Supporting Information

**Tailoring of a** **Visible-Light-Absorbing Biaxial Ferroelectric towards Broadband** **Self-Driven Photodetection**

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Experimental Procedures

**Material Synthesis.** Compound **1** was synthesized from the concentrated aqueous HI solutions (57%) containing PbI2, CH3CH2NH3I and C5H11NH3I with a molar ratio of 3:2:2. Then, the reaction mixture was stirred with heating for 30 min to dissolve the components thoroughly. Subsequently, large-size crystals were grown by the temperature cooling method with the temperature lowing rate of 1 K/day.

**Thermal measurements.** Differential scanning calorimetry (DSC) measurement was performed using the NETZSCH DSC 200 F3 with the heating/cooling rates of 5 K/min.

**Single-crystal X-ray diffraction.** Variable-temperature single crystal diffraction data of **1** were collected on a Bruker D8 Quest/Venture diffractometer with Mo-Ka radiation (λ = 0.77 Å) at 260 K, 320 K and 350 K, respectively. The data reduction and multi-scan absorption correction were performed using the Crystalclear software package (Rigaku, 2005).

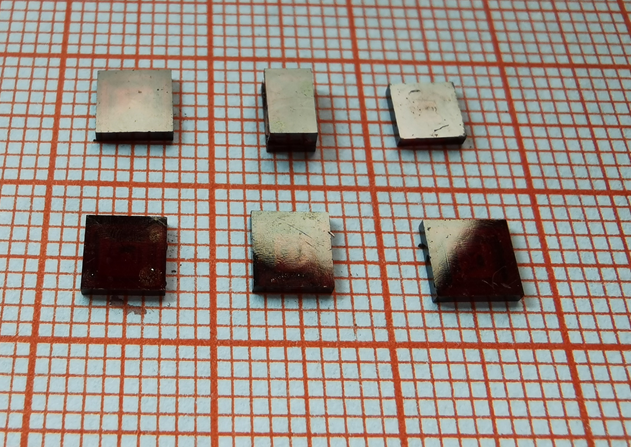
**Optical measurements.** Ultraviolet-visible diffuse reflectance spectrometry was performed on a PerkinElmer Lambda 950 UV-vis-IR spectrophotometer.

**Electrical measurements.** The dielectric constants were measured using the two-probe AC impedance method with an Impedance Analyzer (TH2828A). Photoelectric measurements were measured using a Keithley 6517B source meter.

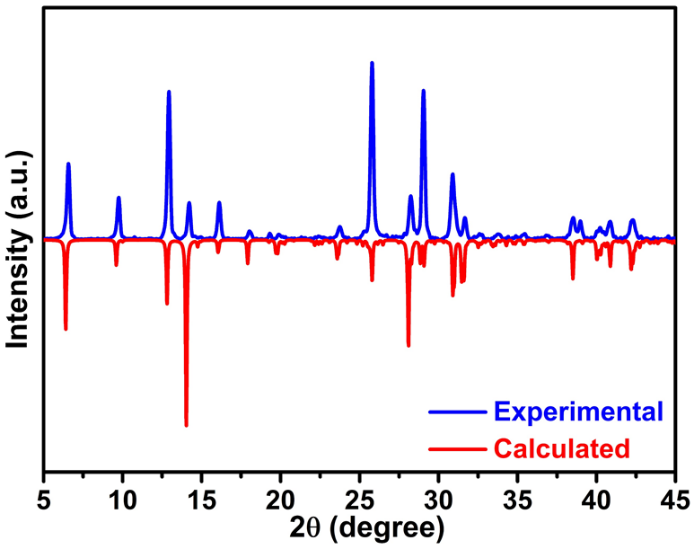
**Ferroelectric measurements.** Single-crystal sample with the thickness of ~1 mm was cut and polished for the measurements of pyroelectric and ferroelectric properties. In order to avoid electric discharge at high electric field, single crystal of **1** was immersed in silicone oil to measure the *P-E* hysteresis loops.

**Computational methods.** Density function theory (DFT) calculations were performed using the plane-wave pseudopotential method implemented in the Cambridge Sequential Total Energy Package (CASTEP) software package. The exchange-correlation potential was calculated using the Ceperley and Alder-Perdew and Zunger (CA-PZ) functional within local-density approximation (LDA). Ultrasoft pseudopotential were adapted, and valence electrons were provided by the package. The numbers of plane waves included in the basis sets were determined by a cutoff energy 280 eV, and the numerical integration of the Brillouin zone was performed using a Monkhorst-Pack κ-point sampling of 1×2×2.

