Supporting Information

Modulated Luminescence of Zero-Dimensional Bimetallic All-Inorganic Halide Clusters

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Experimental Section

Materials. Rubidium chloride (RbCl, Sigma-Aldrich, 99.8%), indium(III) chloride ($InCl_3$, Alfa Aesar, 99.99%), terbium(III) chloride ($TbCl_3$, Sigma-Aldrich, 99.99%), copper(I) chloride (CuCl, Sigma-Aldrich, 99.99%) were used as received without further purification.

Synthesis of $Rb_8CuIn_3Cl_{18}$ SCs. The SCs were grown by vacuum solid-phase reaction method. The specific steps are listed as follows. In a glove box filled with argon, RbCl, CuCl, and $InCl_3$ were weighed in an 8:1:3 mole ratio and ground in a mortar. The ground precursor powder was loaded into a quartz tube with a diameter of 9-mm, vacuumed to below 100 mtorr, and sealed with H_2/O_2 gas torch to form a quartz ampoule. The ampoule was loaded into Al_2O_3 ceramic tubes and annealed in a programmed muffle furnace. Pre-crystallization was carried out by heating at 5 °C min^{-1} to 700 °C, maintaining for 1 day, and then cooling down to room temperature at a rate of 0.2 °C min^{-1}. Re-crystallization was carried out by heating at 5 °C min^{-1} to 400 °C, maintaining for 5 days, and then cooling down to room temperature at 0.1 °C min^{-1}, and finally pure phase $Rb_8CuIn_3Cl_{18}$ SCs can be obtained.

Synthesis of $Rb_8CuTb_3Cl_{18}$ SCs. The SCs were grown by vacuum solid-phase reaction method. The specific steps were similar to $Rb_8CuIn_3Cl_{18}$. RbCl, CuCl, and $TbCl_3$ were weighed in an 8:1:3 mole ratio. Crystallization was carried out at 750 °C.

Characterizations. PXRD patterns were collected with an X-ray diffractometer (Rigaku Ultima IV) using Cu K_α radiation (λ = 0.15406 nm). The EDS elemental mapping was obtained by a field-emission scanning electron microscopy (ZEISS Gemini 300). SCXRD data were collected by a Bruker D8 venture diffractometer with graphite monochromated

Mo K_α radiation (λ = 0.71073 Å). Absorption spectra were obtained using a UV-Vis-NIR spectrophotometer (Shimadzu UV3600) equipped with an integrating sphere. PL spectra were collected using an Edinburgh FLS980 spectrofluorometer.

Theoretical Methods. The calculations were carried out in the Vienna ab initio simulation package (VASP) using DFT.[1] In this work, the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) functional was used to describe the electron exchange and correlation.[2] The projector augmented wave (PAW) potentials were used and the energy cut-off of the plane-wave basis set was 500 eV.[3] To sample the Brillouin zone, a Gamma-centered *k*-point mesh with densities of 0.2 $Å^{-1}$ was used according to the Monkhorst-Pack scheme.[4] The crystal structures were fully relaxed with the criteria for the convergence of the Hellmann-Feynman forces on each atom which was < 0.02 eV $Å^{-1}$. The energy convergence threshold was 1.0×10^{-6} eV.

The formation energy (ΔH) of $Rb_8CuB(III)_3Cl_{18}$ was calculated according to the synthesis route, and the relationship between B(III) ion and structure formation energy was explored (**Fig. 2**). The radii of the B(III) cations used in the calculation are 0.99 Å (Pr^{3+}), 0.923 Å (Tb^{3+}), 0.901 Å (Ho^{3+}), 0.9 Å (Y^{3+}), 0.89 Å (Er^{3+}), 0.861 Å (Lu^{3+}), 0.8 Å (In^{3+}), 0.745 Å (Sc^{3+}) and 0.67 Å (Ti^{3+}). The formation pathways and corresponding ΔH (unit: eV) are as follows:

