Supporting Information

Cage-Incorporation of Secondary Amine in Ruddlesden-Popper 2D Hybrid Perovskite with Strong Photoconductivity and Polarization Response

Beibei Wang,[a] Huaixi Chen,[b] Wuqian Guo,[b] Yi Liu,[b] Shiguo Han,[b] Lina Hua,[b] Liwei Tang,[b] Junhua Luo[b] and Zhihua Sun*[a, b, c]

[a.] *College of Chemistry, Fuzhou University, Fuzhou 350116, China*

[b.] *State Key Laboratory of Structure Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China*

[c.] *Fujian Science & Technology Innovation Laboratory for Optoelectronic Information of China, Fuzhou, Fujian 350108, P. R. China*

E-mail: sunzhihua@fjirsm.ac.cn.

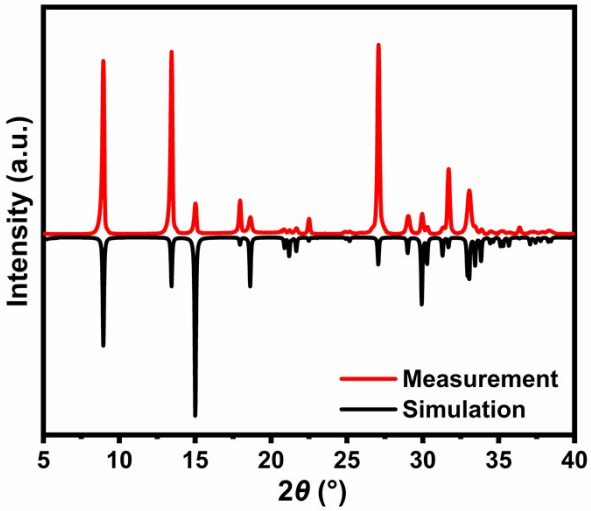

Figure S1. Experimental and calculated powder X-ray diffraction patterns of **1** at room temperature.

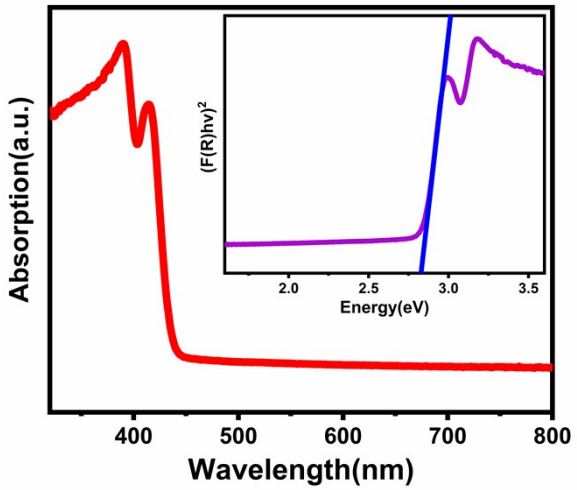

Figure S2. Optical absorption spectrum (Inset: the calculated bandgap) of $(BA)_2PbBr_4$.

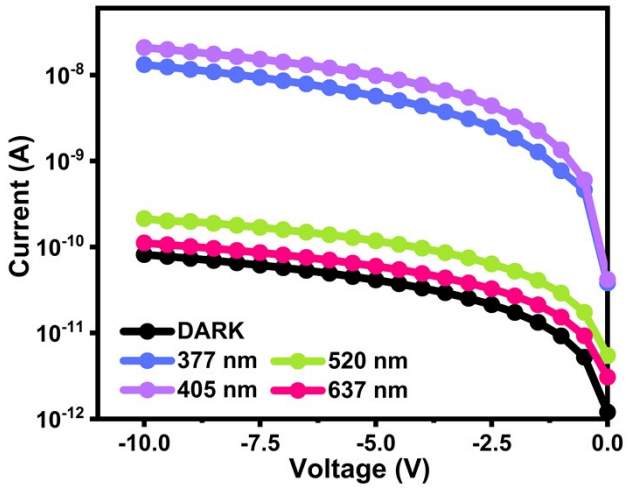

Figure S3: *I*–*V* traces of **1** measured under different wavelength.

