Electronic Supplementary Information

A Chiral Two-dimensional Perovskite-like Lead-Free Bismuth(III) Iodide Hybrid with High Phase Transition Temperature

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Experimental details

Sample preparation. All reagents and solvents in this experiment were of reagent grade and used without further purification. *S*-3-aminopyrrolidinium dihydroiodate (2 mmol), bismuth iodide (2 mmol), and concentrated hydroiodic acid (3 mL) were added into a 25 ml hydrothermal autoclave reactor. The autoclave was heated in an air-dry oven, which kept the temperature at 453 K for two hours and then cooled to ambient temperature at a rate of 5 K/h. We finally obtained dark-red crystals of [(*S*)-3-aminopyrrolidinium·I]$_2$Bi$_{2/3}$I$_4$ (**1**).

Characterization methods. Single-crystal X-ray diffraction data were performed on a Rigaku Oxford Diffraction 2019 diffractometer in the scan mode with Mo-Kα radiation (λ = 0.71073). Data collection, cell refinement, and data reduction were performed using Rigaku CrystalClear 1.3.5. The structures were solved by direct methods and refined by the full-matrix method based on F^2 using the SHELXTL software package. All non-hydrogen atoms were refined anisotropically and the positions of all hydrogen atoms were generated geometrically. The X-ray crystallographic structures have been deposited at the Cambridge Crystallographic Data Centre (deposition numbers CCDC 2244696-2244697) and can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/getstructures. Differential scanning calorimetry (DSC) measurements were carried out on a NETZSCH DSC 214 instrument under N_2 atmosphere in aluminum crucibles. The dielectric measurements were carried out

on a TH2828A impedance analyzer. Powder X-ray diffraction (PXRD) data were measured using a Rigaku D/MAX 2000 PC X-ray diffraction system with Cu Kα radiation in the 2θ range of 10°-40° with a step size of 0.02°. The UV-vis absorption spectrum was obtained using a Shimadzu UV-3600 Plus spectrophotometer. UV-vis absorption of powder in solid was tested *via* absorption mode of integrating sphere (ISR-603) operating in the wavelength range of 200-1000 nm. $BaSO_4$ was used as a 100% reflectance reference. Circular dichroism (CD) spectra are recorded with JASCO J-1700. The CD measurements are performed on the [(*S*)-3-aminopyrrolidinium·I]$_2$Bi$_{2/3}$I$_4$ single-crystalline powder embedded KBr pellets. The thermogravimetric analysis (TGA) measurements were carried out on polycrystalline powder samples by PerkinElmer TGA 8000 at a rate of 30 K/min in an N_2 atmosphere.

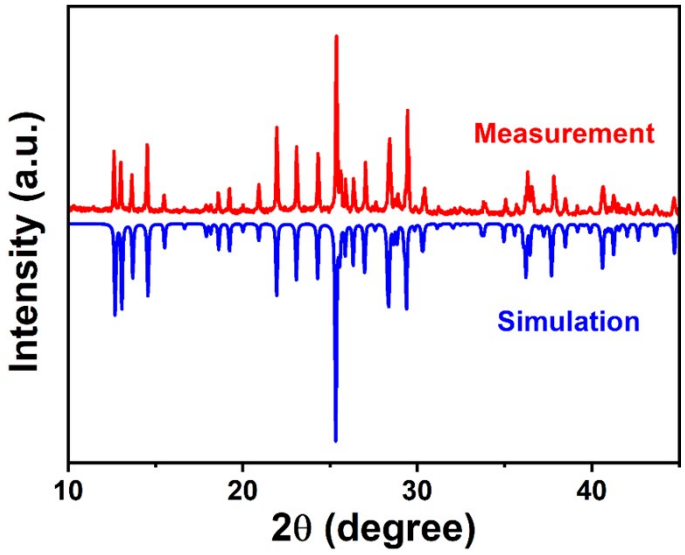

Fig. S1 Experimental PXRD patterns and simulated ones from the crystal structure of **1** at 293 K.

