Electronic Supplementary Information

Interlayer Cations Engineering to Regulate the Photoelectric Properties of Lead Bromine Dion-Jacobson Hybrid Perovskites

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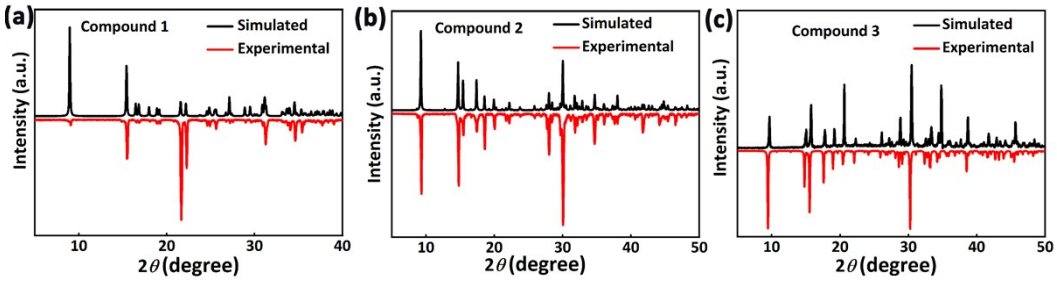

Figure S1. Experimental PXRD patterns of compound **1** (a), **2** (b) and **3** (c) with the simulated ones from crystal structures.

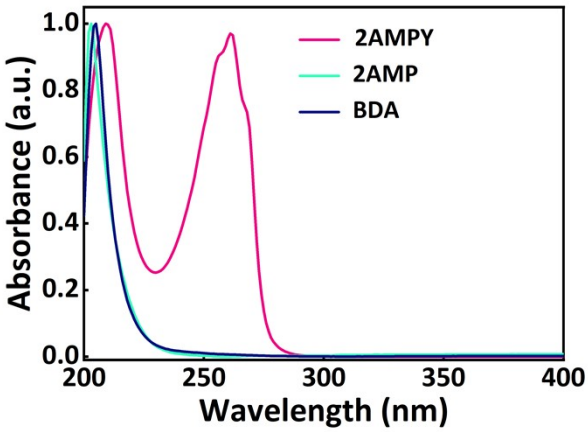

Figure S2. Absorption spectra of 2AMPY, 2AMP and BDA organic cations.

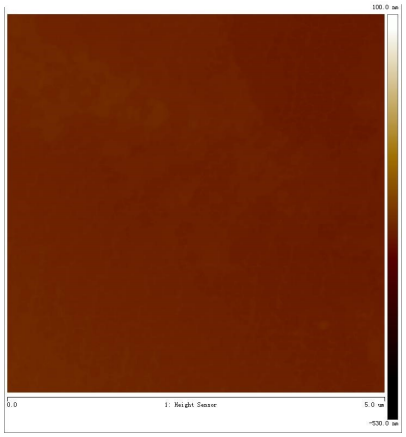

Figure S3. AFM image of crystal **3**.

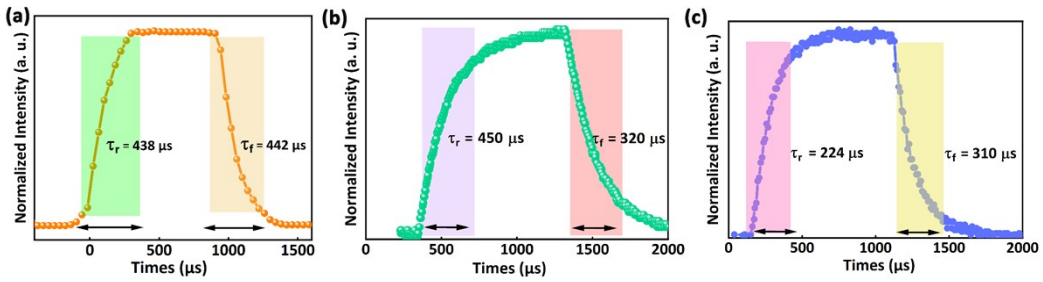

Figure S4. Rise time and decay time of photocurrent response of device **1** (a), **2** (b) and **3** (c).