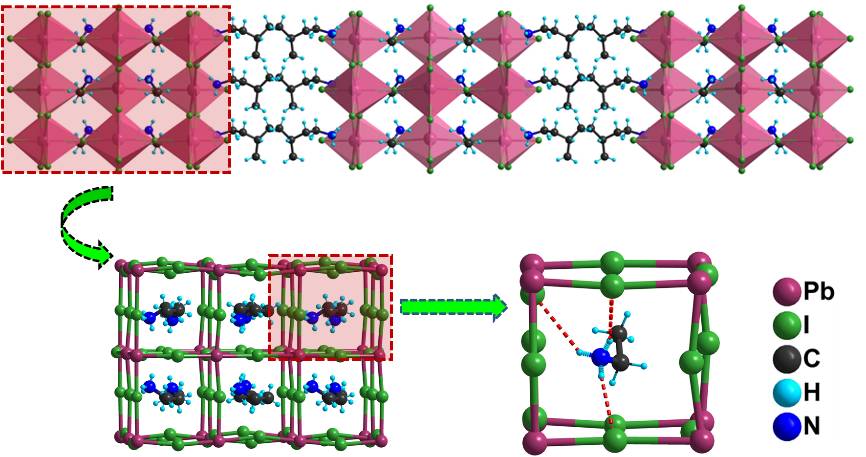
Figures



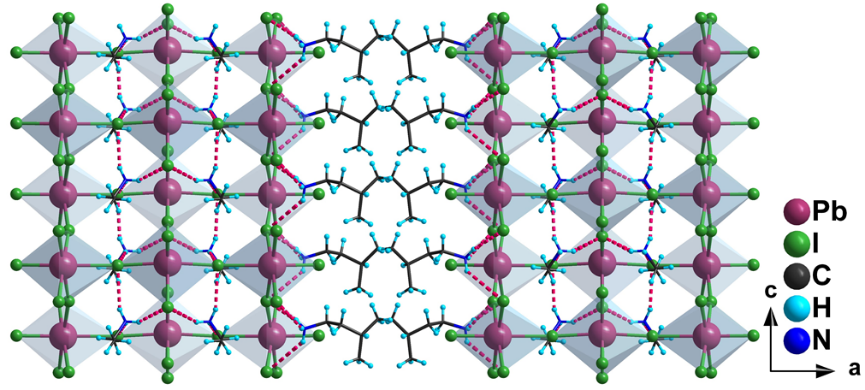
**Figure S1**. Bulk crystal of **1** grown from the concentrated HI solution by the temperature lowering method.



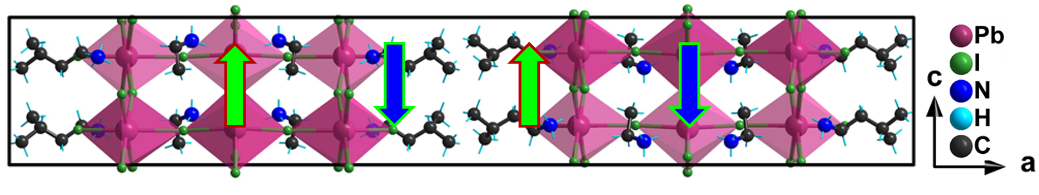
**Figure S2.** Experimental and calculated PXRD patterns of **1** at room temperature.

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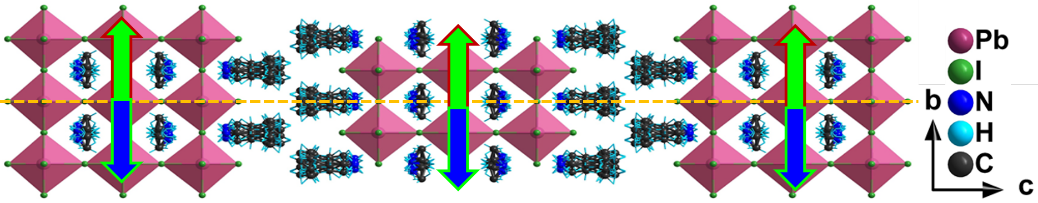
**Figure S3.** The organic ethylammonium cation is confined in the cavity enclosed by distorted corner-sharing PbI6 octahedra, being linked together by the strong N-H···I hydrogen bonds. Red imaginary lines represent the N−H···I hydrogen bonds.

