Supporting Information

AIn_4S_6Cl (A = Rb, Cs) and $Pb_5Sn_3Q_{10}Cl_2$ (Q = S, Se): Quaternary Chalcohalides with Mixed Anionic Coordination Exhibit Photocurrent Responses

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CONTENTS

2. Tables

Table S1. Fractional atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$), formal oxidation states (FOS) and bond valence sum (BVS) of all atoms in **1**-**4**.

Table S2. Selected bond lengths ($Å^2$) of **1**-**4**.

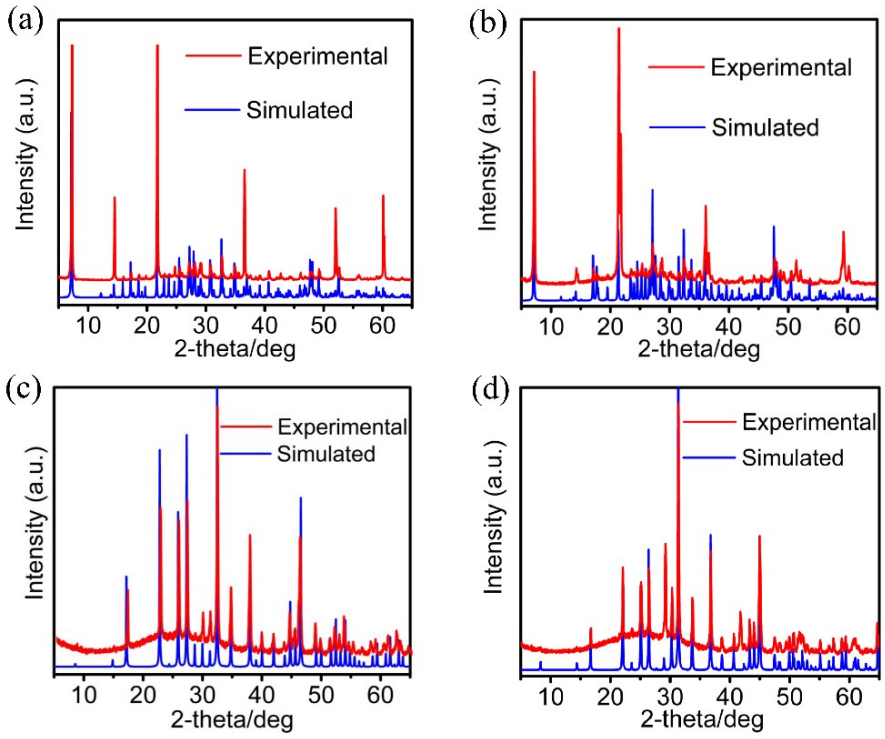

Figure S1. Powder XRD patterns of **1** (a), **2** (b), **3** (c) and **4** (d). Samples of **1** and **2** are flake-like crystals, and samples of **3** and **4** are needle-like crystals. Intensities of some peaks on the experimental patterns don't match those on the simulated ones because of the effect of preferred orientation.

