Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic Supplementary Information (ESI)†

Lead-free double-halide perovskite Cs_3BiBr_6 with well-defined crystal structure and high thermal stability for optoelectronics

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Contents:

Table S1. Crystal data and structure refinements for the Cs_3BiBr_6.

formula	Cs_3BiBr_6
fw	1087.11
T, K	room temp
λ, Å	0.71073
space group	*Pbcm*
a, Å	8.689(2)
b, Å	13.628(1)
c, Å	27.694(9)
α, deg	90
β, deg	90
γ, deg	90
V, $Å^3$	3279.5(6)
Z	8
D_{calcd}, g cm^{-3}	4.404
μ, mm^{-1}	31.89
GOF on F^2	1.062
R1,wR2 [$I > 2\sigma(I)$]^a	0.0495, 0.1412
R1,wR2(all data)	0.0794, 0.1603

^{a}R1 = $\sum||F_o| - |F_c||/\sum|F_o|$, wR2 = $\{\sum w[(F_o)^2 - (F_c)^2]^2/\sum w[(F_o)^2]^2\}^{1/2}$

Table S2. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters ($Å^2$ ×10^3) for Cs_3BiBr_6. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
Bi(1)	7451(1)	806(1)	2500	22(1)
Bi(2)	-2141(1)	-2500	0	21(1)
Cs(3)	3140(1)	-939(1)	1546(1)	35(1)
Cs(2)	8180(1)	-2461(1)	1615(1)	37(1)
Br(5)	6001(1)	-1075(1)	2500	31(1)
Br(6)	8801(1)	2722(1)	2500	30(1)
Br(7)	-2221(2)	-4191(1)	588(1)	57(1)
Br(4)	294(1)	-1717(1)	582(1)	47(1)
Br(3)	9470(1)	202(1)	1752(1)	48(1)
Br(2)	5486(1)	1392(1)	1720(1)	46(1)
Br(1)	-4459(1)	-3387(1)	-581(1)	51(1)
Cs(1)	-2566(1)	-5855(1)	-493(1)	70(1)

Table S3. Bond lengths (Å) and angles (deg) for Cs_3BiBr_6.

