$[Ba_4X][In_{19}S_{32}]$ (X = Cl, Br): two quaternary metal chalcohalides exhibiting remarkable photocurrent responses

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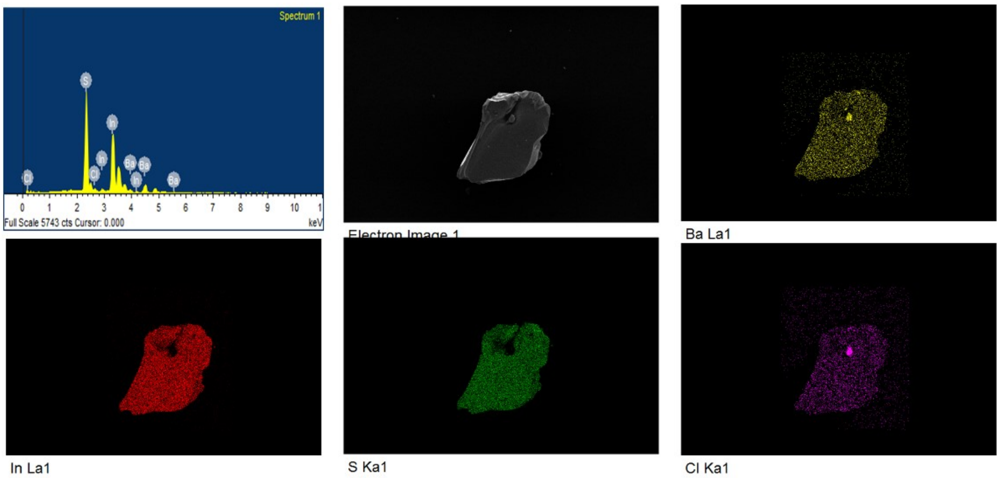

Fig. S1. The SEM pictures and EDS results of $[Ba_4Cl][In_{19}S_{32}]$.

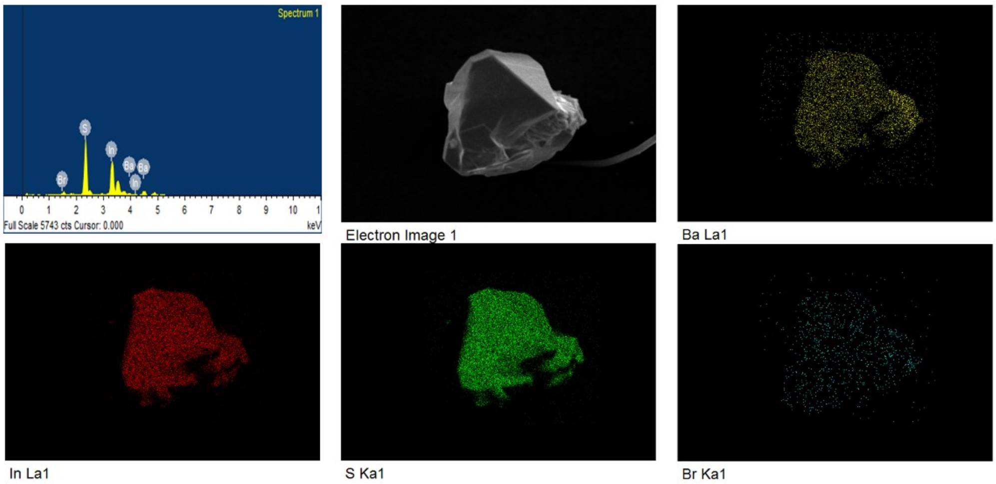

Fig. S2. The SEM pictures and EDS results of $[Ba_4Br][In_{19}S_{32}]$.