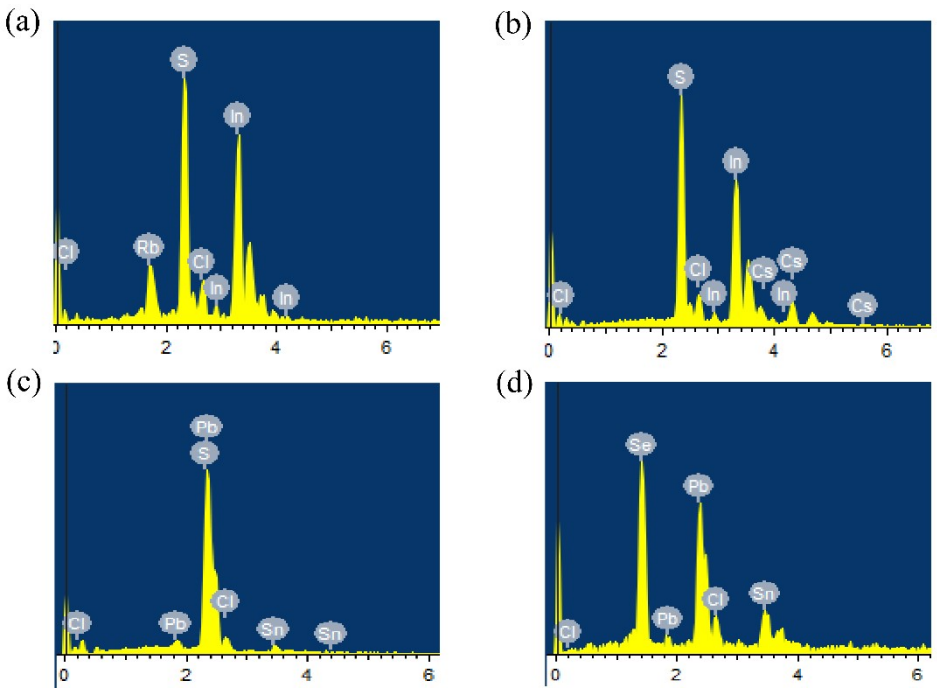

Figure S2. EDX spectra of **1** (a), **2** (b), **3** (c) and **4** (d).

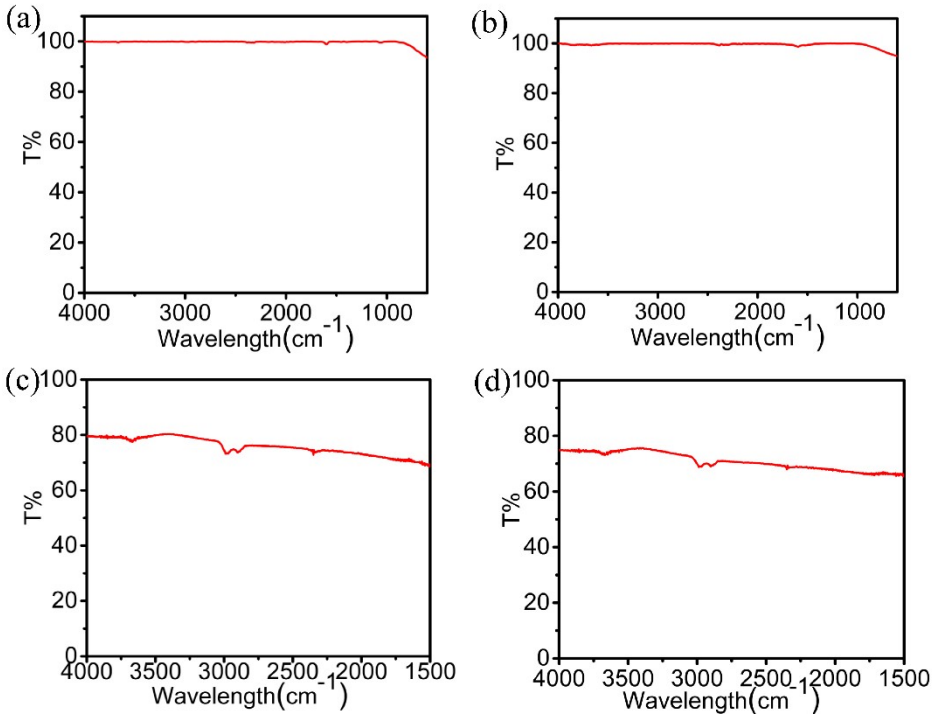

Figure S3. IR spectra of **1** (a), **2** (b), **3** (c) and **4** (d).

