Supporting Information

Tin-based organic-inorganic metal halides with reversible phase transition and thermochromic response

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Experimental Section

Synthetic procedures

All reagents and solvents employed in this work are commercially available without further purification.

$(BPA)_2SnCl_6$ (1). 3-chloropropan-1-ammonium hydrochloride (0.872 g, 4 mmol) and $SnCl_4$ (0.520 g, 2 mmol) were dissolved into about 5 mL hydrochloric acid and the mixture was stirred until the solution was completely clarified. Finally, the solution was left to evaporate slowly at room temperature to obtain colorless flaky single crystals.

$(BPA)_2SnBr_6$ (2). Following synthesis procedures similar to those of compound 1, $SnBr_4$ (0.876 g, 2 mmol) and 3-chloropropan-1-ammonium hydrochloride (0.872 g, 4 mmol) were completely dissolved in about 5 mL hydrobromic acid. At room temperature, green flake crystals were obtained by slow evaporation.

Materials and methods: Dry crystals were ground into powders, and an appropriate quantity of powders was pressed into a thin sheet with a thickness of 5 mm. The process was carried out in a special mold under a pressure of 40 MPa. A simple capacitor was made by fixing the cut sheet on the electrode with copper wires and carbon glue. Finally, the electrode was connected to the Tonghui TH2828A instrument, and the temperature-dependent dielectric constant was tested at frequencies ranging from 5 kHz-1 MHz with AC voltage of 1 V. PerkinElmer diamond instrument was used for differential scanning calorimetry (DSC) measurement. A powder sample with a mass of about 10 mg was weighed and placed in an aluminum crucible, which was sealed with an accompanying pressure, and two heating and cooling cycles were measured at a rate of 20 K min^{-1} in the range of 240-340 K under a nitrogen atmosphere. UV-near-infrared-visible (UV-NIR-vis) spectra were measured on a Cary RF 6000 instrument in the range of 200-800 nm. Firstly, $BaSO_4$ was used as a blank sample to perform a baseline correction. After that, a small quantity of

powders was taken for testing. Powder X-ray diffraction (PXRD) data was measured on the D8 Advance 03030502 instrument in the 2θ range of 5 ~55° with a step size of 0.02°. Thermogravimetric analyses (TGA) were carried out on a TA Q50 system with a heating rate of 10 K min^{-1}. For compounds **1** and **2**, Hirshfeld surfaces and 2D fingerprints were calculated using the CrystalExplorer software with input structure files in CIF format. Density functional theory (DFT) were performed with the Vienna Ab Initio Simulation Package (VASP).

X-ray single crystal diffraction: Single-crystal X-ray diffraction data were collected by using a Bruker D8 APEX-III diffractometer with *Mo-Kα* radiation (λ = 0.71073 Å) (operating at 50 kV and 40 mA). Data reduction and numerical absorption corrections were generated using APEX-III software. Refinement of single crystal data was solved and refined using SHELXT and OLEX2 software packages, all non-hydrogen atoms were anisotropically manipulated.

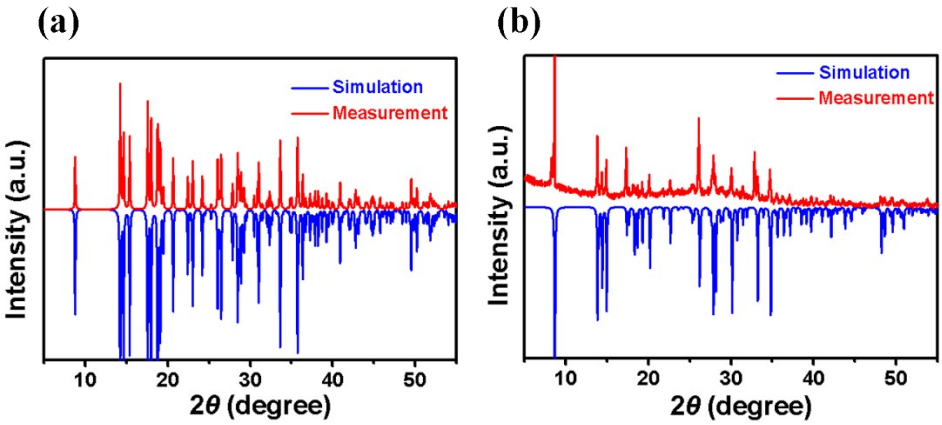

Fig. S1 Powder X-ray diffraction (PXRD) patterns for $(BPA)_2SnCl_6$ (**1**) and $(BPA)_2SnBr_6$ (**2**).