Bi(1)-Br(3)	2.8360(9)	Bi(1)-Br(3)#1	2.8360(8)
Bi(1)-Br(5)	2.8557(11)	Bi(1)-Br(6)	2.8628(11)
Bi(1)-Br(2)	2.8671(8)	Bi(1)-Br(2)#1	2.8671(8)
Bi(2)-Br(7)	2.8233(8)	Bi(2)-Br(7)#2	2.8233(8)
Bi(2)-Br(1)	2.8484(9)	Bi(2)-Br(1)#2	2.8484(9)
Bi(2)-Br(4)	2.8655(9)	Bi(2)-Br(4)#2	2.8655(9)
Cs(3)-Br(1)#5	3.5117(10)	Cs(3)-Br(3)#4	3.5927(11)
Cs(3)-Br(6)#6	3.6278(9)	Cs(3)-Br(5)	3.6329(10)
Cs(3)-Br(7)#7	3.6528(11)	Cs(3)-Br(4)	3.7906(10)
Cs(3)-Br(2)	3.8048(11)	Cs(3)-Br(2)#6	3.8593(11)
Cs(2)-Br(4)#10	3.5490(10)	Cs(2)-Br(2)#6	3.5602(11)
Cs(2)-Br(6)#11	3.5980(10)	Cs(2)-Br(5)	3.6266(10)
Cs(2)-Br(7)#10	3.7120(11)	Cs(2)-Br(3)#11	3.8028(11)
Cs(2)-Br(3)	3.8167(10)	Cs(2)-Br(1)#5	3.8463(12)
Cs(2)-Bi(2)#10	4.4827(5)	Cs(1)-Br(4)#15	3.7600(11)
Cs(1)-Br(4)#9	3.8610(13)	Cs(1)-Br(2)#3	3.8665(13)
Cs(1)-Br(3)#3	4.0110(15)	Cs(1)-Br(1)#16	4.0743(15)
Cs(1)-Br(7)#9	4.1682(17)	Cs(1)-Cs(1)#17	5.2503(15)
Cs(1)-Cs(3)#9	5.2774(9)	Cs(1)-Cs(3)#3	5.3291(9)
Cs(1)-Cs(2)#18	5.4278(10)	Br(3)-Bi(1)-Br(3)#1	93.79(5)
Br(3)-Bi(1)-Br(5)	90.73(3)	Br(3)-Bi(1)-Br(6)	90.63(3)
Br(5)-Bi(1)-Br(6)	178.01(3)	Br(3)-Bi(1)-Br(2)	84.22(3)
Br(3)#1-Bi(1)-Br(2)	178.01(3)	Br(5)-Bi(1)-Br(2)	89.28(3)
Br(6)-Bi(1)-Br(2)	89.42(3)	Br(3)-Bi(1)-Br(2)#1	178.01(3)
Br(3)#1-Bi(1)-Br(2)#1	84.22(3)	Br(5)-Bi(1)-Br(2)#1	89.28(3)
Br(6)-Bi(1)-Br(2)#1	89.42(3)	Br(2)-Bi(1)-Br(2)#1	97.78(4)
Br(7)-Bi(2)-Br(7)#2	177.18(6)	Br(7)-Bi(2)-Br(1)	87.83(3)
Br(7)#2-Bi(2)-Br(1)	90.18(3)	Br(1)-Bi(2)-Br(1)#2	89.98(5)
Br(7)-Bi(2)-Br(4)	89.87(3)	Br(7)#2-Bi(2)-Br(4)	92.21(3)
Br(1)-Bi(2)-Br(4)	176.51(3)	Br(1)#2-Bi(2)-Br(4)	92.66(3)
Br(4)-Bi(2)-Br(4)#2	84.81(4)	Br(7)-Bi(2)-Cs(2)#3	124.57(2)
Br(7)#2-Bi(2)-Cs(2)#3	55.64(2)	Br(1)-Bi(2)-Cs(2)#3	58.31(2)
Br(1)#2-Bi(2)-Cs(2)#3	127.82(2)	Br(4)-Bi(2)-Cs(2)#3	121.32(2)
Br(4)#2-Bi(2)-Cs(2)#3	52.301(19)	Br(7)#2-Bi(2)-Cs(2)#4	124.57(2)
Br(1)-Bi(2)-Cs(2)#4	127.82(2)	Cs(2)#3-Bi(2)-Cs(2)#4	172.876(17)
Br(1)#5-Cs(3)-Br(3)#4	139.59(3)	Br(1)#5-Cs(3)-Br(6)#6	134.31(3)
Br(3)#4-Cs(3)-Br(6)#6	71.90(2)	Br(1)#5-Cs(3)-Br(5)	97.66(3)
Br(3)#4-Cs(3)-Br(5)	120.91(3)	Br(6)#6-Cs(3)-Br(5)	76.27(2)
Br(1)#5-Cs(3)-Br(7)#7	75.40(3)	Br(3)#4-Cs(3)-Br(7)#7	68.88(3)
Br(6)#6-Cs(3)-Br(7)#7	139.06(3)	Br(5)-Cs(3)-Br(7)#7	135.33(3)
Br(1)#5-Cs(3)-Br(4)	77.20(3)	Br(3)#4-Cs(3)-Br(4)	69.78(2)
Br(6)#6-Cs(3)-Br(4)	93.95(2)	Br(5)-Cs(3)-Br(4)	160.80(3)
Br(7)#7-Cs(3)-Br(4)	61.86(2)	Br(1)#5-Cs(3)-Br(2)	89.80(3)
Br(3)#4-Cs(3)-Br(2)	95.41(3)	Br(6)#6-Cs(3)-Br(2)	125.24(2)
Br(5)-Cs(3)-Br(2)	65.41(2)	Br(7)#7-Cs(3)-Br(2)	70.43(2)
Br(4)-Cs(3)-Br(2)	132.26(2)	Br(1)#5-Cs(3)-Br(2)#6	70.40(2)
Br(3)#4-Cs(3)-Br(2)#6	131.49(3)	Br(6)#6-Cs(3)-Br(2)#6	65.06(2)
Br(5)-Cs(3)-Br(2)#6	69.46(2)	Br(7)#7-Cs(3)-Br(2)#6	140.61(3)
Br(4)-Cs(3)-Br(2)#6	91.49(3)	Br(2)-Cs(3)-Br(2)#6	127.246(16)