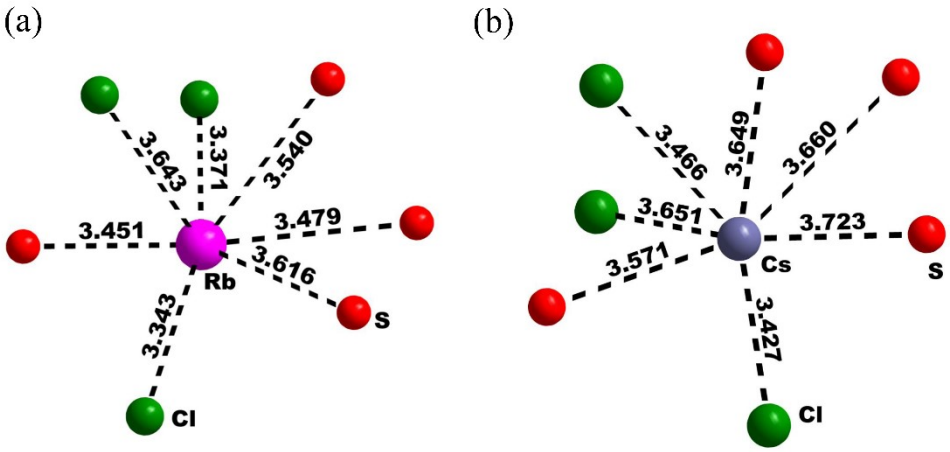

Figure S4. Coordination environments of Rb (a) and Cs (b) atoms in compounds **1** and **2** with distances (Å) near the ionic interactions (dotted lines).

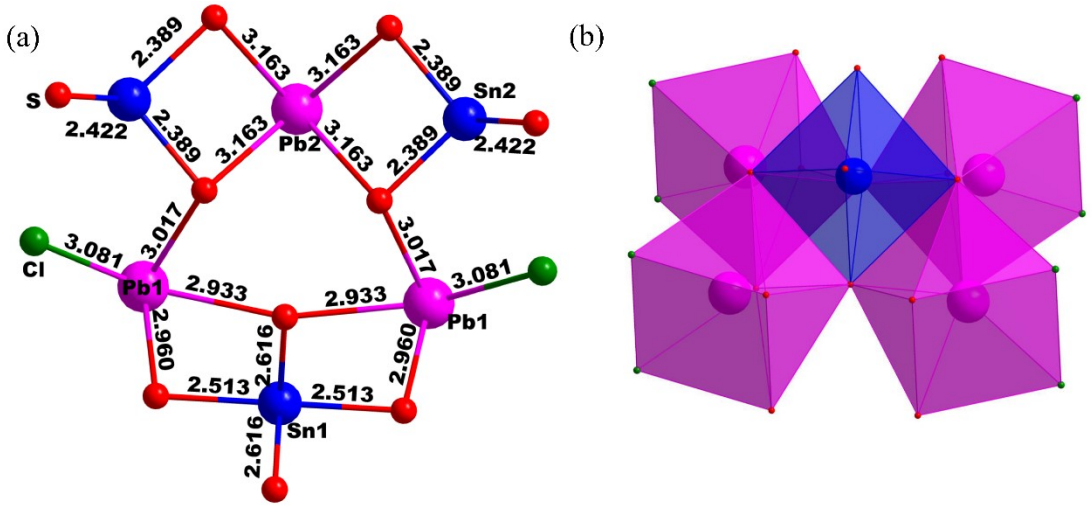

Figure S5. (a) Coordination environments of Sn and Pb atoms in compound **3** with bond lengths (Å) near the covalent bonds. (b) A $[Pb_4SnS_{16}Cl_8]^{28-}$ polyhedral unit.