Rb_3InCl_6: $3RbCl + InCl_3 \rightarrow Rb_3InCl_6$ $\Delta H = -1.0$ eV (1)

$Rb_8CuPr_3Cl_{18}$: $8RbCl + CuCl + 3PrCl_3 \rightarrow Rb_8CuPr_3Cl_{18}$ $\Delta H = -3.38$ eV (2)

$Rb_8CuTb_3Cl_{18}$: $8RbCl + CuCl + 3TbCl_3 \rightarrow Rb_8CuTb_3Cl_{18}$ $\Delta H = -5.12$ eV (3)

$Rb_8CuHo_3Cl_{18}$: $8RbCl + CuCl + 3HoCl_3 \rightarrow Rb_8CuHo_3Cl_{18}$ $\Delta H = -6.08$ eV (4)

$Rb_8CuY_3Cl_{18}$: $8RbCl + CuCl + 3YCl_3 \rightarrow Rb_8CuY_3Cl_{18}$ $\Delta H = -6.11$ eV (5)

$Rb_8CuEr_3Cl_{18}$: $8RbCl + CuCl + 3ErCl_3 \rightarrow Rb_8CuEr_3Cl_{18}$ $\Delta H = -6.18$ eV (6)

$Rb_8CuLu_3Cl_{18}$: $8RbCl + CuCl + 3LuCl_3 \rightarrow Rb_8CuLu_3Cl_{18}$ $\Delta H = -6.20$ eV (7)

$Rb_8CuIn_3Cl_{18}$: $8RbCl + CuCl + 3InCl_3 \rightarrow Rb_8CuIn_3Cl_{18}$ $\Delta H = -5.34$ eV (8)

$Rb_8CuSc_3Cl_{18}$: $8RbCl + CuCl + 3ScCl_3 \rightarrow Rb_8CuSc_3Cl_{18}$ $\Delta H = -4.48$ eV (9)

$Rb_8CuTi_3Cl_{18}$: $8RbCl + CuCl + 3TiCl_3 \rightarrow Rb_8CuTi_3Cl_{18}$ $\Delta H = -2.03$ eV (10)

Table S1 Crystallography and refinement details.

Chemical Formula	**$Rb_8CuIn_3Cl_{18}$**	**$Rb_8CuTb_3Cl_{18}$**
Formula weight	1623.52	7448.64
Temperature/K	100.15	296.15
Crystal system	trigonal	trigonal
Space group	*R/3c*	*R/3c*
a/Å	12.6551(19)	13.0330(5)
b/Å	12.6551(19)	13.0330(5)
c/Å	75.1540(12)	76.4930(5)
α/°	90	90
β/°	90	90
γ/°	120	120
Volume/Å^3	10423(4)	11252.3(11)
Z	3	3
ρ_{calc} g/cm^3	3.307	3.298
μ/mm^{-1}	15.090	17.744
F(000)	9336	9912
Crystal size/mm	0.124 × 0.119 × 0.106	0.080 × 0.080× 0.050
Radiation/Å	MoK_α (λ = 0.71073)	MoK_α (λ = 0.71073)
2θ range for data	4.302 to 50.044	5.584 to 50.050
Index ranges	−10 ≤ h ≤ 15,	−15 ≤ h ≤ 15, −13 ≤ k
Reflections collected	10702	29355
Independent reflections	2048	2224
Data/restraints/parameters	2048/0/92	2224/0/92
Goodness-of-fit on F^2	1.035	1.118
Final R indexes [I>=2σ	R_1 = 0.0482,	R_1 = 0.0675,
Final R indexes [all data]	R1 = 0.0836	R_1 = 0.0831,
Largest diff. peak/hole/e Å^{-3}	2.287/−1.692	4.330/−2.240

Table S2 Bond lengths (Å) for $Rb_8CuIn_3Cl_{18}$.

