Supporting Information

Photophysical properties of tetrabutylammonium metal chloride with different inorganic frameworks

Materials and chemicals

Lead chloride ($PbCl_2$, 99.99%), bismuth chloride ($BiCl_3$, 99.99%), antimony chloride ($SbCl_3$, 99.99%), stannic chloride pentahydrate ($SnCl_4 \cdot 5H_2O$, 99.0%), tetrabutylammonium chloride (TBAC, 99.0%), dimethylformamide (DMF, 99.8%), dichloromethane (DCM, 99.8%), absolute ethyl alcohol (ETOH, 99.8%), were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Hydrochloric acid (HCl, 37%) was purchased from Harbin Polytechnic Chem. Reag. Co., Ltd. All of these raw materials were used without any further purification.

Synthesis of (TBA)$PbCl_3$ (SC-Pb) single crystal: Add 1 mmol of TBAC and 1 mmol of $PbCl_2$ to the glass bottle, then add 4 mL of DMF and stir until completely dissolved to form a precursor solution. The glass bottle containing the precursor solution was placed in a large beaker containing DCM and sealed, and crystallization was carried out by the antisolvent DCM diffusion method.

Synthesis of $(TBA)_3Bi_2Cl_9$ (SC-Bi) single crystal: 0.5 mmol TBAC and 0.5 mmol $BiCl_3$ dissolved in hydrochloric acid, and then the solution volatilized at room temperature in a glass bottle.

Synthesis of $(TBA)_2Sb_2Cl_8$ (SC-Sb) single crystal: 0.5 mmol TBAC and 0.5 mmol $SbCl_3$ dissolved in hydrochloric acid, and then the solution volatilized at room temperature in a glass bottle.

Synthesis of (TBA)$SnCl_5 \cdot 2EtOH$ (SC-Sn) single crystal: 0.5 mmol TBAC and 0.5 mmol $SnCl_4 \cdot 5H_2O$ dissolved in absolute ethyl alcohol, and then the solution volatilized at room temperature in a glass bottle.

Synthesis of Liquid-Pb: 1 mmol TBAC and 0.1 mmol $PbCl_2$ dissolved DMF

Synthesis of Liquid-Bi: 1 mmol TBAC and 0.1 mmol $BiCl_3$ dissolved DMF

Synthesis of Film-Sb: SC-Sb was dissolved in EtOH and then dried by dropping on a

glass slide.

Single crystal X-ray diffraction (SCXRD). Single crystal X-ray data for the $(TBA)PbCl_3$, $(TBA)_3Bi_2Cl_9$, $(TBA)_2Sb_2Cl_8$ and $(TBA)_2SnCl_6$ were collected using a Bruker AXS diffractometer with Mo $K\alpha$ radiation.

Powder X-ray diffraction (PXRD). The PXRD analysis was performed on powder X-ray diffractometer (X'PERT Pro, Panalytical) equipped with Cu $K\alpha$ radiation. Simulated powder patterns were calculated by Material Studio 2017 software using the crystallographic information file (CIF) from single-crystal X-ray experiment.

Energy dispersive spectrometry (EDS). Energy dispersive spectrometry was perfor med on the accessories of a ZEISS G500 scanning electron microscope.

Steady-state PL measurement. The 405 nm continuous-wave (CW) laser (UV-FN-405-200mW, CNI) was used as an excitation light source for steady-state excitation. The steady-state PL spectra were collected by a spectrometer (HR4000CG-UV-NIR, Ocean Optics).

Time-resolved photoluminescence (TRPL). The PL dynamics are excited by 200-ps laser pulses at 405 nm and measured by a time-correlated single photon counting (TCSPC) systems from Boston Electronics with the time resolution of 200 ps to reveal the ultrafast process at the very beginning of the dynamics.

Temperature-dependent PL measurement. The temperature-dependent PL measurement was performed using a vacuum liquid-nitrogen cryostat (Cryo-77, Oriental Koji) and a temperature controller. The 405 nm continuous-wave (CW) laser (UV-FN-405-200mW, CNI) was used as an excitation light source, and spectrometer (HR4000CG-UV-NIR, Ocean Optics) is used to collect spectra.

