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Methylated diammonium spacer modulated three-dimensional lead bromide perovskitoid hybrids with distinct photoconductivity anisotropy

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Experimental

Materials: N-Methyl-1,3-propanediamine (98%), HBr (48 wt % in water) and $Pb(Ac)_2{\cdot}3H_2O$ (99.998%) were purchased from Aladdin Industrial Inc.

Synthesis of 3D (MPDA)Pb_2Br_6 Perovskite: $Pb(Ac)_2{\cdot}3H_2O$ (758 mg, 2 mmol) was dissolved in 7 mL hydrobromic acid and kept stirring at room temperature. And then, N-methyl-1,3-propanediamine (204 μL, 1 mmol) was added to the above solution to generate a yellowish precipitate. Subsequently, the mixture was heated to 90^o in an oil bath and kept stirring for 3 hours until the precipitate was completely dissolved. After that, the precursor solution was transferred to an oven and kept at 90 °C for 6 h, finally cooling to room temperature at a rate of 2 °C/day to grow transparent crystals.

Fabrication of photodetectors: The photodetector device based on (MPDA)Pb_2Br_6 single crystal is fabricated by coating silver electrodes on the (100), (010) and (001) crystal plane of single crystal. The channel area between the electrodes is controlled between 0.05 and 0.2mm^2. The crystal face is determined by comparing the crystal shape simulated by the Materials Studio software with the actual crystal shape.

Characterization: The crystal structure was analyzed by Mo Ka radiation diffractometer (Bruker APEX-II CCD). Kα ray diffraction (XRD) patterns were collected using a powder Kα ray diffractometer (D8 propulsion, Bruker). The microscopic morphology of the crystals was acquired with a field emission SEM (Sigma500). The optical absorption spectrum was measured on a UV-VIS-NIR spectrophotometer (UV-3600 Plus, Nishito). PL spectroscopy at different temperatures were conducted by a Raman system (FST2 Ahdx DZ, Zolix) with temperature control system. The dielectric constant was tested at room temperature by employing TH 2832 LCR. The electrical and optoelectrical performance was performed with the Keithley 2400 digital source meter. A 150 W low-pressure UV-enhanced xenon lamp was used as the light source and monochromatic light was obtained using a grating spectrometer. The optical power density was calibrated using a standard Si photodetector.

First-Principles Calculations. All calculations were carried out by the Vienna Ab initio Simulation Package (VASP) based on the Density functional theory (DFT). The Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) functional were used to describe the interatomic exchange-correlation functional for electronic structure investigations. Considering the presence of heavy element, the spin-orbit coupling (SOC) corrections was involved during the calculations. Moreover, 500 eV was selected for the energy cutoff. The energy and force convergence criteria were set as 10^{-6} eV and 0.01 eV/Å. The 3 × 6 × 8 k-point meshes were built for (NMPDA)Pb_2Br_6 in first Brillouin zone integration, respectively.

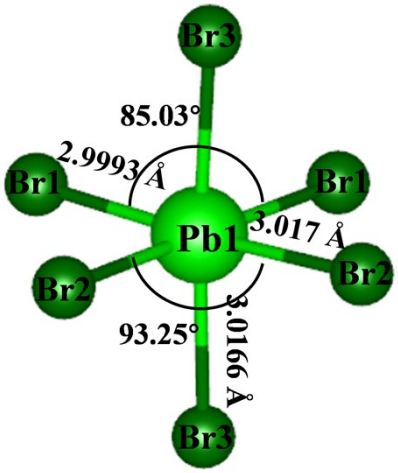

Fig. S1 Selected Pb–Br bond lengths and Br–Pb–Br bond angles for (NMPDA) Pb_2Br_6.

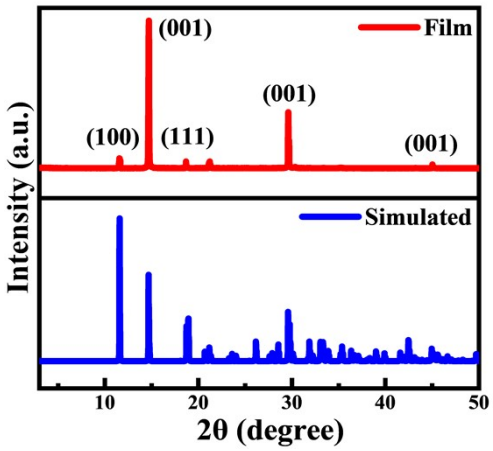

Figure. S2 PXRD patterns of (NMPDA)Pb_2Br_6 thin film synthesized from the perovskite precursor via spin-coating.