In1	Rb1	4.015(2)	In3	Cl4	2.456(3)	Rb2	Cl4^{1}	3.488(3)
In1	Rb2^{1}	4.388(13)	In3	Cl5	2.519(3)	Rb2	Cl6^{13}	3.761(3)
In1	Rb2^{2}	4.387(13)	In3	Cl5^{10}	2.519(3)	Rb3	Rb4	4.445(13)
In1	Rb2	4.393(13)	In3	Cl6^{10}	2.598(3)	Rb3	Cu1^{14}	3.890(14)
In1	Rb2^{3}	4.392(13)	In3	Cl6	2.598(3)	Rb3	Cl1^{2}	3.256(3)
In1	Rb2^{4}	4.388(13)	Rb1	Rb3^{2}	4.468(13)	Rb3	Cl2	3.155(3)
In1	Cl1	2.528(3)	Rb1	Rb4^{11}	4.241(2)	Rb3	Cl3	3.378(3)
In1	Cl1^{3}	2.528(3)	Rb1	Cl1	3.276(3)	Rb3	Cl4	3.228(3)
In1	Cl1^{5}	2.528(3)	Rb1	Cl1^{5}	3.276(3)	Rb3	Cl5^{15}	3.320(3)
In1	Cl2	2.481(3)	Rb1	Cl1^{3}	3.276(3)	Rb3	Cl5^{7}	3.294(3)
In1	Cl2^{5}	2.481(3)	Rb1	Cl4^{1}	3.726(3)	Rb3	Cl6^{15}	3.356(3)
In1	Cl2^{3}	2.481(3)	Rb1	Cl4^{2}	3.726(3)	Rb3	Cl6^{16}	3.361(3)
In2	Rb2^{1}	4.405 (13)	Rb1	Cl4^{4}	3.726(3)	Rb4	Cl3^{7}	3.336(3)
In2	Rb2^{6}	4.405 (12)	Rb1	Cl5^{11}	3.312(3)	Rb4	Cl3^{9}	3.336(3)
In2	Rb2^{7}	4.405 (12)	Rb1	Cl5^{12}	3.313(3)	Rb4	Cl3	3.336(3)
In2	Rb2^{8}	4.405 (12)	Rb1	Cl5^{13}	3.312(3)	Rb4	Cl4	3.708(3)
In2	Rb4^{6}	4.096(18)	Rb2	Cl1^{2}	3.566(3)	Rb4	Cl4^{7}	3.708(3)
In2	Rb4	4.096(18)	Rb2	Cl1	3.487(3)	Rb4	Cl4^{9}	3.708(3)
In2	Cl3^{8}	2.518(3)	Rb2	Cl1^{3}	3.949(3)	Rb4	Cl5^{7}	3.358(3)
In2	Cl3^{1}	2.518(3)	Rb2	Cl2	3.302(3)	Rb4	Cl5^{9}	3.358(3)
In2	Cl3^{9}	2.518(3)	Rb2	Cl2^{2}	3.756(3)	Rb4	Cl5	3.358(3)
In2	Cl3^{6}	2.518(3)	Rb2	Cl2^{8}	3.447(3)	Cu1	Cl6^{17}	2.261(3)
In2	Cl3^{7}	2.518(3)	Rb2	Cl3^{1}	3.789(3)	Cu1	Cl6^{18}	2.261(3)
In2	Cl3	2.518(3)	Rb2	Cl3^{8}	3.557(3)	Cu1	Cl6	2.261(3)
In3	Cl4^{10}	2.456(3)	Rb2	Cl3	3.467(3)			