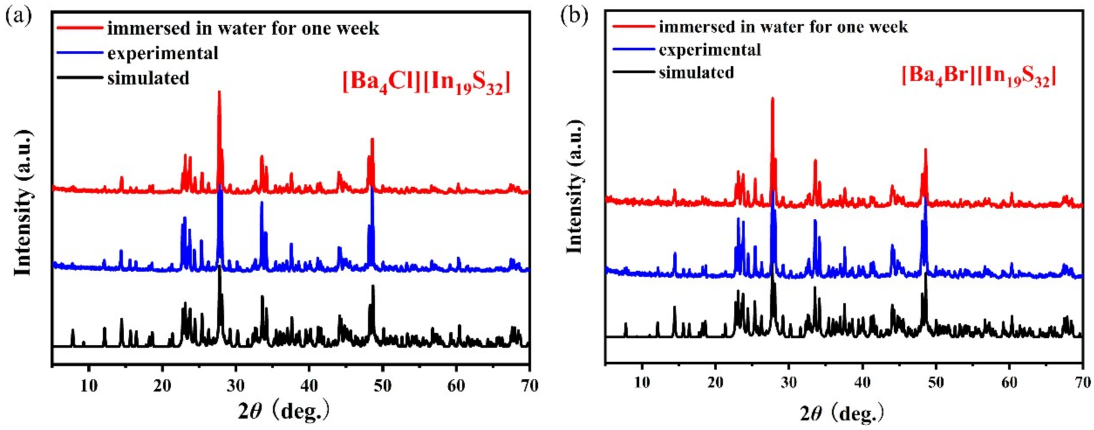

Fig. S3. Simulated (black), original synthesized (blue) and immersed in water for one week (red) PXRD patterns of $[Ba_4X][In_{19}S_{32}]$ (X = Cl, Br).

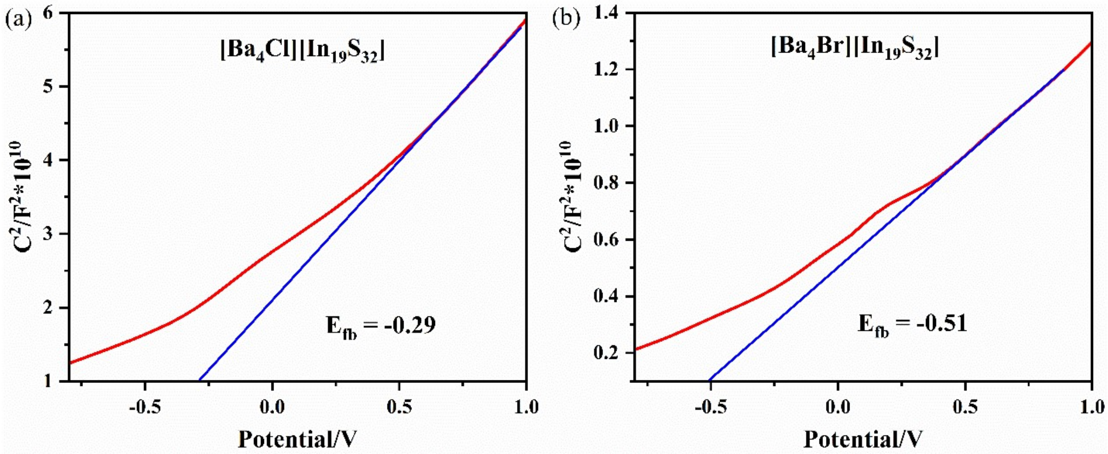

Fig. S4. Mott-Schottky plot of the as-prepared $[Ba_4X][In_{19}S_{32}]$ (X = Cl, Br) sample.