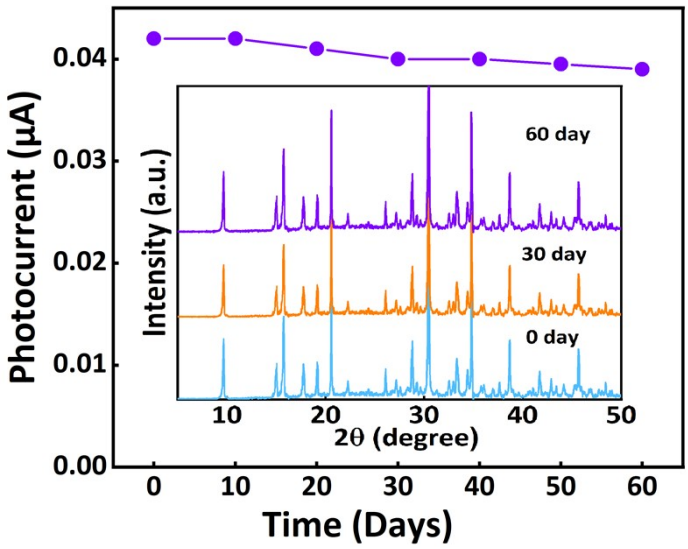

Figure S5. The stability test of device **3**.

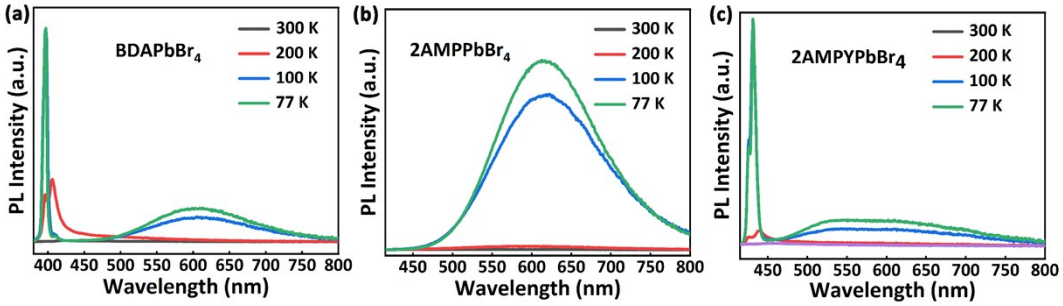

Figure S6 Steady-state PL emission spectra of $(BDA)PbBr_4$ **(1)**, $(2AMP)PbBr_4$ **(2)** and $(2AMPY)PbBr_4$ **(3)**.

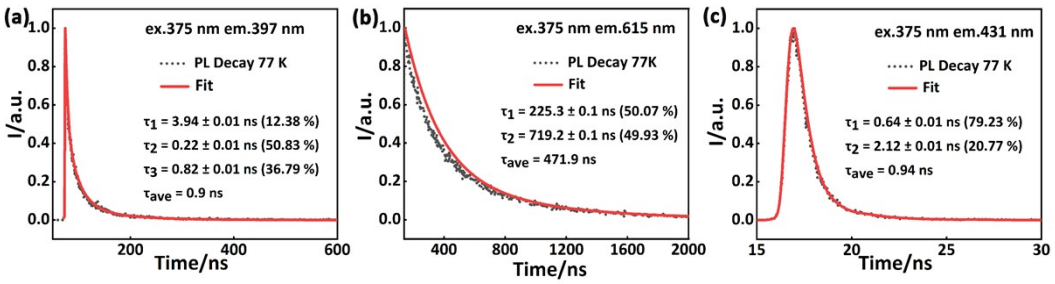

Figure S7 Time-resolved PL spectra of $(BDA)PbBr_4$ **(1)**, $(2AMP)PbBr_4$ **(2)** and $(2AMPY)PbBr_4$ **(3)**.

Table S1. Crystal data and structure refinements for $2AMPPbBr_4$ (**2**).