Br(1)#5-Cs(3)-Cs(2)#4	116.88(2)	Br(3)#4-Cs(3)-Cs(2)#4	51.834(17)
Br(6)#6-Cs(3)-Cs(2)#4	48.245(17)	Br(5)-Cs(3)-Cs(2)#4	124.39(2)
Br(7)#7-Cs(3)-Cs(2)#4	96.59(2)	Br(4)-Cs(3)-Cs(2)#4	47.135(16)
Br(2)-Cs(3)-Cs(2)#4	147.04(2)	Br(2)#6-Cs(3)-Cs(2)#4	82.247(19)
Br(1)#5-Cs(3)-Cs(2)	51.81(2)	Br(3)#4-Cs(3)-Cs(2)	168.55(2)
Br(6)#6-Cs(3)-Cs(2)	100.12(2)	Br(5)-Cs(3)-Cs(2)	48.030(16)
Br(7)#7-Cs(3)-Cs(2)	120.33(2)	Br(4)-Cs(3)-Cs(2)	119.82(2)
Br(2)-Cs(3)-Cs(2)	82.421(18)	Br(2)#6-Cs(3)-Cs(2)	46.561(17)
Cs(2)#4-Cs(3)-Cs(2)	128.764(18)	Br(1)#5-Cs(3)-Cs(2)#8	115.06(2)
Br(3)#4-Cs(3)-Cs(2)#8	50.589(17)	Br(6)#6-Cs(3)-Cs(2)#8	110.54(2)
Br(5)-Cs(3)-Cs(2)#8	100.47(2)	Br(7)#7-Cs(3)-Cs(2)#8	49.021(18)
Br(4)-Cs(3)-Cs(2)#8	98.42(2)	Br(2)-Cs(3)-Cs(2)#8	46.383(17)
Br(2)#6-Cs(3)-Cs(2)#8	169.52(2)	Cs(2)#4-Cs(3)-Cs(2)#8	101.992(12)
Cs(2)-Cs(3)-Cs(2)#8	128.753(15)	Br(1)#5-Cs(3)-Cs(1)#9	54.49(2)
Br(3)#4-Cs(3)-Cs(1)#9	111.25(2)	Br(6)#6-Cs(3)-Cs(1)#9	86.661(19)
Br(5)-Cs(3)-Cs(1)#9	115.10(2)	Br(7)#7-Cs(3)-Cs(1)#9	96.77(2)
Br(4)-Cs(3)-Cs(1)#9	46.948(19)	Br(2)-Cs(3)-Cs(1)#9	144.28(2)
Br(2)#6-Cs(3)-Cs(1)#9	46.972(19)	Br(4)#10-Cs(2)-Br(2)#6	130.86(3)
Br(4)#10-Cs(2)-Br(6)#11	98.75(2)	Br(2)#6-Cs(2)-Br(6)#11	128.84(3)
Br(4)#10-Cs(2)-Br(5)	131.80(3)	Br(2)#6-Cs(2)-Br(5)	72.94(2)
Br(6)#11-Cs(2)-Br(5)	83.38(2)	Br(4)#10-Cs(2)-Br(7)#10	67.16(2)
Br(2)#6-Cs(2)-Br(7)#10	72.51(3)	Br(6)#11-Cs(2)-Br(7)#10	129.35(3)
Br(5)-Cs(2)-Br(7)#10	143.10(3)	Br(4)#10-Cs(2)-Br(3)#11	92.38(3)
Br(2)#6-Cs(2)-Br(3)#11	95.99(3)	Br(6)#11-Cs(2)-Br(3)#11	66.32(2)
Br(5)-Cs(2)-Br(3)#11	130.47(3)	Br(7)#10-Cs(2)-Br(3)#11	66.08(2)
Br(4)#10-Cs(2)-Br(3)	69.92(2)	Br(2)#6-Cs(2)-Br(3)	132.25(3)
Br(6)#11-Cs(2)-Br(3)	69.66(3)	Br(5)-Cs(2)-Br(3)	65.87(2)
Br(7)#10-Cs(2)-Br(3)	135.06(3)	Br(3)#11-Cs(2)-Br(3)	128.952(17)
Br(4)#10-Cs(2)-Br(1)#5	67.81(2)	Br(2)#6-Cs(2)-Br(1)#5	70.08(2)
Br(6)#11-Cs(2)-Br(1)#5	157.06(3)	Br(5)-Cs(2)-Br(1)#5	92.02(2)
Br(7)#10-Cs(2)-Br(1)#5	64.18(2)	Br(3)#11-Cs(2)-Br(1)#5	130.25(2)
Br(3)-Cs(2)-Br(1)#5	87.91(3)	Br(4)#10-Cs(2)-Bi(2)#10	39.705(15)
Br(2)#6-Cs(2)-Bi(2)#10	91.17(2)	Br(6)#11-Cs(2)-Bi(2)#10	136.53(2)
Br(5)-Cs(2)-Bi(2)#10	130.393(19)	Br(7)#10-Cs(2)-Bi(2)#10	38.893(14)
Br(3)#11-Cs(2)-Bi(2)#10	97.059(19)	Br(3)-Cs(2)-Bi(2)#10	97.40(2)
Br(1)#5-Cs(2)-Bi(2)#10	39.062(14)	Br(4)#10-Cs(2)-Cs(3)#10	51.523(16)
Br(2)#6-Cs(2)-Cs(3)#10	177.59(2)	Br(6)#11-Cs(2)-Cs(3)#10	48.779(16)
Br(5)-Cs(2)-Cs(3)#10	105.75(2)	Br(7)#10-Cs(2)-Cs(3)#10	109.21(2)
Br(3)#11-Cs(2)-Cs(3)#10	83.313(19)	Br(3)-Cs(2)-Cs(3)#10	47.739(17)
Br(1)#5-Cs(2)-Cs(3)#10	112.13(2)	Bi(2)#10-Cs(2)-Cs(3)#10	91.205(13)
Br(4)#10-Cs(2)-Cs(3)	108.27(2)	Br(2)#6-Cs(2)-Cs(3)	51.916(18)
Br(6)#11-Cs(2)-Cs(3)	130.99(2)	Br(5)-Cs(2)-Cs(3)	48.140(17)
Br(7)#10-Cs(2)-Cs(3)	99.02(2)	Br(3)#11-Cs(2)-Cs(3)	147.90(2)
Br(3)-Cs(2)-Cs(3)	82.11(2)	Br(1)#5-Cs(2)-Cs(3)	45.860(15)
Br(4)#10-Cs(2)-Cs(3)#6	111.53(2)	Br(2)#6-Cs(2)-Cs(3)#6	50.687(18)
Br(6)#11-Cs(2)-Cs(3)#6	105.37(2)	Br(5)-Cs(2)-Cs(3)#6	114.19(2)
Br(7)#10-Cs(2)-Cs(3)#6	47.979(16)	Br(3)#11-Cs(2)-Cs(3)#6	46.881(17)
Br(3)-Cs(2)-Cs(3)#6	175.04(2)	Br(1)#5-Cs(2)-Cs(3)#6	97.03(2)
Br(1)-Cs(1)-Br(4)#15	124.20(3)	Br(1)-Cs(1)-Br(7)	63.09(2)
Br(4)#15-Cs(1)-Br(7)	61.13(2)	Br(1)-Cs(1)-Br(4)#9	171.21(4)
Br(4)#15-Cs(1)-Br(4)#9	60.93(2)	Br(7)-Cs(1)-Br(4)#9	121.71(3)