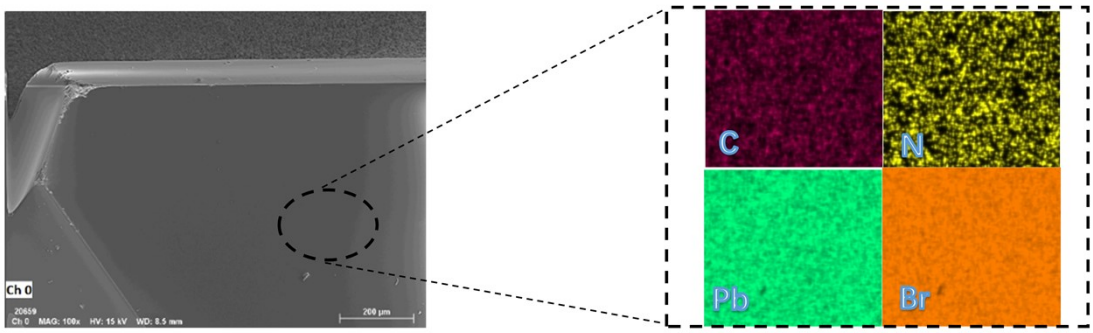

Fig. S3 EDS mapping of C, N, Pb and Br for (NMPDA)Pb_2Br_6.

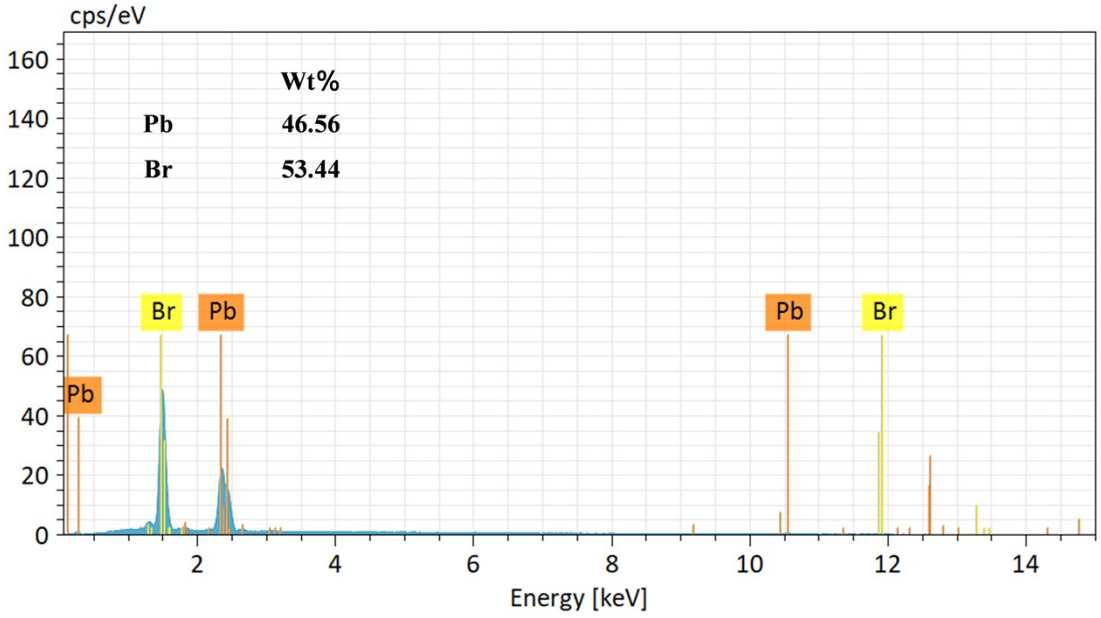

Fig. S4 Energy Dispersive Spectrometer of (NMPDA)Pb_2Br_6.

