Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting information

A Polar Two-Dimensional Lead-Free Hybrid Perovskite for Self-Powered Polarization-Sensitive Photodetection

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Experimental Section

General characterizations

Powder X-ray diffraction (PXRD) patterns were obtained on a Rigaku SmartLab X-ray diffraction instrument. Ultraviolet-vis (UV-vis) absorption spectra were measured with Shimadzu UV-2600 equipped with ISR-2600Plus integrating sphere. The single crystal growth was carried out using a home-made hydrothermal growth system.

Single-crystal X-ray Diffraction.

Crystallographic data of the compound were collected on a Rigaku Oxford Diffraction Supernova Dual Source, Cu at Zero equipped with an AtlasS2 CCD using Mo Kα radiation and an XtaLAB Synergy R, DW system, HyPix diffractometer. Rigaku CrysAlisPro software was used to collect data, refine cell, and to reduce data. SHELXL-2018 with the OLEX2 interface was used to solve the structures by direct methods. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were generated geometrically.

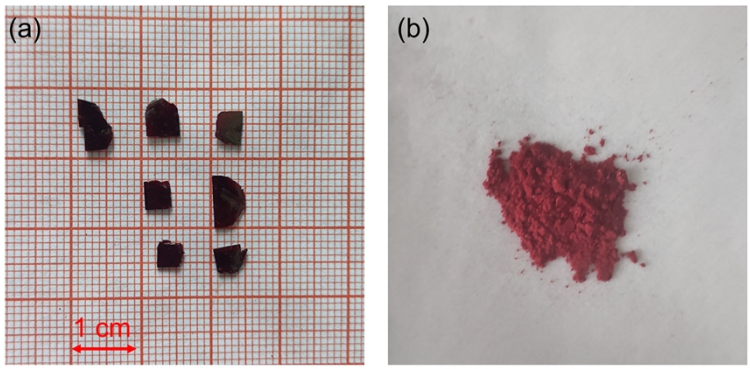

Figure S1. (a) Single crystal and (b) powder sample of $(4BrPEA)_3BiI_6$.

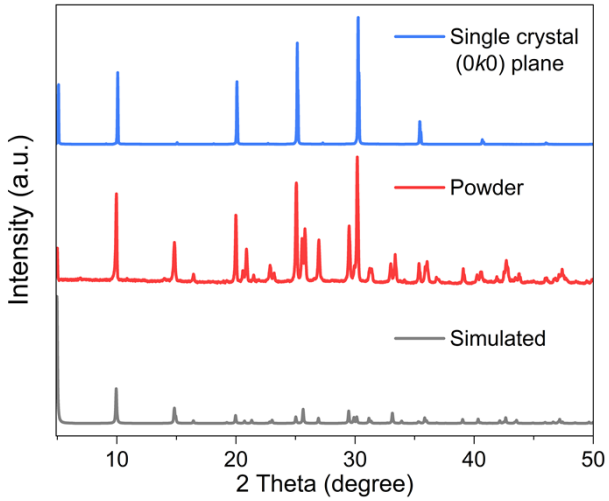

Figure S2. PXRD patterns of $(4BrPEA)_3BiI_6$ single crystal and powder sample.

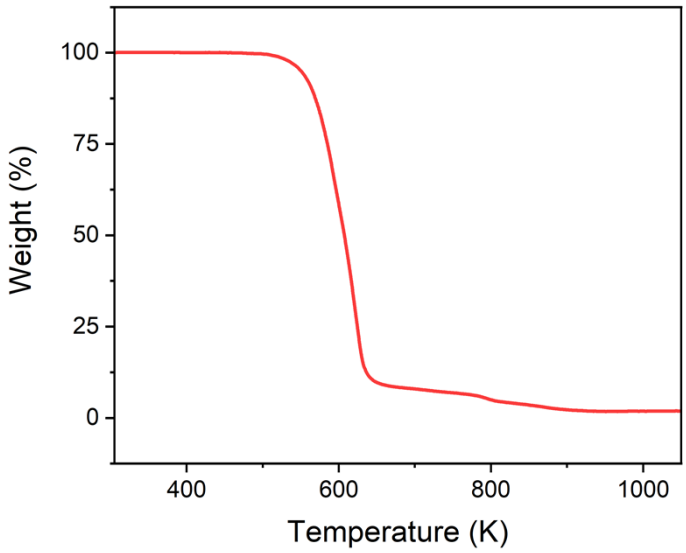

Figure S3. Thermogravimetric analysis of $(4BrPEA)_3BiI_6$.