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**Figure S4.** Diagram of N-H∙∙∙I Hydrogen bonds between inorganic perovskite sheets and organic isopentylammonium/ethylammonium cations of **1** at FEP. Red imaginary lines represent the N−H···I hydrogen bonds.



**Figure S5.** The unit cell of crystal structure of **1** at AFEP. The green and blue arrowheads denote antiparallel alignment of dipoles related to dynamic orientation of structural moieties.



**Figure S6.** Schematic representation of crystal structure for **1** at PEP. The yellow-dashed line denotes the crystallographic mirror plane.

**Table S1.** Crystal data and structure refinement for **1** at different temperatures: FEP (260 K); AFEP (320 K) and PEP (350 K).

|  |  |  |  |
| --- | --- | --- | --- |
| Temperature | FEP (at 260 K) | AFEP (at 320 K) | PEP (at 350 K) |
| Empirical formula | C14H44I10N4Pb3 | C14H44I10N4Pb3 | C14H44I10N4Pb3 |
| Crystallographic system, space group | Orthorhombic,  *Cmc*21 | Orthorhombic,  *Pmcn* | Tetragonal,  *I*4/*mmm* |
|  | 55.225(6) Å | 54.941(11) Å | 6.3847(10) Å |
| Cell parameters | 8.9515(8) Å | 8.9136(17) Å | 6.3847(10) Å |
|  | 9.0019(9) Å | 8.9822(15) Å | 55.873(9) Å |
| V (Å3) | 4450.1(7) | 4398.8(14) | 2277.6(8) |
| Z | 4 | 4 | 2 |
| Calculated density (g/cm3) | 3.223 | 3.260 | 3.148 |
| F(000) | 3728.0 | 3728.0 | 1864.0 |
| Theta range (º) | 4.426-55.08 | 5.082-52.836 | 5.834-52.652 |
| Limiting indices | -71 ≤ h ≤ 71 | -68 ≤ h ≤ 48 | -7 ≤ h ≤ 7 |
| -11 ≤ k ≤ 11 | -11 ≤ k ≤ 10 | -7 ≤ k ≤ 7 |
| -10 ≤ l ≤ 11 | -11 ≤ l ≤ 10 | -69 ≤ l ≤ 69 |
| Reflections collected / unique | 18281/4535 | 19201/4506 | 8673/778 |
| Rint = 0.0998 | Rint = 0.1074 | Rint = 0.0678 |
| Data/restraints/parameters | 4535/110/150 | 4506/110/150 | 778/169/100 |
| GOF. | 1.051 | 1.064 | 1.046 |
| Final R indices [I > 2σ(I)] | *R*1 = 0.0944,  *wR*2 = 0.2500 | *R*1 = 0.1376,  *wR*2 = 0.2576 | *R*1 = 0.0605, *wR*2 = 0.1164 |
|  |  |  |  |

**Table S2.** Bond Lengths of Pb-I of crystal **1** at FEP (260 K).

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Atom | Atom | Bond length (Å) | Atom | Atom | Bond length (Å) |
| Pb2 | I5*#*1 | 3.238(2) | Pb1 | I4 | 3.4608(18) |
| Pb2 | I5 | 3.323(2) | Pb1 | I3 | 3.1763(19) |
| Pb2 | I4*#*2 | 3.1924(16) | Pb1 | I3*#*4 | 3.2109(19) |
| Pb2 | I4 | 3.1923(16) | Pb1 | I1 | 3.195(2) |
| Pb2 | I6 | 3.243(3) | Pb1 | I1*#*5 | 3.178(2) |
| Pb2 | I6*#*3 | 3.183(2) | Pb1 | I2 | 2.998(2) |

Symmetry transformations used to generate equivalent atoms:

