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A polar two-dimensional lead-free hybrid perovskite for self-powered polarization-sensitive photodetection†

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Two-dimensional (2D) lead hybrid perovskites have attracted great attention due to their excellent stability and unique physical and chemical properties. Nevertheless, the toxicity of lead remains an urgent issue. Lead-free homovalent substituents (Sn^{2+} and Ge^{2+}) suffer from poor oxygen-sensitive stability, posing a serious challenge to their device applications. Compared to homovalent substituents, heterovalent substituted perovskites based on the VA group elements, especially bismuth, exhibit excellent stability, making them more competitive. However, 2D Bi-based perovskites with the composition $2\text{D A}_2\text{BiX}_4$ (A = organic cation; $\text{X} = \text{Cl}^-$, Br^- or I^-) cannot be formed considering the charge balance. Here, by reducing the occupancy rate of Bi^{3+} ions, we successfully obtained the first polar 2D Bi-based perovskite $(4\text{BrPEA})_3\text{BiI}_6$ ($4\text{BrPEA} = 4\text{-bromophenethylammonium}$) with an A_2PbX_4 -like layered structure. $(4\text{BrPEA})_3\text{BiI}_6$ exhibits a narrow bandgap (2.00 eV) and excellent photoelectric response performance. Specifically, a single crystal device based on $(4\text{BrPEA})_3\text{BiI}_6$ has been explored for self-powered polarization-sensitive photodetection with a large photocurrent anisotropic ratio ω of 2.16. This work demonstrates the great potential of heterovalent substituted 2D lead-free perovskites and opens up a new way to expand the synthesis of environmentally friendly and high-performance self-powered polar optoelectronic semiconductor materials.

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Introduction

Lead-based hybrid perovskites, represented by $\text{CH}_3\text{NH}_3\text{PbI}_3$, have attracted significant attention in various fields, including photovoltaics,¹ light-emitting diodes,² photoluminescence,³ ferroelectricity,^{4–6} and photodetection,^{7,8} on account of their excellent physical and chemical properties.^{9–11} However, their instability and toxicity greatly hinder further commercial development.^{12–14} Usually, the stability issues can be effectively addressed by employing dimensional reduction technology to construct 2D hybrid perovskites.¹⁵ 2D perovskites possess excellent chemical stability compared to typical 3D $\text{CH}_3\text{NH}_3\text{PbI}_3$ due to their quantum well structure of hydrophobic organic cations and inorganic perovskite layers. The alternant quantum well structure also introduces natural structural anisotropy for 2D perovskites, which facilitates the realiz-

ation of polarization-sensitive detection.^{16–19} In particular, polar 2D perovskites exhibit the bulk photovoltaic effect (BPVE), which can produce stable open-circuit voltage and short-circuit current under illumination, making them candidates for highly efficient self-powered polarization-sensitive photodetectors.¹⁷ Although considerable progress has been made in lead-based 2D perovskite self-powered polarization-sensitive photodetection, the toxicity of lead remains a pressing issue.

Lead-free is the development trend of green chemistry in perovskites. To obtain 2D lead-free hybrid perovskites, two strategies have been developed: homovalent substitution and heterovalent substitution. Although Group IVA homovalent substituent (Sn^{2+} and Ge^{2+}) perovskites have produced decent optical and electrical properties, their poorer oxygen-sensitive stability than lead-based perovskites poses a serious challenge to their device applications.¹² Compared to homovalent substitution, heterovalent substitution based on the VA group element bismuth is more competitive. Bi^{3+} has the same $6\text{S}^26\text{P}^0$ external electron configuration and a similar ionic radius to Pb^{2+} , and its stability and semiconductor properties have been widely demonstrated.¹⁴ However, due to the total charge δ of the composition A_2BiX_4 (A = organic cation; $\text{X} = \text{Cl}^-$, Br^- or I^-) greater than 0, the typical (100)-oriented 2D