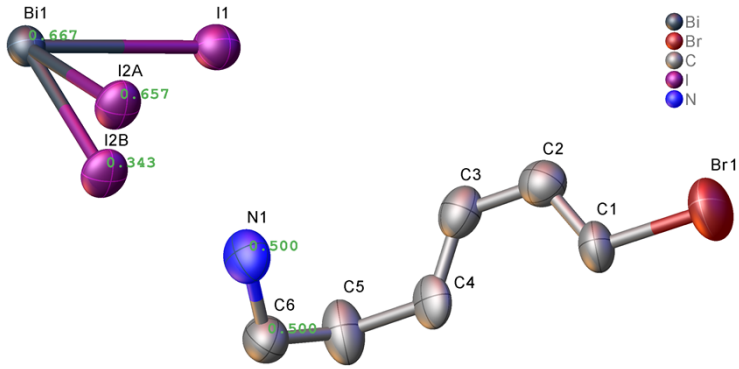

Figure S4. The asymmetric unit of $(4BrPEA)_3BiI_6$. The black label represents the atomic number while the green label represents the chemical occupancy.

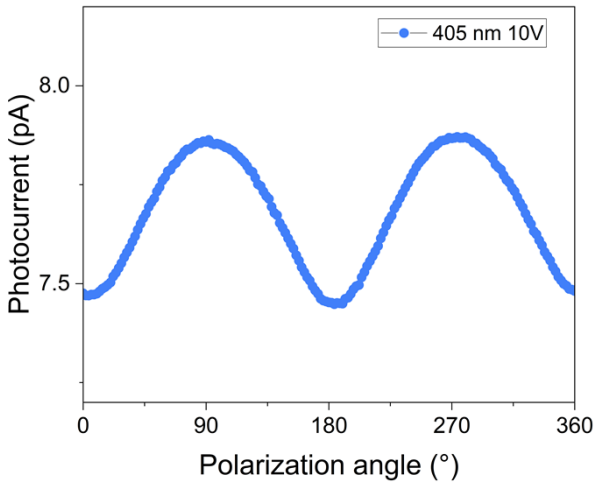

Figure S5. Polarization-dependent photocurrent measured at 10 V bias.

Table S1. Crystal data and structure refinement details for $(4BrPEA)_3BiI_6$.

Empirical formula	$C_8H_{11}NBrBi_{0.33}I_2$
Formula weight	524.63
Temperature / K	292(2)
Crystal system	Orthorhombic
Space group	*Fmm*2
a / Å	8.5646(5)
b / Å	35.477(5)
c / Å	8.5649(5)
α / °	90
β / °	90
γ / °	90
Volume / Å^3	2602.4(4)
Z	8
ρ_{calc} / cm^3	2.678
μ / mm^{-1}	12.357
F(000)	1878.0
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection / °	4.592 to 52.594
Index ranges	$-10 \leq h \leq 10$, $-44 \leq k \leq 44$, $-10 \leq l \leq 10$
Reflections collected	6692
Independent reflections	1418 [R_{int} = 0.0299, R_{sigma} = 0.0253]
Data/restraints/parameters	1418/3/86
Goodness-of-fit on F^2	1.081
Final *R* indexes [*I*>=2σ (*I*)]	R_1 = 0.0248, wR_2 = 0.0576
Final *R* indexes [all data]	R_1 = 0.0281, wR_2 = 0.0584
Largest diff. peak/hole / e Å^{-3}	1.84/-1.49
Flack parameter	-0.012(12)

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^bwR_2(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

Table S2. Bond lengths for $(4BrPEA)_3BiI_6$.

Atom−Atom	Lengths / Å	Atom−Atom	lengths / Å
Bi1−I1	3.1640 (8)	C3−H3	0.9300
Bi1−I1^{i}	3.1639 (8)	C3−C4	1.377 (12)
Bi1−I2A^{ii}	3.0404 (15)	C4−C5	1.491 (17)
Bi1−I2A^{iii}	3.0404 (15)	C5−H5A	0.9700
Bi1−I2A^{i}	3.0680 (16)	C5−H5A^{iv}	0.9700
Bi1−I2A	3.0680 (16)	C5−H5B	0.9700
Bi1−I2B^{i}	3.109 (2)	C5−H5B^{iv}	0.9700
Bi1−I2B^{iii}	3.106 (3)	C5−C6	1.494 (17)
Bi1−I2B^{ii}	3.106 (3)	N1−H1A	0.8900
Bi1−I2B	3.109 (2)	N1−H1B	0.8900
Br1−C1	1.892 (12)	N1−H1C	0.8900
C1−C2	1.373 (11)	N1−C6	1.47 (2)
C1−C2^{iv}	1.373 (11)	C6−H6A	0.9700
C2−H2	0.9300	C6−H6B	0.9700
C2−C3	1.383 (12)		

Symmetry codes: (i) −x+1, −y+1, z; (ii) x+1/2, y, z+1/2; (iii) −x+1/2, −y+1, z+1/2; (iv) −x, y, z; (v) x−1/2, y, z−1/2.

Table S3. Bond angles for $(4BrPEA)_3BiI_6$.