Br(1)-Cs(1)-Br(2)#3	85.43(2)	Br(4)#15-Cs(1)-Br(2)#3	150.04(3)
Br(7)-Cs(1)-Br(2)#3	147.92(3)	Br(4)#9-Cs(1)-Br(2)#3	90.32(2)
Br(1)-Cs(1)-Br(3)#3	86.44(3)	Br(4)#15-Cs(1)-Br(3)#3	121.74(3)
Br(7)-Cs(1)-Br(3)#3	121.50(3)	Br(4)#9-Cs(1)-Br(3)#3	84.79(2)
Br(2)#3-Cs(1)-Br(3)#3	58.05(2)	Br(1)-Cs(1)-Br(1)#16	89.81(3)
Br(4)#15-Cs(1)-Br(1)#16	71.08(2)	Br(7)-Cs(1)-Br(1)#16	67.83(3)
Br(4)#9-Cs(1)-Br(1)#16	98.84(3)	Br(2)#3-Cs(1)-Br(1)#16	108.43(3)
Br(3)#3-Cs(1)-Br(1)#16	166.20(3)	Br(1)-Cs(1)-Br(7)#9	114.83(3)
Br(4)#15-Cs(1)-Br(7)#9	62.02(2)	Br(7)-Cs(1)-Br(7)#9	87.81(3)
Br(4)#9-Cs(1)-Br(7)#9	59.91(2)	Br(2)#3-Cs(1)-Br(7)#9	112.59(3)
Br(3)#3-Cs(1)-Br(7)#9	60.10(2)	Br(1)#16-Cs(1)-Br(7)#9	133.08(3)

Symmetry transformations used to generate equivalent atoms: #1 x,y,-z+1/2; #2 x,-y-1/2,-z; #3 x-1,-y-1/2,-z ; #4 x-1,y,z; #5 x+1,-y-1/2,-z; #6 -x+1,y-1/2,z ; #7 -x,y+1/2,z; #8 -x+1,y+1/2,z; #9 -x,-y-1,-z; #10 x+1,y,z; #11 -x+2,y-1/2,z; #12 -x+2,y+1/2,-z+1/2 ; #13 -x+2,y+1/2,z ; #14 -x+1,y+1/2,-z+1/2; #15 -x,y-1/2,z; #16 -x-1,-y-1,-z; #17 x,-y-3/2,-z; #18 -x+1,-y-1,-z .

Table S4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for Cs_3BiBr_6. The anisotropic displacement factor exponent takes the form: $-2 \pi^2 [h^2 a^{*2} U11 + ... + 2 h k a^* b^* U12]$.

atom	U11	U22	U33	U23	U13	U12
Bi(1)	19(1)	22(1)	25(1)	0	0	2(1)
Bi(2)	25(1)	20(1)	19(1)	0(1)	0	0
Cs(3)	28(1)	46(1)	32(1)	6(1)	2(1)	2(1)
Cs(2)	32(1)	47(1)	30(1)	-3(1)	1(1)	0(1)
Br(5)	33(1)	28(1)	33(1)	0	0	-4(1)
Br(6)	32(1)	26(1)	32(1)	0	0	-2(1)
Br(7)	114(1)	25(1)	32(1)	9(1)	-6(1)	-2(1)
Br(4)	45(1)	65(1)	31(1)	-9(1)	-1(1)	-27(1)
Br(3)	50(1)	40(1)	55(1)	-6(1)	29(1)	5(1)
Br(2)	50(1)	41(1)	47(1)	4(1)	-24(1)	8(1)
Br(1)	48(1)	60(1)	46(1)	-2(1)	-21(1)	-17(1)
Cs(1)	103(1)	58(1)	47(1)	-9(1)	-19(1)	29(1)

Table S5. Crystallographic and electronic parameters for the known perovskites.

