Supporting Information

Bilayered Two-Dimensional Hybrid Perovskite with the Cage-Templated Secondary Cation for High Efficiency Photodetection

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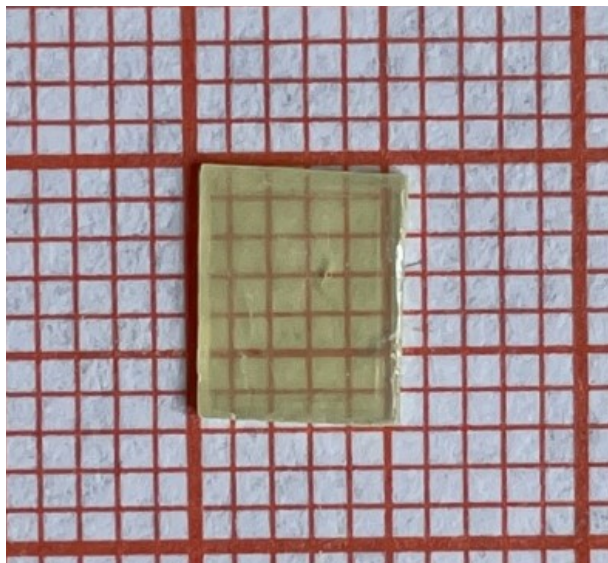**Table of Contents:**

Figure:

Figure

Figure S1. Single-crystal sample of **1**.

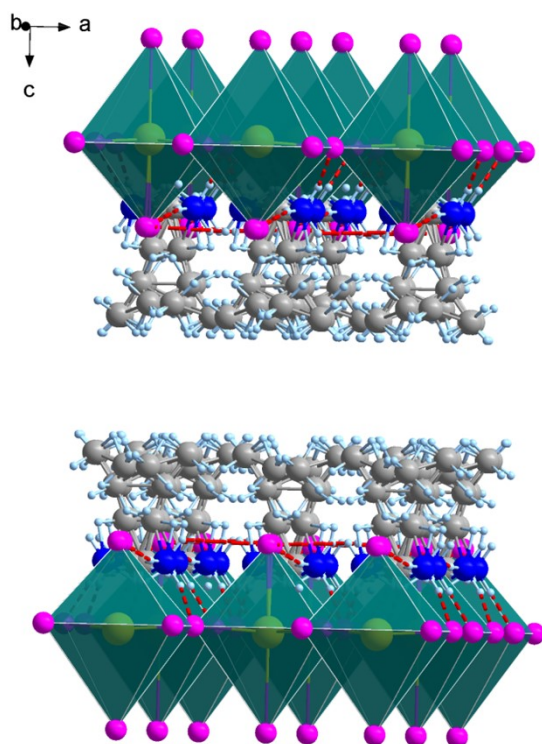**Figure S2.** The inorganic perovskite bilayers are connected with organic IA$^+$ cation layers by weak N-H···Br hydrogen bonds.
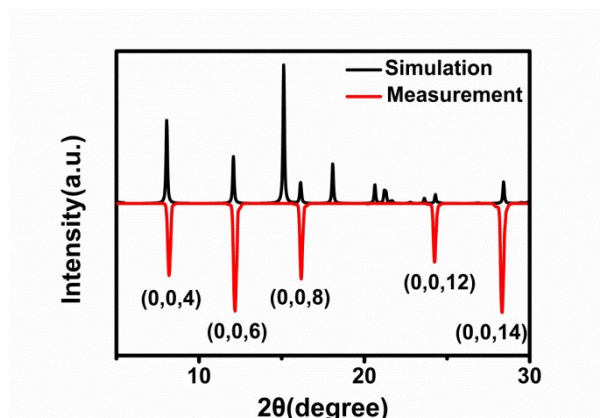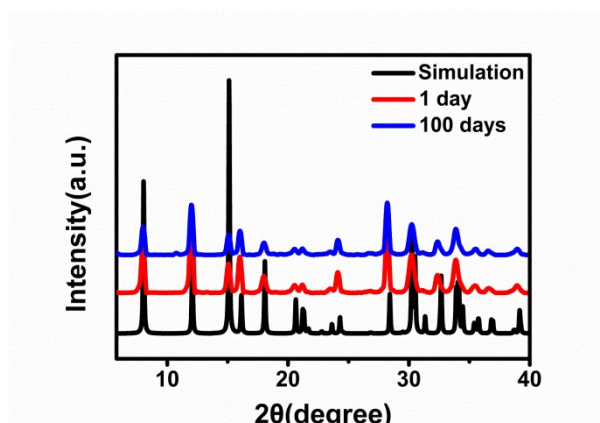
Figure S4. Powder X-ray diffraction patterns of **1** recorded on the sample after 1 day and 100 days, respectively.

Figure S5. Thermogravimetric (TG) curve of **1**.

Table S1 Crystal data for **1**.