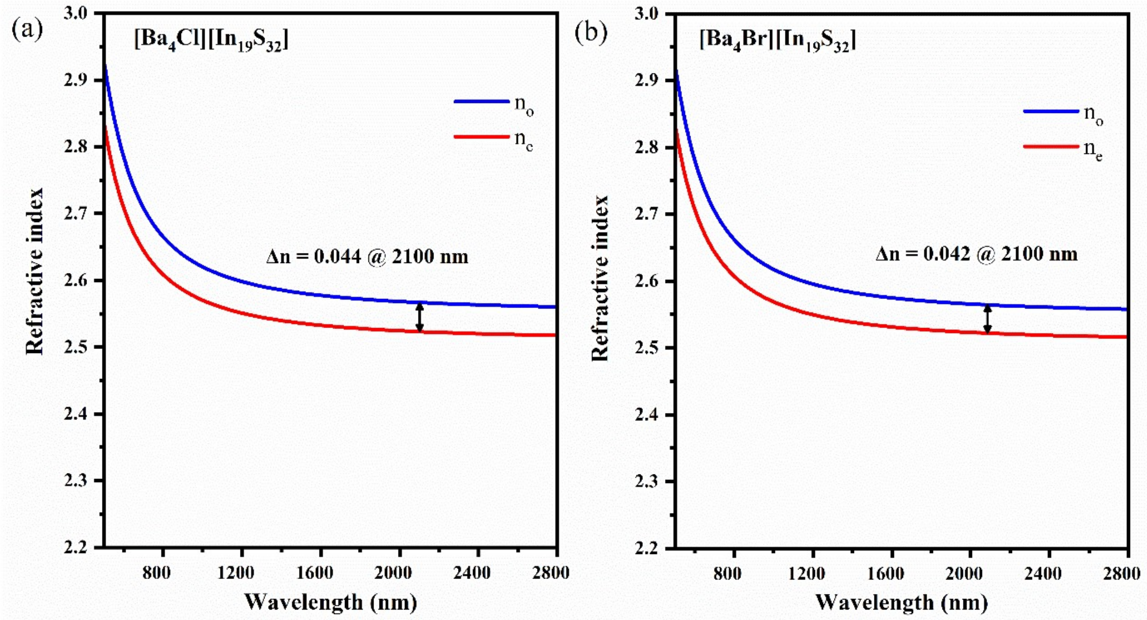

Fig. S5. The calculated birefringence of (a) $[Ba_4Cl][In_{19}S_{32}]$ and (b) $[Ba_4Br][In_{19}S_{32}]$.

Table S1 Atomic coordinates and equivalent isotropic displacement parameters for $[Ba_4Cl][In_{19}S_{32}]$.

Atom	Wyckoff position	x	y	z	U_{eq} (Å^2) [a]
Ba1	16h	0	0.63499(2)	0.27935(3)	0.02049(9)
In1	32i	0.15969(2)	0.66916(2)	0.49465(2)	0.01213(8)
In2	4b	0	0.75	0.625	0.0106(13)
In3	8c	0.25	0.75	0.25	0.01451(11)
In4	16f	0.15612(2)	0.5	0.5	0.01268(9)
In5	16g	0.16931(2)	0.41931(2)	0.875	0.01001(9)
S1	16h	0.07802(5)	0.75	0.46454(10)	0.0121(2)
S2	32i	0.08358(4)	0.58594(3)	0.50463(7)	0.01075(17)
S3	16h	0.23954(5)	0.75	0.48824(9)	0.0101(2)
S4	32i	0.16714(3)	0.50986(4)	0.74671(7)	0.01004(17)
S5	32i	0.1586(4)	0.32653(4)	0.75989(7)	0.01307(17)
Cl1	4a	0	0.75	0.125	0.0153(4)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S2 Atomic coordinates and equivalent isotropic displacement parameters for $[Ba_4Br][In_{19}S_{32}]$.

Atom	Wyckoff position	x	y	z	U_{eq} (Å^2) [a]
Ba1	16h	0.5	0.63128(2)	0.71854(2)	0.02263(8)
In1	32i	0.34055(2)	0.66911(2)	0.50579(2)	0.0133(6)
In2	4a	0.5	0.75	0.375	0.01119(12)
In3	8d	0.25	0.75	0.75	0.01534(10)
In4	16f	0.34323(2)	0.5	0.5	0.01383(8)
In5	16g	0.33057(2)	0.41943(2)	0.125	0.01109(7)
S1	16h	0.42166(5)	0.75	0.53405(9)	0.0129(2)
S2	32i	0.41592(3)	0.58568(3)	0.49488(6)	0.01176(15)
S3	16h	0.261(4)	0.75	0.51192(8)	0.0105(2)
S4	32i	0.33296(3)	0.50974(3)	0.25337(6)	0.01094(15)
S5	32i	0.4232(3)	0.40907(3)	0.00981(7)	0.01406(16)
Br1	4b	0.5	0.75	0.875	0.01638(18)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S3 Selected band distances (Å) and band angles (°) for $[Ba_4Cl][In_{19}S_{32}]$.