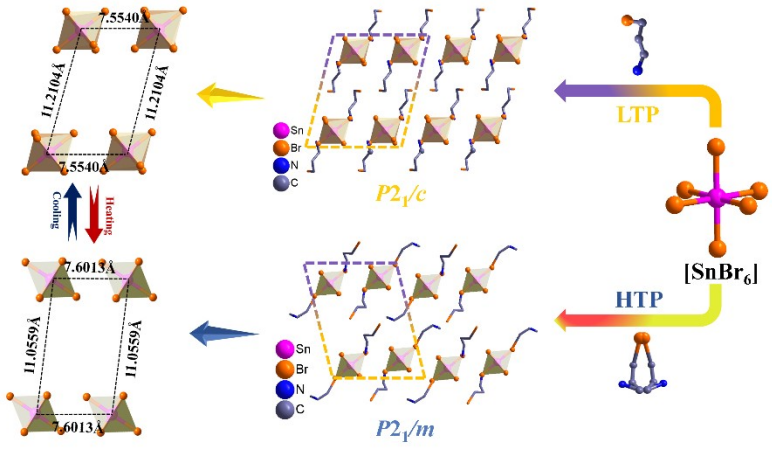

Fig. S2 Schematic diagram of the LTP and HTP structures in compound **2**. For clarity, all H atoms were omitted.

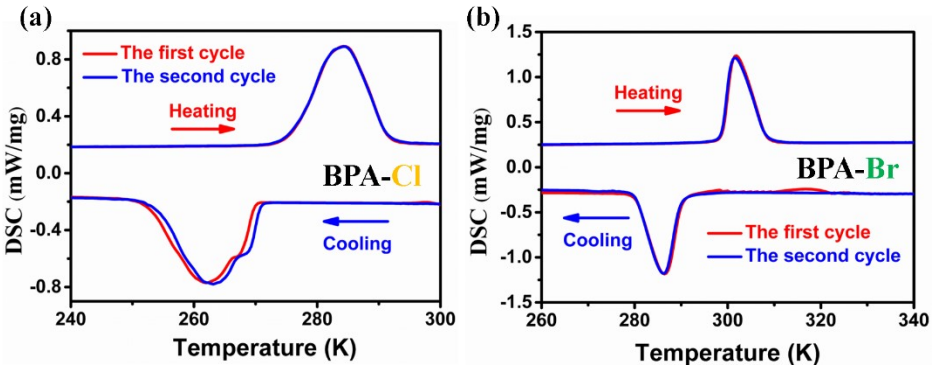

Fig. S3 DSC curves of **1** (a) and **2** (b) in a heating-cooling run at the first cycle and the second cycle respectively.

