A chiral switchable photovoltaic ferroelectric 1D perovskite


Spin and valley degrees of freedom in materials without inversion symmetry promise previously unknown device functionalities, such as spin-valleytronics. Control of material symmetry with electric fields (ferroelectricity), while breaking additional symmetries, including mirror symmetry, could yield phenomena where chirality, spin, valley, and crystal potential are strongly coupled. Here we report the synthesis of a halide perovskite semiconductor that is simultaneously photoferroelectricity switchable and chiral. Spectroscopic and structural analysis, and first-principles calculations, determine the material to be a previously unknown low-dimensional hybrid perovskite (R)-(−)-1-cyclohexylethylammonium/(S)-(+)-1 cyclohexylethylammonium) PbI2. Optical and electrical measurements characterize its semiconducting, ferroelectric, switchable pyroelectricity and switchable photoferroelectric properties. Temperature dependent structural, dielectric and transport measurements reveal a ferroelectric-paraelectric phase transition. Circular dichroism spectroscopy confirms its chirality. The development of a material with such a combination of these properties will facilitate the exploration of phenomena such as electric field and chiral enantiomer–dependent Rashba-Dresselhaus splitting and circular photogalvanic effects.

INTRODUCTION
Recently, ferroelectric semiconductors with strong spin-orbit coupling emerged as theoretically promising candidates for previously unavailable electronic functionalities such as spin-orbitronics, by exploiting the electric field–switchable Rashba-Dresselhaus effect (1–6). The ability to break inversion symmetry in a field-dependent manner is the primary source of this phenomenon. Breaking additional symmetries, such as chirality, in spin-orbit ferroelectric semiconductors would introduce additional perturbations in the Rashba-Dresselhaus physics that could lead to further fine-grained control of the coupled optical, spin, valley, and electronic properties of these materials [e.g., chirality-controlled circular photogalvanic effect (7, 8)].

Bringing together spin-orbit-split ferroelectricity and chirality necessitates overcoming two challenges. First, most ferroelectric materials with strong spin-orbit coupling (2–6) have too low of a bandgap for unambiguously achieving ferroelectricity in experiment, resulting in a long-standing debate about whether these materials are even ferroelectric. Second, common chiral materials (9) that exhibit spin-selectivity to photons (10, 11) and electrons (12, 13), such as sodium ammonium tartrate, (S)-alanine, and cholesteric liquid crystals, typically have large bandgaps with response only in the ultraviolet (UV) and poor carrier mobilities. Here, we theoretically design and experimentally realize an electrically switchable, chiral, spin-orbit ferroelectric material in a hybrid lead halide perovskite semiconductor.

Organic-inorganic halide perovskites (14–17) have shown great potential in photovoltaic and electro-optical devices due to their excellent semiconducting properties. The lead iodine octahedra in hybrid perovskites control the band-edge electronic structure and make them good semiconductors with strong spin–orbit coupling, while the organic groups serve as structural and chemical stabilizers. The organic groups provide the flexibility to explore unique functionalities, such as the ferroelectricity and chirality explored here (Fig. 1), while retaining the desirable semiconducting behavior. Taking such design approach, notable seminar works (18–24) in this field on hybrid perovskite have been inspiring the search of unprecedented materials performance and previously unknown properties. Recently, Xiong et al. (18) reported the two-dimensional (2D) ferroelectric perovskite in the form of chiral enantiomers. Here, specifically, by using chiral (R)-(−)-1-cyclohexyl-ethylamine (R-CYHEA, C8H15NH2) or (S)-(++)-1-cyclohexyl-ethylamine (S-CYHEA, C8H15NH2) for the organic group, we have successfully designed and synthesized a pair of enantiomers (R)-CYHEAPbI3 and (S)-CYHEAPbI3, which have been found to be chiral and electrically switchable photoferroelectric perovskite semiconductors. PbI6 octahedra determine the band structure and transport property, while the organic groups are responsible for chirality and ferroelectricity by removing the material’s mirror and inversion symmetry, respectively (Fig. 1).