Atom−Atom−Atom	Angle / °	Atom−Atom−Atom	Angle / °
I1^{i}–Bi1−I1	175.99 (5)	C2^{iv}–C1−C2	122.1 (11)
I2A−Bi1−I1	91.59 (2)	C1−C2−H2	120.8
I2A−Bi1−I1^{i}	91.59 (2)	C1−C2−C3	118.4 (9)
I2A^{iii}–Bi1−I1^{i}	88.782 (16)	C3−C2−H2	120.8
I2A^{i}–Bi1−I1^{i}	91.59 (2)	C2−C3−H3	119.6
I2A^{iii}–Bi1−I1	88.782 (16)	C4−C3−C2	120.9 (9)
I2A^{ii}–Bi1−I1	88.782 (16)	C4−C3−H3	119.6
I2A^{ii}–Bi1−I1^{i}	88.782 (16)	C3^{iv}–C4−C3	119.3 (12)
I2A^{i}–Bi1−I1	91.59 (2)	C3^{iv}–C4−C5	120.3 (6)
I2A^{ii}–Bi1−I2A^{i}	89.934 (9)	C3−C4−C5	120.3 (6)
I2A^{ii}–Bi1−I2A^{iii}	105.06 (8)	C4−C5−H5A^{iv}	108.5 (4)
I2A^{i}–Bi1−I2A	75.07 (8)	C4−C5−H5A	108.5
I2A^{iii}–Bi1−I2A^{i}	165.01 (8)	C4−C5−H5B	108.5
I2A^{ii}–Bi1−I2A	165.01 (8)	C4−C5−H5B^{iv}	108.5 (2)
I2A^{iii}–Bi1−I2A	89.934 (9)	C4−C5−C6	114.9 (11)
I2A^{i}–Bi1−I2B^{ii}	110.47 (5)	H5A−C5−H5A^{iv}	91.6
I2A^{ii}–Bi1−I2B^{iii}	84.52 (10)	H5A−C5−H5B	107.5
I2A^{ii}–Bi1−I2B^{i}	69.48 (5)	H5A^{iv}–C5−H5B^{iv}	107.5
I2A−Bi1−I2B^{i}	95.53 (10)	H5A−C5−H5B^{iv}	17.4
I2A−Bi1−I2B^{iii}	110.47 (5)	H5B−C5−H5A^{iv}	17.4
I2A−Bi1−I2B^{ii}	174.45 (10)	H5B−C5−H5B^{iv}	122.3
I2A^{iii}–Bi1−I2B^{ii}	84.52 (10)	C6−C5−H5A^{iv}	121.7 (14)
I2A^{i}–Bi1−I2B^{i}	20.46 (5)	C6−C5−H5A	108.5
I2A^{iii}–Bi1−I2B^{iii}	20.54 (5)	C6−C5−H5B	108.5

I2A^{ii}–Bi1–I2B^{ii}	20.54 (5)	C6–C5–H5B^{iv}	93.7 (13)
I2A^{i}–Bi1–I2B^{iii}	174.45 (10)	H1A–N1–H1B	109.5
I2A^{iii}–Bi1–I2B^{i}	174.53 (10)	H1A–N1–H1C	109.5
I2B^{ii}–Bi1–I1	88.30 (2)	H1B–N1–H1C	109.5
I2B–Bi1–I1	91.061 (14)	C6–N1–H1A	109.5
I2B^{iii}–Bi1–I1	88.30 (2)	C6–N1–H1B	109.5
I2B^{i}–Bi1–I1	91.061 (14)	C6–N1–H1C	109.5
I2B^{ii}–Bi1–I2B	154.00 (14)	C5–C6–H6A	108.4
I2B^{iii}–Bi1–I2B	90.02 (2)	C5–C6–H6B	108.4
Bi1^{v}–I2A–Bi1	165.01 (8)	N1–C6–C5	115.4 (19)
Bi1^{v}–I2B–Bi1	154.00 (13)	N1–C6–H6A	108.4
C2–C1–Br1	119.0 (6)	N1–C6–H6B	108.4
C2^{iv}–C1–Br1	119.0 (6)	H6A–C6–H6B	107.5

Symmetry codes: (i) −x+1, −y+1, z; (ii) x+1/2, y, z+1/2; (iii) −x+1/2, −y+1, z+1/2; (iv) −x, y, z; (v) x−1/2, y, z−1/2.

Table S4. N–H···I hydrogen bond lengths extracted from the crystal structure of $(4FPEA)_3BiI_6$ and $(4BrPEA)_3BiI_6$.

$(4FPEA)_3BiI_6$	$(4BrPEA)_3BiI_6$
2.738 Å	2.753 Å
2.77 Å	2.827 Å
2.807 Å	3.065 Å
2.842 Å	3.092 Å
2.904 Å	3.162 Å
2.928 Å	
2.945 Å	
2.992 Å	
2.993 Å	
3.087 Å	