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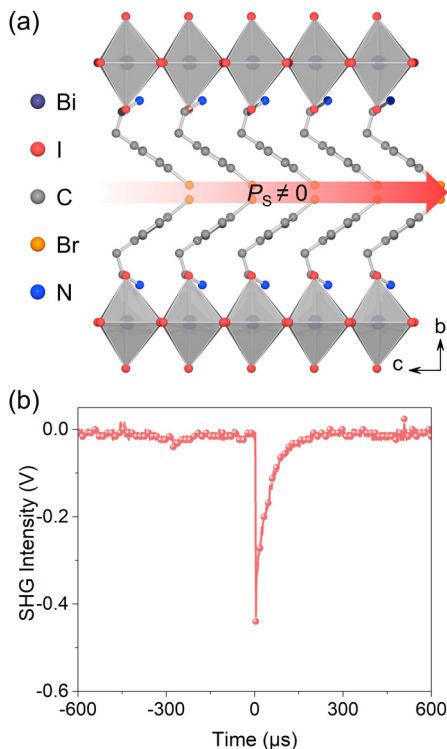


Fig. 1 (a) 2D polar structure of $(4\text{BrPEA})_3\text{BiI}_6$ viewed along the a -axis. (b) The second harmonic generation signals of $(4\text{BrPEA})_3\text{BiI}_6$.

cal polarization of $(4\text{BrPEA})_3\text{BiI}_6$ was analyzed. $(4\text{BrPEA})_3\text{BiI}_6$ and $(4\text{FPEA})_3\text{BiI}_6$ are composed of similar organic cations, with the only difference being the halogen species on the *para*-position of the benzene ring. In $(4\text{FPEA})_3\text{BiI}_6$, the 4FPEA cations exhibit an edge-to-face parallel arrangement with C–F $\cdots\pi$ interaction distances ranging from 3.713 to 3.830 Å (Fig. 2a and b). While in $(4\text{BrPEA})_3\text{BiI}_6$, the orientation of the 4BrPEA cations exhibits vertical arrangement to adapt to strong C–Br $\cdots\pi$ interactions (3.417–3.424 Å) (Fig. 2c and d). In $(4\text{BrPEA})_3\text{BiI}_6$ and $(4\text{FPEA})_3\text{BiI}_6$, the main interaction between the $[\text{BiI}_6]^{3-}$ layer and the organic amine cations is the N–H $\cdots\text{I}$ hydrogen bond, and the bond length range is roughly the same (Table S4, ESI †). Therefore, in $(4\text{BrPEA})_3\text{BiI}_6$, the strong C–Br $\cdots\pi$ interactions drive the orientation arrangement of cations within the organic layer, which leads to the separation of positive and negative charges along the c -axis and ultimately results in the polar structure.²⁸

Semiconductor and optoelectronic properties

2D lead-free hybrid perovskites based on bismuth are expected to exhibit semiconducting-related optoelectronic behavior comparable to those of lead-based compounds. To characterize the semiconducting properties of $(4\text{BrPEA})_3\text{BiI}_6$, ultraviolet-visible (UV-vis) absorption spectra were recorded. As shown in Fig. 3, $(4\text{BrPEA})_3\text{BiI}_6$ exhibits an absorption cutoff of around 670 nm and a bandgap of 2.00 eV derived from the Kubelka–Munk function. Compared with the reported 2D Pb-based hybrid perovskites, such as $(4\text{BrPEA})_2\text{PbI}_4$,²⁹ $(4\text{AMP})\text{PbI}_4$