RESULTS AND DISCUSSION
We use a solution method to synthesize chiral perovskites from each molecular enantiomer, resulting in needle-like yellow crystals with millimeter dimensions (Fig. 2, A and B). Optical images (Fig. 2C) show that the materials from the R-CYHEA and S-CYHEA precursors exhibit similar shapes and colors (in unpolarized light). Nuclear magnetic resonance (NMR) and Fourier transform infrared spectroscopy...
(FTIR) confirm the identity of the organic molecule within each crystal, as shown in Fig. 2 (D and E). Most NMR peaks remain unchanged from the molecule, and a new peak at 7.6 parts per million (ppm) \(^{1}H\) NMR [500 MHz, dimethyl sulfoxide (DMSO)–\(d_6\): \(\delta = 7.60 \text{ (s, 3H)}, 3.00 \text{ to } 2.98 \text{ (m, 1H)}, 1.72 \text{ to } 0.94 \text{ (m, 14H)}\)] indicates the incomplete reaction of amino group and hydroiodic acid (HI) (fig. S1). The peaks in FTIR from N–H bonds at around 3200 cm\(^{-1}\) are shifted from that in R-CYHEA/S-CYHEA because of the formation of \(–\text{NH}_3^+\) from \(–\text{NH}_2\) (fig. S2). Simultaneously, Raman spectroscopy (see Materials and Methods) confirms the presence of lead iodide octahedra with the characteristic peak at around 100 cm\(^{-1}\) seen for most lead iodide perovskites (25, 26), as shown in fig. S3 (see Materials and Methods for further details on the synthesis and spectroscopic measurements).

X-ray diffraction (XRD) then provides us with detailed structural information, as shown in figs. S4 to S8 and discussed further in Materials and Methods. Powder XRD of the materials synthesized from R-CYHEAI and S-CYHEAI are mutually quite similar to each other (figs. S4 and S5) and exhibit none of the peaks of PbI\(_2\) or the molecular precursors. This indicates the structural similarity of the two enantiomers and complete transformation from the precursors. XRD of the films grown on different substrates are shown in figs. S6 to S8.

Rietveld refinements and single-crystal XRD measurements (Fig. 2, G and H) on the needle-like single crystals at \(-173^\circ\) and \(20^\circ\)C (figs. S9 to S11 and tables S1 to S3) help determine lattice parameters and atomic positions in greater detail. The existence of a single fast axis in the transmission of linearly polarized white light (Fig. 2) and the Kikuchi pattern in our electron backscatter diffraction (EBSD) measurements (fig. S15) confirm that these needles are indeed single crystals. A combination of XRD crystal determination software, density measurements (fig. S16), and first-principles calculations (fig. S17) jointly establishes the space group of the crystal to be \(P2_1\) with angle \(\beta = 89.5121^\circ\) (see more discussions on tables S1 to S3 and fig. S11). Figure 2G shows the single-crystal diffraction pattern of the crystal, and Fig. 2H presents the corresponding digitally reconstructed precession photograph. On the basis of first-principles calculations and single-crystal XRD at low and room temperatures, we find that the lattice expands slightly from \(a = 8.612 \text{ Å}, b = 7.954 \text{ Å}, c = 21.719 \text{ Å at } -173^\circ\text{C to } a = 8.628 \text{ Å}, b = 8.211 \text{ Å, and } c = 22.994 \text{ Å at room temperature, with the angle and space group remaining unchanged.}\) The structure and density identify the stoichiometry of the synthesized materials to be R-CYHEAPbI/S-CYHEAPbI\(_3\) (Fig. 2I). First-principles density functional theory (DFT) calculations fill in the finer structural details beyond XRD resolution. These calculations show that opposite rotation of the amine groups on either side of the [001] plane breaks inversion symmetry along the \(b\)-direction, giving rise to polarization in the structure (fig. S17).

We then investigate the semiconducting property with optical and optoelectronic measurements. Photoluminescence spectroscopy (PL) measurements from a 405-nm excitation laser reveal a weak white PL (fig. S18), attributed to the Stokes process in low-dimensional halide perovskites (27–29), with response persisting to longer wavelengths including 635 nm as shown in figs. S21 and S22. A strong absorption transition ranging from \(\sim 360 \text{ to } 410 \text{ nm}\) indicates exitonic behavior (figs. S19 and S20) (30), once again consistent with the low-dimensional structure of the crystals (Fig. 2I).

