Halogen engineering of organic-inorganic hybrid perovskites with nonlinear optical, fluorescence properties and phase transition

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Synthetic procedures

Synthesis of (4-methoxybenzylammonium)$_2$ZnI$_4$ (1)

All of reagents involved in the experiments were purchased from chemical companies and were used without any further purification. HI, 4-methoxybenzylamine, and zinc bromide were dissolved in methanol to obtain an alcohol solution and the mixed solution was stirred for a few minutes. The target product was got by slow evaporation of the mixed solution at room temperature after several days. Finally, colorless target crystals were obtained.

Synthesis of (4-methoxybenzylammonium)$_2$ZnBr$_4$ (2)

On the basis of synthesis **1**, zinc iodide was replaced by zinc bromide and finally yellow target crystals were obtained.

Materials and methods

Dielectric constants were recorded on a Tonghui TH2828A instrument at frequencies of 5 kHz, 10 kHz, 100 kHz, and 1 MHz with a measured AC voltage of 1 V. Differential scanning calorimetry (DSC) was measured on a NETZSCH DSC 3500 instrument by heating and cooling at a rate of 20 K/min under a nitrogen atmosphere. UV-near-infrared-visible (UV-NIR-vis) spectra were obtained on a Cary RF 6000 instrument, and the fluorescence spectra was determined on an FLS 9801 instrument. Powder X-ray diffraction (PXRD) data for two compounds were measured on a D8 Advance 03030502 at room temperature. Diffraction patterns were collected in the 2θ range of 5~55° with a step size of 0.02°. The CIE coordination was calculated by 1931 CIE package. Crystallographic data of the title compounds was restored by SPEX-III software, and absorption was corrected by multi-scan (ω) mothed. Furthermore, the crystal structure factors were solved by least squares. Meanwhile, structural factors were refined by SHLXT and OLEX software, and non-hydrogen atoms were refined and positioned by operation of anisotropy. The figures of the title compounds were carried out by DIAMOND package.

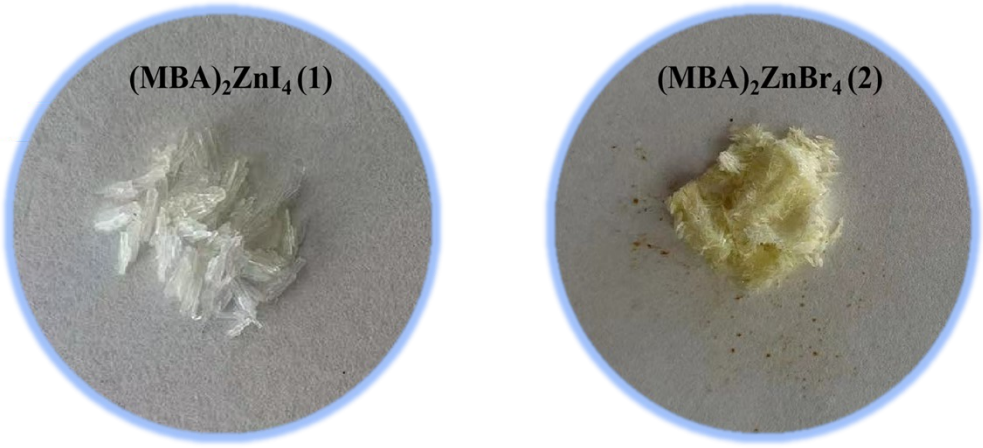

Fig. S1 Single crystals of compounds **1** and **2**.