	Space group	a	b	c
Cs_3BiCl_6	C2/c	27.017	8.252	13.121
Rb_3BiBr_6	Pnma	13.311	26.63	8.603
Cs_2SnCl_6	Fm-3m	10.347	10.347	10.347
Cs_2SnBr_6	Fm-3m	10.771	10.771	10.771
Cs_2SnI_6	Fm-3m	11.631	11.631	11.631
$Cs_2AgInCl_6$	Fm-3m	10.469	10.469	10.469
Cs_3BiBr_6	Pbcm	8.689	13.628	27.694

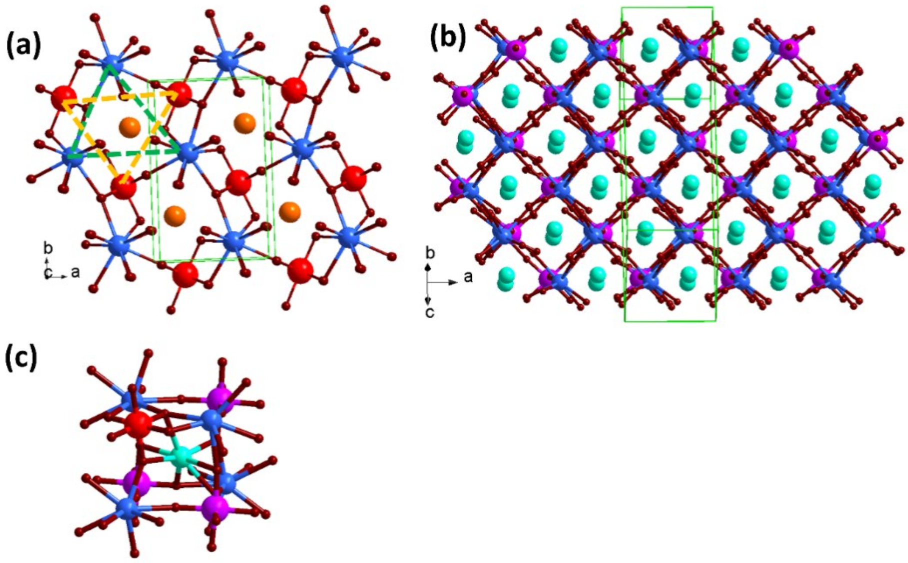

Fig. S1 View of the structures constructed by (a) Bi1, Cs3; and (b) Bi1, Bi2, Cs3 on the mirror plane, respectively. (c) A basic unit constructed from the Bi1, Bi2, Cs3. Color code: Bi1, red; Bi2, purple; Cs1, green; Cs2, orange; Cs3, blue; Br, Brown.

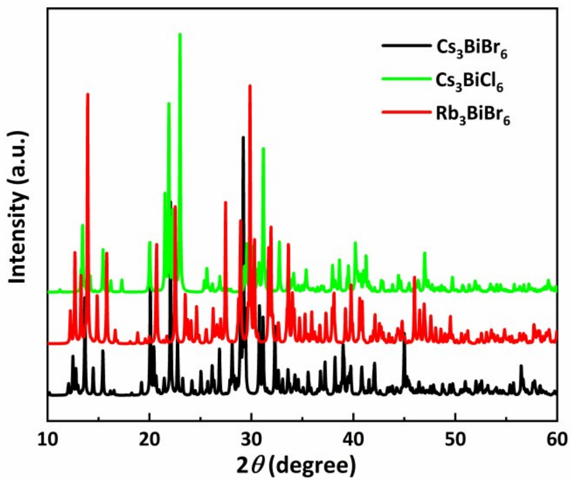

Fig. S2 Comparison of XRD pattern for Cs_3BiBr_6,Rb_3BiBr_6, Cs_3BiCl_6.

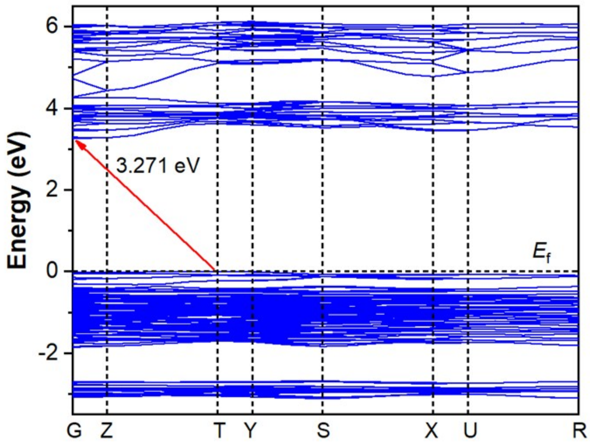

Fig. S3 The bandgap calculated from the DFT.