Next, to test ferroelectricity in our material, we performed temperature-dependent second-harmonic generation (TD-SHG) to analyze this phase transition (Fig. 3A). The SHG signal markedly decreases (by half in intensity) at around \(85^\circ\)C, indicating a phase transition (at \(100^\circ\)C, the phase transition is complete) from a low-temperature SHG-active structure to a high-temperature structure, which shows no or much weaker SHG signal under our experiment condition. Figure S23 presents the SHG spectrum from the R

**Fig. 1. Design principle.** Lead halogen octahedra control the semiconducting property independently from the organic molecule that can be engineered to introduce a previously unknown properties, such as the simultaneous ferroelectricity and chirality achieved here.

symmetry crystal. In addition, we used the double-wave technique (31–33) to characterize the polarization–electric field (PE) loops, as shown in Fig. 3B, clearly indicating that the synthesized crystal is ferroelectric (fig. S24). The polarization of around 0.03 μC/cm² is small compared with commercial ferroelectric materials because of the combination of a low intrinsic DFT-predicted polarization (see more discussion in fig. S17 and the associated description) and lack of alignment between the polarization and measurement axes (DFT predicts b axis, fig. S17). The orientation dependence of the polarization is further confirmed by direction-dependent PE loops in fig. S26. Polarization endurance and retention results are shown in fig. S28. Further study shows that the polarization reaches 1.2 μC/cm² for a single-crystal sample, which will be discussed later.

Having established that our material is both ferroelectric and semiconducting, we measure the typical switchable diode effect (34–37) shown in Fig. 3C. The photoresponse of our devices was measured without external bias, and we found that the direction of photocurrent is dependent on the previous poling process (history of applied electric fields). Specifically, we find a negative photocurrent at 0 V after applying 10 V on the device for 200 s, and a positive photocurrent...
the experimental absorbance results as shown in fig. S20. Including SOC brings the gap in much closer agreement with (i and ii) and X_2PbI_4 (band structure for chiral CYHEA (i and iii) and nonchiral CYHEA (ii and iv) XPbI_3 shown in the device. LED, light-emitting diode. PVK, perovskite. (E) Electronic band structure for chiral CYHEA (i and iii) and nonchiral CYHEA (ii and iv) XPbI_3 (i and ii) and X_2PbI_4 (iii and iv) stoichiometries including spin-orbit coupling (SOC). Bandgaps increase and switch from direct to indirect on going from X_2PbI_4 to XPbI_3 for each material. Including SOC brings the gap in much closer agreement with the experimental absorbance results as shown in fig. S20.

Fig. 3. Switchable photovoltaic ferroelectric effect. (A) TD-SHG reveals a transition from an inversion symmetry broken to an inversion-symmetric phase at 85°C. Inset: SHG peak at 540 nm from a 1080-nm infrared laser. a.u., arbitrary units. (B) PE loop of our perovskite confirming its ferroelectricity. Test was done at 800 Hz. (C) Switchable diode effect: After poling with +10 V and −10 V for 200 s, the photocurrent without bias is negative and positive, respectively, because of (D) band structure of our polycrystal device under zero bias, positive bias, and negative bias, respectively. A reversal in the band bending and resulting diode orientations are shown in the device. LED, light-emitting diode. PVK, perovskite. (E) Electronic band structure for chiral CYHEA (i and iii) and nonchiral CYHEA (ii and iv) XPbI_3 (i and ii) and X_2PbI_4 (iii and iv) stoichiometries including spin-orbit coupling (SOC). Bandgaps increase and switch from direct to indirect on going from X_2PbI_4 to XPbI_3 for each material. Including SOC brings the gap in much closer agreement with the experimental absorbance results as shown in fig. S20.
pared with traditional chiral organics (fig. S31). Signal to the higher absorption of our semiconducting material compared with traditional chiral organics (fig. S31). Hence, we may attribute our high CD signal to the higher absorption of our semiconducting material compared with traditional chiral organics (fig. S31). Larger absorption coefficient. Hence, we may attribute our high CD signal to the higher absorption of our semiconducting material compared with traditional chiral organics (fig. S31).