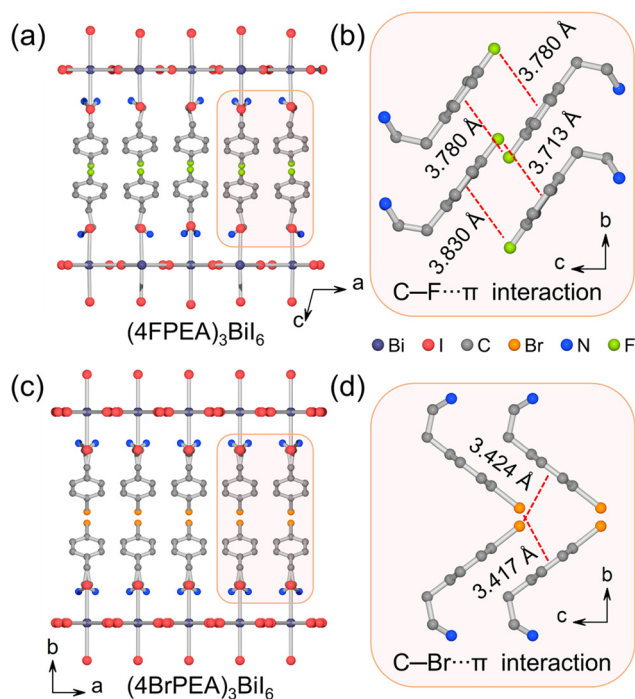


Fig. 2 (a) Crystal structure of $(4\text{FPEA})_3\text{BiI}_6$ viewed along the b -axis. (b) C–F $\cdots\pi$ interactions in $(4\text{FPEA})_3\text{BiI}_6$. (c) Crystal structure of $(4\text{BrPEA})_3\text{BiI}_6$ viewed along the c -axis. (d) C–Br $\cdots\pi$ interactions in $(4\text{BrPEA})_3\text{BiI}_6$.

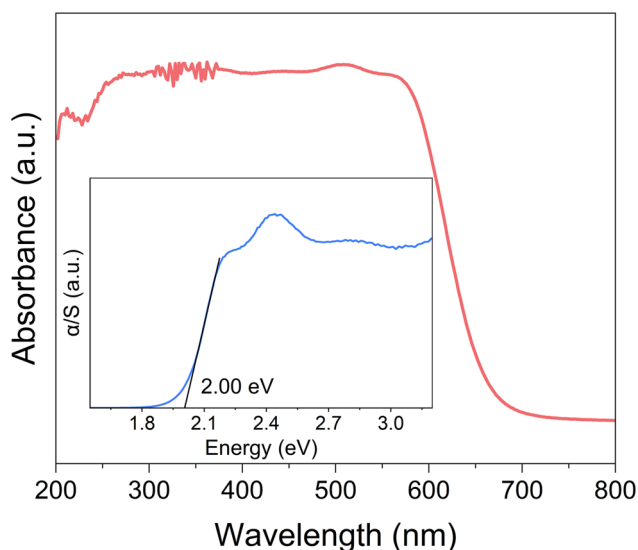


Fig. 3 UV-vis absorption spectra of $(4\text{BrPEA})_3\text{BiI}_6$. Insert: the optical bandgap.

$(4\text{AMP}) = 4\text{-}(aminomethyl)piperidinium$),³⁰ and $(\text{BA})_2\text{PbI}_4$ ($\text{BA} = n\text{-butylammonium}$),³¹ 2D lead-free Bi-based perovskites exhibit a smaller bandgap.

Band gap analysis shows that $(4\text{BrPEA})_3\text{BiI}_6$ has the potential to be an optoelectronic material.^{14,32–34} Therefore, we further investigated its photoresponse behavior upon 405 nm LED light irradiation under a 10 V bias. Fig. 4a shows the

