

Electronic Supplementary Information (ESI)

Modulating the birefringence of two-dimensional hybrid lead bromide perovskites by pyridine derivative cations

Li-Ling Zhang,^{a,‡} Hua Huang,^{a,‡} Qingran Ding,^a Hui-Ping Xiao,^a Qing-Yan Liu^{*a} and Yu-Ling Wang^{*a}

¹College of Chemistry and Materials, Key Lab of Fluorine and Silicon for Energy Materials and Chemistry of Ministry of Education and National Engineering Research Centre for Carbohydrate Synthesis, Jiangxi Normal University, Nanchang 330022, Jiangxi.

[‡]These authors contributed equally to this work.

Corresponding Authors (email: qyliu@jxnu.edu.cn; ylwang@jxnu.edu.cn)

1. Characterization.

Physical Measurements. FT-IR spectra were recorded from KBr disc on a Perkin-Elmer Spectrum One FT-IR spectrometer ranging from 400 to 4000 cm⁻¹. Thermogravimetric analyses were performed under a nitrogen atmosphere with a heating rate of 10 °C/min using a PE Diamond thermogravimetric analyser. Powder X-ray diffraction analyses were performed on a Rigaku DMAX 2500 diffractometer with Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$). The UV-vis-NIR diffuse reflection data was recorded at room temperature using BaSO₄ powder sample as a standard (100% reflectance) on a PerkinElmer Lambda-950 UV/vis/NIR spectrophotometer (scanning wavelength is between 200 and 800 nm). The exposure of the samples to the controlled humid environments was performed on an XK-CTS80Z incubator (Shenzhen selenium control testing equipment corp.).

Crystallographic Study. X-ray single-crystal diffraction experiment was carried out a Rigaku Oxford SuperNova diffractometer equipped with an EOS detector (Mo-K α radiation, $\lambda = 0.71073$ Å). Absorption correction and data reduction were handled with a *CrysAlisPro package*.¹ The *SHELXT-2015*² and *SHELXL-2018*³ were applied to structure solution and refinement. The hydrogen atoms were added theoretically. Non-hydrogen atoms were refined anisotropically. Details of crystal parameters, data collection, and structure refinement are summarized in Table S1. The important bond lengths and bond angles are listed in Table S2.

Birefringence Measurement. The birefringence of crystal **1** and **2** was obtained through a polarizing microscope (Nikon LV1000) equipped with a Berek compensator at a wavelength of 550 nm. Small crystals were chosen for the measurements. The following formula was listed to calculate birefringence: $R = |N_e - N_o| = \Delta n \times T$, where R denotes the optical path difference, Δn represents birefringence, and T denotes the thickness of the crystal.

Computational Methods. The first-principles calculations for compound **1** and **2** were performed by CASTEP⁴ on a plane-wave pseudopotential total energy package based density functional theory (DFT).⁵ The functional developed by Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA)^{6,7} form was adopted to describe the exchange-correlation energy. The ultrasoft pseudopotentials were used to model the effective interaction between atom cores and valence electrons. H 1s¹, C 2s²2p², N 2s²2p³, Cl 3s²3p⁵, Br 4s²4p⁵ and Pb 6s²6p² electrons were treated as valence electrons. The kinetic energy cutoff of 380 eV and dense 2 \times 2 \times 1 Monkhorst-Pack⁸ k-point meshes in the Brillouin zones were chosen. The linear optical properties were examined based on the dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$. The imaginary part of dielectric function ϵ_2 can be calculated based on the electronic structures and the real part is

obtained by the Kramers-Kronig transformation, accordingly the refractive indices and the birefringence (Δn) can be calculated. The frequency-dependent refractive indices were calculated to demonstrate the validity of birefringence measurements.

Table S1. Crystal data and structural refinement data.

	1	2
formula	C ₁₀ H ₁₀ N ₂ SPbBr ₄	C ₂₄ H ₂₈ Cl ₄ N ₄ Pb ₃ Br ₁₀
fw	717.09	1934.97
temp (K)	296(2)	293(2)
cryst syst	Orthorhombic	Monoclinic
space group	<i>Pbcm</i>	<i>P2₁/c</i>
<i>Z</i>	4	2
<i>a</i> (Å)	6.0548(3)	12.8848(13)
<i>b</i> (Å)	11.8366(4)	21.3978(15)
<i>c</i> (Å)	22.8759(10)	8.2775(10)
α (deg)	90	90
β (deg)	90	99.031(10)
γ (deg)	90	90
<i>V</i> (Å ³)	1639.48(12)	2253.9(4)
<i>D</i> _{calcd} (g·cm ⁻³)	2.905	2.851
μ (mm ⁻¹)	20.151	20.301
no. of reflns collected	9490	21454
independent reflns	2084	5264
obsd reflns.[<i>I</i> > 2 σ (<i>I</i>)]	1693	3667
<i>F</i> (000)	1288	1728
<i>R</i> [int]	0.0566	0.0791
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0361	0.0547
<i>wR</i> ₂ (<i>I</i> > 2 σ (<i>I</i>))	0.0704	0.1261