Electric field dipole and magnetic field dipole moment operators, $\mathbf{M}$ and $\mathbf{\mu}$, respectively. $\mathcal{E}$, $\hbar$, and $N_A$ are the wave functions of ground state and excited state of electrons. $\mu$ and $M$ represent the electric field dipole and magnetic field dipole moment operators, respectively. $C_{\mathcal{E}}$ is CD signal. On the basis of this equation, CD signal can be described in the following equation (44, 45)

$$
\frac{3K\hbar c}{16\pi^3 N_A} \int \Delta \mathbf{e} \cdot d\mathbf{\lambda} = \text{Im} \left( \int \mathbf{\Psi}_e \cdot \mathbf{\mu} \cdot \mathbf{\Psi}_g \, dt \cdot \int \mathbf{\Psi}_e \cdot M \cdot \mathbf{\Psi}_g \, dt \right)
$$

$K$ is a constant to convert the unit of molecular extinction coefficient to molecular ellipticity, $c$, $\hbar$, and $N_A$ stand for light speed, reduced Planck constant, and Avogadro’s number, respectively. $\beta$ is a proportionality coefficient. $\mathbf{\Psi}_e$ and $\mathbf{\Psi}_g$ are the wave functions of ground state and excited state of electrons. $\mathbf{\mu}$ and $M$ represent the electric field dipole and magnetic field dipole moment operators, respectively. $\Delta \mathbf{e}$ is CD signal. On the basis of this equation, CD signal can be described in the following equation:

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$$

In summary, we have theoretically predicted, experimentally synthesized, and comprehensively established a previously unknown low-dimensional hybrid perovskite material with both ferroelectricity and optical chirality. Structural, spectroscopy, and DFT analysis have shown that the pair of synthesized material enantiomers do not have inversion symmetry. Electrical and optoelectronic transport characteristics show the existence of PE loop, switchable and hysteresis-like pyroelectric response, and a switchable photoferroelectric effect. On the basis of single-crystal material, temperature-dependent synchrotron XRD, DSC, temperature-dependent dielectric constant, and temperature-dependent pyroelectric current all show the existence of a ferroelectric-paraelectric phase transition at around 100°C. CD spectroscopy and theoretical analysis demonstrate the large chirality comparable to existing chiral organics. This new class of materials will form the foundation for exploiting chirality as an additional control on the ferroelectrically manipulated spin-orbit splitting in switchable Rashba-Dresselhaus materials (e.g., chirality-selected circular photogalvanic materials).

CONCLUSION

MATERIALS AND METHODS

Synthesis

R-CYHEAPbI$_3$/S-CYHEAPbI$_3$ was synthesized by a solution method. Lead iodide (PbI$_2$) (0.25 mmol; Sigma Aldrich), R-CYHEA/S-CYHEA (1 mmol; Sigma-Aldrich), and hydriodic acid aqueous solution (HI) (6 ml, ≥47.0%; Sigma-Aldrich) were mixed in a round-bottom flask in silicon oil bath. The flask was heated to 150°C for 2 hours with refluxing. Excess R-CYHEA/S-CYHEA and HI were used deliberately.
to advance the reaction and to make sure that PbI$_2$ was completely consumed and can be removed after the reaction by filtration. After the heating process, a clear solution was obtained, and by slowly decreasing the temperature to room temperature at 0.1°C/min, large needle-like single crystals were successfully synthesized.

A chemical vapor deposition (CVD) method was also used to synthesize this material. We used a home-made CVD system (Extech 48VFL13 PID controller). Mica (SPI Grade V-5) was used as a substrate. The temperature at the furnace center was around 400°C, where one of the precursors, PbI$_2$, was placed. The other precursor, R-CYHEA/S-CYHEA, which was prepared by mixing R-CYHEA/S-CYHEA and HI in an ice water bath, was placed in an upstream position, 5 cm away from the zone center, while substrates was placed at downstream position. The system was pumped to 0.5 torr before the deposition, after which the base pressure was maintained to be around 200 torr with a flow rate of 200 standard cubic centimeter per minute of argon. After 30-min growth, we successfully got some needle-like crystals on the substrate.

