

Support Information

Experimental Section

Synthesis and crystal growth: All reagents and solved used in the synthesis are commercially available. $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ (3.79 g, 10 mmol) was dissolved in 40% w/w aqueous HBr solution (30.0 mL) by heating to boiling under constant magnetic stirring to give a yellowish solution. Subsequent addition of formamidiniumacetate (0.512 g, 6.67 mmol) to the hot solution formed red precipitation, which dissolved under stirring to afford a yellow solution. Moreover, $\text{n-CH}_3(\text{CH}_2)_3\text{NH}_2$ (0.49 g, 6.67 mmol) was added to the above solution to afford a yellow precipitate, which was subsequently dissolved under heating the solution to boiling. As the solution was subjected to a controlled cooling rate of 0.5°C/h to 65°C , the small crystallite formed on the solution surface. When the temperature was further lowered to 55°C , the crystallite grew large enough to begin to slowly sink to the bottom of the container. As we allowed the process to continue until the temperature dropped to 30°C , a bigger single crystal was harvested. The powder X-ray diffraction further verified the purity of 1 (Figure S1). Powder X-ray diffractometry (PXRD) data were recorded on a Mini Flex II Powder X-ray diffractometer.

Ferroelectric measurements: The temperature-dependent P - E hysteresis loops and I - E curves were measured on a ferroelectric analyzer (Radiant Precision Premier II) using the double-wave method. To avoid electric discharge at high electric field, single crystal of 1 was immersed in silicone oil to measure the P - E hysteresis loops. The temperature was carefully controlled by an oil bath. Two pairs of electrodes were formed orthogonally with each other on a single crystal of 1 with carbon paste.

Optical measurements: The UV absorptions in solid state were measured at room temperature on a PE Lambda 900 UV-Visible spectrophotometer. The fluorescence measurements were performed on an Edinburgh Analytical instrument FLS920. The conoscopic interference pattern was observed using a Nikon Eclipse LV100POL polarizing microscope. The temperature during measurements was controlled at 290 K using a Linkam TS1500 heating stage.

Photoelectric measurements: Photoelectric measurements were performed with a planar electrode configurations. Two symmetric Au electrodes with a defined gap of $200\ \mu\text{m}$ were sputtered on the flat side of a well-polished single crystal. The electrode materials were proven not to have any obvious influence on the photoelectric properties. Before the photoelectric measurements, the sample was poled by a nonpolar electrical plus in field strength range of -20 - $30\ \text{KV/cm}$. The current vs voltage (I - V) and photocurrent vs time (I - t) with light on or off (measured at zero bias) were measured using a high precision electrometer (Keithley6517B). A THORLABS 405 nm pigtailed laser diode (LP405-MF300, $200\ \text{mW/cm}^2$) was used for visible light illumination. The incident light intensity was measured by light power meter. The transient photoresponse time was measured using a 1 GHz bandwidth oscilloscope (Tektronix MDO3104) under a nanosecond 355 nm laser (pulse width $\sim 2\ \text{ns}$) at zero bias. The temperature during measurements was controlled at 290 K using a Linkam TS1500 heating stage.

Respond time was recorded by the high-speed Tektronix MDO3014 Oscilloscope. Conductivity was tested in the heating mode with range from 300-400 K by using a direct-current two-terminal method. The UV absorptions in solid state were measured at room temperature on a PE Lambda 900 UV-Visible spectrophotometer. The fluorescence measurements were performed on an Edinburgh Analytical instrument FLS920. The responsivity (R) of and the corresponding detectivity (D^*) of the device are calculated from the following equations:

$$R = (I_{\text{on}} - I_{\text{off}}) / P_{\text{in}}$$

$$D^* = R / (2qI_{\text{off}}/S)^{1/2}$$

where I_{on} is the photocurrent, I_{off} is the dark current, P_{in} is the incident light power, S is the effective area of light, and q is the electron charge.