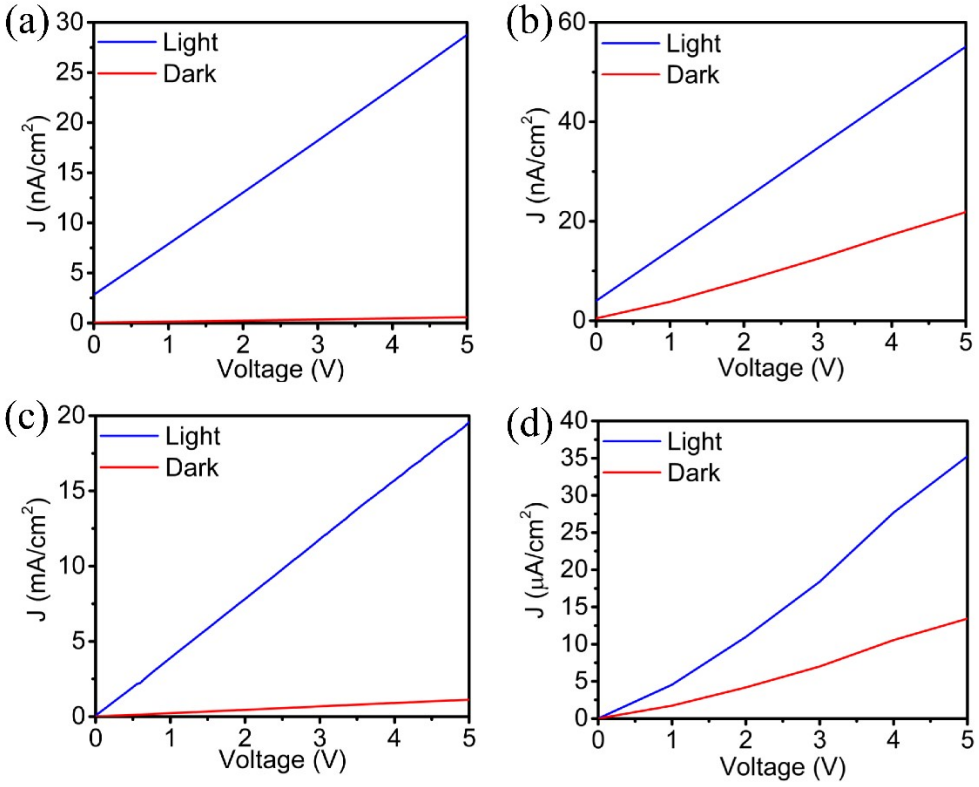

Figure S6. On-Off I-V curves of **1-4** with and without Xenon lamp irradiation.

Table S1. Fractional atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$), formal oxidation states (FOS) and bond valence sum (BVS) of all atoms in **1-4**.

1						
Atom	*x*	*y*	*z*	*U*(eq)	FOS	BVS
Rb1	4066.5(1)	-2616.2(6)	-1387.8(1)	45.3(5)	1	0.806
In1	905.8(1)	648.1(3)	6281.8(9)	16.3(3)	3	3.087
In2	-849.8(1)	-1358.0(3)	-1291.6(9)	17.4(3)	3	3.195
In3	5741.1(1)	660.8(3)	8762.3(1)	16.7(3)	3	3.067
In4	-4099.5(1)	672.8(3)	3777.7(1)	17.4(3)	3	3.044
S1	-4128(4)	-1193.0(1)	3771(3)	15.4(6)	-2	-1.984
S2	-2407(3)	21.4(1)	6164(3)	16.6(6)	-2	-1.891

S3	-4499(4)	-1268.0(1)	-1272(3)	16.7(6)	-2	-2.189
S4	2773(4)	-15.9(1)	8623(3)	15.0(6)	-2	-1.920
S5	991(4)	-1221.1(1)	1441(3)	17.1(6)	-2	-2.158
S6	930(4)	-1275.5(1)	-4035(3)	17.4(7)	-2	-2.150
Cl1	911(4)	2375.8(1)	11188(4)	35.9(9)	-1	-0.908

2

Atom	*x*	*y*	*z*	*U*(eq)	FOS	BVS
Cs1	2109(2)	4002 (2)	2413.0(5)	34.7(4)	1	0.957
In1	1449.3(1)	4018.6(1)	645.5(5)	15.2(3)	3	3.006
In2	6642.3(1)	4143.8(1)	1339.1(5)	16.4(3)	3	3.202
In3	8936.1(1)	9093.7(1)	656.3(5)	15.5(4)	3	3.050
In4	3919.3(1)	9258.8(1)	654.1(5)	15.5(4)	3	3.042
S1	1514(5)	844(6)	1181.4(1)	12.9(8)	-2	-1.971
S2	3886(5)	5976(6)	1206.0(1)	14.6(8)	-2	-2.184
S3	9353(6)	5943(6)	1259.1(1)	16.1(9)	-2	-1.871
S4	3635(5)	2232(6)	9988.9(1)	12.9(8)	-2	-1.903
S5	8828(5)	2586(6)	9979.1(1)	14.3(8)	-2	-2.127
S6	6596(5)	513(6)	1242.0(1)	12.7(8)	-2	-2.232
Cl1	6888(7)	4033(7)	2349.4(1)	28.8(1)	-1	-0.970

