Luminescent 3D Chiral Hybrid Metal-halide Perovskites for Piezoelectric Energy Harvesting and Ultrasound Detection

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Material and methods

Preparation. The (*R/S*-3AQ)RbI_3 crystals were prepared by a simple room-temperature solvent evaporation method. Rubidium iodide (1 mmol), (*R*)-(+)-3-aminoquinuclidine dihydro-chloride or (*S*)-(-)-3-aminoquinuclidine dihydro-chloride (1 mmol), concentrated hydroiodic acid (2 mL) and deionized water (5 mL) were mixed to a clear solution through ultrasonic stirring. Additional hypophosphorous acid (50%, 0.5 mL) was added to prevent the oxidation of the I^- ion. Colorless block crystals, (*R/S*-3AQ)RbI_3, were obtained after evaporating at room-temperature for about two weeks.

Crystal data collection and refinement. The collection of single crystal X-ray diffraction (XRD) data of two compounds was conducted on a Rigaku XtaLAB MM007 CCD diffractometer. The final structures were solved and refined by the crystallographic program SHELXT[1] and SHELXL-2016,[2] respectively, on the Olex^2 software.[3] All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically. The unit cell parameters and structure refinement details are listed in Table S1.

Preparation of (*R*-3AQ)RbI_3 polycrystalline film and device. A solution with a concentration of 20 mg·mL^{-1} was prepared by dissolving the 100 mg (*R*-3AQ)RbI_3 crystals into 5 mL deionized water. The (*R*-3AQ)RbI_3 film was prepared on the surface of commercial PET substrate, which surface has been coated with PEDOT:PSS, through a heat-evaporating method. (*R*-3AQ)RbI_3 solution (300 μL) was dropped onto the preheated substrate and annealed under 70 °C for 2 h to obtain the (*R*-3AQ)RbI_3 film with 2.0×1.7 cm^2. A polydimethylsiloxane (PDMS) layer was prepared on the surface of the (*R*-3AQ)RbI_3 film by using the spin-coating method to ensure the mechanical stability of the film as well as avoid the short current of the device. A copper tape was adhered to the film surface as the top electrode. Two wires were soldered to the surface of the top and bottom electrodes, respectively. Finally, the device was encapsulated with polyimide (PI) tape.

Physical Measurements. Powder XRD data was measured on a Rigaku MiniFlex600 X-ray diffractometer using Cu-Kα / Mo-Kα radiation ($\lambda = 1.5406$ Å). Measurement 2θ

ranged from 3° to 50° with a step size of 0.02° and scanning speed of 3°/min. TGA data were measured on the Rigaku TG8121 thermoanalyzer in the atmosphere of N_2. The data was collected in the range of 25−800 ^{o}C with a heating rate of 10 ^{o}/min. Differential scanning calorimetry (DSC) experiments were performed on a TA DSC25 under a nitrogen atmosphere in aluminum crucibles with a heating or cooling rate of 10 K/min. Photoluminescence (PL) spectra have been experimented on a Hitachi F7000 luminescence spectrometer (Japan). Photoluminescence lifetime was measured on an Edinburgh FS-5 spectrophotometer using a 405 nm laser. Circular dichroism (CD) spectra were acquired on a CD spectrometer (J-810, JASCO). The measurement of the piezoelectric sensing performance of the (R-3AQ)RbI_3 device was conducted on a homemade system composed of the digital oscilloscope (Keysight DSCX3024T), vibration exciter, pressure sensor, and so on. The ultrasound detecting system consists of an ultrasonic pulse generator receiver (JSR DPR300), digital oscilloscope, and ultrasonic transducer.

First-principles calculations.

The first-principles calculations were performed on the Vienna ab initio simulation package (VASP) based on the Density Functional Theory (DFT) plane-wave pseudopotential method to calculate the electronic structure and elastic constants (C_{ij}) of (R-3AQ)RbI_3 using its structure at 300 K.[4-6] The exchange-correlation energy functional Perdew–Burke–Ernzerh of generalized gradient approximation was applied to optimize the atomic positions and lattice parameters until the total energy converged to within 10^{-7} eV and the residual forces on each atom were less than 0.01 eV $Å^{-1}$.[7-8] The energy cut-off was set to 500 eV and the Monkhorst−Pack-type k point was 2×2×1. The C_{ij} were obtained by the finite-strain method with the maximum strain amplitude of 0.015 Å and 6 steps for each strain. The piezoelectric strain constants [d] were calculated by using density functional perturbation theory.