Fitted photo-phonon coupling constants (γ_{OL}): adopt the electron-phonon coupling model to evaluate the electron-phonon coupling strength with the following equation:

$$FWHM = \Gamma_0 + \gamma_{ac}T + \gamma_{LO}\left(e^{E_{LO}/k_BT} - 1\right)^{-1} \quad (1)$$

where Γ_0 is the nonuniform broadening contribution at 0 K, which is independent of temperature. $\gamma_{ac}T$ is the homogeneous broadening term, which arises from acoustic phonon scattering through the deformation potential with charge electronic-acoustic

phonon coupling strength of γ_{ac}. The whole third term represents the longitudinal optical phonon (Fröhlich) interactions. And corresponding γ_{OL} *and* E_{LO} are electronic-optical phonon coupling constant and the phonon energy, respectively.

Fitted lifetime (τ): The experimental data can be fitted by the following double exponential decay. I(t) and the average lifetime (τ) can be described as,

$$I(t) = A + \int_0^t \left(Be^{-(t-t')/\tau_1} + Ce^{-(t-t')/\tau_2} \right) e^{-\left(t'/\tau_{fwhm}\right)^2} dt' \quad (2)$$

$$\tau = \left(B\tau_1^2 + C\tau_2^2\right) \Big/ \left(B\tau_1 + C\tau_2\right) \quad (3)$$

where $I(t)$ is the normalized PL intensity at time t. A is the baseline of PL, while B and C are the amplitudes of the entire normalized PL. τ_1 and τ_2 are the short-lifetime and long-lifetime components of PL, respectively. The instrumental response function (IRF) is considered as a Gaussian function to convolute with the PL decays. The width of IRF τ_{fwhm} is recorded at the wavelength of the excitation.

Table S1. Crystal date and structure refinement for SC-Bi, SC-Sb and SC-Sn

Compound	SC-Bi	SC-Sb	SC-Sn
Chemical formula	$C_{48}H_{108}N_3Bi_2Cl_9$	$C_{32}H_{72}N_2Sb_2Cl_8$	$C_{20}H_{48}NO_2SnCl_5$
Formula weight	1464.38	1012.01	630.53
Temperature	296(2) K	296(2)K	296(2)
Space group	$P2_1/n$	$P2_1/c$	P-1
a/Å	11.3458(11)	18.688(8)	11.1104(19)
b/Å	22.317(2)	13.552(5)	12.108(2)
c/Å	28.552(3)	19.240(8)	13.108(3)
α/°	90	90	109.091(4)
β/°	96.561(2)	101.902(9)	105.943(4)
γ/°	90	90	94.281(4)
Volume/Å^3	7182.4(12)	4768(3)	1575.8(5)
Density/g·cm^{-3}	1.354	1.410	1.329
F(000)	2944	2064	652
Data collection range	2.216<*θ*<25.219	2.227<*θ*<25.007	2.401<*θ*<25.204
Index ranges	-12 ≤*h*≤13	-21≤*h*≤22	-13≤*h*≤13
	-26 ≤*k*≤26	-13≤*k*≤16	-14≤*k*≤14
	-33 ≤*l*≤34	-22≤*l*≤20	-15≤*l*≤15
Independent reflections	12796 [R_{int}=0.1686]	8335 [R_{int}=0.0814]	5616 [R_{int}=0.0663]
Data/restraints/ parameters	12796/313/559	8335/2/405	5616/145/262
Final R indices [*I*>=2*σ*(*I*)]	R_1 = 0.0963[a]	R_1 = 0.0535	R_1 = 0.0705
	wR_2 = 0.1305[b]	wR_2 = 0.1345	wR_2 = 0.1624
R indexes [all data]	R_1 =0.2127	R_1 =0.1198	R_1 =0.1381
	wR_2=0.164	wR_2=0.1764	wR_2=0.1940
Largest diff. peak and hole	0.976 and -0.799 e·Å^{-3}	0.652 and -0.644 e·Å^{-3}	0.735 and -0.523 e·Å^{-3}

a) $R_1 = \sum||F_o|-|F_c||/\sum|\underline{F_o}|\cdot b)$ $wR_2 = [\sum w(F_o^2-F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