In1–$S4^{9}$	2.6691(8)	In4–S4	2.6096(7)
In1–S2	2.5521(8)	In4–$S4^{2}$	2.6686(8)
In1–$S2^{9}$	2.6327(8)	In4–$S4^{10}$	2.6686(8)
In1–S3	2.5700(8)	In4–S2	2.5432(8)
In1–S1	2.6174(8)	In4–$S2^{9}$	2.5431(8)
In1–$S5^{10}$	2.6721(8)	In5–S4	2.4506(8)
In2–S1	2.4384(10)	In5–$S4^{6}$	2.4506(8)
In2–$S1^{7}$	2.4384(10)	In5–S5	2.4326(8)
In2–$S1^{8}$	2.4384(10)	In5–$S5^{6}$	2.4326(8)
In2–$S1^{3}$	2.4384(10)	Ba1–Cl1	3.0632(3)
In3–S3	2.5104(10)	Ba1–$S2^{1}$	3.2229(8)
In3–$S3^{11}$	2.5104(10)	Ba1–S2	3.2229(8)
In3–$S5^{12}$	2.6973(8)	Ba1–$S3^{2}$	3.3169(11)
In3–$S5^{13}$	2.6973(8)	Ba1–$S1^{3}$	3.6943(8)
In3–$S5^{10}$	2.6973(8)	Ba1–S1	3.6944(8)
In3–$S5^{14}$	2.6973(8)	Ba1–$S5^{4}$	3.4578(8)
In4–$S4^{9}$	2.6097(7)	Ba1–$S5^{5}$	3.4578(8)
$S4^{10}$—In1—$S5^{9}$	93.84(2)	S2—In4—$S4^{9}$	98.38(3)
$S2^{10}$—In1—$S4^{10}$	85.60(2)	S2—In4—S4	88.70(2)
S2—In1—$S4^{10}$	85.36(3)	$S2^{9}$—In4—$S4^{9}$	88.70(2)
S2—In1—$S2^{10}$	88.11(3)	$S2^{9}$—In4—$S4^{10}$	174.76(2)
S2—In1—S3	177.64(3)	$S2^{9}$—In4—S2	99.69(4)
S2—In1—S1	92.53(3)	$S4^{6}$—In5—S4	109.57(4)
$S2^{10}$—In1—$S5^{9}$	178.22(3)	S5—In5—S4	116.48(3)
S2—In1—$S5^{9}$	93.54(3)	$S5^{6}$—In5—$S4^{6}$	116.48(3)

S3—In1—S4^{10}	92.41(3)	S5^{6}—In5—S4	109.79(3)
S3—In1—S2^{10}	90.95(3)	S5—In5—S4^{6}	109.78(3)
S3—In1—S1	89.76(3)	S5—In5—S5^{6}	94.29(4)
S3—In1—S5^{9}	87.39(3)	Ba1^{16}—Cl1—Ba1^{3}	106.223(5)
S1—In1—S4^{10}	174.51(3)	Ba1—Cl1—Ba1^{16}	106.224(5)
S1—In1—S2^{10}	99.41(3)	Ba1—Cl1—Ba1^{3}	116.182(11)
S1—In1—S5^{9}	81.22(3)	Ba1^{16}—Cl1—Ba1^{17}	116.182(11)
S1^{7}—In2—S1^{8}	92.69(5)	Ba1^{3}—Cl1—Ba1^{17}	106.223(5)
S1^{10}—In2—S1	92.69(5)	Ba1—Cl1—Ba1^{16}	106.224(5)
S1^{7}—In2—S1^{3}	118.46(3)	Cl1—Ba1—S2	132.823(15)
S1^{8}—In2—S1	118.46(3)	Cl1—Ba1—S2^{1}	132.824(15)
S1^{7}—In2—S1	118.46(3)	Cl1—Ba1—S3^{2}	140.621(19)
S1^{3}—In2—S1^{8}	118.46(3)	Cl1—Ba1—S1	71.365(14)
S3—In3—S3^{11}	180.0	Cl1—Ba1—S1^{3}	71.365(14)
S3^{11}—In3—S5^{12}	88.06(2)	Cl1—Ba1—S5^{4}	79.039(15)
S3^{11}—In3—S5^{9}	91.94(2)	Cl1—Ba1—S5^{5}	79.039(14)
S3—In3—S5^{13}	88.06(2)	S2—Ba1—S2^{1}	71.80(3)
S3^{11}—In3—S5^{14}	88.06(2)	S2^{1}—Ba1—S3^{2}	75.76(2)
S3—In3—S5^{12}	91.94(2)	S2—Ba1—S3^{2}	75.76(2)
S3—In3—S5^{9}	88.06(2)	S2^{1}—Ba1—S1^{3}	64.952(18)
S3^{11}—In3—S5^{13}	91.94(2)	S2—Ba1—S1	64.951(18)
S3—In3—S5^{14}	91.94(2)	S2—Ba1—S1^{3}	97.85(2)
S5^{9}—In3—S5^{14}	100.19(4)	S2^{1}—Ba1—S1	97.85(2)
S5^{14}—In3—S5^{13}	180.00(3)	S2^{1}—Ba1—S5^{4}	102.00(2)
S5^{9}—In3—S5^{13}	79.81(4)	S2^{1}—Ba1—S5^{5}	142.64(2)
S5^{12}—In3—S5^{14}	79.81(4)	S2—Ba1—S5^{5}	102.00(2)
S5^{12}—In3—S5^{13}	100.19(4)	S2—Ba1—S5^{4}	142.64(2)