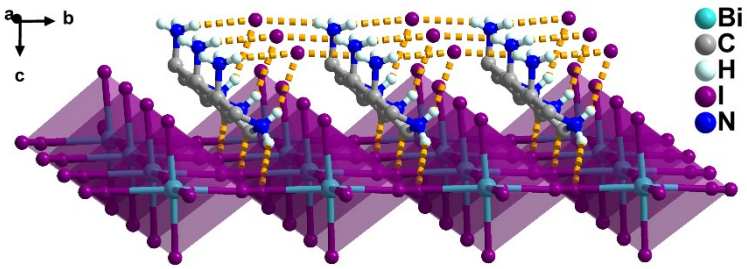

Fig. S2 Hydrogen bonding of **1** along *b* axis at 293 K. Some hydrogen atoms are omitted for clarity. The yellow dotted lines represent hydrogen bonds.

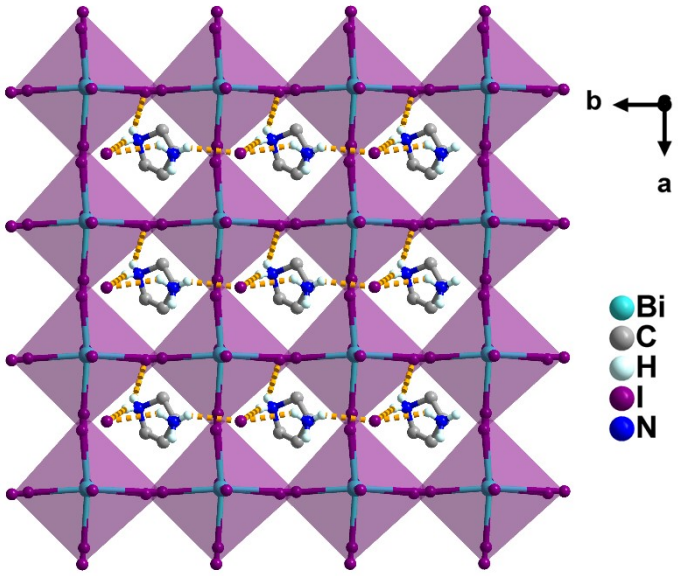

Fig. S3 Hydrogen bonding of **1** along the *c* axis at 293 K. Some hydrogen atoms are omitted for clarity. The yellow dotted lines represent hydrogen bonds.

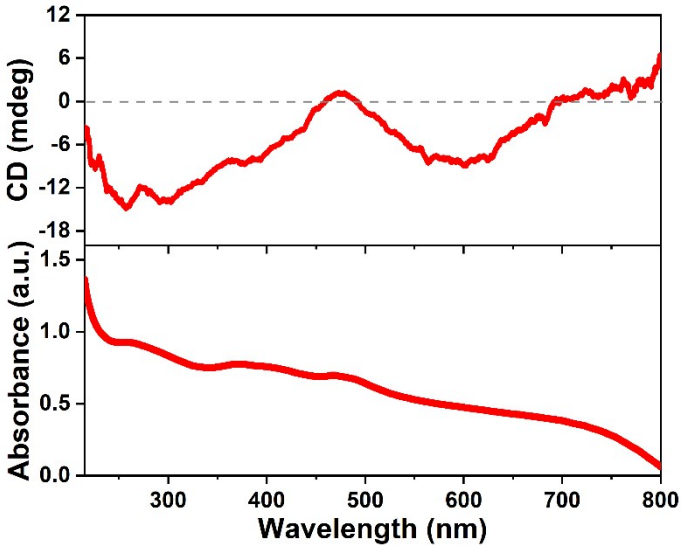

Fig. S4 CD (top) and absorption (bottom) spectra of [(*S*)-3-aminopyrrolidinium·I]$_2$Bi$_{2/3}$I$_4$.