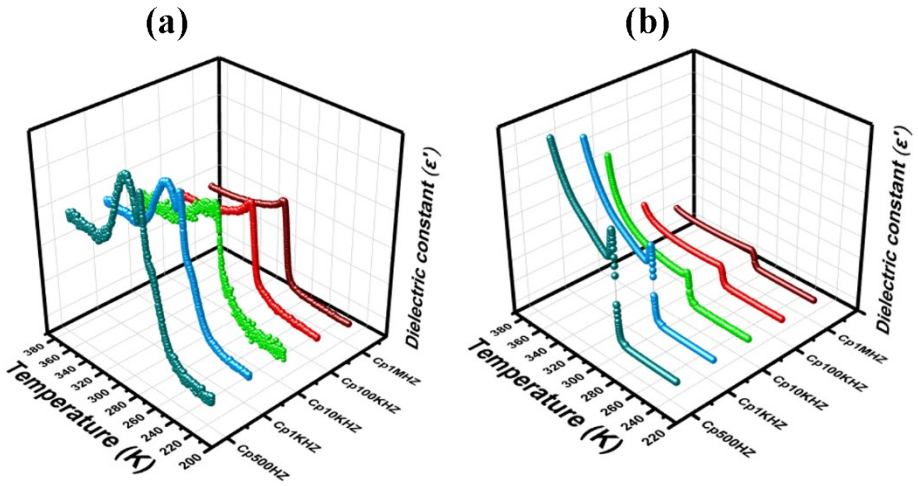

Fig. S4 The dielectric measurements of **1** (a) and **2** (b) at 500Hz, 1KHz, 10KHz, 100KHz and 1MHz upon heating.

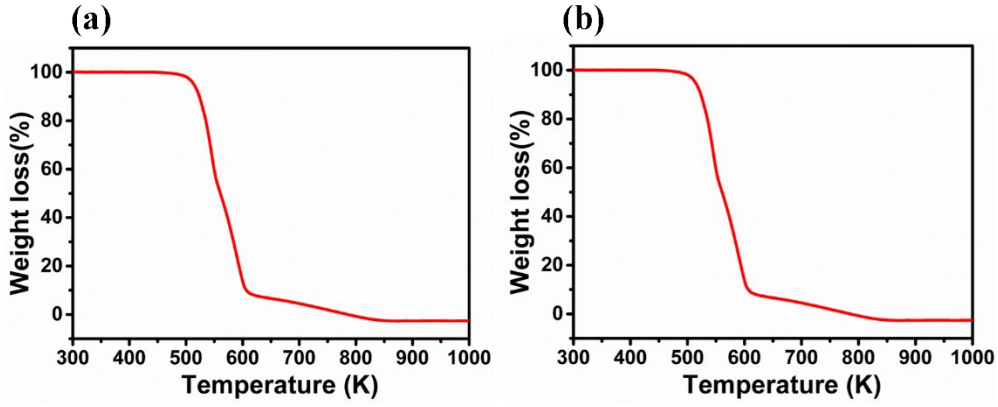

Fig. S5 TGA curves of **1** (a) and **2** (b) in the temperature range of 300-1000K.

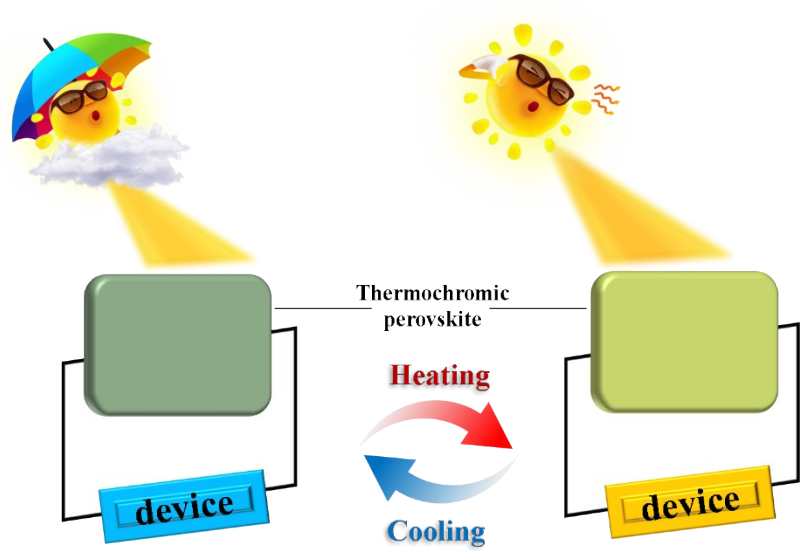

Fig. S6 The schematic of color-change smart window.