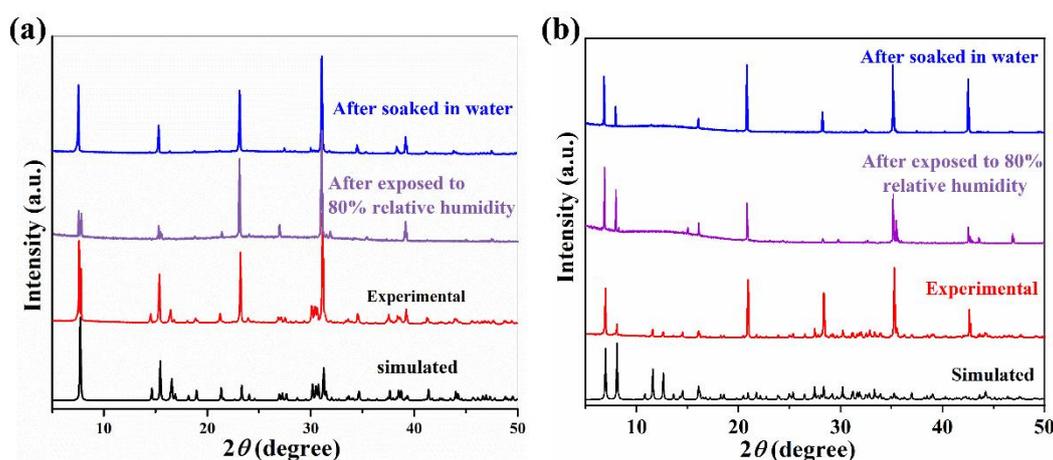
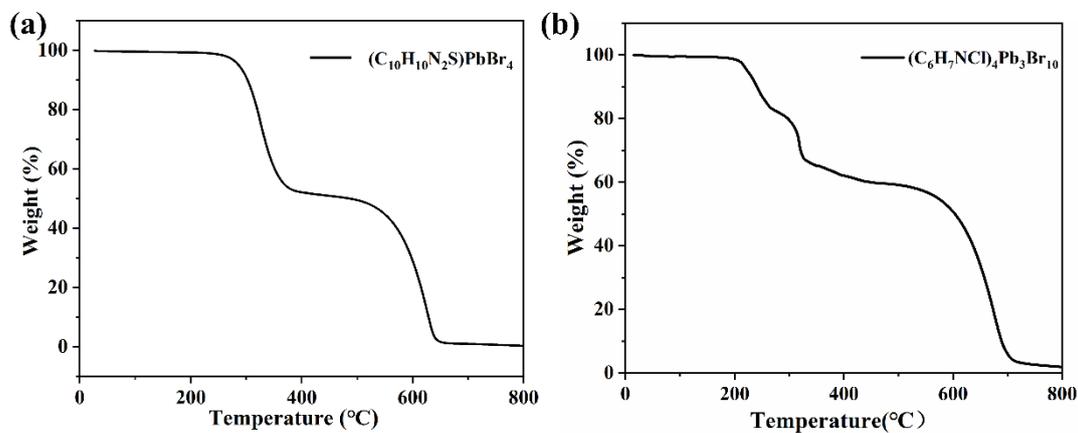
^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$

Table S2. Selected Bond Lengths (Å) of **1** and **2**.^a

Compound 1					
Bond	distance	Bond	distance	Bond	distance
Pb1–Br1	2.9989(9)	Pb1–Br2	2.9940(8)	Pb1–Br3	2.9667(7)
Pb1–Br1A	3.0626(9)	Pb1–Br2B	3.0376(8)	Pb1–Br3C	2.9667(7)
Compound 2					
Bond	distance	Bond	distance	Bond	distance
Pb1–Br1	2.9849(12)	Pb1–Br2	3.0100(13)	Pb1–Br3	3.1050(14)
Pb1–Br4	3.0992(13)	Pb1–Br5	2.9396(14)	Pb1–Br1B	3.0568(13)
Pb2–Br2	3.0456(13)	Pb2–Br2A	3.0457(13)	Pb2–Br3	3.0055(12)
Pb2–Br3A	3.0056(12)	Pb2–Br4	3.0873(13)	Pb2–Br4A	3.0873(13)

^aSymmetry codes: for **1**: A 1+x, y, z; B 1-x, 1/2+y, -z+3/2; C x, y, -z+3/2; D x, 1/2-y, 1-z. For **2**: A -x, -y, -z; B x, -y+1/2, z+1/2.