Figures

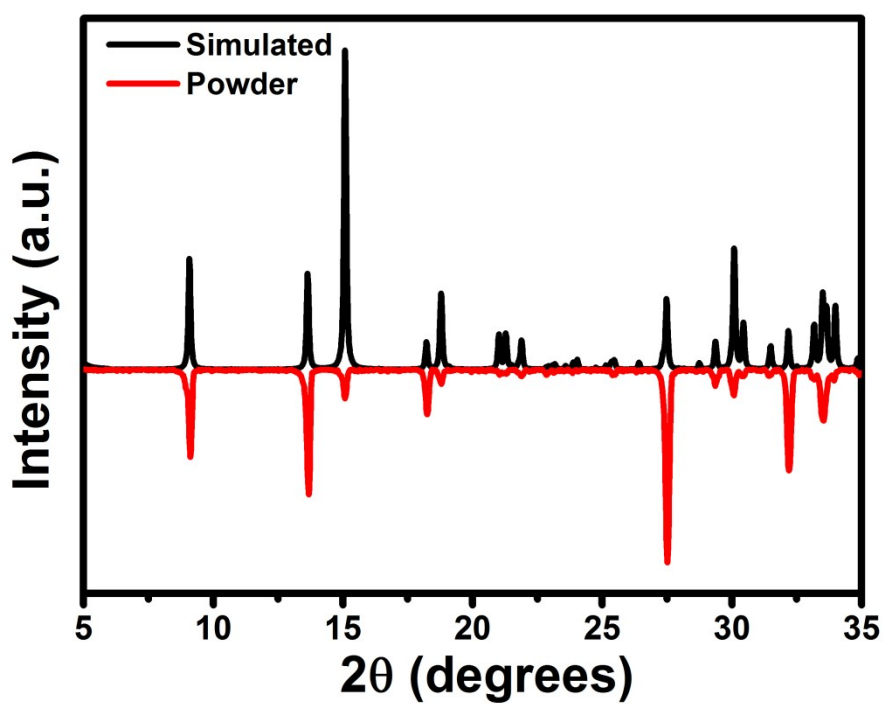


Figure S1. Experimental and simulated PXRD patterns for **1**.

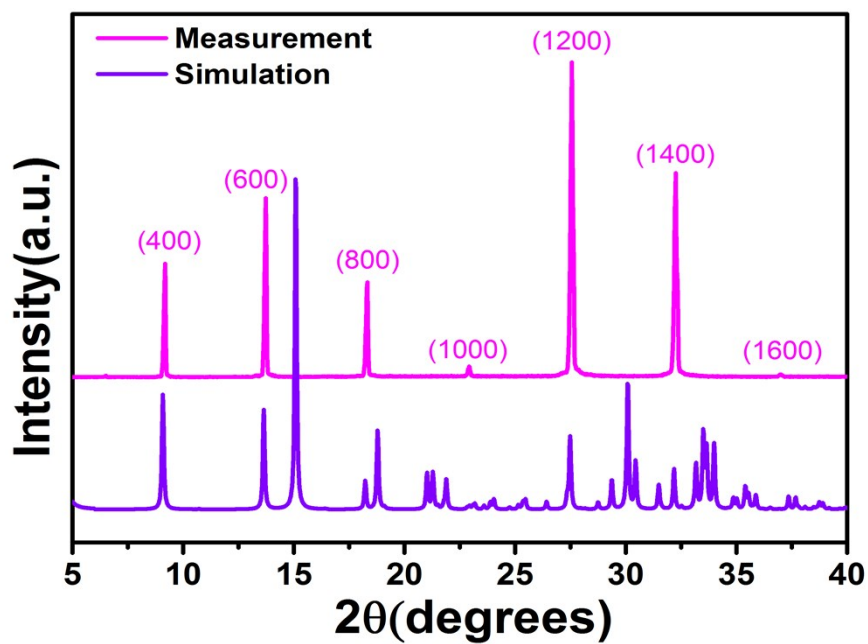


Figure S2. XRD patterns of the crystallographic facets of **1** showing high crystalline quality. The purple and pink curves indicate simulated and experimental XRD patterns, respectively.