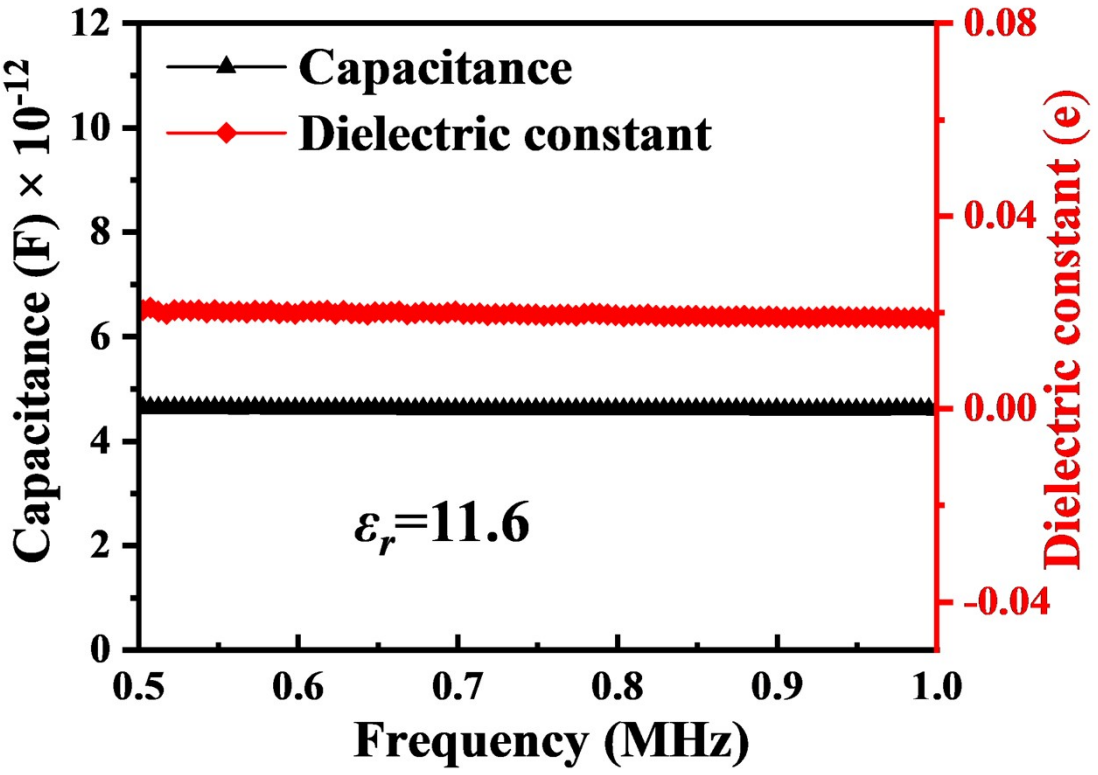

Fig. S5 The frequency dependent capacitance and dielectric constant of (NMPDA)Pb_2Br_6.

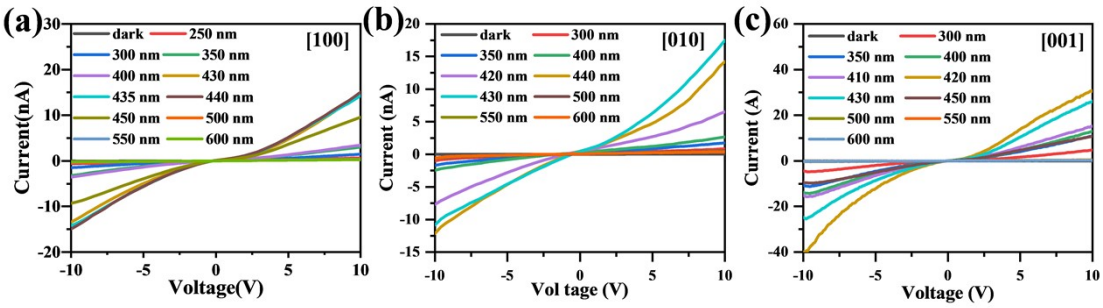

Fig. S6 Wavelength-dependent *I*–*V* curves for (a) [100], (b) [010] and (c) [001] axis of $(NMPDA)Pb_2Br_6$.