Table S1 Crystal data and structure refinement of (R-3AQ)RbI_3 and (S-3AQ)RbI_3.

	(R-3AQ)RbI_3		(S-3AQ)RbI_3	
T/K	100(15)	465(15)	150(10)	465(10)
CCDC	2434215	2366228	2434285	2434284
Formula	$C_7H_{16}I_3N_2Rb$		$C_7H_{16}I_3N_2Rb$	
M_w	594.39		594.39	
Crystal system	trigonal	cubic	trigonal	cubic
Space group	$P3_121$	$Pm\bar{3}m$	$P3_121$	$Pm\bar{3}m$
a (Å)	10.0749(10)	7.3138(7)	10.0786(2)	7.3079(2)
b (Å)	10.0749(10)	7.3138(7)	10.0786(2)	7.3079(2)
c (Å)	25.0784(19)	7.3138(7)	25.1161(7)	7.3079(2)
α (°)	90	90	90	90
β (°)	90	90	90	90
γ (°)	120	90	120	90
V (Å^3)	2204.5(6)	391.22(11)	2209.44(12)	390.28(3)
Radiation	Cu Kα	Cu Kα	Mo Kα	Mo Kα
2θ range for data collection (°)	10.138-153.61	12.102-145.3	4.666-54.546	5.574-54.944
$\rho_{calcd.}$/ (g·cm^{-3})	2.686	2.692	2.679	2.699
μ / mm^{-1}	53.858	50.651	9.619	9.083
F (000)	1608.0	280.0	1608.0	280.0
GOF	1.089	1.218	1.009	1.210
$R_1{}^a$ [I >2s(I)]	R_1=0.0310,	R_1=0.0480,	R_1=0.0357,	R_1=0.0403,
	wR_2=0.0831	wR_2=0.01254	wR_2=0.0741	wR_2=0.1359
$wR_2{}^b$(all data)	R_1=0.0312,	R_1=0.0499,	R_1=0.0403,	R_1=0.0438,
	wR_2=0.0833	wR_2=0.1282	wR_2=0.0758	wR_2=0.1452

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

Table S2. Summary of the elastic and piezoelectric properties of (R-3AQ)RbI_3. All the elastic tensors are obtained from DFT calculations. The maximal and minimal values of Young's modulus (E), shear modulus (G), and Poisson's ratio (v) were determined by using the ELATE software. Anisotropy of X is denoted by $A_X = X_{max}/X_{min}$.

		(R-3AQ)RbI_3
C_{ij} (GPa)	C_{11}	17.707
	C_{12}	6.451
	C_{13}	6.381
	C_{14}	1.806
	C_{33}	16.139
	C_{44}	6.126
E (GPa)	E_{max}	18.373
	E_{min}	10.857
	A_E	1.692
G (GPa)	G_{max}	7.70
	G_{min}	4.053
	A_G	1.9
v	v_{max}	0.483
	v_{min}	0.0969
	A_v	4.98
Bulk modulus (GPa)		9.98