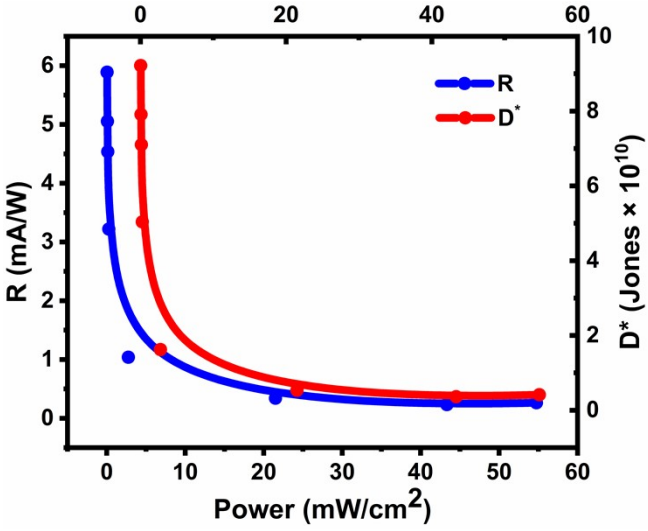

Figure S4. Detectivity *D** and responsivity *R* of the single crystal of **1** under changed incident light power.

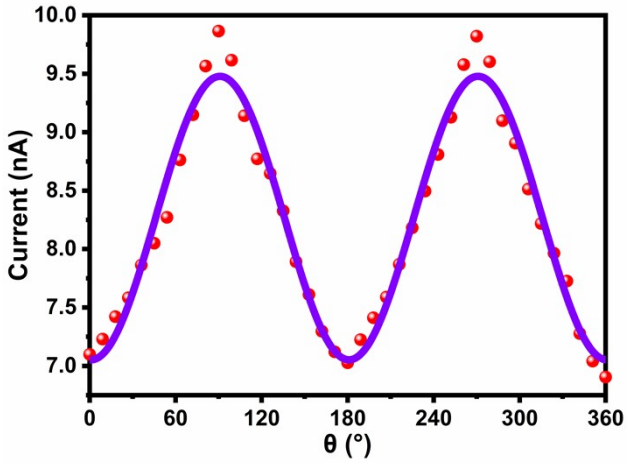

Figure S5. Polarization-dependent photocurrents.

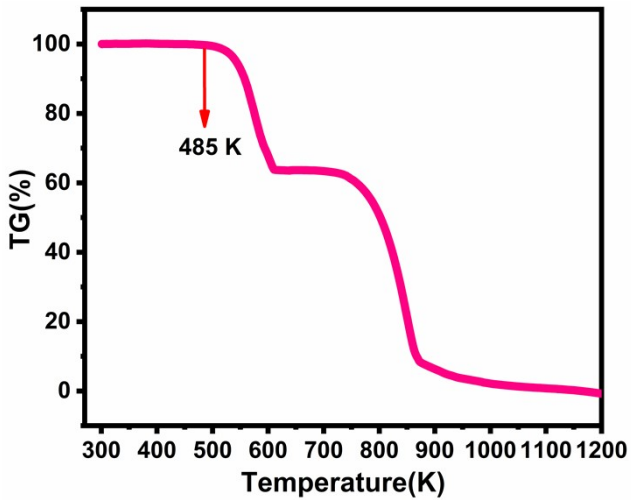

Figure S6. Thermal analysis of **1** showing its thermal stability up to ~485 K.