3

Atom	*x*	*y*	*z*	*U*(eq)	FOS	BVS
Pb1	3593.9(3)	6842.8(5)	5000	20.3(3)	2	2.095
Pb2	0	5000	5000	58.6(6)	2	1.810
S1	2350(3)	5000	5000	15.6(2)	-2	-1.881
S2	1219(3)	0	0	11.4(1)	-2	-2.094
S3	9138(2)	6467(3)	0	17.2(9)	-2	-2.087
S4	0	1466(4)	5000	11.8(1)	-2	-1.830

Cl1	2500	7500	0	18.7(2)	-1	-0.903
Sn1	0	0	0	13.5(5)	4	3.696
Sn2	8348 (8)	5000	0	15.6(4)	4	3.939

4

Atom	*x*	*y*	*z*	*U*(eq)	FOS	BVS
Pb1	3558.9(3)	1853.0(5)	0	22.7(4)	2	2.071
Pb2	0	0	10000	61.7(7)	2	1.637
Sn1	5000	0	5000	11.4(5)	4	3.593
Sn2	1650.3(7)	0	5000	11.8(4)	4	3.856
Se1	5000	1503.2(6)	0	10.0(5)	-2	-1.797
Se2	2391.4(9)	0	0	12.1(5)	-2	-1.823
Se3	4152.5(8)	3496.7(2)	5000	14.0(4)	-2	-2.045
Se4	3743.5(1)	0	5000	9.8(5)	-2	-2.102
Cl1	2500	2500	5000	17.4(1)	-1	-0.802

Table S2. Selected bond lengths (Å) of **1**-**4**.

1

bond	length/Å	bond	length/Å
In1–S1	2.515(3)	In3–S3	2.562(3)
In1–S5	2.566(3)	In3–S5	2.566(3)
In1–S6	2.593(3)	In3–S4	2.573(3)
In1–S2	2.677(3)	In3–S4	2.717(3)
In1–S2	2.679(3)	In3–S2	2.812(3)
In1–S4	2.703(3)	In4–S1	2.551(3)
In2–S6	2.408(3)	In4–S3	2.567(3)

In2–S5	2.418(3)	In4–S6	2.571(3)
In2–S3	2.420(3)	In4–S4	2.594(3)
In2–Cl1	2.506(3)	In4–S2	2.657(3)
In3–S1	2.552(3)	In4–S2	2.871(3)

2

Bond	Length/Å	Bond	Length/Å
In1–S1	2.531(4)	In3–S5	2.574(4)
In1–S2	2.561(4)	In3–S4	2.586(4)
In1–S3	2.612(4)	In3–S3	2.583(4)
In1–S6	2.683(4)	In3–S6	2.665(4)
In1–S3	2.706(4)	In3–S6	2.868(4)
In1–S4	2.723(4)	In4–S5	2.552(4)
In2–S3	2.405(4)	In4–S1	2.567(4)
In2–S2	2.423(4)	In4–S4	2.579(4)
In2–S5	2.422(4)	In4–S2	2.581(4)
In2–Cl1	2.519(5)	In4–S4	2.740(4)
In3–S1	2.550(4)	In4–S6	2.800(4)

3

Bond	Length/Å	Bond	Length/Å
Pb1–S2	2.9600	Sn1–S2	2.5126
Pb1–S3	3.0180	Sn1–S4	2.6163
Pb1–S4	2.9329	Sn2–S1	2.4224
Pb1–Cl1	3.0808	Sn2–S3	2.3894

4

Bond	Length/Å	Bond	Length/Å
Pb1–Se1	3.0914	Sn1–Se1	2.7383
Pb1–Se3	3.1240	Sn1–Se4	2.6692

Pb1–Se4	3.0716	Sn2–Se2	2.5584
Pb1–Cl1	3.1562	Sn2–Se3	2.5178