**Thin film preparation**

Thin films were prepared by a spin-coating method (Headway Manual Spin Coater). R-CYHEAPbI$_3$/S-CYHEAPbI$_3$ was dissolved in acetone, and the saturated solution was spin-coated on silicon wafers (Si, n-type, 1.0 to 1.3 × 10$^{15}$ /cm$^3$-phosphor doped, Silicon Valley Microelectronics), fluorine-doped tin oxide–coated glasses (FTO; ~7 ohms/sq.; Sigma-Aldrich), freshly cleaved sodium chloride substrates (NaCl; Ted Pella Inc.), freshly cleaved potassium chloride substrates (KCl; Ted Pella Inc.), quartz slides (Technical Glass Products, Inc.) and glass slides (VWR) at 2000, 4000, 6000, 8000, and 10000 rpm for 30 s. After the spin-coating process, high-quality films were easily prepared, and annealing was not required.

**Device preparation**

For electrical measurements, 40-nm-thick round gold electrodes with a diameter of around 1 mm was deposited on the thin films by an electronic-beam (e-beam) deposition method to form usable devices with Temescal e-beam evaporator. Those devices were used for PE loop and photoresponse tests.

Our single-crystal device was prepared with a submillimeter-size single-crystal sample between two piles of silver paste on a glass substrate, forming a lateral device. This device was used for temperature-dependent dielectric constant measurement and pyroelectric tests (fig. S25).

**NMR and FTIR measurement**

Our material was dissolved in DMSO-$d_6$ for NMR measurement with 500 MHz Agilent NMR Spectrometer. A thin film on NaCl was used for FTIR measurement with a PerkinElmer Spectrum One FTIR spectrometer.

**Optical measurements**

Optical images and transmission of linear-polarized white light were measured with our Nikon Ti-S optical microscope. Thin films on KCl were used for Raman spectrum measurement with a WITec alpha300 confocal Raman microscope and a 532 nm continuous wave (CW) laser. PL measurement was done at room temperature with a home-built PL system [Thorlabs 4 Megapixel Monochrome Scientific charge-coupled device (CCD) camera, Princeton Instruments SP-2358 spectrograph, Nikon Ti-S optical microscope, and PicoQuant 405-nm pulsed laser]. Transmission spectrum was measured using a thin film on NaCl with a USB4000-UV-VIS spectrometer. The photoresponse of this material was measured with a home-made system (Autolab PGSTAT302N potentiostat and Thorlabs Compact Laser Diode Module with Shutter, 405/635 nm, 4.0 mW). Devices on FTO was used in these measurements. SHG measurement was performed with a home-made system (Keopsys KPS-BT2-YFL-1083-40-COL 1083 nm, 3-W CW fiber laser, Thorlabs 4 Megapixel Monochrome Scientific CCD camera, Princeton Instruments SP-2358 spectrograph, and Nikon Ti-S optical microscope). TD-SHG was performed with a Linkam Scientific Instruments TMS94 temperature controller.

**XRD measurements**

Powder XRD was performed using Cu Kα radiation on a Bruker D8 Focus diffractometer with a LynxEye detector. Rietveld refinements
were performed in TOPAS (Bruker AXS). Single-crystal XRD experiments were carried out by mounting needle-like crystals on a loop with a tiny amount of Paratone-N oil \([T = -163 \ (2\text{°C})]\) or epoxy \((T = 25\text{°C})\). All reflection intensities were measured using a SuperNova diffractometer (equipped with an Atlas detector) with Mo Kα radiation \((\lambda = 0.71073 \ \text{Å})\) under the CrystAlisPro software suite (version 1.171.36.28, Agilent Technologies, 2012). CrystAlisPro was also used to index the cell dimensions and to perform data reduction. The generation of the initial models and subsequent structure refinements were conducted using SIR971 (46) and SHExLX-20132 (47), respectively. After the refinement of all of the atomic positions, the collected data were corrected for absorption (i.e., a face-indexed analytical absorption correction was applied using CrystAlisPro). The displacement parameters were then refined as anisotropic, and weighting schemes were applied during the final stages of refinement.