Table S1 Crystallographic data and structural refinement details of compound **1**

Compound	$(BPA)_2SnCl_6$	
	LTP	HTP
CCDC Code	2231652	2231653
Formula	$C_6H_{18}Br_2Cl_6N_2Sn$	$C_6H_{18}Br_2Cl_6N_2Sn$
Fw	481.71	609.43
Temp(K)	273.0	300.0
Crystal Syst	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/m$
a(Å)	10.715(5)	11.040(3)
b(Å)	7.267(2)	7.3622(15)
c(Å)	12.829(5)	12.282(3)
α/°	90	90
β/°	109.487(6)	105.063(6)
γ/°	90	90
V(Å^3)	941.8(6)	964.0(4)
Z	2	2
μ(mm^{-1})	6.434	6.286
GOF on F^2	1.039	1.053
R_1[[I > 2σ(I)]	0.1289	0.1576
wR_2 (all data)	0.2076	0.3278

Table S2 Crystallographic data and structural refinement details of compound **2**

Compound	$(BPA)_2SnBr_6$	
	LTP	HTP
CCDC Code	2231654	2231655
Formula	$C_6H_{18}Br_8N_2Sn$	$C_3H_9Br_8NSn$
Fw	876.19	737.17
Temp(K)	240.0	333.0
Crystal Syst	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/m$
a(Å)	10.886(8)	11.0559(15)
b(Å)	7.493(5)	7.6425(6)
c(Å)	13.119(8)	12.6907(15)
α/°	90	90
β/°	110.449(13)	105.813(13)
γ/°	90	90
V(Å^3)	1002.7(12)	1031.7(2)
Z	2	2
μ(mm^{-1})	17.200	14.766
GOF on F^2	1.057	0.956
R_1[[I > 2σ(I)]	0.1478	0.1984
wR_2 (all data)	0.2368	0.3662

Table S3 Selected bond lengths /Å and angles/° for compound **1**

Compound **1**			
LTP		HTP	
Sn1-Cl1	2.4538(18)	Sn1-Cl1^1	2.455(4)
Sn1-Cl1^1	2.4537(18)	Sn1-Cl1	2.455(4)
Sn1-Cl2	2.4501(16)	Sn1-Cl2	2.449(7)
Sn1-Cl2^1	2.4501(16)	Sn1-Cl3^1	2.446(4)
Sn1-Cl3	2.4462(16)	Sn1-Cl3	2.446(4)
Sn1-Cl3^1	2.4462(16)	Sn1-Cl4	2.441(6)
Br1-C1	1.926(10)	Br1-C1	1.75(4)
N1-C3	1.502(9)	N1-C3	1.53(2)
C1-C2	1.497(11)	C1-C2	1.49(2)
C2-C3	1.518(10)	C2-C3	1.520(14)
Cl^1-Sn1-Cl1	180.0	Br2-C4	2.00(2)

Cl2[1]-Sn1-Cl1[1]	90.10(6)	N2-C6	1.52(2)
Cl2[1]-Sn1-Cl1	89.90(6)	C4-C5	1.52(2)
Cl2[1]-Sn1-Cl1	89.90(6)	C5-C6	1.521(15)
Cl2-Sn1-Cl1[1]	89.90(6)	Cl[1]-Sn1-Cl1	89.8(2)
Cl2-Sn1-Cl2[1]	180.0	Cl2-Sn1-Cl1	89.95(17)
Cl3-Sn1-Cl1	88.81(6)	Cl2-Sn1-Cl1[1]	89.95(17)
Cl3[1]-Sn1-Cl1	91.19(6)	Cl3[1]-Sn1-Cl1	88.74(16)
Cl3[1]-Sn1-Cl1[1]	88.81(6)	Cl3[1]-Sn1-Cl1[1]	178.54(17)
Cl3-Sn1-Cl1[1]	91.19(6)	Cl3-Sn1-Cl1	178.54(17)
Cl3[1]-Sn1-Cl2[1]	89.68(6)	Cl3-Sn1-Cl1[1]	88.74(16)
Cl3-Sn1-Cl2	89.68(6)	Cl3[1]-Sn1-Cl2	89.65(17)
Cl3-Sn1-Cl2[1]	90.32(6)	Cl3-Sn1-Cl2	89.66(17)
Cl3-Sn1-Cl3[1]	180.0	Cl3-Sn1-Cl3[1]	92.7(2)
C2-C1-Br1	112.0(6)	Cl4-Sn1-Cl1	89.35(17)
C1-C2-C3	111.2(7)	Cl4-Sn1-Cl1[1]	89.35(17)
N1-C3-C2	111.1(6)	Cl4-Sn1-Cl2	179.0(2)
		Cl4-Sn1-Cl3[1]	91.03(17)
		Cl4-Sn1-Cl3	91.03(17)
		C2-C1-Br1	168(4)
		C1-C2-C3	115(3)
		C2-C3-N1	105(2)
		C5-C4- Br2	155(6)
		C4-C5-C6	108(3)
		N2-C6-C5	111(3)