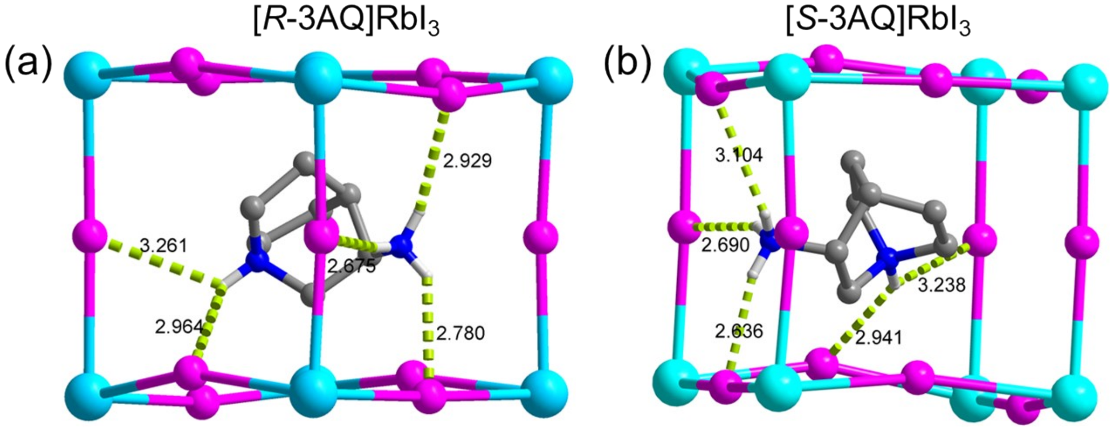

Figure S1. Hydrogen bond plots of (R-3AQ)RbI_3 and (S-3AQ)RbI_3 at 300 K. Lime dotted lines represent the hydrogen bonds. The unit of bond length is Å. Colour codes: Rb, aqua; N, blue; I, violet; C, gray; H, white.

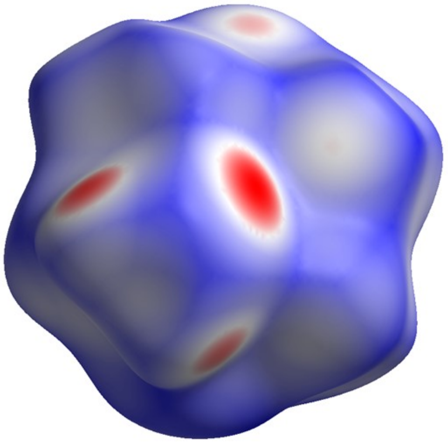

Figure S2. Hirshfeld surface of the R-3AQ^{2+} cation at 300 K.

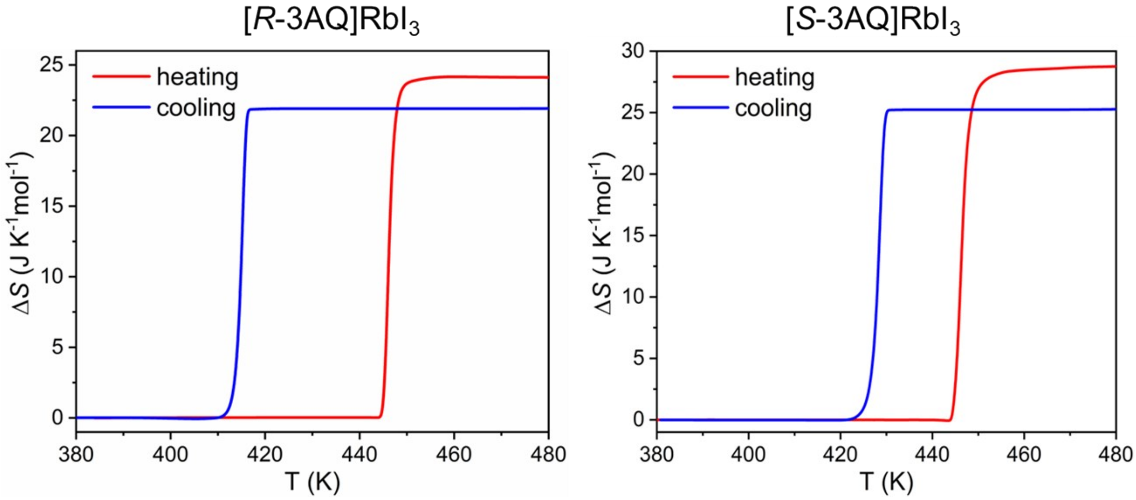

Figure S3. The corresponding entropy changes as a function of the temperature of (*R*-3AQ)RbI_3 and (*S*-3AQ)RbI_3, respectively.

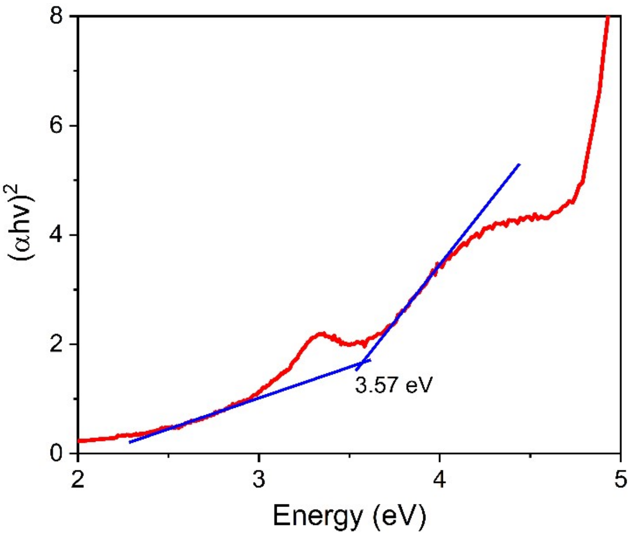

Figure S4. Tauc plot from absorbance spectrum of (*R*-3AQ)RbI_3 for determining the bandgap.