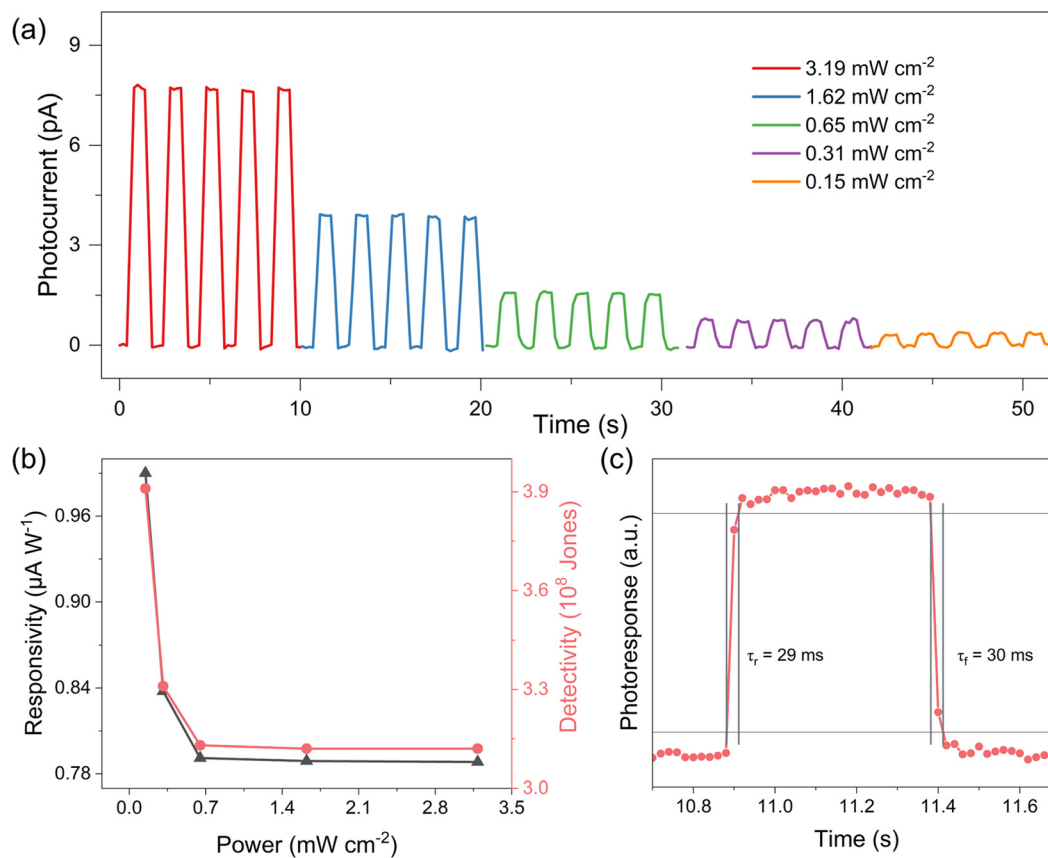


Fig. 4 (a) The $I-t$ curve of the $(4\text{BrPEA})_3\text{BiI}_6$ single crystal device at 405 nm under 10 V bias. (b) The calculated R and D^* related to the optical density. (c) The rise and decay time.

time-dependent photocurrent ($I-t$) of the $(4\text{BrPEA})_3\text{BiI}_6$ single crystal device at different optical power densities. The photocurrent reaches 7.6 pA under an optical power P of 3.19 mW cm^{-2} , and the corresponding $I_{\text{ph}}/I_{\text{dark}}$ ratio is 10^2 . Even under an optical power of 0.15 mW cm^{-2} , $(4\text{BrPEA})_3\text{BiI}_6$ still exhibits significant photocurrent. The calculated responsivity R and specific detectivity D^* related to optical density are negatively correlated with radiation intensity (Fig. 4b). Under 0.15 mW cm^{-2} irradiation, the calculated D^* and R values are 3.91×10^8 Jones and $0.99\text{ }\mu\text{A W}^{-1}$, respectively, which were comparable to some reported lead-free perovskites (Table 1).^{35,36} In addition, the $(4\text{BrPEA})_3\text{BiI}_6$ device shows a fast rise/decay time of 29/

30 ms at 405 nm (Fig. 4c), which is superior to some reported lead-free perovskite photodetectors (Table 1).