^{1}1/3+Y, 2/3−X+Y, 2/3−Z; ^{2}4/3−X, 5/3−Y,2/3−Z; ^{3}2-Y, 1+X−Y,+Z; ^{4}4/3−Y+X, 2/3+X, 2/3−Z; ^{5}1+Y−X, 2−X,+Z; ^{6}4/3−X, 2/3−Y, 2/3−Z; ^{7}1+Y−X, 1−X,+Z; ^{8}1/3−Y+X, −1/3+X, 2/3−Z; ^{9}1−Y, +X−Y, +Z; ^{10}+Y, +X, 1/2−Z; ^{11}4/3−Y,5 /3−X, 1/6+Z; ^{12}4/3+Y−X, 2/3+Y, 1/6+Z; ^{13}1/3+X, 2/3+X−Y, 1/6+Z; ^{14}1+Y, 1+X, 1/2−Z; ^{15}1−X, 1−X+Y, 1/2−Z; ^{16}1−Y+X, 1−Y, 1/2−Z; ^{17}−Y, +X−Y, +Z; ^{18}+Y−X, −X, +Z

Table S3 Cu−Cl bond lengths in typical Cu(I)-based halides.

Formula	Average Cu−Cl distance (Å)	Dimension	Coordination number	Ref.
Rb_2CuCl_3	2.394	1D	4	[5]
$Rb_4Cu_5Cl_9$	2.365	1D	4	[6]
$CsCu_2Cl_3$	2.389	1D	4	[7]
$Cs_3Cu_2Cl_5$	2.354	0D	3, 4	[8]
$Rb_8CuSc_3Cl_{18}$	2.254	0D	3	[9]
$Rb_8CuY_3Cl_{18}$	2.254	0D	3	[9]

Table S4 Bond lengths (Å) for $Rb_8CuTb_3Cl_{18}$.

Tb2	Rb4[1]	4.206(3)	Tb3	Cl5	2.663(4)	Rb4	Cl4[3]	3.807(6)
Tb2	Rb4	4.205(3)	Tb3	Cl6[9]	2.730(5)	Rb4	Cl4[2]	3.807(6)
Tb2	Rb2[2]	4.512(2)	Tb3	Cl6	2.731(5)	Rb1	Cl5[13]	3.346(5)
Tb2	Rb2[3]	4.512(2)	Tb3	Cl4[9]	2.586(5)	Rb1	Cl5[14]	3.346(5)
Tb2	Rb2	4.512(2)	Tb3	Cl4	2.586(5)	Rb1	Cl5[15]	3.346(5)
Tb2	Rb2[4]	4.512(2)	Rb3	Rb4	4.562(18)	Rb1	Cl4[16]	3.835(6)
Tb2	Cl3[1]	2.642(4)	Rb3	Rb1[7]	4.591(18)	Rb1	Cl4[4]	3.835(6)
Tb2	Cl3[4]	2.642(4)	Rb3	Rb2[4]	4.892(3)	Rb1	Cl4[7]	3.835(6)
Tb2	Cl3[2]	2.642(4)	Rb3	Cu1[10]	3.987(2)	Rb1	Cl1[6]	3.342(6)
Tb2	Cl3[5]	2.642(4)	Rb3	Cl5[2]	3.357(5)	Rb1	Cl1[8]	3.342(6)
Tb2	Cl3	2.642(4)	Rb3	Cl5[10]	3.393(5)	Rb1	Cl1	3.342(6)
Tb2	Cl3[3]	2.642(4)	Rb3	Cl3	3.370(5)	Rb2	Cl3	3.564(5)
Tb1	Rb1	4.123(3)	Rb3	Cl6[11]	3.480(5)	Rb2	Cl3[4]	3.954(6)
Tb1	Rb2[6]	4.510(2)	Rb3	Cl6[10]	3.460(5)	Rb2	Cl3[5]	3.586(6)
Tb1	Rb2[4]	4.539(2)	Rb3	Cl4	3.269(5)	Rb2	Cl6[15]	3.846(6)
Tb1	Rb2	4.510(2)	Rb3	Cl1[7]	3.256(5)	Rb2	Cl4[4]	3.492(6)
Tb1	Rb2[7]	4.539(2)	Rb3	Cl2	3.191(5)	Rb2	Cl1[7]	3.721(6)
Tb1	Rb2[7]	4.539(2)	Rb4	Rb1[12]	4.240(4)	Rb2	Cl1	3.476(7)
Tb1	Cl1[8]	2.660(5)	Rb4	Cl5[3]	3.392(5)	Rb2	Cl2[7]	3.950(7)
Tb1	Cl1[6]	2.660(5)	Rb4	Cl5	3.391(5)	Rb2	Cl2[5]	3.517(7)
Tb1	Cl1	2.660(5)	Rb4	Cl5[2]	3.392(5)	Rb2	Cl2	3.360(6)
Tb1	Cl2[6]	2.600(5)	Rb4	Cl3	3.407(5)	Cu1	Cl6[17]	2.256(5)
Tb1	Cl2[8]	2.600(5)	Rb4	Cl3[2]	3.407(5)	Cu1	Cl6[18]	2.256(5)
Tb1	Cl2	2.600(5)	Rb4	Cl3[3]	3.407(5)	Cu1	Cl6	2.256(5)
Tb3	Cl5[9]	2.663(4)	Rb4	Cl4	3.807(6)			

