3)	C6–C7–C8	119.0(5)
Br4–In1–Br2	89.46(1)	C3–C8–C7	121.5(5)
Br4–In1–Br5	90.66(1)	C11–C10–C9	111.4(4)
O1–In1–Br1	85.46(8)	C12–C11–C10	121.6(5)
O1–In1–Br2	87.91(8)	C12–C11–C16	118.2(5)
O1–In1–Br4	84.85(8)	C16–C11–C10	120.2(4)
O1–In1–Br5	85.01(8)	C11–C12–C13	121.1(5)
C2–C1–N1	110.0(4)	C14–C13–C12	119.8(5)
N2–C9–C10	111.2(4)	C15–C14–C13	119.8(5)
C1–C2–C3	112.0(4)	C14–C15–C16	119.9(5)
C4–C3–C2	121.2(4)	C11–C16–C15	121.2(5)
1 (293 K)			
In1–Br2A	2.656(3)	C15–C14	1.39

In1–Br2	2.656(3)	C14–C13	1.39
In1–Br3	2.686(8)	C13–C12	1.39
In1–Br3A	2.686(8)	C8–C3	1.330(2)
In1–Br1	2.596(2)	C8–C7	1.29(2)
In1–O1	2.302(6)	C3–C2	1.55(2)
N2–C9	1.446(1)	C3–C4	1.41(2)
N1–C1A	1.478(2)	C5–C4	1.374(2)
C11–C16	1.39	C5–C6	1.369(1)
C11–C12	1.39	C7–C6	1.27(2)
C11–C10	1.613(2)	C10–C9	1.246(2)
C16–C15	1.39	C2–C1A	1.41(4)
Br2A–In1–Br2	92.68(7)	C12–C11–C10	116.3(8)
Br2–In1–Br3	89.61(7)	C11–C16–C15	120
Br2A–In1–Br3A	89.61(7)	C16–C15–C14	120
Br3A–In1–Br3	86.56(8)	C15–C14–C13	120
Br1–In1–Br2A	96.29(4)	C12–C13–C14	120
Br1–In1–Br2	96.29(4)	C13–C12–C11	120
Br1–In1–Br3A	93.04(4)	C7–C8–C3	127.8(17)
Br1–In1–Br3	93.04(4)	C8–C3–C2	131.7(16)
O1–In1–Br2A	82.53(14)	C8–C3–C4	113.1(14)
O1–In1–Br2	82.53(14)	C4–C3–C2	114.8(12)
O1–In1–Br3	88.21(15)	C6–C5–C4	126.2(12)
O1–In1–Br3A	88.21(15)	C6–C7–C8	122.8(14)
C2–C1A–N1	120(2)	C9–C10–C11	116.6(15)
N2–C9–C10	120.1(14)	C1A–C2–C3	112.1(16)
C16–C11–C12	120	C5–C4–C3	113.5(10)
C16–C11–C10	123.7(8)	C7–C6–C5	111.8(12)
A=1+X, 1/2-Y, +Z			

2 (110 K)

In1−Cl1	2.355(2)	C10−C11	1.515(3)
In1−Cl2	2.355(2)	C1−C2	1.510(3)
In1−Cl4	2.348(7)	C4−C5	1.514(3)

In1−Cl3	2.337(9)	C7−C8	1.520(3)
N1−C10	1.519(3)	C12−C11	1.531(3)
N1−C1	1.521(3)	C5−C6	1.514(3)
N1−C4	1.514(3)	C8−C9	1.517(3)
N1−C7	1.524(3)	C2−C3	1.532(3)
Cl1−In1−Cl2	107.15(3)	C4−N1−C1	108.07(17)
Cl4−In1−Cl1	109.11(2)	C4−N1−C7	111.44(17)
Cl4−In1−Cl2	108.40(3)	C11−C10−N1	117.05(19)
Cl3−In1−Cl1	111.36(3)	C2−C1−N1	116.51(19)
Cl3−In1−Cl2	108.66(3)	C5−C4−N1	115.71(18)
Cl3−In1−Cl4	112.00(3)	C8−C7−N1	114.73(19)
C10−N1−C1	110.92(16)	C4−C5−C6	109.7(2)
C10−N1−C7	107.19(17)	C9−C8−C7	110.6(2)
C1−N1−C7	109.74(16)	C1−C2−C3	108.2(2)
C4−N1−C10	109.50(17)	C10−C11−C12	107.6(2)

2 (380 K)

In1−Cl2	2.324(3)	N1−C1	1.519(1)
In1−Cl3A	2.31(8)	C10−C11	1.424(1)
In1−Cl1A	2.29(2)	C7−C8	1.386(1)
In1−Cl4A	2.346(9)	C4−C5	1.344(1)
In1−Cl4	2.350(1)	C1−C2	1.356(2)
In1−Cl3	2.326(7)	C11−C12	1.477(2)
In1−Cl1	2.315(4)	C2−C3	1.511(2)
N1−C10	1.541(1)	C8−C9	1.450(1)
N1−C7	1.479(1)	C6−C5	1.515(1)
N1−C4	1.487(1)		
Cl2−In1−Cl4A	112.0(6)	C7−N1−C1	110.0(9)
Cl2−In1−Cl4	101.2(8)	C4−N1−C10	110.4(9)
Cl2−In1−Cl3	108.5(7)	C4−N1−C1	110.4(8)
Cl3A−In1−Cl2	125(4)	C1−N1−C10	106.6(8)
Cl3A−In1−Cl4A	99(4)	C11−C10−N1	119.1(1)
Cl1A−In1−Cl2	118(2)	C8−C7−N1	124.8(1)

Cl1A−In1−Cl3A	116(5)	C5−C4−N1	126.0(1)
Cl3−In1−Cl4	105.0(9)	C2−C1−N1	122.0(1)
Cl1−In1−Cl2	110.81(2)	C10−C11−C12	116.4(1)
Cl1−In1−Cl4	120.2(1)	C1−C2−C3	113.1(1)
Cl1−In1−Cl3	110.4(3)	C7−C8−C9	121.2(1)
C7−N1−C10	111.2(7)	C4−C5−C6	118.5(1)
C7−N1−C4	108.4(7)		

Table S3. Selected hydrogen bonds for compounds **1**.

1 (110 K)					
D–H···A	d(D−H)	d(H···A)	d(D···A)	∠(DHA)	A
N1–H1B···Br2	0.89	2.52	3.356(6)	156	[1/2-x, -1/2+y, 1/2-z]
N2–H2C···Br4	0.89	2.50	3.376(6)	168	[-1/2-x, -1/2+y, 1/2-z]
1 (293 K)					
N1–H1A···Br2	0.89	2.51	3.389(3)	169	[x, 1/2-y, z]
N1–H1C···Br2	0.89	2.82	3.389(3)	124	
N2–H2B···Br3	0.89	2.73	3.514(3)	148	[-x, -1/2-y, z]