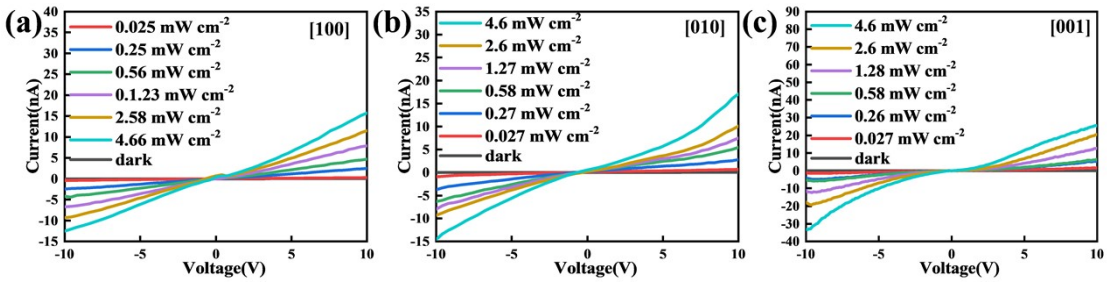

Fig. S7 Optical power density-dependent *I*–*V* curves for (a) [100], (b) [010] and (c) [001] axis under 440, 430 and 420 nm irradiation of $(NMPDA)Pb_2Br_6$.

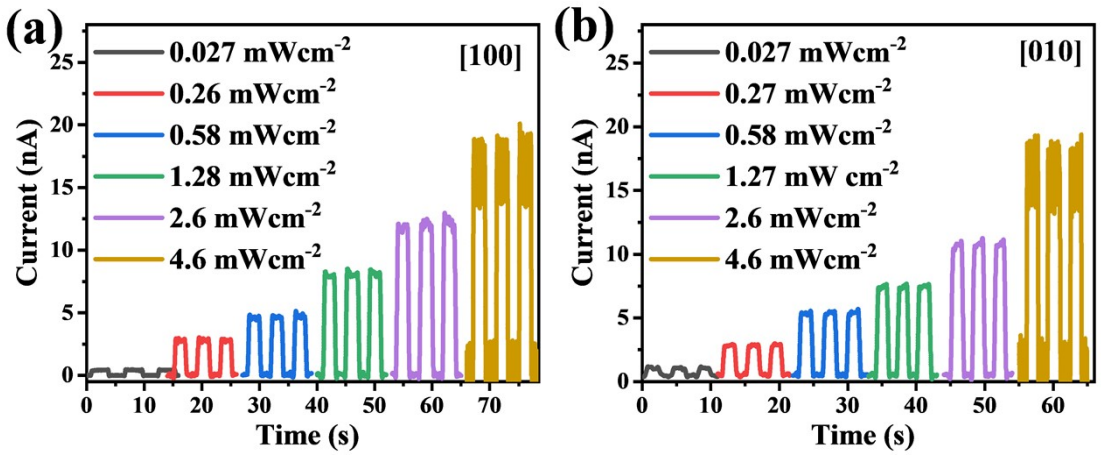

Fig. S8 Temporal photoresponse of (NMPDA)Pb_2Br_6 single crystal device along (a) [100] and (b) [010] crystallography axes under 440 and 430 nm irradiation at 10 V bias voltage.