[1]4/3−X, 2/3−Y, 2/3−Z; [2]1+Y−X, 1−X, +Z; [3]1−Y, +X−Y, +Z; [4]1/3+Y, 2/3−X+Y, 2/3−Z; [5]1/3−Y+X, −1/3+X, 2/3−Z; [6]2+Y−X, 2−X, +Z; [7]7/3−X, 5/3−Y, 2/3−Z; [8]2−Y, +X−Y, +Z; [9]2/3−Y+X, 4/3−Y, 5/6−Z; [10]2/3+Y, 1/3+X, 5/6−Z; [11]5/3−X, 1/3−X+Y, 5/6−Z; [12]4/3−Y, 5/3−X, 1/6+Z; [13]2/3+X, 1/3+X−Y, −1/6+Z; [14]5/3+Y−X, 1/3+Y, −1/6+Z; [15]5/3−Y, 4/3−X, −1/6+Z; [16]4/3−Y+X, −1/3+X, 2/3−Z; [17]1−Y, 1+X−Y, +Z; [18]+Y−X, 1−X, +Z

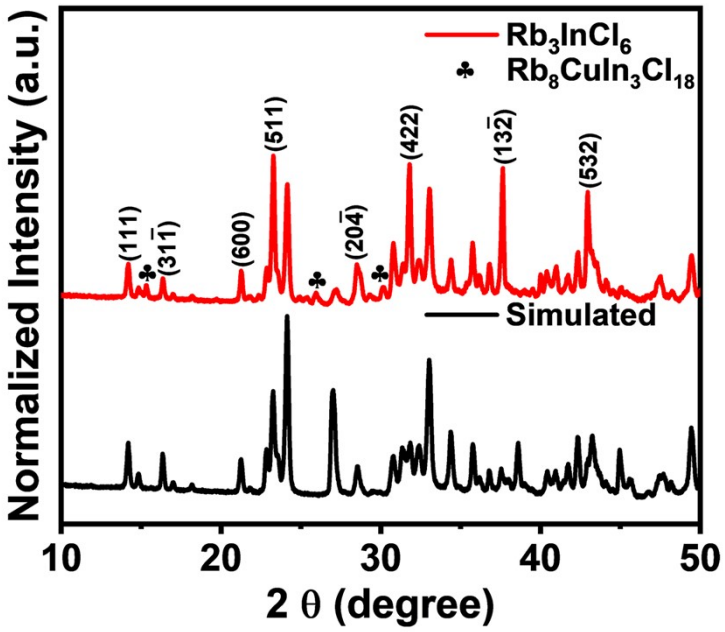

Fig. S1. The PXRD patterns of the product directly prepared at 700 °C.