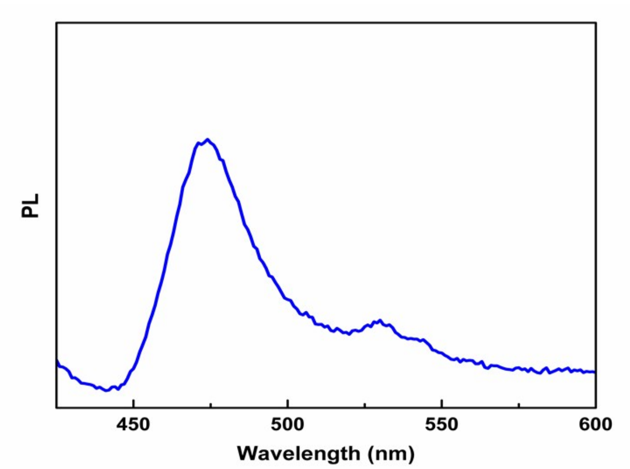

Fig. S4 The PL spectra for the Cs_3BiBr_6.

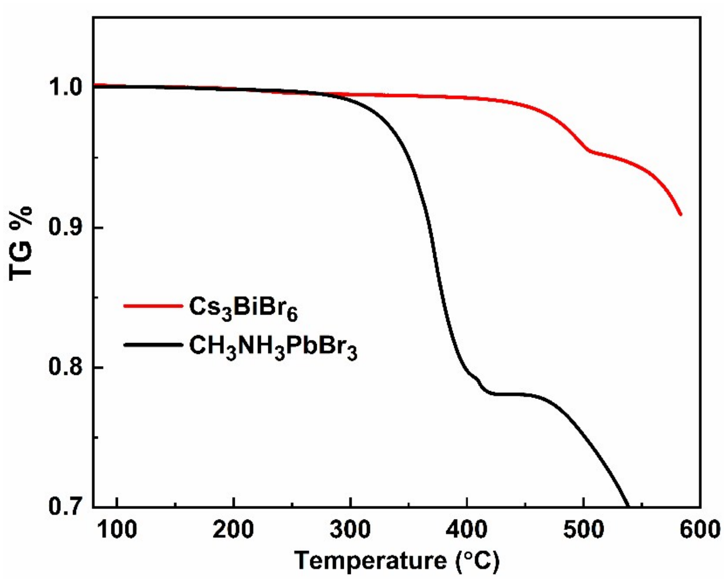

Fig. S5 TGA curves of Cs_3BiBr_6 and $CH_3NH_3PbBr_3$.

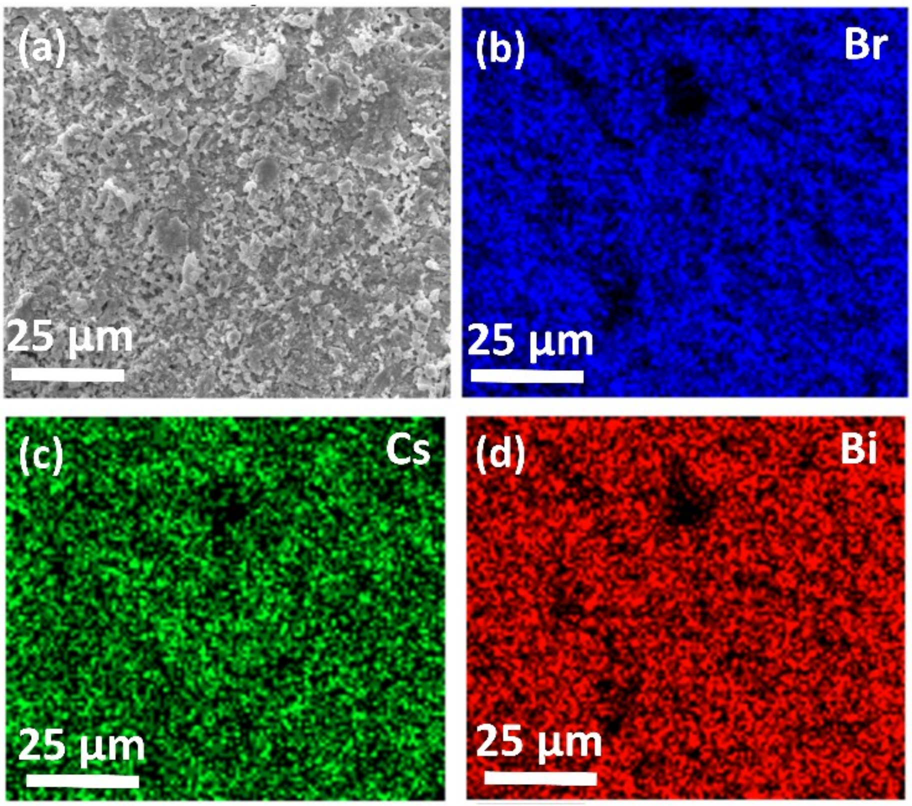

Fig. S6 (a) Electron micrograph of the microstructure for the photodetector. (b)-(d) Energy dispersive X-ray (EDX) mapping of the element distribution: (b) Br, (c) Cs, (d) Bi.