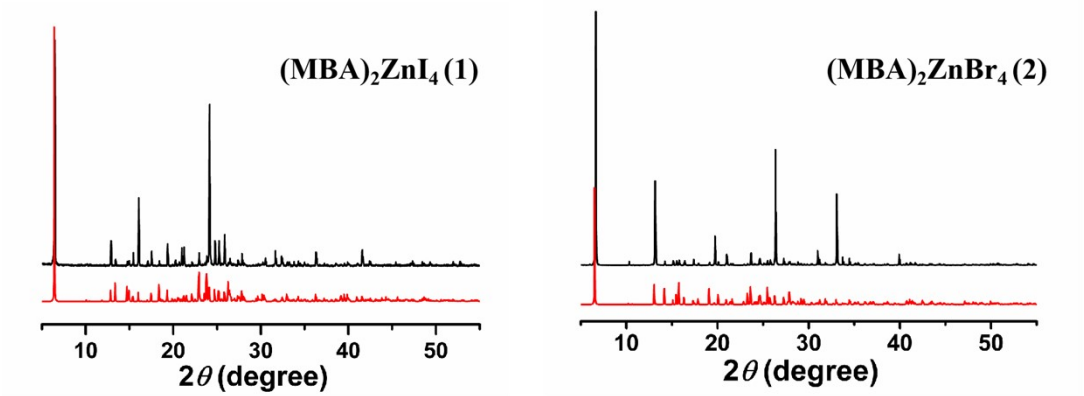

Fig. S2 Powder X-ray diffraction (PXRD) for compounds **1** and **2**.

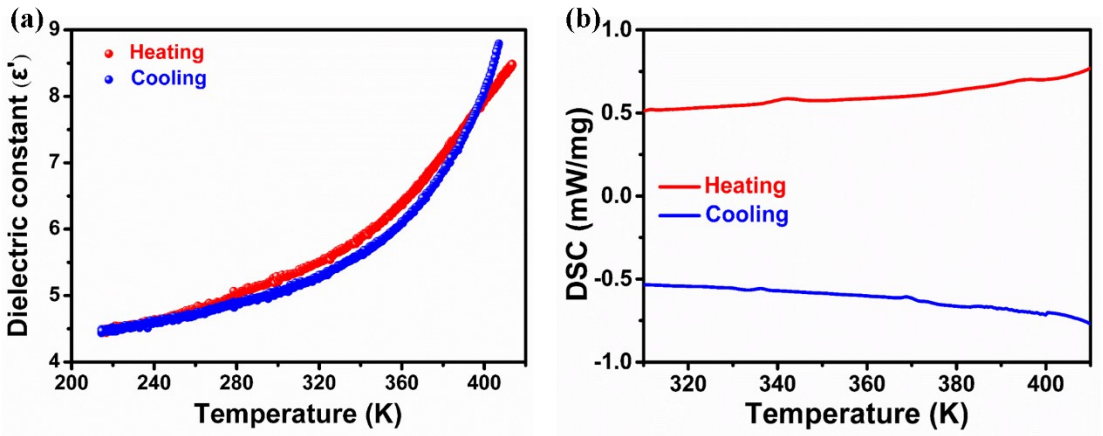

Fig. S3 (a and b) Dielectric and DSC curves of **2**.

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

Compound	$(MBA)_2ZnI_4$	
	LTP	HTP
CCDC Code	2212096	2212097
Formula	$C_{16}H_{24}I_4N_2O_2Zn$	$C_{16}H_{24}I_4N_2O_2Zn$
Fw	849.34	849.34
Temp(K)	300	363
Crystal Syst	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a(Å)	17.3830(7)	11.330(4)
b(Å)	8.2623(4)	8.298(3)
c(Å)	18.0124(7)	27.754(9)
α/°	90	90
β/°	102.45(3)	90.45(3)
γ/°	90	90
V(Å^3)	2526.08(19)	2609.2(15)
Z	4	4
μ(mm^{-1})	5.872	5.685
GOF on F^2	1.050	1.074
R_1[[I > 2σ(I)]	0.0353	0.0447
wR_2 (all data)	0.0615	0.0999