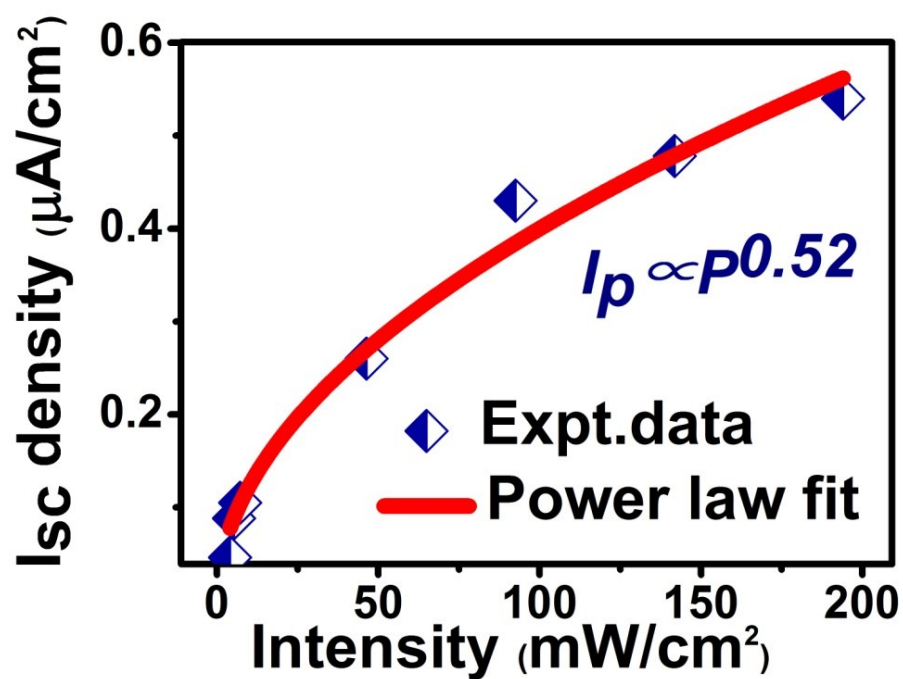


Figure S3. power law fitting of the relation between I_{sc} and light intensity.

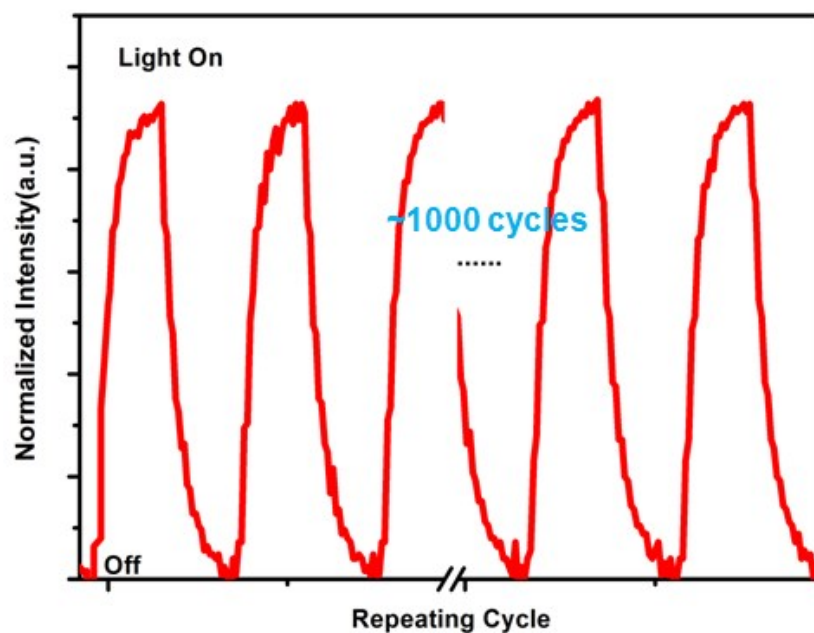


Figure S4. Repetitive switching cycles of photoresponse for 1, showing no obvious attenuation.