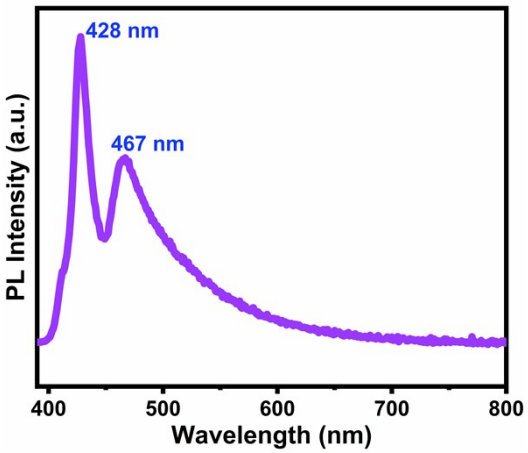

Figure S7. Photoluminescence (PL) spectra of **1**.

Tables

Table S1 Crystal data and structure refinement for **1.**

Empirical formula	$C_{10}H_{32}Br_7N_3Pb_2$
Formula weight	1168.13
Temperature/K	300.0
Crystal system	monoclinic
Space group	*C*2/*m*
a/Å	8.379(3)
b/Å	8.498(2)
c/Å	20.187(8)
α/°	90
β/°	101.917(13)
γ/°	90
Volume/Å^3	1406.5(8)
Z	2
ρ_{calc}g/cm^3	2.758
μ/mm^{-1}	21.898
F(000)	1044.0
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	6.906 to 49.984
Index ranges	-9 ≤ h ≤ 9, -10 ≤ k ≤ 10, -24 ≤ l ≤ 24
Reflections collected	15109
Independent reflections	1316 [R_{int} = 0.0893, R_{sigma} = 0.0454]
Data/restraints/parameters	1316/95/105
Goodness-of-fit on F^2	1.093
Final R indexes [I>=2σ (I)]	R_1 = 0.0757, wR_2 = 0.2239
Final R indexes [all data]	R_1 = 0.0812, wR_2 = 0.2313
Largest diff. peak/hole / e Å^{-3}	1.72/-2.97

Table S2 Bond Lengths for **1.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
$Pb^{(1)}$	$Br^{(3)}$	2.847(2)	$Br^{(3)}$	$Br^{(3)1}$	0.964(4)
$Pb^{(1)}$	$Br^{(3)1}$	2.847(2)	$N^{(2)}$	$C^{(6)}$	1.509(12)
$Pb^{(1)}$	$Br^{(2)2}$	2.9864(11)	$C^{(6)}$	$C^{(5)}$	1.493(10)
$Pb^{(1)}$	$Br^{(2)3}$	2.9864(11)	$C^{(5)}$	$C^{(4)}$	1.488(12)
$Pb^{(1)}$	$Br^{(2)}$	2.9855(11)	$C^{(4)}$	$C^{(3)}$	1.502(13)
$Pb^{(1)}$	$Br^{(2)1}$	2.9855(11)	$C^{(2)}$	$N^{(1)}$	1.497(13)
$Pb^{(1)}$	$Br^{(1)}$	3.1901(13)	$N^{(1)}$	$C^{(1)}$	1.502(13)