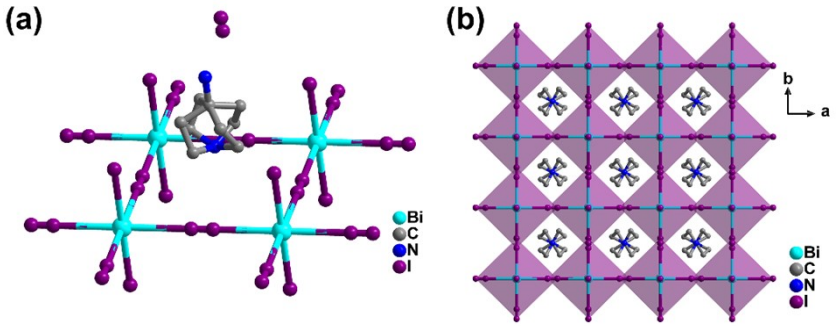

Fig. S5 Structural unit (a) and packing view along the *c* axis (b) of **1** at 420 K. Hydrogen atoms are omitted for clarity.

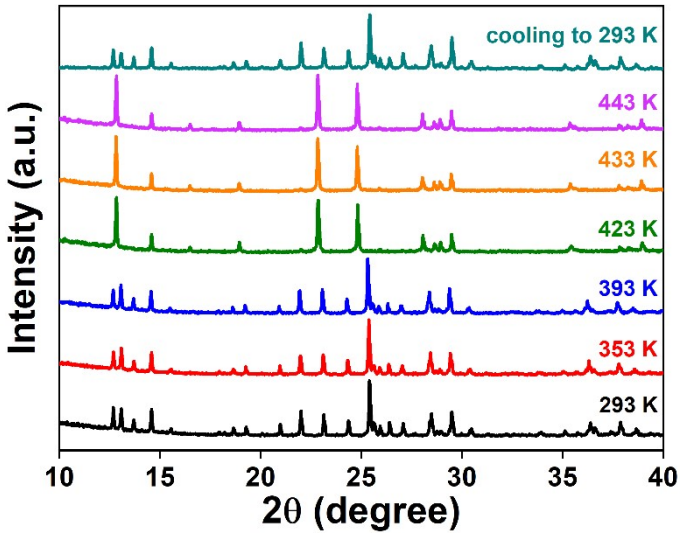

Fig. S6 Variable temperature PXRD patterns of **1**.

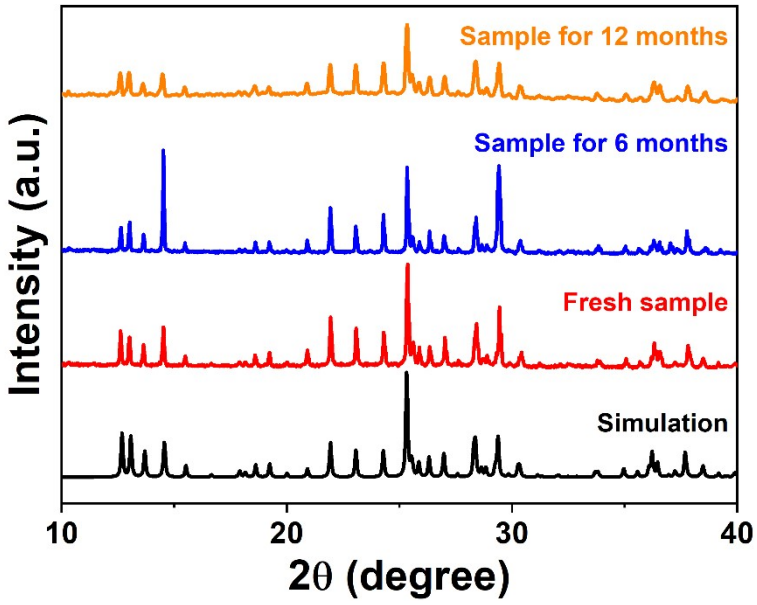

Fig. S7 PXRD patterns of **1** recorded after 6 months and 12 months upon exposure to air at room temperature.