#1 1-X,1-Y,1/2+Z; #2 1-X, +Y, +Z; #3 1-X,2-Y,1/2+Z; #4 +X,1-Y, -1/2+Z; #5 +X, 2-Y,1/2+Z

**Table S3.** Bond angles of I-Pb-I of crystal **1** at FEP (260 K).

|  |  |  |  |
| --- | --- | --- | --- |
| Bond | Bond angle (˚) | Bond | Bond angle (˚) |
| I5*#*1-Pb2-I5 | 88.38(3) | I3-Pb1-I4 | 82.38(6) |
| I5*#*1-Pb2-I6 | 173.11(6) | I3*#*4-Pb1-I4 | 82.45(6) |
| I4*#*2-Pb2-I5 | 85.53(4) | I3-Pb1-I3*#*4 | 89.61(2) |
| I4*#*2-Pb2-I5*#*1 | 90.40(5) | I3-Pb1-I1 | 177.49(6) |
| I4-Pb2-I5*#*1 | 90.40(5) | I3-Pb1-I1*#*5 | 92.15(5) |
| I4-Pb2-I5 | 85.54(4) | I1-Pb1-I4 | 95.96(6) |
| I4-Pb2-I4*#*2 | 171.01(8) | I1*#*5-Pb1-I4 | 96.06(6) |
| I4*#*2-Pb2-I6 | 89.07(5) | I1*#*5-Pb1-I3*#*4 | 177.53(6) |
| I4-Pb2-I6 | 89.07(5) | I1-Pb1-I3*#*4 | 88.31(5) |
| I6*#*3-Pb2-I5 | 177.06(7) | I1*#*5-Pb1-I1 | 89.89(2) |
| I6-Pb2-I5 | 84.73(6) | I2-Pb1-I4 | 169.49(6) |
| I6*#*3-Pb2-I5*#*1 | 94.56(7) | I2-Pb1-I3*#*4 | 90.60(8) |
| I6*#*3-Pb2-I4 | 94.43(4) | I2-Pb1-I3 | 89.72(8) |
| I6*#*3-Pb2-I4*#*2 | 94.43(4) | I2-Pb1-I1*#*5 | 91.15(8) |
| I6*#*3-Pb2-I6 | 92.33(3) | I2-Pb1-I1 | 91.70(8) |

Symmetry transformations used to generate equivalent atoms:

#1 1-X, 1-Y, 1/2+Z; #2 1-X, +Y, +Z; #3 -X, 2-Y, 1/2+Z; #4 +X, 1-Y, -1/2+Z; #5 +X, 2-Y, 1/2+Z

**Table S4.** N-H∙∙∙I Hydrogen bonds of crystal **1** at FEP (260 K).

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| D-H···A | d(D-H) | d(H···A) | < DHA | d(D···A) |
| N1-H1C∙∙∙I4 | 0.890 | 2.779 | 163.79 | 3.642 |
| N1-H1D∙∙∙I4#1 | 0.890 | 2.865 | 156.97 | 3.700 |
| N1-H1E∙∙∙I6#2 | 0.890 | 3.061 | 144.60 | 3.822 |
| N2-H2B∙∙∙I1 | 0.890 | 2.789 | 131.14 | 3.440 |
| N2-H2C∙∙∙I3#3 | 0.890 | 2.755 | 166.91 | 3.627 |

Symmetry transformations used to generate equivalent atoms:

*#*1 X, -Y+1, Z+1/2; *#*2 -X+1, -Y+1, Z+1/2, *#*3 X, -Y+1, Z-1/2

**Table S5.** Bandgap of **1** and some other lead-halide perovskite ferroelectric.

|  |  |  |
| --- | --- | --- |
| Compound | Bandgap | Refs |
| **1** | ~**1.80 eV** | **This work** |
| (C4H9NH3)2(C2H5NH3)2Pb3I10 | ~1.90 eV | [1] |
| (4,4-difluorocyclohexylammnium)2PbI4 | ~2.38 eV | [2] |
| [(CH3)3NCH2I]PbI3 | ~2.82 eV | [3] |
| [4-(aminomethyl)-piperidinium]2PbI4 | ~2.38 eV | [4] |
| R-1-(4-chlorophenyl)-ethylammonium]2PbI4 | ~2.34 eV | [5] |
| S-1-(4-chlorophenyl)-ethylammonium]2PbI4 | ~2.36 eV |
| (C4H9NH3)2(CH3NH3)2Pb3Br10 | ~2.42 eV | [6] |
| (C4H9NH3)2(CH3NH3)Pb2Br7 | ~2.55 eV | [7] |
| (C4H9NH3)2(NH2CHNH2)Pb2Br7 | ~2.35 eV | [8] |
| (C4H9NH3)2CsPb2Br7 | ~2.68 eV | [9] |
| (ethylammonium)4Pb3Br10 | ~2.70 eV | [10] |
| (cyclohexylammonium)2PbBr4 | ~2.95 eV | [11] |
| (benzylammonium)2PbCl4 | ~3.65 eV | [12] |
| (C4H9NH3)2PbCl4 | ~3.49 eV | [13] |

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