2. Results and discussion

**Fig. S1** PXRD patterns for compound (a) **1** and (b) **2**.**Fig. S2** TGA curves for compound (a) **1** and (b) **2**.

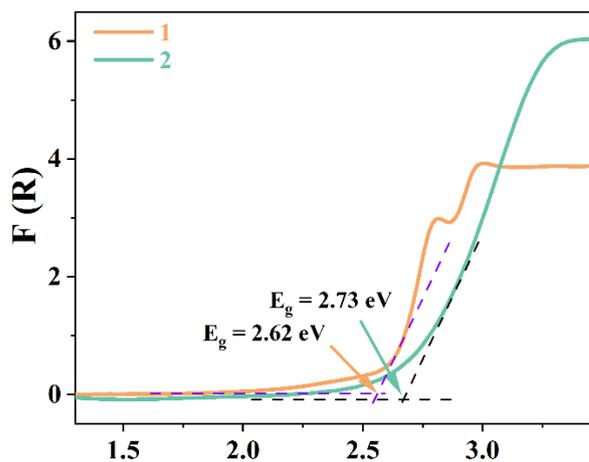


Fig. S3 UV-visible-near-infrared diffuse reflectance spectra of compound **1** and (b) **2**.

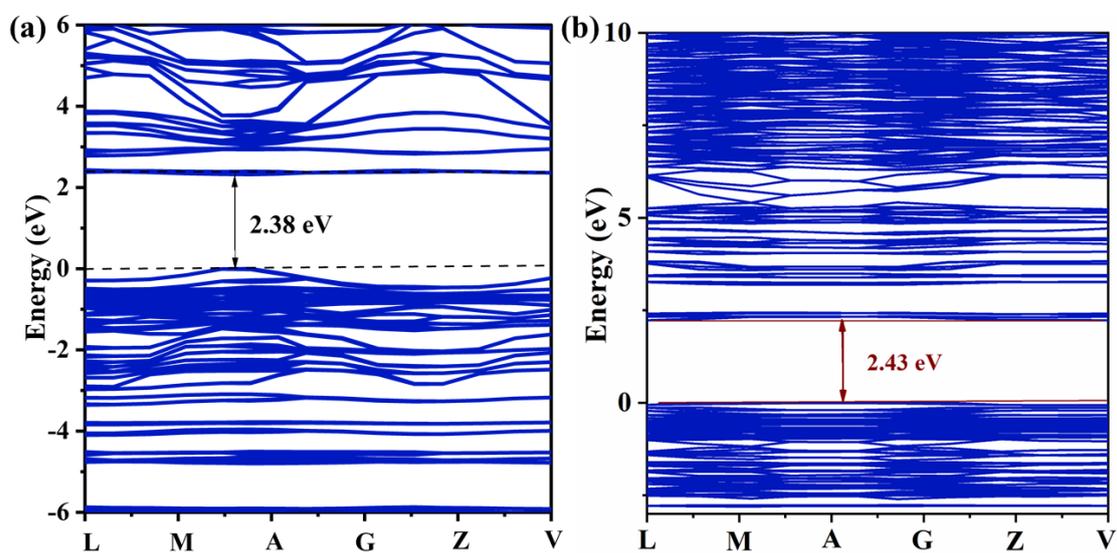


Fig. S4 Electronic band structures for compound (a) **1** and (b) **2**.

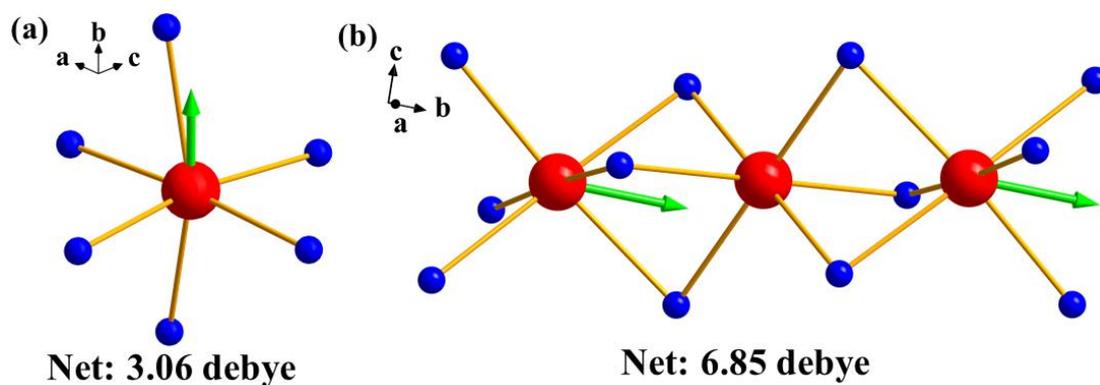


Fig. S5 Dipole moment vectors of the PbBr_6 octahedrons in compound (a) **1** and (b) **2**.

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