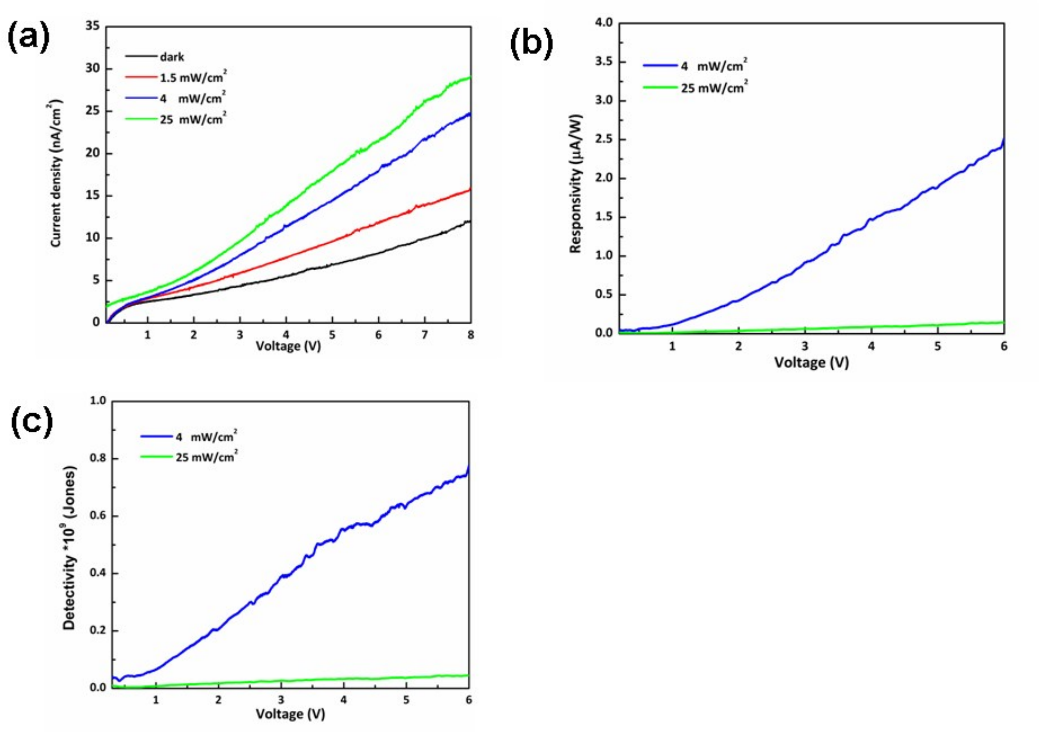

Fig. S7 (a) I-V characteristics under different power density. (b) Photocurrent responses under various light densities at bias voltage of 0- 6 V. (c) Comparison of the detectivity at two different light densities.

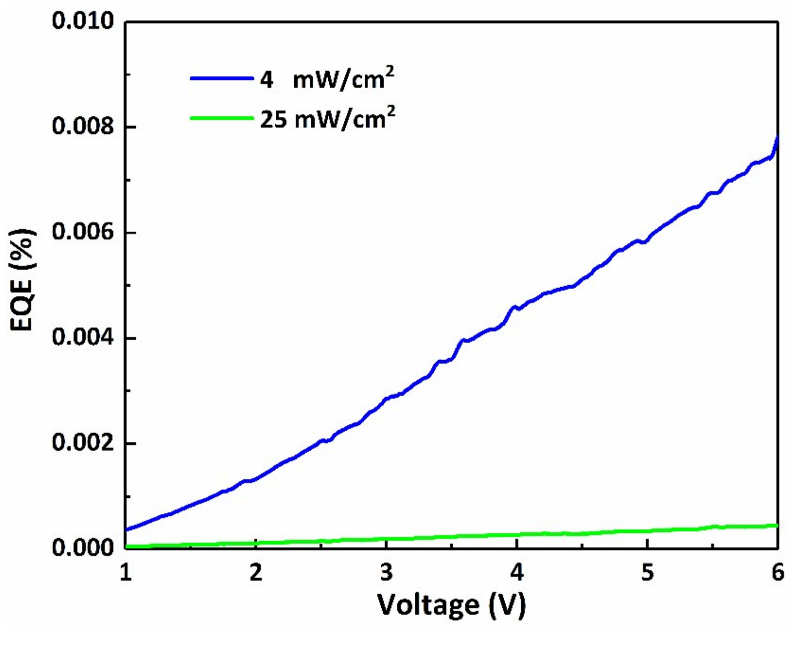

Fig. S8 EQE versus voltage under light illumiantion of 4 mW/cm^2 and 25 mW/cm^2.