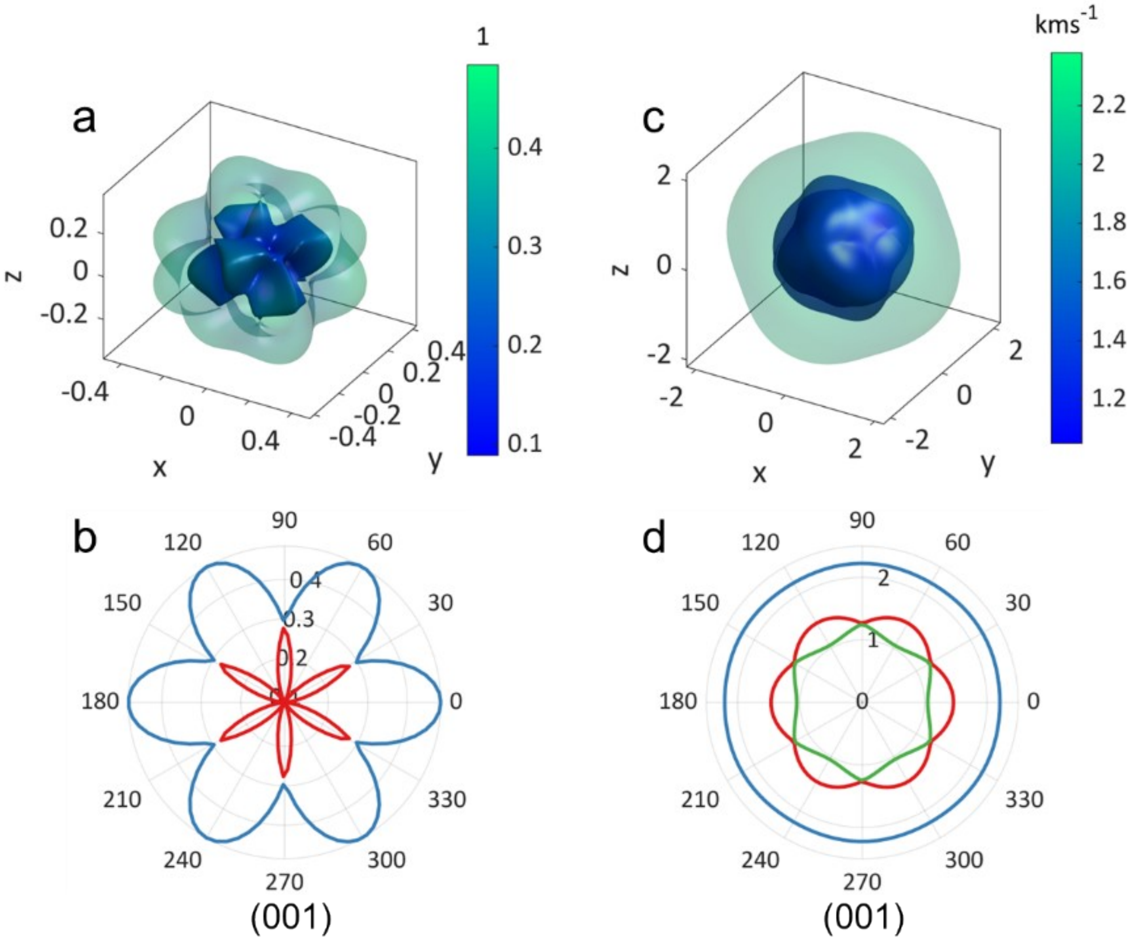

Figure S5. 3D and 2D representations of (a-b) Poisson's ratio and (c-d) acoustic velocity of (R-3AQ)RbI$_3$. The transparent outer layer and non-transparent inner layer in (a) represent the maximum and minimum values, respectively. Notably, a transparent outer layer and two non-transparent inner layers in (c) correspond to one longitudinal and two transverse modes of sound velocities.

Reference

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