Self-powered polarization-sensitive photodetection

Polar hybrid perovskites have also shown great potential in self-powered photodetection based on the BPVE.^{40,41} The inherent polar structure drives us to further explore the BPVE behavior based on single crystal devices. Fig. 5a shows the current-voltage ($I-V$) photocurrent curves measured along the c -axis and a -axis ($P = 2.94\text{ mW cm}^{-2}$). The $I-V$ curve on the c -axis shows obvious short-circuit current ($I_{\text{sc}} = -1.3\text{ pA}$) and open circuit voltage ($V_{\text{oc}} = 1.45\text{ V}$), while the current curve on the a -axis almost passes through the origin. The $I-t$ curve measured along the c -axis under 0 V shows that the photocurrent increases sharply under illumination, and the $I_{\text{ph}}/I_{\text{dark}}$ ratio is about 50 (Fig. 5b) ($P = 4.04\text{ mW cm}^{-2}$). The value of V_{oc} is larger than many Pb-based hybrid perovskites, such as $(\text{BPA})_2\text{PbBr}_4$ ($V_{\text{oc}} = 0.85\text{ V}$) and $(\text{BA})_2(\text{FA})\text{Pb}_2\text{I}_7$ ($V_{\text{oc}} = 0.3\text{ V}$).^{16,17}

The 2D $(4\text{BrPEA})_3\text{BiI}_6$ perovskite structure has inherent structural anisotropy and can be used for polarization-sensitive photosensitive detection. Therefore, based on excellent BPVE activity, we further investigated the self-powered polarization-sensitive photoresponse of $(4\text{BrPEA})_3\text{BiI}_6$. A 405 nm LED is used as the light source, ordinary light is converted into line-

Table 1 Summary of the reported lead-free perovskite photodetectors

Compound	D^* (Jones)	R (A W^{-1})	Rise/decay time (ms)	Ref.
$\text{Cs}_3\text{Bi}_2\text{I}_9$	1.2×10^{10}	$0.59\text{ }\mu$	88.66/109.3	35
$\text{MA}_3\text{Bi}_2\text{I}_9$	9.23×10^{11}	1.9 m	26.81/41.98	37
HDABiI_5	5.3×10^8	6.8 m	52/35	23
$\text{Cs}_3\text{Bi}_2\text{I}_6\text{Br}_3$	4.60×10^{11}	15 m	40.7/27.1	38
$\text{AG}_3\text{Bi}_2\text{I}_9$	8.8×10^{10}	14.8 m	0.152/0.187	39
CsSnI_3	3.85×10^5	54 m	83.8/243.4	36
$(4\text{BrPEA})_3\text{BiI}_6$	3.91×10^8	$0.99\text{ }\mu$	29/30	This work

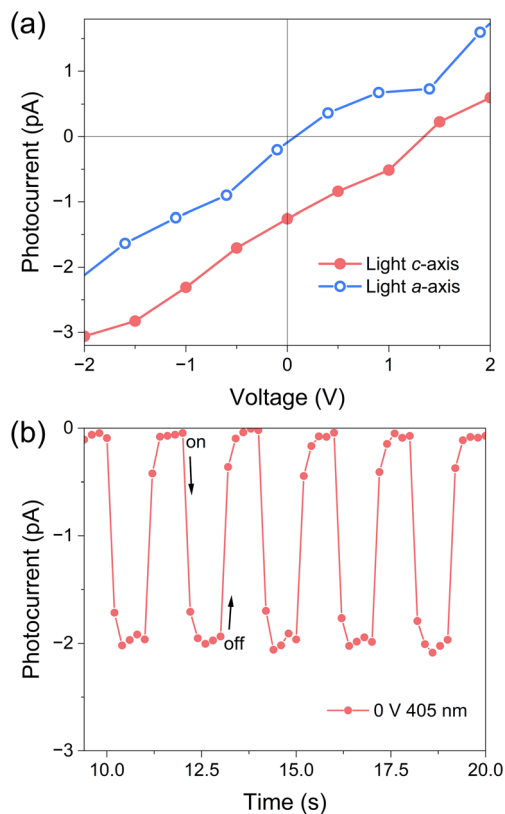


Fig. 5 (a) I - V photocurrent curves measured along the c -axis and a -axis. (b) The I - t curve measured along the c -axis under 0 V bias.