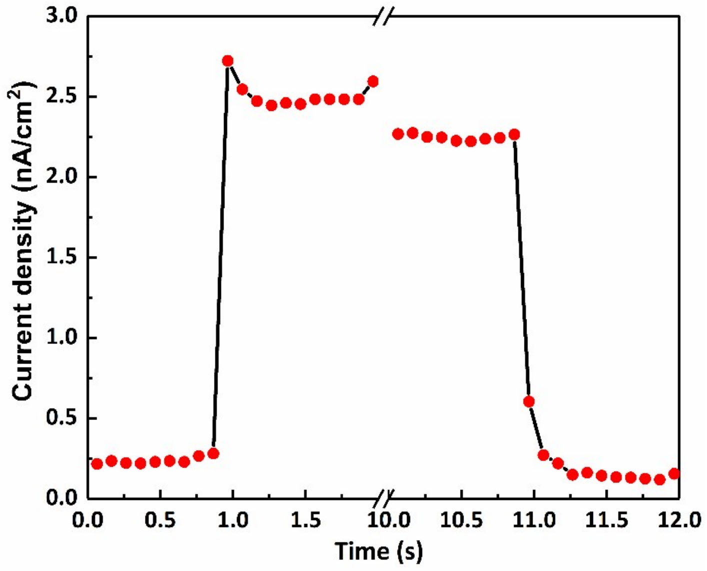

Fig. S9 The high-resolution I-t curve of Cs3BiBr$_6$ devices towards 400 nm illumination with a powder intensity of 25 mW/cm^2.

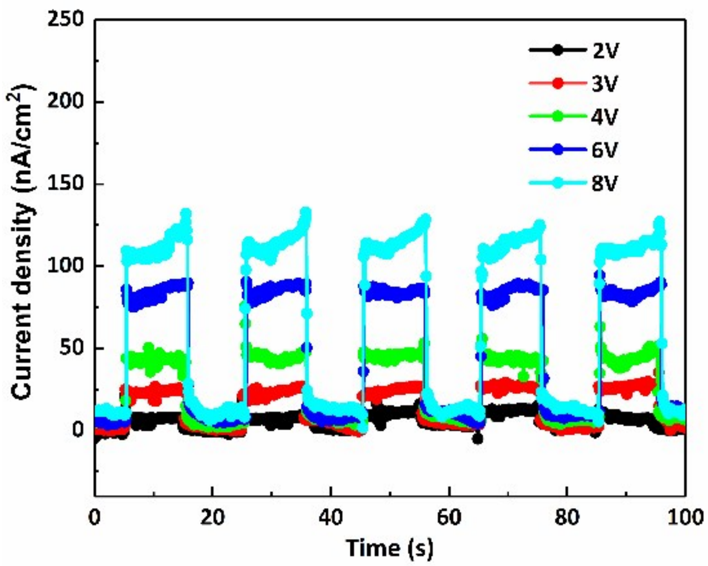

Fig. S10 Photoresponse of Cs_3BiBr_6 under white light illumination with power density of 350 mW/cm^2.

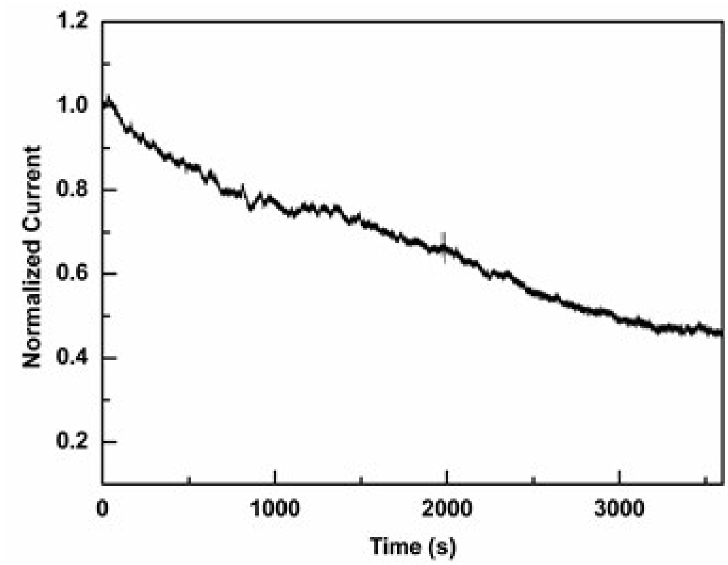

Fig. S11 The stability for the photodetector under light illumination.