[1]+X, 1-Y, +Z; [2]1/2+X, 1/2-Y, +Z; [3]1/2+X, 1/2+Y, +Z

Table S3 Bond Angles for **1.**

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
$Br^{(3)}$	$Pb^{(1)}$	$Br^{(3)1}$	19.50(8)	$Br^{(2)1}$	$Pb^{(1)}$	$Br^{(2)3}$	89.10(2)
$Br^{(3)}$	$Pb^{(1)}$	$Br^{(2)2}$	80.91(7)	$Br^{(2)}$	$Pb^{(1)}$	$Br^{(2)2}$	89.10(2)
$Br^{(3)}$	$Pb^{(1)}$	$Br^{(2)}$	80.76(7)	$Br^{(2)3}$	$Pb^{(1)}$	$Br^{(2)2}$	90.69(4)
$Br^{(3)1}$	$Pb^{(1)}$	$Br^{(2)}$	94.62(7)	$Br^{(2)1}$	$Pb^{(1)}$	$Br^{(1)}$	92.30(3)
$Br^{(3)1}$	$Pb^{(1)}$	$Br^{(2)3}$	80.91(7)	$Br^{(2)2}$	$Pb^{(1)}$	$Br^{(1)}$	92.21(3)
$Br^{(3)}$	$Pb^{(1)}$	$Br^{(2)1}$	94.62(7)	$Br^{(2)}$	$Pb^{(1)}$	$Br^{(1)}$	92.30(3)
$Br^{(3)1}$	$Pb^{(1)}$	$Br^{(2)2}$	94.76(7)	$Br^{(2)3}$	$Pb^{(1)}$	$Br^{(1)}$	92.21(3)
$Br^{(3)}$	$Pb^{(1)}$	$Br^{(2)3}$	94.76(7)	$Br^{(3)1}$	$Br^{(3)}$	$Pb^{(1)}$	80.25(4)
$Br^{(3)1}$	$Pb^{(1)}$	$Br^{(2)1}$	80.77(7)	$Pb^{(1)}$	$Br^{(2)}$	$Pb^{(1)4}$	175.49(6)
$Br^{(3)1}$	$Pb^{(1)}$	$Br^{(1)}$	170.25(4)	$Pb^{(1)5}$	$Br^{(1)}$	$Pb^{(1)}$	180.0
$Br^{(3)}$	$Pb^{(1)}$	$Br^{(1)}$	170.25(4)	$C^{(5)}$	$C^{(6)}$	$N^{(2)}$	112.2(11)
$Br^{(2)}$	$Pb^{(1)}$	$Br^{(2)3}$	175.49(6)	$C^{(4)}$	$C^{(5)}$	$C^{(6)}$	114.2(10)
$Br^{(2)1}$	$Pb^{(1)}$	$Br^{(2)2}$	175.49(6)	$C^{(5)}$	$C^{(4)}$	$C^{(3)}$	116.6(11)
$Br^{(2)}$	$Pb^{(1)}$	$Br^{(2)1}$	90.75(4)	$C^{(2)}$	$N^{(1)}$	$C^{(1)}$	113.6(15)

^{1}+X, 1-Y, +Z;^{2} 1/2+X, 1/2-Y, +Z; ^{3}1/2+X, 1/2+Y,+Z; ^{4}-1/2+X, -1/2+Y, +Z; ^{5}1-X, 1-Y, 1-Z

Table S4 N-H···Br Hydrogen bonds of **1** at 300 K.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
$N1^{a}$-$H1B^{a}$	0.890	2.728	169.77	3.607	Br1 [x-1, y, z]
$N2^{a}$-$H2A^{a}$	0.890	2.641	128.50	3.270	Br3 [x+1/2, y-1/2, z]
$N2^{a}$-$H2A^{a}$	0.890	1.689	131.93	2.378	Br3 [x+1/2, -y+1/2, z]
$N2^{a}$-$H2B^{a}$	0.890	2.187	152.62	3.006	Br2 [x+1/2, -y+1/2, z]
$N2^{a}$-$H2C^{a}$	0.890	1.760	137.34	2.489	Br2 [x+1, y, z]

Table S5 Absorption cutoff wavelengths, bandgaps and PL peak position of **1**, $(DMA)PbBr_3$, $(DMA)_7Pb_4Br_{15}$ and $(BA)_2PbBr_4$.

Compound	Absorption cutoff wavelength (nm)	Bandgap (eV)	PL peak
1	466	2.67	at 467 nm
$(DMA)PbBr_3$	425	3.0	at 620 nm
$(DMA)_7Pb_4Br_{15}$	425	2.8	at 438 nm
$(BA)_2PbBr_4$	439	2.83	at 411 nm [1]

[1] L. Dou, A. B. Wong, Y. Yu, M. Lai, N. Kornienko, S. W. Eaton, A. Fu, C. G. Bischak, J. Ma, T. Ding, N. S. Ginsberg, L.-W. Wang, A. P. Alivisatos and P. Yang, *Science*, 2015, **349**, 1518-1521.