arly polarized light through a polarizer, and the angle of LPL is controlled through a $1/2$ wave plate (Fig. 6a) inside the bc -plane. The initial polarization angle (defined as 0°) of LPL is parallel to the b -axis. As shown in Fig. 6a, when the polarization angle of LPL is parallel to the b -axis, the photocurrent reaches its minimum value (I_{valley}). The value of photocurrent varies with the polarization angle, and when the LPL angle is parallel to the c direction, the maximum photocurrent value (I_{peak}) can be obtained. The polar coordination plot of the photocurrent and the polarization angle shows a clear double-lobed shape, and the calculated photocurrent anisotropy ratio ω ($I_{\text{peak}}/I_{\text{valley}}$) is 2.16. The I - t curve under pulsed light shows a clear polarization angle dependence, which proves the reproducibility and stability of the detector. Fig. 6e summarizes the performance of the reported perovskite and lead-based perovskite polarization-sensitive single crystal detectors.^{17,23,42-47} The ω value of $(4\text{BrPEA})_3\text{BiI}_6$ exceeds that of many lead-free perovskites and is even comparable to Pb-based perovskites.

The polarization-dependent photocurrent measured at 10 V bias is shown in Fig. S5,[†] and the photocurrent displays a small ω value of 1.05. This result demonstrates the enormous potential of BPVE-enhanced self-powered LPL detectors. The large ω value of $(4\text{BrPEA})_3\text{BiI}_6$ at 0 V can be attributed to the angle dependence of the BPVE, which can be expressed as

$$J_z = I\beta_{31} \sin^2(\theta) + I\beta_{33} \cos^2(\theta)$$

where I is the light intensity, θ is the angle between the LPL polarization plane and the z axis (polar axis), and β_{31} and β_{33}