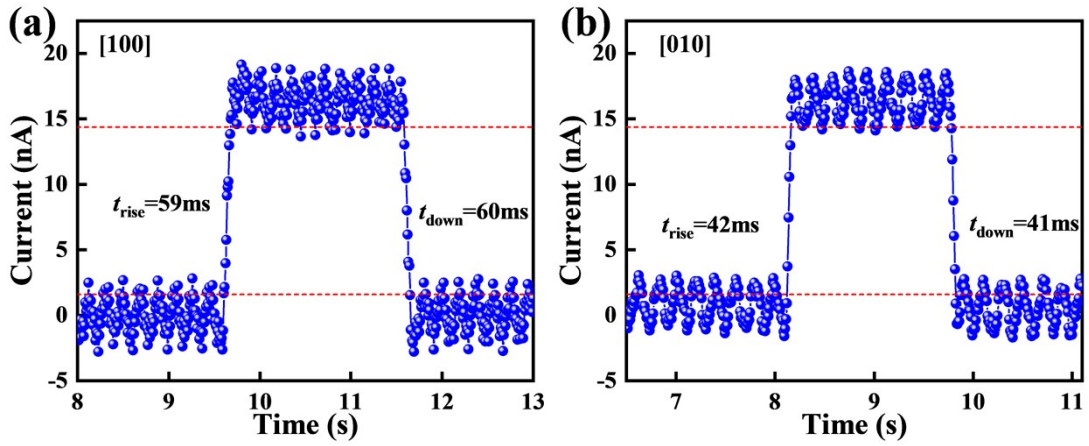

Fig. S9 The rise and fall time for (a) [100] and (b) [010] axis under 440 and 430 nm irradiation at 10 V bias voltage for (NMPDA)Pb_2Br_6.

Table S1. Bond angle derived from the single crystal X-ray data of $(NMPDA)Pb_2Br_6$.

Atom–Atom–Atom	Angle (°)
Br1 Pb1 Br1	85.03
Br1 Pb1 Br2	89.84
Br1 Pb1 Br3	89.47
Br1 Pb1 Br3	89.47
Br2 Pb1 Br1	91.88
Br2 Pb1 Br2	93.25
Br2 Pb1 Br3	90.04
Br2 Pb1 Br3	90.04
Br3 Pb1 Br1	89.91
Br3 Pb1 Br1	89.91
Br3 Pb1 Br2	90.52
Br3 Pb1 Br2	90.52
Pb1 Br1 Pb1	94.97
Pb1 Br2 Pb1	157.51
Pb1 Br3 Pb1	178.94

Table S2. Bond length derived from the single crystal X-ray data of $(NMPDA)Pb_2Br_6$.

Compound	Atom-Atom	Bond Length (Å)
$(NMPDA)Pb_2Br_6$	Pb1 Br1	2.99
	Pb1 Br1	3.02
	Pb1 Br2	3.01
	Pb1 Br2	3.00
	Pb1 Br3	3.01
	Pb1 Br3	3.01

Table S3. Summary of distortion parameters and bond angle variance for $(NMPDA)Pb_2Br_6$.

Compound	$(NMPDA)Pb_2Br_6$
Average bond length	3.0113 Å
Polyhedral volume	36.3516 $Å^3$
Distortion index (bond length)	0.00244
Effective coordination number	5.9986
Δ_d ($\times 10^{-5}$)	4
λ_{oct}	1.00103
σ^2_{oct} ($deg.^2$)	3.6340

$$\Delta_d = \frac{1}{6}\sum_{i=1}^{6}\left[\frac{di - dm}{dm}\right]^2 \quad \textbf{(Equation S1)}$$

$$\lambda_{oct} = \sum_{i=1}^{12}\left[\frac{di}{d0}\right]^2 \quad \textbf{(Equation S2)}$$

$$\sigma^2_{oct} = \frac{1}{11}\sum_{i=1}^{12}(\alpha i - 90)^2 \quad \textbf{(Equation S3)}$$

Table S4. The extracted carrier effective mass for $(NMPDA)Pb_2Br_6$.

Effect mass ($\times m_0$)	**$(NMPDA)Pb_2Br_6$**
Electron	Z-U: 0.796
	Z-T: 0.871
	Z-Γ: 0.187
	Z-R: 0.856
Hole	Z-U1.626
	Z-T: 1.206
	Z-Γ: 0.209
	Z-R: 1.206

Table S5. Detection performance parameters along all three directions for (NMPDA)Pb_2Br_6.

(NMPDA)Pb_2Br_6			
direction	[100]	[010]	[001]
μτ ($cm^2 V^{-1}$)	$3.5*10^{-4}$	$3.9*10^{-5}$	$6.85*10^{-4}$
τ_{rise} (ms)	41	42	27
τ_{decay} (ms)	79	39	29
I_{on}/I_{off}	640	825	$3*10^3$
Responsivity (A W^{-1})	0.074 @0.025 mW cm^{-2}	0.085 @0.026 mW cm^{-2}	0.275 @0.026 mW cm^{-2}
Detectivity (Jones)	$3.7*10^{11}$ @0.025 mW cm^{-2}	$5.82*10^{11}$ @0.026 mW cm^{-2}	$2.12*10^{12}$ @0.026 mW cm^{-2}