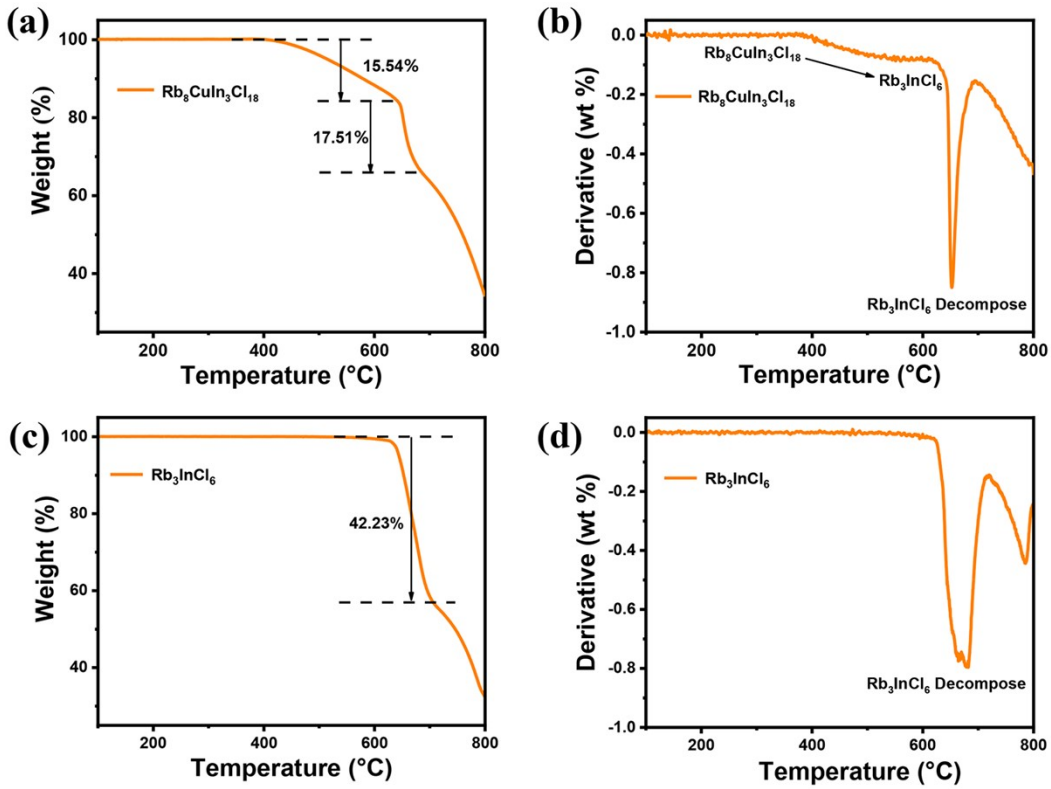

Fig. S2. TG and DTG curves of (a, b) $Rb_8CuIn_3Cl_{18}$ and (c, d) Rb_3InCl_6 SCs.