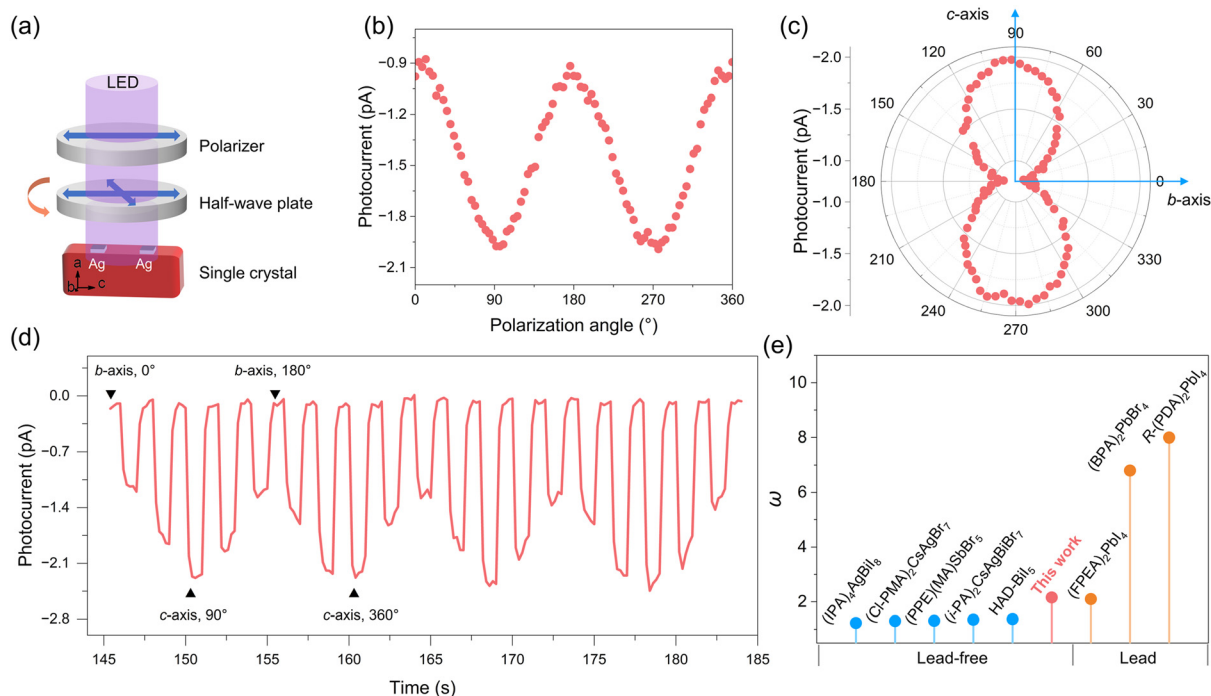


Fig. 6 (a) Schematic diagram of the polarization-sensitive photodetection device. (b) Angle-dependent photocurrent measured under 0 V bias. (c) Polar plots of the angle-dependent photocurrents measured under 0 V bias. (d) Angle-dependent I - t measurements at 405 nm pulsed light. (e) Comparison of the ω values for 2D perovskite photodetectors.

are the bulk photovoltaic coefficients.^{48–51} Weak coupling occurs when the direction of LPL is perpendicular to the polar axis (*c*-axis), resulting in a low I_{valley} . While strong coupling occurs when the LPL is parallel to the polar axis, which promotes carrier separation, resulting in a large I_{peak} and ultimately highly sensitive polarization-sensitive detection.

Conclusions

In summary, by reasonably reducing the occupancy rate of Bi^{3+} on the 2D layer, we successfully obtained the first 2D polar Bi-based perovskite $(4\text{BrPEA})_3\text{BiI}_6$ with an A_2PbX_4 -like structure. $(4\text{BrPEA})_3\text{BiI}_6$ single crystal devices exhibit photocurrent anisotropy ω values (2.16) comparable to Pb-based perovskite devices. This work provides an effective approach for the targeted design of green, lead-free, high-performance, 2D polarization-sensitive perovskites. At the same time, the narrow bandgap, low toxicity, high chemical stability, and excellent self-powered photodetection performance of $(4\text{BrPEA})_3\text{BiI}_6$ also show its great application potential in solar cells and other photovoltaic conversion devices.

Experimental

Chemicals

Bismuth trioxide (Bi_2O_3 , 99.0%), 4-bromophenethylamine (4BrPEA, 98%), hypophosphorous acid (H_3PO_2 , AR, 50 wt% in H_2O), and hydroiodic acid (HI, AR, 55.0–58%, contains $\leq 1.5\%$ H_3PO_2 as a stabilizer) were all commercially obtained without further purification.

Synthesis of $(4\text{BrPEA})_3\text{BiI}_6$

Bi_2O_3 (0.233 g, 0.5 mmol) was dissolved in 57% hydroiodic (HI) solution (100 mL) and then H_3PO_2 (5 mL) and 4BrPEA (0.600 g, 3 mmol) were slowly added dropwise. The mixture was stirred continuously at 373 K for 30 minutes until the precipitate was completely dissolved to give a clear red solution. Slowly cooling the red solution at a rate of 5 K day^{-1} from 373 K to 298 K resulted in the formation of dark red plate-shaped crystals of $(4\text{BrPEA})_3\text{BiI}_6$.

Device fabrication

The surfaces of the single crystal were coated with silver paste along the different axes. The effective area of the crystal device was determined to be $1 \times 0.3 \text{ mm}^2$ by the Phenix MC-D310U high-definition digital camera.

Photocurrent measurement

The photocurrent was measured using a PDA FS380 (Primarius) source meter. The 405 nm LED was obtained from Thorlabs. The polarizer (Glan–Taylor prism) converted the LED laser beam into polarized light, and the polarization angle of the polarized light was then adjusted by a half-wave plate. The state of the polarization state of linearly polarized

light was calibrated by a polarimeter system (PAX1000). The light intensity was measured using a digital console with a photodiode sensor (PM120VA, Thorlabs).

Author contributions

C.-D. L. performed most of the experiments and wrote the original manuscript. C.-C. F. and B.-D. L. participated in the writing and revision of the manuscript. W. Z. was responsible for funding acquisition, supervision, writing review, and editing. All authors discussed the results and commented on the manuscript.

Conflicts of interest

There are no conflicts to declare.

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