The crystallographic phase transition of 1D pervoskite single crystal was characterized by in situ temperature-dependent synchrotron high-energy XRD measurements, which were performed at the 11-ID-C beamline of the Advanced Photon Source at Argonne National Laboratory. High-energy x-rays of 0.111665 Å wavelength were used to obtain 2D diffraction patterns in the transmission geometry using a PerkinElmer large area detector placed downstream at 1.5 m away from the sample. The single-crystal Laue diffraction was collected as a function of heating temperature from 0° to 175°C in 5°C for each step. For each temperature point, the single long-acquisition 2D image is the cumulative collection of the single-crystal diffraction as a function of rotation along the crystallographic zone axis of the longer side of the small needle-like single crystal. The temperature control was realized by an Oxford Instrument cryosteamer/heater system, which flushes the dry-heated N2 gas to the capillary glass tube enclosing the 1D perovskite needle-like small single crystal.

**EBSD measurements**

EBSD measurements were performed with an Oxford AZTEC system on our needle-like single crystals.

**Electrical property measurements**

PE loop measurements were performed with a home-built double-wave method system (BK Precision 2190D oscilloscope, AFG1062 Tektronix Arbitrary Waveform Generator) at different frequency. Detailed information about the double-wave method can be found in fig. S24.

Switchable diode effect was measured with a home-built system consisting of an Autolab PGSTAT302N potentiostat and a radio shack 10-mm blue light-emitting diode lamp (465 to 467.5 nm).

The temperature dependence of dielectric constant was measured with a home-built system (AFG1062 Tektronix Arbitrary Waveform Generator, BK Precision 2190D oscilloscope, and Falco Systems WMA-02 amplifier), and temperature was controlled by a cryostage (Linkam Scientific Instruments, TMS94). Impedance was measured, WMA-02 amplifier), and temperature was controlled by a cryostage with a home-built system (AFG1062 Tektronix Arbitrary Waveform Generator) with an Autolab PGSTAT302N potentiostat and a radio

Pyroelectric current was measured with a potentiostat (Autolab PGSTAT302N) and a cryostage (Linkam Scientific Instruments, TMS94). Similar to PE loop measurements, pyroelectric coefficient versus poling electric field loop was obtained by poling our device at a series of voltage (2000, 1000, 500, 0, −500, −1000, −2000, −1000, −500, 0, 500, 1000, and 2000 V) and measured the pyroelectric coefficient after each poling. The temperature dependence of pyroelectric current was measured with a ramp speed of 10°C/min.

**DSC measurements**

DSC was measured with a differential scanning calorimeter (TA Instruments, DSC-Q100) under nitrogen atmosphere. Temperature range was set to be 20° to 120°C with a ramp speed of 10°C/min.

**CD measurements**

CD was performed on a Jasco 815 CD spectrometer.

**DFT calculations**

We performed DFT calculations using the open-source plane-wave software: JDFTx (48) with the Heyd-Scuseria-Ernzerhof (HSE06) (49) exchange-correlation functional, ultrasoft pseudopotentials (50), and a kinetic energy cutoff of 20 Hartrees for wave functions and 100 Hartrees for the charge density. We used DFT + D2 (51) pair-potential corrections for the van der Waals interaction and integrated over the Brillouin zone using a \(2 \times 2 \times 1 \) Γ-centered \(k\)-point mesh. The band structure was then calculated on a high-symmetry \(k\)-point path using maximally localized wannier functions.

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**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/6/9/eaay4213/DC1

Section S1. Structural characterization

Section S2. Optical characterization

Section S3. Ferroelectricity and pyroelectricity

Section S4. Photoferroelectricity

Section S5. Chirality

Fig. S1. NMR result of R-CYHEA.

Fig. S2. FTIR result of R-CYHEA.

Fig. S3. Raman results of R-CYEHAPbI3 on KCl.

Fig. S4. Powder XRD result of R-CYEHAPbI3.

Fig. S5. Powder XRD result of C-CYEHAPbI3.

Fig. S6. XRd result of R-CYEHAPbI3 grown on Si.

Fig. S7. XRD result of R-CYEHAPbI3 grown on mica.