$S5^{12}$—In3—$S5^{9}$	180.0	$S3^{2}$—Ba1—S1	140.019(17)
S4—In4—$S4^{9}$	169.04(4)	$S3^{2}$—Ba1—$S1^{3}$	140.019(17)
$S4^{10}$—In4—$S4^{2}$	89.21(3)	$S3^{2}$—Ba1—$S5^{4}$	67.113(19)
S4—In4—$S4^{10}$	81.91(3)	$S3^{2}$—Ba1—$S5^{5}$	67.113(19)
$S4^{9}$—In4—$S4^{2}$	81.91(3)	$S1^{3}$—Ba1—S1	57.05(3)
S4—In4—$S4^{2}$	90.28(2)	$S5^{4}$—Ba1—$S1^{3}$	113.05(2)
$S4^{9}$—In4—$S4^{10}$	90.28(2)	$S5^{4}$—Ba1—S1	150.40(2)
$S2^{9}$—In4—S4	98.38(3)	$S5^{5}$—Ba1—S1	113.05(2)
$S2^{9}$—In4—$S4^{2}$	85.55(2)	$S5^{5}$—Ba1—$S1^{3}$	150.40(2)
S2—In4—$S4^{10}$	85.55(2)	$S5^{4}$—Ba1—$S5^{5}$	60.05(3)
S2—In4—$S4^{2}$	174.75(2)		

Symmetry codes: ^{1}-X,+Y,+Z; ^{2}3/4-Y,1/4+X,-1/4+Z; ^{3}-X,3/2-Y,+Z; ^{4}1/4-Y,3/4-X,-3/4+Z; ^{5}-1/4+Y,3/4-X,-3/4+Z; ^{6}-1/4+Y,1/4+X,7/4-Z; ^{7}3/4-Y,3/4+X,5/4-Z; ^{8}-3/4+Y,3/4-X,5/4-Z; ^{9}+X,1-Y,1-Z; ^{10}3/4-Y,3/4-X,5/4-Z; ^{11}1/2-X,3/2-Y,1/2-Z; ^{12}1/2-X,1/2+Y,-1/2+Z; ^{13}+X,1/2+Y,1-Z; ^{14}1/2-X,1-Y,-1/2+Z; ^{15}-1/4+Y,3/4-X,1/4+Z; ^{16}-3/4+Y,3/4-X,1/4-Z; ^{17}3/4-Y,3/4+X,1/4-Z

Table S4 Selected band distances (Å) and band angles (°) for $[Ba_4Br][In_{19}S_{32}]$.