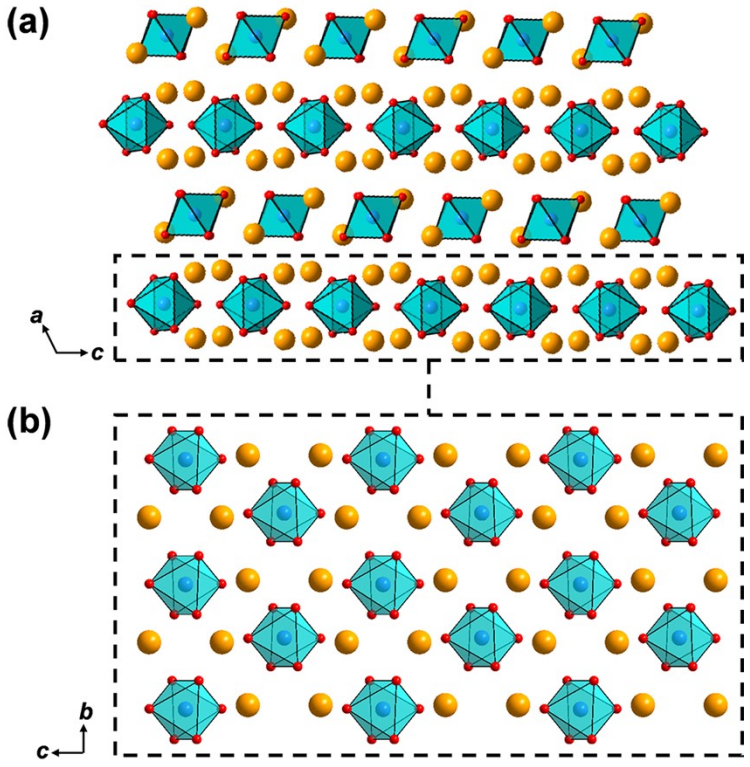

Fig. S3. (a) The crystal structure of Rb_3InCl_6 SCs, and (b) the isolated $[InCl_6]^{3-}$ octahedron layer.

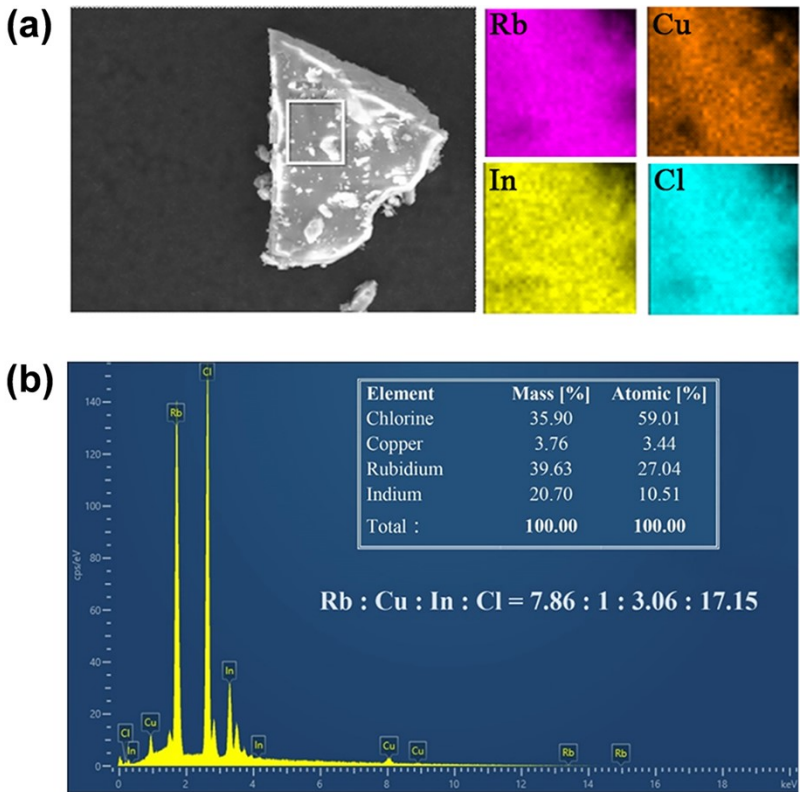

Fig. S4. (a) Elemental mapping images of a $Rb_8CuIn_3Cl_{18}$ SC for Rb, Cu, In, and Cl elements. (b) Atomic ratio of Rb/Cu/In/Cl.