Compound	**$2AMPPbBr_4$**
Temperature	298 K
Formula	$C_{12}H_{32}N_4Pb_2Br_8$
Weight	1286.02
Crystal system	orthorhombic
Space group	*P*bcn
a (Å)	17.7922(9)
b (Å)	16.4220(7)
c (Å)	19.1417(11)
β (°)	90
V (Å³)	5592.9
Z	8
ρcalc g/cm³	3.055
R_{int}	0.13
R_1	0.06
wR_2	0.19
GOF	1.051

Table S2. The selected bond lengths for $2AMPPbBr_4$ (**2**) at 298 K.

$2AMPPbBr_4$					
Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Pb01	Br04	3.1030(12)	Pb02	Br05[3]	2.9403(11)
Pb01	Br05	3.1440(11)	Pb02	Br05	2.9403(11)
Pb01	Br06	2.9659(11)	Pb02	Br07	3.1973(11)

2AMPPbBr$_4$					
Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Pb01	Br07[1]	2.9426(11)	Pb03	Br06[4]	3.1448(11)
Pb01	Br08	2.9047(13)	Pb03	Br09	2.9738(11)
Pb01	Br09[2]	3.0986(11)	Pb03	Br06[5]	3.1448(11)

[1]1/2+X,-1/2+Y,1/2-Z; [2]+X,1-Y,-1/2+Z; [3]1-X,+Y,1/2-Z; [4]3/2-X,3/2-Y,1/2+Z; [5]-1/2+X,3/2-Y,1-Z; [6]1-X,+Y,3/2-Z; [7]1/2+X,3/2-Y,1-Z; [8]-1/2+X,1/2+Y,1/2-Z; [9]+X,1-Y,1/2+Z

Table S3. The selected bond angles for 2AMPPbBr$_4$ (**2**) at 298 K.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
Br04	Pb01	Br05	85.07(3)	Br05[3]	Pb02	Br07[3]	164.08(3)
Br06	Pb01	Br04	99.47(3)	Br07[3]	Pb02	Br07	106.48(4)
Br06	Pb01	Br05	94.57(3)	Br06[4]	Pb03	Br06[5]	109.15(4)
Br06	Pb01	Br09[1]	171.97(4)	Br09[6]	Pb03	Br06[5]	84.59(3)
Br07[2]	Pb01	Br04	98.07(3)	Br09[6]	Pb03	Br06[4]	166.05(3)
Br07[2]	Pb01	Br05	174.87(3)	Br09[6]	Pb03	Br09	81.81(5)
Br07[2]	Pb01	Br06	88.93(3)	Pb02	Br05	Pb01	163.58(5)
Br07[2]	Pb01	Br09[1]	93.73(3)	Pb01	Br03	Pb03[7]	170.44(4)
Br08	Pb01	Br04	166.71(3)	Pb01[8]	Br07	Pb02	171.06(4)
Br08	Pb01	Br05	83.47(3)	Pb03	Br09	Pb01[9]	171.83(4)
Br08	Pb01	Br06	88.15(3)	Br0A	Pb03	Br06[5]	93.78(3)
Br08	Pb01	Br07[2]	92.91(4)	Br0A[6]	Pb03	Br06[5]	90.03(3)
Br08	Pb01	Br09[1]	84.16(3)	Br0A	Pb03	Br09	88.51(4)
Br09[1]	Pb01	Br04	87.66(3)	Br0B[3]	Pb02	Br0B	170.55(5)
Br09[1]	Pb01	Br05	82.31(3)	Br0B[3]	Pb02	Br07[3]	102.64(3)
Br05[3]	Pb02	Br05	82.95(4)	Br0B[3]	Pb02	Br07	83.10(3)
Br05	Pb02	Br07	164.08(3)	Br0A[6]	Pb03	Br0A	173.43(5)
Br05[3]	Pb02	Br07	86.28(3)	Br0A[6]	Pb03	Br09	86.52(4)

Table S4. Detailed Pb-Br-Pb (deg) angles solved from the crystal structures of BDAPbBr$_4$ (**1**), 2AMPPbBr$_4$ (**2**) and 2AMPYPbBr$_4$ (**3**).

Compound	**avg horizontal Pb-Br-Pb angle**	**avg axial Pb-Br-Pb angle**	**avg Pb-Br-Pb angle**
BDAPbBr$_4$	148.4	149.8	149.1
2AMPPbBr$_4$	167.6	170.8	169.2
2AMPYPbBr$_4$	171.5	175.9	173.7