Table S6 Figure-of-merits for some photodetectors based on 2D perovskites.

	Responsivity (mA W^{-1})	Detectivity (Jones)	Response time	Ref
Our work	31.1	2.0×10^{11}	τ_{rise} = 20 μs τ_{decay} = 8 μs	
$(BA)_2(GA)Pb_2I_7$	12.01	3.3×10^{11}	τ_{rise} = 320 μs τ_{decay} = 315 μs	[1]
$(iso\text{-}BA)_2(MA)Pb_2I_7$	12.1	1.05×10^{11}	τ_{rise} = 310 μs τ_{decay} = 370 μs	[2]
$(C_4H_9NH_3)_2(MA)_2Pb_3Br_{10}$		3.6×10^{10}	τ_{rise} = 150 μs τ_{decay} = 570 μs	[3]
$(C_4H_9NH_3)_2(CH_3NH_3)Pb_2I_7$	7.3			[4]
$(C_4H_9NH_3)_2PbI_4$	3.0			
$(C_5H_{11}NH_3)_2(CH_3NH_3)Pb_2I_7$	3.8	2.9×10^{10}	τ_{rise} = 1.52 μs τ_{decay} = 1.67 μs	[5]
$[CH_3(CH_2)_3NH_3]_2(CH_3NH_3)Pb_2Br_7$		1.1×10^{10}	τ_{rise} = 20 μs τ_{decay} = 28 μs	[6]
$(EA)_2(MA)_2Pb_3Br_{10}$	1.35	1.16×10^{9}	τ_{rise} = 96 μs τ_{decay} = 123 μs	[7]
$(AMP)(MA)Pb_2I_7$	0.16	5.0×10^{10}	τ_{rise} = 40 ms τ_{decay} = 40 ms	[8]

[1] L. Lu, Y. Ma, J. Wang, Y. Liu, S. Han, X. Liu, W. Guo, H. Xu, J. Luo and Z. Sun, *Chem. Eur. J.*, 2021, **27**, 9267-9271.

[2] Y. Liu, Z. Wu, X. Liu, S. Han, Y. Li, T. Yang, Y. Ma, M. Hong, J. Luo, and Z. Sun, *Adv. Opt Mater.*, 2019, **7**, 1901049-1901054.

[3] L. Li, Z. Sun, P. Wang, W. Hu, S. Wang, C. Ji, M. Hong, J. Luo, *Angew. Chem. Int. Ed.*, 2017, **56**, 12150 -12154

[4] J. Zhou, Y. Chu and J. Huang, *ACS Appl. Mater. Inter.*, 2016, **8**, 25660-25666.

[5] S. Han, P. Wang, J. Zhang, X. Liu, Z. Sun, X. Huang, L. Li, C. Ji, W. Zhang, B. Teng, W. Hu, M. Hong and J. Luo, *Laser Photonics Rev.*, 2018, **12**, 1800060.

[6] L. Li, X. Liu, Y. Li, Z. Xu, Z. Wu, S. Han, K. Tao, M. Hong, J. Luo and Z. Sun, *J. Am. Chem. Soc.*, 2019, **141**, 2623-2629.

[7] X. Liu, S. Wang, P. Long, L. Li, Y. Peng, Z. Xu, S. Han, Z. Sun, M. Hong, J. Luo, *Angew. Chem. Int. Ed.*, 2019, ***58***, 14504.–14508

[8] I.-H. Park, K. C. Kwon, Z. Zhu, X. Wu, R. Li, Q.-H. Xu and K. P. Loh, *J. Am. Chem. Soc.*, 2020, **142**, 18592-18598.