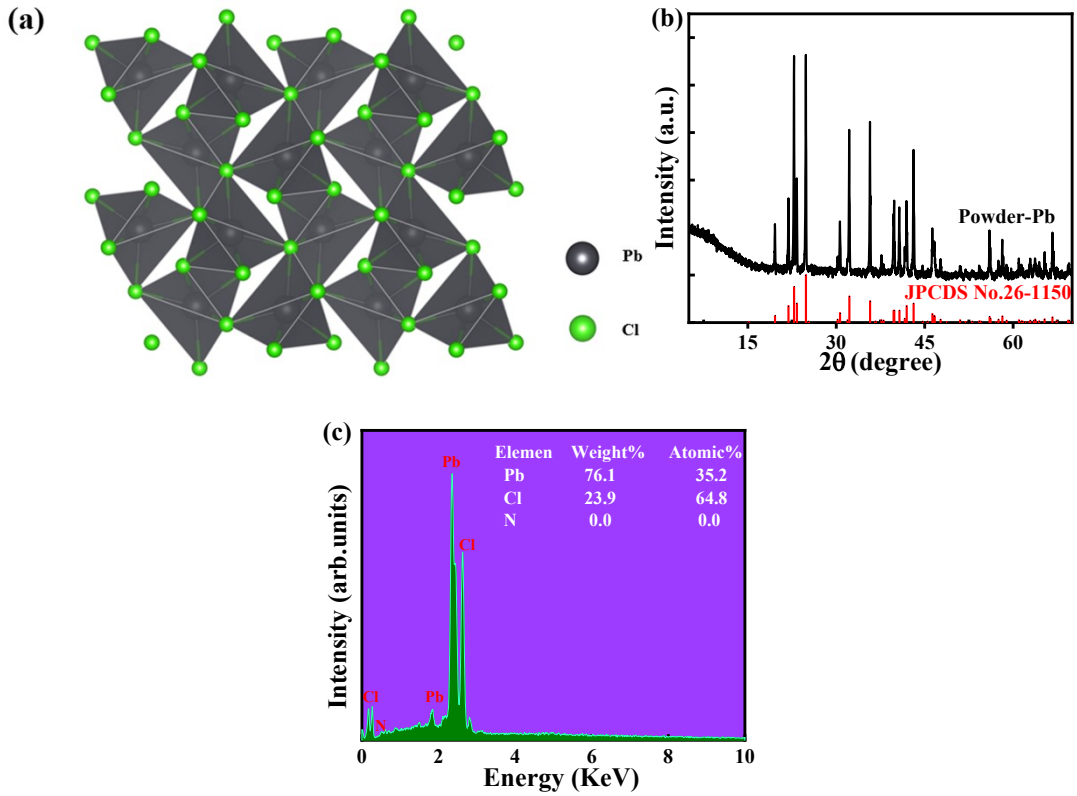

Fig. S1 (a) Schematic diagram of the crystal structure of SC-Pb (b) Powder XRD of SC-Pb and standard card of cotunnite. (c) EDS of SC-Pb.

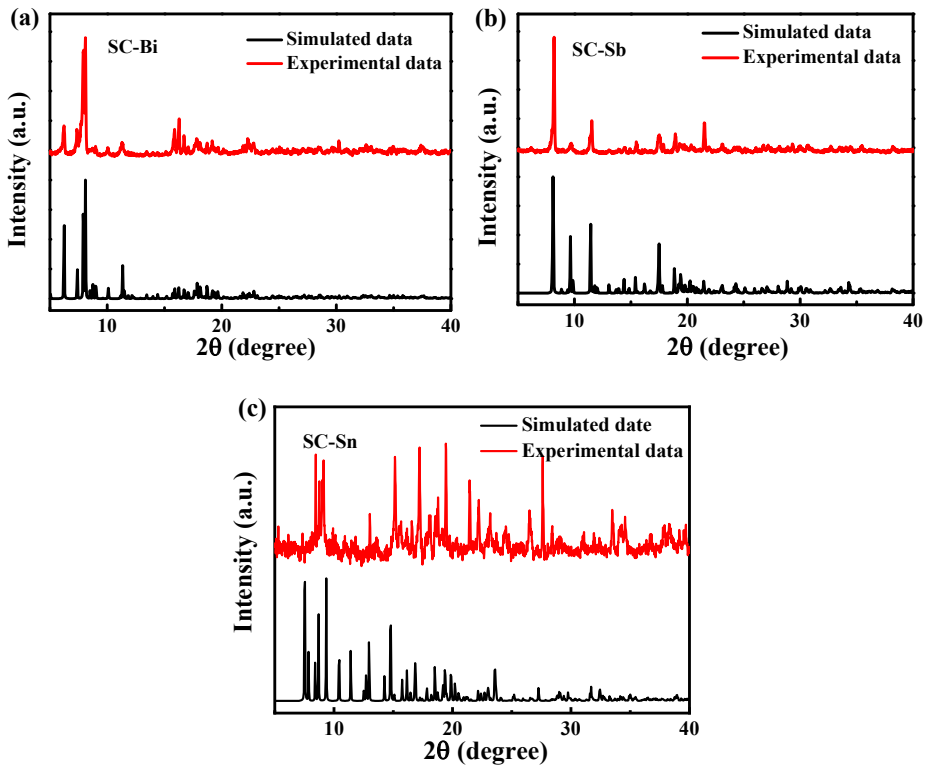

Fig. S2 The simulated and experimental powder XRD patterns of SC-Bi (a), SC-Sb (b) and SC-Sn (c), respectively.