Empirical formula	$C_{12}H_{36}Br_7N_3Pb_2$
Formula weight	1196.19
Temperature/K	249.99
Crystal system, space group	Orthorhombic, *Fmmm*
a/Å	8.333(2)
b/Å	8.372(2)
c/Å	43.928(12)
β/°	90
Volume/Å^3	3064.7(14)
Z, ρ_{calc}g/cm^3	2, 2.593
μ/mm^{-1}	20.103
F(000)	2152.0
Radiation	Mo$K\alpha$ (λ = 0.71073)
2-θ range for data collection(°)	6.962 to 55.156
Index ranges	-8 ≤ h ≤ 10, -10 ≤ k ≤ 10, -53 ≤ l ≤ 56
Reflections collected	5089
Independent reflections	1016 [R_{int} = 0.0860, R_{sigma} = 0.0686]
Data/restraints/parameters	1016/111/105
Goodness-of-fit on F^2	1.090
Final R indexes [I>=2σ (I)]	R_1 = 0.0870, wR_2 = 0.2396
Final R indexes [all data]	R_1 = 0.1093, wR_2 = 0.2581
Largest diff. peak/hole / e Å^{-3}	1.92/-1.97

Table S2. Bond lengths of **1** at 250K.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pb1	Br2[1]	2.9566(6)	C1	C2	1.487(11)
Pb1	Br2	2.9566(6)	C1	N1	1.497(12)
Pb1	Br2[2]	2.9566(6)	C2	C3	1.490(11)
Pb1	Br2[3]	2.9566(6)	C3	C5	1.504(12)
Pb1	Br1[4]	2.803(3)	C3	C4	1.505(13)
Pb1	Br1	2.803(3)	C7	N2	1.501(13)
Pb1	Br3	3.1930(11)	N2	C6	1.497(14)
Br1	Br1[4]	0.809(6)			

[1]1-x,+y,+z; [2]-1/2+x,1/2+y,+z; [3]3/2-x,1/2+y,+z; [4]1-x,1-y,+z

Table S3. Bond angles of **1** at 250K.

bond	Angle/°	Bond	Angle/°
Br2[1]-Pb1-Br2	89.60(2)	Br1-Pb1-Br2[1]	81.37(7)
Br2-Pb1-Br2[2]	174.46(11)	Br1-Pb1-Br2[3]	93.11(7)
Br2[1]-Pb1-Br2[3]	174.46(11)	Br1-Pb1-Br2[2]	93.11(7)
Br2[3]-Pb1-Br2[2]	89.60(2)	Br1[4]-Pb1-Br1	16.60(12)
Br2[1]-Pb1-Br2[2]	90.13(2)	Br1-Pb1-Br3	171.70(6)
Br2-Pb1-Br2[3]	90.13(2)	Br1[4]-Pb1-Br3	171.70(6)
Br2[1]-Pb1-Br3	92.77(5)	Pb1[5]-Br2-Pb1	174.46(11)
Br2[3]-Pb1-Br3	92.77(5)	Br1[4]-Br1-Pb1	81.70(6)
Br2[2]-Pb1-Br3	92.77(5)	Pb1-Br3-Pb1[6]	180.0
Br2-Pb1-Br3	92.77(5)	C2-C1-N1	113.1(9)
Br1[4]-Pb1-Br2[2]	81.37(7)	C1-C2-C3	117.8(8)
Br1[4]-Pb1-Br2[1]	93.11(7)	C2-C3-C5	115.8(10)
Br1-Pb1-Br2	81.37(7)	C2-C3-C4	104.2(9)
Br1[4]-Pb1-Br2[3]	81.37(7)	C5-C3-C4	110.0(9)
Br1[4]-Pb1-Br2	93.11(7)	C6-N2-C7	111.5(10)

[1]1-x,+y,+z; [2]-1/2+x,1/2+y,+z; [3]3/2-x,1/2+y,+z; [4]1-x,1-y,+z; [5]1/2+x,-1/2+y,+z; [6]1-x,1-y,1

Table S4 N-H⋯Br Hydrogen bonds of **1** at 250K.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)
N1^a-H1C⋯Br1[1]	0.900	2.765	167.66	3.649
N1^a-H1C⋯Br1[2]	0.900	2.012	165.96	2.893
N1^a-H1D⋯Br2[3]	0.900	1.761	137.07	2.497
N1^a-H1E⋯Br1	0.900	2.736	124.31	3.327
N1^a-H1E⋯Br1[4]	0.900	3.011	123.87	3.591
N2^a-H2C⋯Br3[5]	0.900	2.288	138.17	3.019
N2^a-H2D⋯Br2[6]	0.900	2.530	159.37	3.387

[1]x-1/2, y-1/2, z; [2]-x+1/2, -y+1/2, z; [3]-x+1, y, z; [4]-x+1, -y+1, z; [5]-x+1, -y+1, -z+1; [6]x-1/2, y+1/2, z

Table S5. Parameter comparison of photodetectors using different materials

Photodetectors	Responsivity (mA W^{-1})	Detectivity (Jones)	Ref
$(IA)_2(DMA)Pb_2Br_7$	110	2.8×10^{11}	Our work
$(C_5H_{11}NH_3)_2(CH_3NH_3)Pb_2I_7$	3.8	2.9×10^{10}	1
$(C_4H_9NH_3)_2(MA)_2Pb_3Br_{10}$	-	3.6×10^{10}	2
$(iso\text{-}BA)_2PbI_4$	560	1.23×10^{10}	3
$(BA)_2(GA)Pb_2I_7$	12.01	3.3×10^{11}	4
$(iso\text{-}BA)_2(MA)Pb_2I_7$	12.1	1.05×10^{11}	5
$(HDA)CsPb_2Br_7$	210	1.5×10^9	6

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