Fig. S8. XRD result of R-CYEHAPbI3 grown on NaCl.

Fig. S9. Rietveld modeling (red curve) of room temperature powder x-ray data (black crosses) and corresponding difference curve (blue) for powdered R-CYEHAPbI3.

Fig. S10. Single-crystal XRD results of R-CYEHAPbI3.

Fig. S11. Diffraction analysis.

Fig. S12. Single-crystal synchrotron XRD results.

Fig. S13. Analysis of synchrotron diffraction result.

Fig. S14. Peak intensities have changed after temperature increases from 0° to 175°C.

Fig. S15. EBSD of single-crystal sample.

Fig. S16. Schematic drawing of the system that we used to measure the volume of the crystal in density determination.

Fig. S17. Theoretical electronic band structure and polarization.

Fig. S18. PL of R-CYEHAPbI3.

Fig. S19. Transmission spectrum of S-CYEHAPbI3.

Fig. S20. Absorption spectrum of S-CYEHAPbI3.

Fig. S21. Photoresponse of R-CYEHAPbI3 on FTO under 405-nm laser.

Fig. S22. Photoresponse of R-CYEHAPbI3 on FTO under 635-nm laser.

Fig. S23. SHG spectrum of R-CYEHAPbI3.

Fig. S24. Comparison of Sawyer-Tower method and double wave method used in PE loop measurements.

Fig. S25. Our single-crystal device.

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\[ \epsilon' = \frac{d}{2\pi f S \epsilon_0 Z^2 + Z'^2} \]

\( \epsilon' \) is the real part of dielectric constant \((\epsilon = \epsilon' - i\epsilon'')\), \(d\) is the distance between two electrodes, \(S\) is the device area, \(f\) is the frequency of applied sine wave, \(\epsilon_0\) is the vacuum permittivity, and \(Z\) is the impedance \((Z = Z' + iZ'')\).


Acknowledgments

Funding: J.S. and R.S. acknowledge start-up funding from the Department of Materials Science and Engineering at Rensselaer Polytechnic Institute, NSF under award nos. 1635520, 1916652, and 1712752, the Air Force Office of Scientific Research under award no. FA9550-18-1-0116, and the Office of Naval Research under award no. N000141812408. L.Z. thanks the funding support from the New York State’s Empire State Development’s Division of Science, Technology and Innovation through Focus Center Contract C150117. Calculations were performed at the Center for Computational Innovations at Rensselaer Polytechnic Institute. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under contract no. DE-AC02-06CH11357. This material is partially based on work supported by the NSF-MIP Platform for the Accelerated Realization, Analysis, and Discovery of Interface Materials (PARADIM) under cooperative agreement no. DMR-1539918.

Author contributions: Y.H. and Z.C. grew the materials and fabricated the films. Y.H., Z.C., and J.J. conducted the electrical and optoelectrical transport studies. F.F. and R.S. conducted computational simulations. H.Z. and Y.R. conducted and analyzed temperature-dependent synchrotron XRD. W.A.P. and M.A.S. conducted and analyzed single-crystal XRD. Z.Z. and E.F.P. conducted and analyzed DSC and NMR results. Y.H., Y.G., R.H., J.J., L.Z., and Y.W. conducted device fabrication. Y.H. and Y.G. conducted and analyzed CD spectra. B.W. and D.G. conducted FTIR study and helped on XRD study. Y.H. and J.J. conducted and analyzed SHG. L.Z. conducted and analyzed atomic force microscopy and scanning electron microscopy studies. Z.L. and X.S. conducted EBSD study. X.S. conducted physical vapor deposition growth. Y.H. and F.F. wrote the manuscript. T.-M.L., E.W., R.S., J.F., and J.S. all participated in the analysis of data and revision of the manuscript. J.S. and R.S. conceived and supervised the project. Competing interests: The authors declare that they have no competing interests. Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

Submitted 17 June 2019
Accepted 5 December 2019
Published 28 February 2020
10.1126/sciadv.aay4213

A chiral switchable photovoltaic ferroelectric 1D perovskite

Sci Adv 6 (9), eaay4213.
DOI: 10.1126/sciadv.aay4213