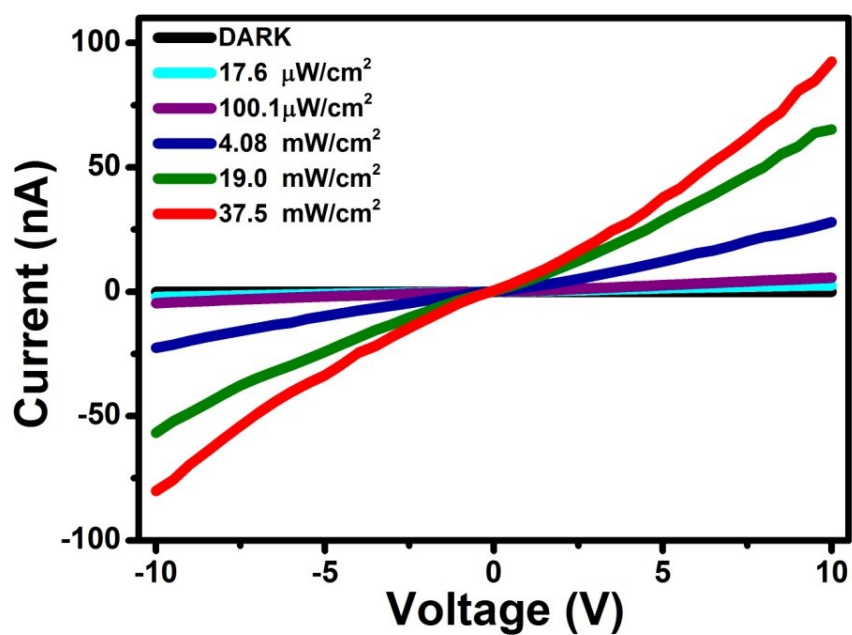


Figure S5. I–V curves of the **1** single crystal photodetector measured in dark and under illumination with different light intensities. **1** exhibits sizable on/off current ratios ($\sim 10^4$).

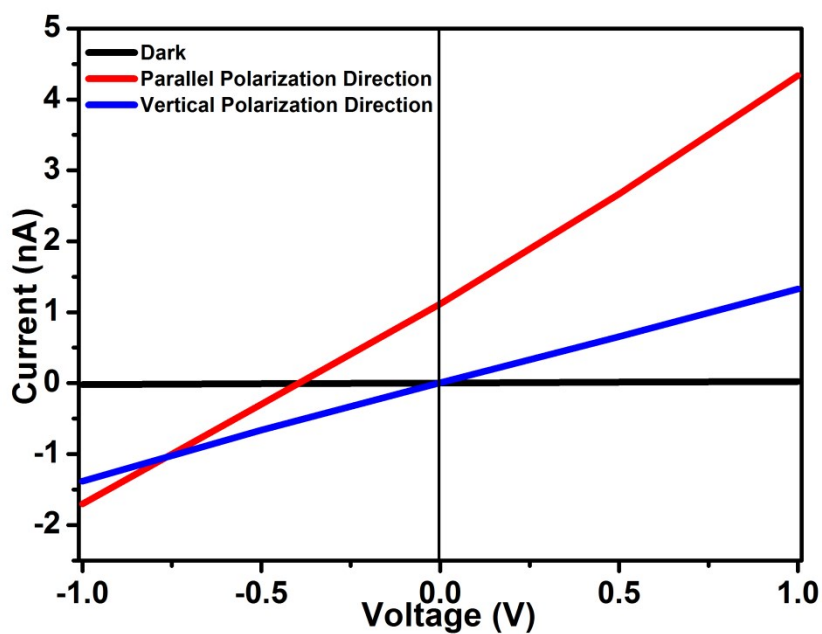


Figure S6. I–V traces measured along the polarization revealing a strong photovoltaic behavior. I–V traces collected perpendicular to its polarization direction.

Table S1 Basic parameters of semiconductors used in self-powered photodetectors.

Self-powered Photodetectors	V_{oc}	I_{sc}	Detection Limit	Responsivity	Detectivity (Jones)	Rise Time	Decay Time
WSe ₂ /MoS ₂ ¹	~0.27 V	~0.22 μ A	0.50 μ W cm ⁻¹	44 mA W ⁻¹	-	-	-
g-C ₃ N ₄ -PVDF ²	~2.7 V	-	0.10 mW cm ⁻¹	1.7 μ A W ⁻¹	-	6.2 s	12.9 s
BiFeO ₃ ³	~0.7 V	-	45 μ W cm ⁻¹	0.66 mA W ⁻¹	5.13×10 ⁷	-	-
BaTiO ₃ ⁴		~40 nA	3.5 mW cm ⁻¹	0.45 μ A W ⁻¹	4×10 ⁵	-	1.6 s
PZT ⁵	~2.85 V	~28.76 nA	15.7 mW cm ⁻¹	1 V W ⁻¹	-	2.2 s	22.6 s
Polyaniline/MgZnO ⁶	~2.5 V	~0.44 pA	130 μ W cm ⁻¹	160 μ A W ⁻¹	1.5×10 ¹¹	4.8 S	5.1 S
ZnO microwire/p-Si films ⁷	~2 V	~71 nA	0.58 mW cm ⁻¹	-	-	<0.3 S	<0.3 S
Present Work	~0.4 V	~2.2 nA	82 nW cm⁻¹	0.51mA W⁻¹	1.47×10¹²	220 μs	370 μs

References

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