In1–S4^{9}	2.6783(7)	In4–S4^{4}	2.6089(7)
In1–S3	2.5718(7)	In4–S4	2.6090(7)
In1–S2^{9}	2.6349(7)	In4–S4^{9}	2.6675(8)
In1–S2	2.5505(7)	In4–S4^{1}	2.6675(8)
In1–S1	2.6129(8)	In4–S2^{4}	2.5467(8)
In1–S5^{10}	2.6683(7)	In4–S2	2.5468(8)
In2–S1^{6}	2.4372(10)	In5–S4	2.4509(7)
In2–S1^{7}	2.4372(10)	In5–S4^{5}	2.4509(7)
In2–S1^{8}	2.4372(10)	In5–S5^{5}	2.4339(8)
In2–S1	2.4372(10)	In5–S5	2.4338(8)
In3–S3^{11}	2.5118(9)	Ba1–Br1	3.1521(3)
In3–S3	2.5117(9)	Ba1–S3^{1}	3.2563(11)
In3–S5^{9}	2.6991(8)	Ba1–S2	3.1954(7)
In3–S5^{6}	2.6991(8)	Ba1–S2^{2}	3.1955(7)
In3–S5^{10}	2.6991(8)	Ba1–S5^{3}	3.4638(8)
In3–S5^{12}	2.6991(8)	Ba1–S5^{4}	3.4638(8)
S3—In1—S4^{9}	92.36(2)	S2^{3}—In4—S4	98.23(2)
S3—In1—S2^{9}	90.87(3)	S2—In4—S4^{1}	175.11(2)
S3—In1—S1	89.43(2)	S2—In4—S4^{9}	85.48(2)
S3—In1—S5^{10}	87.28(3)	S23—In4—S4^{3}	88.41(2)
S2—In1—S4^{9}	85.18(2)	S2—In4—S4	88.41(2)
S2^{9}—In1—S4^{9}	85.16(2)	S5^{12}—In3—S5^{6}	99.70(3)
S2—In1—S3	177.33(3)	S5^{9}—In3—S5^{10}	99.70(3)
S2—In1—S2^{9}	87.87(2)	S5^{12}—In3—S5^{10}	80.30(3)
S2—In1—S1	93.10(2)	S5^{10}—In3—S5^{6}	180.0
S2^{9}—In1—S5^{10}	177.75(2)	S2^{3}—In4—S4^{1}	85.48(2)

S2—In1—S5^{10}	93.93(2)	S2^{3}—In4—S4^{9}	175.11(2)
S1—In1—S4^{9}	175.15(3)	S2^{3}—In4—S2	99.40(3)
S1—In1—S2^{9}	99.33(3)	S4—In5—S4^{5}	109.83(4)
S1—In1—S5^{10}	81.94(3)	S5^{5}—In5—S4	116.41(2)
S5^{10}—In1—S4^{9}	93.64(2)	S5—In5—S4	109.55(2)
S1^{6}—In2—S1	117.99(3)	S5—In5—S4^{5}	116.41(2)
S1^{7}—In2—S1^{8}	117.99(3)	S5^{5}—In5—S4^{5}	109.55(2)
S1^{7}—In2—S1	93.51(5)	S5—In5—S5^{5}	94.62(4)
S1^{8}—In2—S16	117.99(3)	Ba1—Br1—Ba1^{13}	105.756(5)
S1^{7}—In2—S1	117.99(3)	Ba1^{14}—Br1—Ba1^{13}	117.188(10)
S1^{7}—In2—S1^{6}	93.51(5)	Ba1—Br1—Ba1^{14}	105.756(5)
S3—In3—S3^{11}	180.00(5)	Ba1^{8}—Br1—Ba1^{13}	105.756(5)
S3^{11}—In3—S5^{9}	87.83(2)	Ba1^{14}—Br1—Ba1^{8}	105.756(5)
S3^{11}—In3—S5^{6}	87.83(2)	Ba1—Br1—Ba1^{8}	117.188(10)
S3—In3—S5^{9}	92.17(2)	Br1—Ba1—S31	140.554(18)
S3—In3—S5^{6}	92.17(2)	Br1—Ba1—S2	131.217(15)
S3—In3—S5^{12}	87.83(2)	Br1—Ba1—S2^{2}	131.217(15)
S3^{11}—In3—S5^{10}	92.17(2)	Br1—Ba1—S5^{3}	78.247(14)
S3^{11}—In3—S5^{12}	92.17(2)	Br1—Ba1—S5^{4}	78.247(14)
S3—In3—S5^{10}	87.83(2)	S31—Ba1—S5^{4}	67.879(19)
S5^{12}—In3—S5^{9}	180.0	S3^{1}—Ba1—S5^{3}	67.879(19)
S5^{9}—In3—S5^{6}	80.30(3)	S2^{2}—Ba1—S3^{1}	77.440(19)
S4^{3}—In4—S4	169.76(3)	S2—Ba1—S3^{1}	77.441(19)
S4^{3}—In4—S4^{9}	90.54(2)	S2—Ba1—S2^{2}	73.20(3)
S4^{3}—In4—S4^{1}	82.18(2)	S2—Ba1—S5^{3}	102.709(18)
S4^{1}—In4—S4^{9}	89.64(3)	S2^{2}—Ba1—S5^{3}	145.00(2)
S4—In4—S4^{9}	82.18(2)	S2—Ba1—S5^{4}	145.00(2)