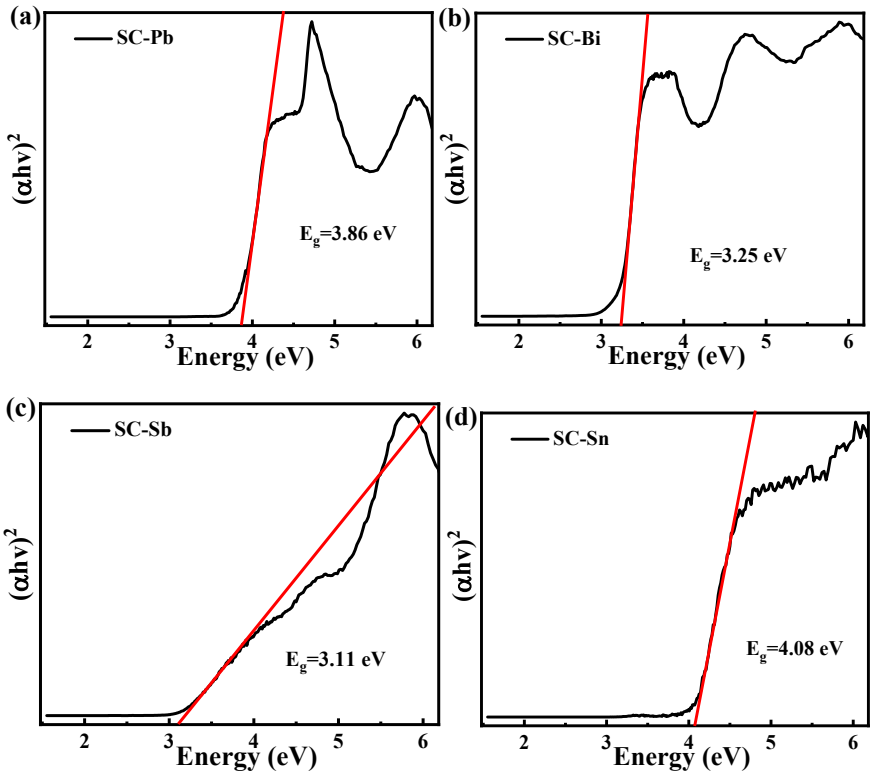

Fig. S3 The optical band gap is calculated by the Tauc-plot formula based on the absorption spectra. the band gap obtained of (a) SC-Pb, (b) SC-Bi, (c) SC-Sb, (d)SC-Sn.