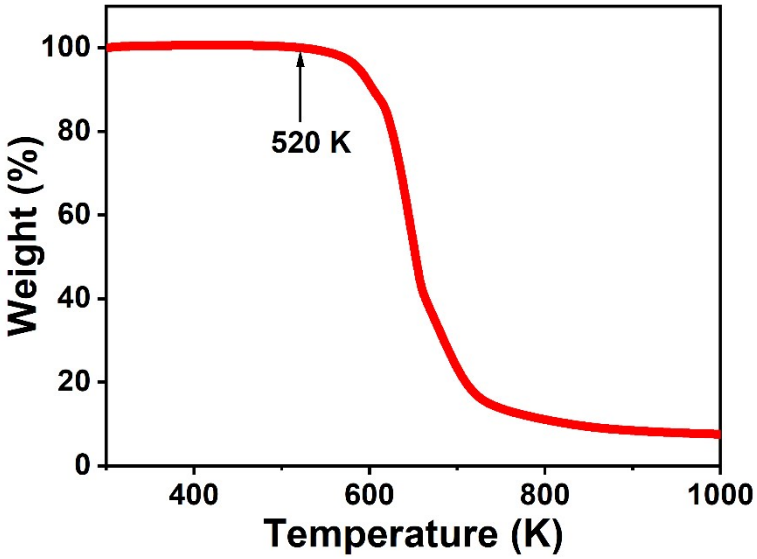

Fig. S8 TGA curve of **1**, exhibiting its thermal stability up to 520 K.

Table S1. Crystal data and structural refinements for **1** at 293 K and 420 K.

Compound	[(*S*)-3-aminopyrrolidinium·I]$_2$Bi$_{2/3}$I$_4$	
Temperature	293 K	420 K
Formula	$C_8H_{24}Bi_{0.67}I_6N_4$	$C_8H_{24}Bi_{0.67}I_6N_4$
Formula weight	1077.04	1077.04
Crystal system	tetragonal	tetragonal
Space group	$P4_12_12$	$I422$
a, b, c (Å)	7.0067(1) 7.0067(1) 48.305(3)	7.1350(5) 7.1350(5) 24.284(4)
α, β, γ (°)	90 90 90	90 90 90
Volume /Å^3	2371.48(16)	1236.3(3)
Z	4	1
R_1 [$I>2\sigma(I)$]	0.0520	0.0962
wR_2 [$I>2\sigma(I)$]	0.1386	0.2234
GOF	1.085	1.007

Table S2. Selected I−Bi bond lengths [Å] and I−Bi−I bond angles [°] for **1** at 293 K.

bond lengths [Å]		bond angles [°]	
Bi1-I1	3.0330(16)	I1-Bi1-I1^{i}	174.50(7)
Bi1-I1^{i}	3.0331(16)	I1-Bi1-I2	97.24(6)
Bi1-I2	3.091(3)	I2-Bi1-I2^{i}	83.57(9)
Bi1-I2^{i}	3.091(3)	I3^{iii}-Bi1-I2^{i}	170.15(7)
Bi1-I3^{ii}	3.083(3)	I3^{ii}-Bi1-I2^{i}	88.38(6)
Bi1-I3^{iii}	3.083(3)	I3^{ii}-Bi1-I2	170.15(7)
		I3^{iii}-Bi1-I2	88.38(6)
		I3^{ii}-Bi1-I3^{iii}	100.16(10)
		I1-Bi1-I2^{i}	86.88(6)
		I1^{i}-Bi1-I2	86.88(6)
		I1^{i}-Bi1-I2^{i}	97.24(6)
		I1^{i}-Bi1-I3^{iii}	87.95(6)
		I1-Bi1-I3^{ii}	87.95(6)
		I1-Bi1-I3^{iii}	88.52(6)
		I1^{i}-Bi1-I3^{ii}	88.52(6)
		I3-I2-Bi1	176.7(3)
		I2-I3-Bi1^{iv}	166.9(3)

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

Table S3. Bond lengths [Å] and angles [°] of hydrogen bonding of **1** at 293 K.

D—H···A	D—H	H···A	D···A[Å]	D—H···A[°]	A-symop
N1-H1A···I4	0.89	2.86	3.664(10)	150	
N1-H1B···I3	0.89	2.88	3.678(10)	150	
N2-H2A···I4	0.89	2.78	3.670(10)	173	3/2-x,1/2+y, 5/4-z
N2-H2B···I4	0.89	2.83	3.530(10)	136	
N2-H2C···I4	0.89	2.79	3.541(10)	143	-1+x,y,z