S4—In4—S4[1]	90.54(2)	S2[2]—Ba1—S5[4]	102.708(18)
S2—In4—S4[3]	98.23(2)	S5[4]—Ba1—S5[3]	60.32(2)

Symmetry codes: [1]-1/4+Y,3/4-X,1/4+Z; [2]1-X,+Y,+Z; [3]+X,1-Y,1-Z; [4]1-X,1-Y,1-Z; [5]3/4-Y,3/4-X,1/4-Z; [6]-1/4+Y,5/4-X,3/4-Z; [7]5/4-Y,1/4+X,3/4-Z; [8]1-X,3/2-Y,+Z; [9]-1/4+Y,1/4+X,3/4-Z; [10]3/4-Y,1/4+X,3/4+Z; [11]1/2-X,3/2-Y,3/2-Z; [12]3/4-Y,5/4-X,3/4+Z; [13]-1/4+Y,5/4-X,7/4-Z; [14]5/4-Y,1/4+X,7/4-Z

Table S5 Photocurrent responses of some crystalline compounds.

Compound	Photocurrent response	Bias voltage	Substrate
$Cs_3CuAs_4S_8$[1]	5 μA cm^{-2}	-	ITO
$Cs_3CuAs_4Se_8$[1]	5 μA cm^{-2}	-	ITO
$Rb_2Ba_3Cu_2Sb_2S_{10}$[2]	6 nA cm^{-2}	0.174 V	ITO
$SrCuSbS_3$[3]	0.54 μA cm^{-2}	1.0 V	FTO
$BaCuSbS_3$[4]	55 nA cm^{-2}	-	ITO
$Ba_5Bi_2Co_2S_{10}$[5]	4 mA cm^{-2}	1.0 V	-
$Rb_2CuSb_7S_{12}$[6]	10 μA cm^{-2}	0.18 V	ITO
$Pb_3P_2S_8$[7]	45 μA cm^{-2}	-	FTO
$Ba_3HgGa_2S_7$[8]	12.2 μA cm^{-2}	1.0 V	ITO
Lu5GaS9[9]	150 nA cm^{-2}	-	ITO
$Zn_4B_6O_{12}S$[10]	2.1 μA cm^{-2}	0.6 V	ITO
$[(Ba_{19}Cl_4)(Ga_6Si_{12}O_{42}S_8)]$[11]	150 nA cm^{-2}	-	ITO
$Sr_6Cd_2Sb_6S_{10}O_7$[12]	2 μA cm^{-2}	0.4 V	ITO
$RbIn_4S_6Cl$[13]	28.75 nA cm^{-2}	5 V	-
$CsIn_4S_6Cl$[13]	55.12 nA cm^{-2}	5 V	-
$Pb_5Sn_3S_{10}Cl_2$[13]	19.58 mA cm^{-2}	5 V	-
$Pb_5Sn_3Se_{10}Cl_2$[13]	36.12 μA cm^{-2}	5 V	

"-" indicates no available data.

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