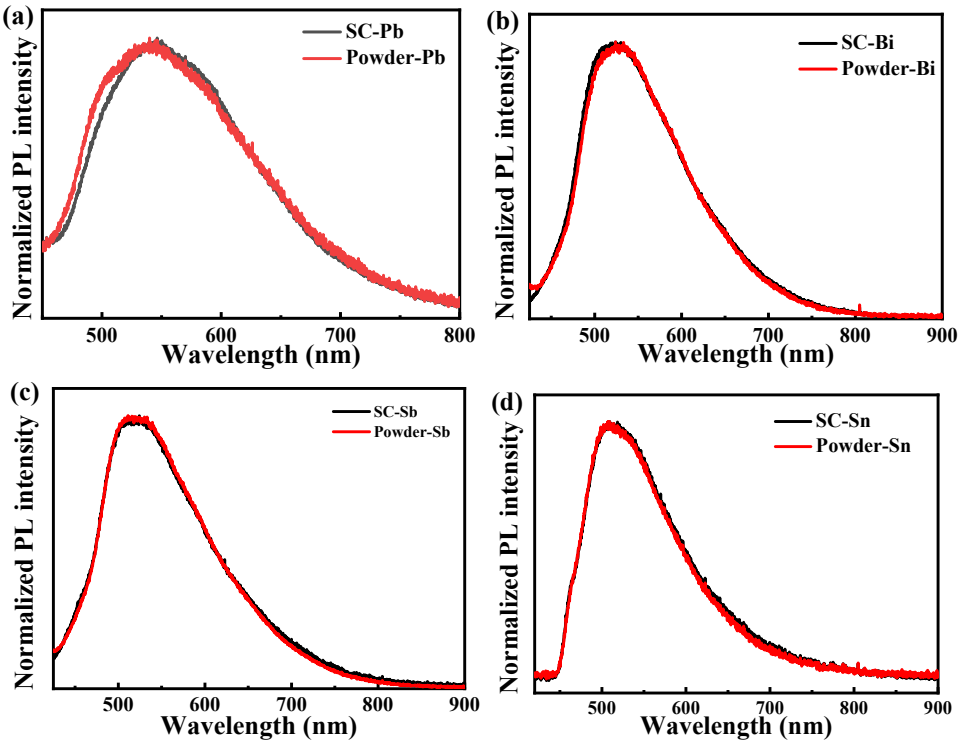

Fig. S4 The spectra of PL of SC-Pb (a), SC-Bi (b), SC-Sb (c), SC-Sn (d) and PL spectra of their ground into powder, respectively.

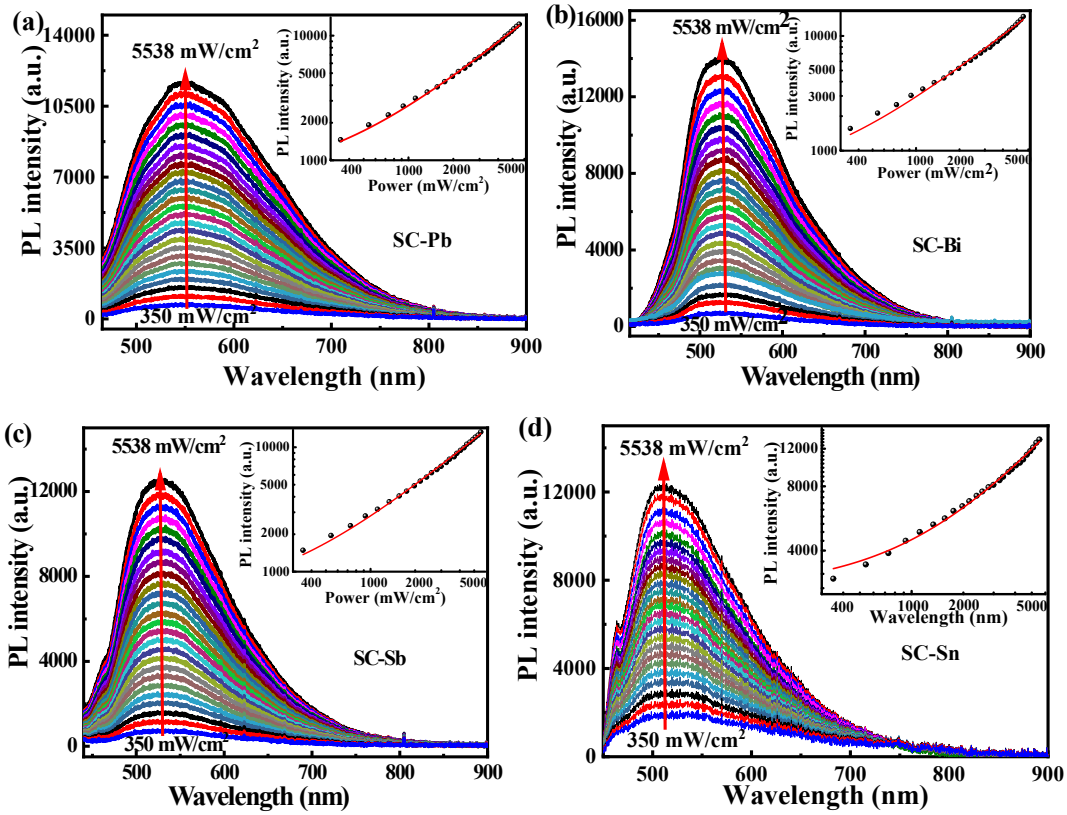

Fig. S5 The power-dependent PL spectra of SC-Pb (a), SC-Bi (b), SC-Sb (c) and SC-Sn (d), respectively.

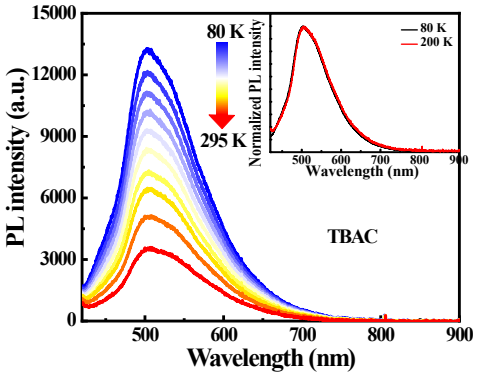

Fig. S6 PL spectra of TBAC at different temperature, inset shows the normalized spectra at 80 K and 200 K.