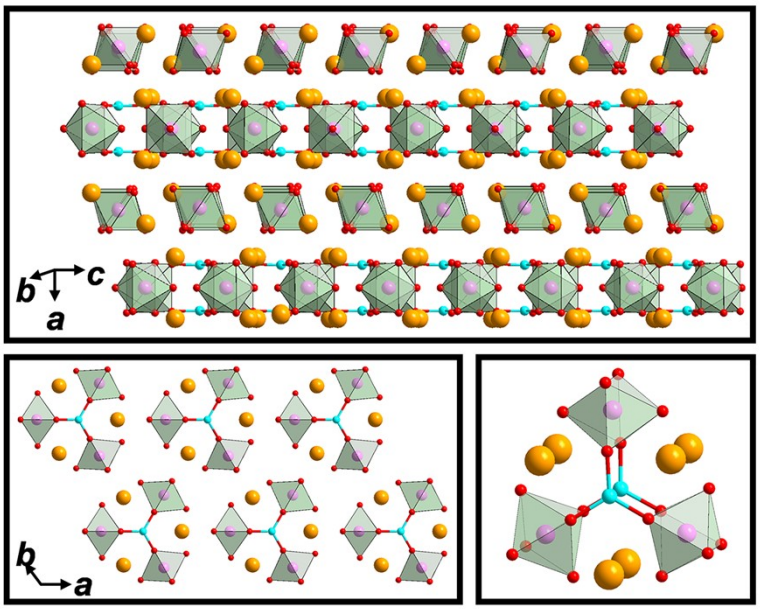

Fig. S5. View of structural characteristics of $Rb_8CuTb_3Cl_{18}$ SCs.

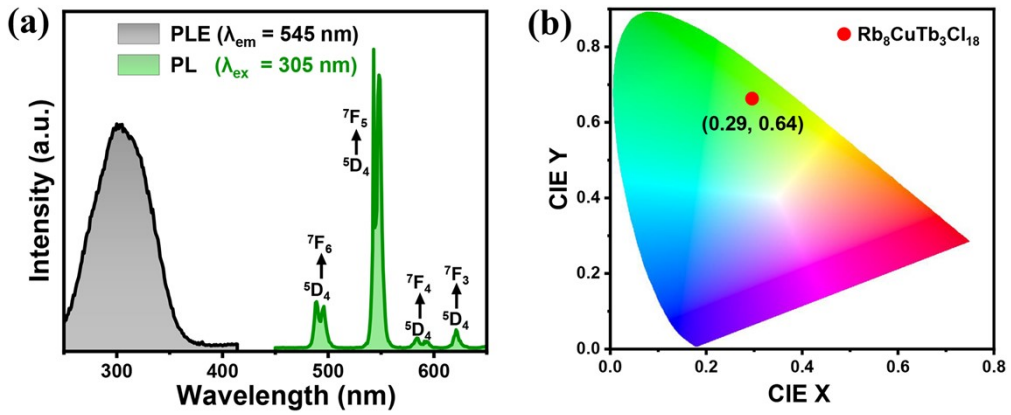

Fig. S6. (a) Excitation (black line) and emission (green line) spectra of $Rb_8CuTb_3Cl_{18}$. (b) Chromaticity CIE coordinate.

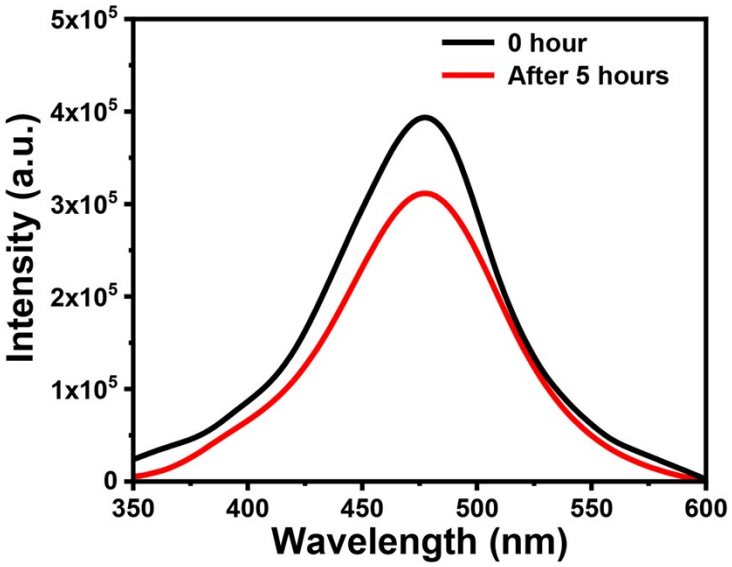

Fig. S7. The stability of PL spectra of $Rb_8CuIn_3Cl_{18}$.

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