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

Compound	$(MBA)_2ZnBr_4$
CCDC Code	2212095
Formula	$C_{16}H_{24}Br_4N_2O_2Zn$
Fw	661.38
Temp(K)	273
Crystal Syst	Monoclinic
Space group	$P2_1$
a(Å)	10.871(4)
b(Å)	7.644(3)
c(Å)	13.574(5)
α/°	90
β/°	92.486(9)
γ/°	90
V(Å^3)	1126.9(7)
Z	2
μ(mm^{-1})	8.193
GOF on F^2	0.993
R_1[[I > 2σ(I)]	0.0423
wR_2 (all data)	0.0800

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

Compound **1**			
LTP		HTP	
I1-Zn1	2.6081(7)	I1-Zn1	2.6059(13)
I3-Zn1	2.6120(7)	I2-Zn1	2.6314(12)
I2-Zn1	2.6078(7)	I3-Zn1	2.6152(15)
I4-Zn1	2.6233(7)	I4-Zn1	2.6255(15)
O1-C5	1.365(6)	N1B-C1B	1.465(15)
O1-C8	1.423(7)	O2-C5	1.373(12)
N2-C16	1.473(7)	O2-C9	1.447(15)
O2-C15	1.366(7)	C11-C16	1.384(12)
O2-C9	1.421(8)	C11-C12	1.351(14)
C5-C6	1.381(7)	C11-C10B	1.490(14)
C5-C4	1.366(7)	C2-C7	1.376(12)
C2-C7	1.371(8)	C2-C1A	1.513(13)
C2-C3	1.377(8)	N2B-C10B	1.455(14)
C2-C1	1.496(8)	O3-C17	1.364(13)
C12-C16	1.513(8)	O3-C14	1.400(13)
C12-C11	1.380(8)	C2-C3	1.387(12)
C12-C13	1.373(7)	C16-C15	1.349(12)
C6-C7	1.381(7)	C7-C6	1.375(13)
N1-C1	1.456(8)	C5-C6	1.356(13)
C4-C3	1.390(8)	C5-C4	1.391(14)
C11-C10	1.390(8)	C5-O1	1.406(14)
C13-C14	1.363(8)	C14-C15	1.332(13)
C10-C15	1.362(8)	C14-C13	1.376(14)
C15-C14	1.378(8)	C14-O3	1.400(17)
I1-Zn1-I3	108.58(3)	C4-C3	1.367(13)
I1-Zn1-I4	108.93(3)	C13-C12	1.407(14)
I3-Zn1-I4	109.06(3)	N2A-C10A	1.482(14)
I2-Zn1-I1	109.38(2)	O3-C17	1.364(13)
I2-Zn1-I3	108.23(2)	I1-Zn1-I2	108.11(5)
I2-Zn1-I4	112.58(3)	I1-Zn1-I4	109.89(4)
		I3-Zn1-I1	110.00(4)
		I3-Zn1-I2	107.34(4)
		I3-Zn1-I4	112.77(4)
		I4-Zn1-I2	108.59(4)

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

Compound **2**			
Br1-Zn1	2.4085(17)	O2-C10	1.368(12)
Br2-Zn1	2.4020(17)	N2-C16	1.465(13)
Br3-Zn1	2.4086(17)	C10-C11	1.400(14)
Br4-Zn1	2.4052(16)	C10-C15	1.366(14)
O1-C5	1.378(11)	C11-C12	1.380(15)
O1-C8	1.423(14)	C12-C13	1.382(15)
N1-C1	1.407(14)	C13-C14	1.400(14)
C1-C2	1.501(14)	C13-C16	1.517(13)
C2-C3	1.372(14)	C14-C15	1.399(14)
C2-C7	1.383(14)	Br1-Zn1-Br3	109.27(6)
C3-C4	1.375(14)	Br2-Zn1-Br1	111.08(6)
C4-C5	1.381(14)	Br2-Zn1-Br3	110.30(5)
C5-C6	1.379(14)	Br2-Zn1-Br4	107.28(6)
C6-C7	1.388(13)	Br4-Zn1-Br1	110.71(6)
O2-C9	1.424(12)	Br4-Zn1-Br3	108.13(6)