Table S4 Selected bond lengths /Å and angles/° for compound **2**

Compound **2**			
LTP		HTP	
Sn1-Br1	2.573(2)	Sn1-Br1	2.582(5)
Sn1- Br1[1]	2.573(2)	Sn1- Br2[1]	2.578(3)
Sn1-Br2	2.588(2)	Sn1-Br2	2.578(3)
Sn1- Br2[1]	2.588(2)	Sn1-Br3	2.586(5)
Sn1-Br3	2.571(2)	Sn1- Br4[1]	2.575(3)
Sn1-Br3[1]	2.571(2)	Sn1- Br4	2.575(3)
Br4-C1	1.920(13)	Br5-C3	2.303(19)
N1-C3	1.462(9)	N1-C1	1.50(2)

C1-C2	1.539(9)	C1-C2	1.484(12)
C2-C3	1.538(9)	C2-C3	1.482(12)
Br1-Sn1- Br1[1]	180.0	Br6-C4	2.346(19)
Br1-Sn1- Br2	90.77(7)	N2-C6	1.47(2)
Br1[1]-Sn1- Br2	89.23(7)	C4-C5	1.47(2)
Br1[1]-Sn1- Br2[1]	90.77(7)	C5-C6	1.474(12)
Br1-Sn1- Br2[1]	89.23(7)	Br1-Sn1- Br3	179.84(16)
Br2[1]-Sn1- Br2	180.0	Br2[1]-Sn1- Br1	89.48(12)
Br3-Sn1-Br1	90.34(8)	Br2-Sn1- Br1	89.48(12)
Br3[1]-Sn1- Br1[1]	90.34(8)	Br2[1]-Sn1- Br2	92.14(16)
Br3-Sn1-Br1[1]	89.66(8)	Br2[1]-Sn1- Br3	90.63(12)
Br3[1]-Sn1- Br1	89.66(8)	Br2-Sn1- Br3	90.63(12)
Br3-Sn1- Br2[1]	89.89(7)	Br4[1]-Sn1- Br1	90.01(13)
Br3[1]-Sn1- Br2[1]	90.11(7)	Br4-Sn1- Br1	90.01(13)
Br3[1]-Sn1- Br2	89.89(7)	Br4-Sn1- Br2[1]	88.63(12)
Br3-Sn1- Br2	90.11(7)	Br4[1]-Sn1- Br2[1]	179.07(13)
Br3[1]-Sn1- Br3	180.00(7)	Br4-Sn1- Br2	179.07(13)
C2-C1-Br4	110.6(9)	Br4[1]-Sn1- Br2	88.63(12)
C3-C2-C1	111.2(10)	Br4-Sn1- Br3	89.88(11)
N1-C3-C2	111.8(9)	Br4[1]-Sn1- Br3	89.88(11)
		Br4[1]-Sn1- Br4	90.59(16)
		C2-C1-N1	107(3)
		C1-C2-C3	107(2)
		C2-C3-Br5	156(3)
		C5-C4- Br6	169(5)
		C4-C5-C6	114(3)
		N2-C6-C5	111(3)