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Supporting Information for

A Novel Copper-Rich Open-Framework Chalcogenide Constructed from Octahedral Cu_4Se_6 and Icosahedral Cu_8Se_{13} Nanocluster

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EXPERIMENTAL SECTION

Materials. Copper (Cu, 99.9%, powder), tin (Sn, 99.9%, powder), selenium (Se, 99.9%, powder), sodium chloride (NaCl, 99%, solid), cesium chloride (CsCl, 99%, solid), 1, 3-di-piperdypropane (>97%, liquid), N-(2-aminoethyl)piperazine (>99%, liquid) and piperidine (PR, >99%, liquid) were all used as supplied without further purification.

Synthesis of CuSnSe-1. Cu (50 mg, 0.180 mmol), Sn (40 mg, 0.430 mmol), Se (197 mg, 2.495 mmol) were mixed with piperidine (1.967 g, 23.1 mmol) in a 23-ml Teflon-lined stainless autoclave and stirred for 0.5 h. Then the vessel was sealed and heated at 180°C for 12 days. Black block crystals (yield: 170 mg, 18.7% based on Cu) with pure phase were obtained by filtration after being washed with ethanol for several times.

Synthesis of SnSe compound. Sn (133 mg, 1.12 mmol), Se (230 mg, 2.913 mmol), 1, 3-Di-piperdypropane (1.156g, mmol) were mixed with ethylene glycol (3ml), deionized water (2.5 ml), and N-(2-aminoethyl)piperazine (1 ml) in a 23-ml Teflon-lined stainless autoclave and stirred for 0.5 h. Then the vessel was sealed and heated at 180°C for 12 days. Red block crystals were obtained by filtration after being washed with ethanol for several times. It is isostructrual to a known two dimensional SnSe framework.

Single Crystal Characterization. The single crystal X-ray diffraction measurement was performed on Agilent diffractometers with graphite monchromated Mo Kα (λ = 0.71073 A) radiation at 223K. The structure was solved by direct method using SHELXS-97 and the refinement against all reflections of the compound was performed using SHELXL-97. Not all the protonated piperidine molecules located in the void space of the framework can be identified owing to their serious disorder. The SQUEEZR subroutine in PLATON was used to treat the data.

Powder X-ray Diffraction (PXRD). PXRD data were collected on a desktop diffractometer (D2 PHASER, Bruker, Germany) using Cu-Kα (λ=1.54056 A) radiation operated at 30 kV and 10 mA. The samples were ground into fine powders in an agate mortar for several minutes before the test.

Elemental Analysis. Energy dispersive spectroscopy (EDS) analysis was performed on scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS) detector. An accelerating voltage of 25 kV and 40s accumulation time were applied. EDS results clearly confirm the presence of Cu/Sn/Se elements. Elemental analysis of C, H, and N was performed on VARIDEL III elemental analyzer {Calcd. (wt%): C, 11.33; N, 2.65; H, 2.27. Found: C, 10.97; N, 2.78; H, 2.31}. The elemental ratio of Cu/Sn/Se was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) on Leeman's PROFILE SPEC spectrometer {Calcd. (wt%): Cu, 20.17%; Sn, 14.17%; Se, 48.70%; Found: Cu, 20.91%; Sn, 14.13%; Se, 44.99%}. The results were consistent with the SCXRD analysis. (The smaller amount of Se measured by ICP-AES may be caused by the loss of hydrogen selenide in the sample-preparation process)

Elements	C	H	N	Cu	Sn	Se
Calculated (wt.%)	11.33	2.27	2.65	20.17	14.17	48.70
Found (wt.%)	10.97	2.31	2.78	20.91	14.13	44.99

Thermogravimetric (TG) Measurement. A Shimadzu TGA-50 thermal analyzer was used to measure the TG curve by heating the sample from room temperature to 600 ^{o}C with heating rate of 5^{o}C/min under nitrogen flow.

UV-Vis Absorption. Room-temperature solid-state UV-Vis diffusion reflectance spectra of crystal samples were measured on a SHIMADZU UV-3600 UV-Vis-NIR spectrophotometer coupled with an integrating sphere by using $BaSO_4$ powder as the reflectance reference. The absorption spectra were calculated from reflectance spectra by using the Kubelka-Munk function: $F(R)=\alpha/S=(1-R)^2/2R$, where R, α, and S are the reflection, the absorption and the scattering coefficient, respectively.

Fourier Transform Infrared Absorption. Fourier transform-Infrared spectral analysis was performed on a Thermo Nicolet Avatar 6700 FT-IR spectrometer with cesium iodide optics allowing the instrument to observe from 600-4000 cm^{-1}.

Ion Exchange. The sample of CuSnSe-1 (20 mg) was dipped in 20 mL aqueous solution of CsCl (1 M) in glass vial, which was slowly shaken by hand for several seconds, then heated at 60 ^{o}C in oven. During treatment, the CsCl solution (1 M) was refreshed twice. After 24 hrs, the crystals were taken out of solution and washed with water to remove residual Cs^+ ions adsorbed on the crystal surface. The products were characterized by EA {Found: C, 5.64; H, 1.55; N, 1.35.} and EDS.

XPS and AES Measurements. X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) were collected with a Leeman prodigy spectrometer equipped with a monochromatic Al Kα X-ray source and a concentric hemispherical analyzer.

Photoelectric Response. To prepare the working electrode, 2 mg of CuSnSe-1/SnSe crystals were first ground into fine powders, and then added into 60μL of 0.5% nafion (D-521 dispersion, 5% in water and 1-propanol). After ultrasonic treatment for 10 minutes, the obtained suspensions were dropped onto the surface of ITO substrate, and then dried at room temperature. The photocurrent experiments were performed on a CHI760E electrochemistry workstation in standard three-electrode configuration, with the sample coated ITO glass (the effective area is around 1 cm^2) as the working electrode, a Pt wire as the auxiliary electrode, and a saturated calomel electrode (SCE) as the reference electrode. The light source is a 150 W high pressure xenon lamp, located 20 cm away from the surface of the ITO electrode. Sodium sulfate aqueous solution (0.5 M, 100 mL) was used as the supporting electrolyte.

Table S1 Crystal data and refinement results of **CuSnSe-1**.

	CuSnSe-1
Formula	$Cu_{16}Sn_6Se_{31}(C_5NH_{12})_{10}$
Fromula weight	5038.26
Crystal system	Cubic
Z	4
Space group	Pa-3
a (Å)	21.7015(12)
α (deg.)	90
V (Å^3)	10220.4(10)
$F(000)$	7272
D (g cm^{-3})	2.714
μ (mm^{-1})	15.731
Crystal morphology	block
$2\theta_{max}$(deg.)	45.72
Collected reflections	28182
Independent reflections	2331 (R_{int}= 0.0597)
Observed reflections	1842
Parameters/restrain/data	81/0/2331
GOF on F^2	1.032
R_1, wR_2 ($I>2\sigma(I)$)	0.0598, 0.1551
R_1, wR_2 (all data)	0.0739, 0.1656
Diff peak, hole (e Å^{-3})	2.485, -1.251

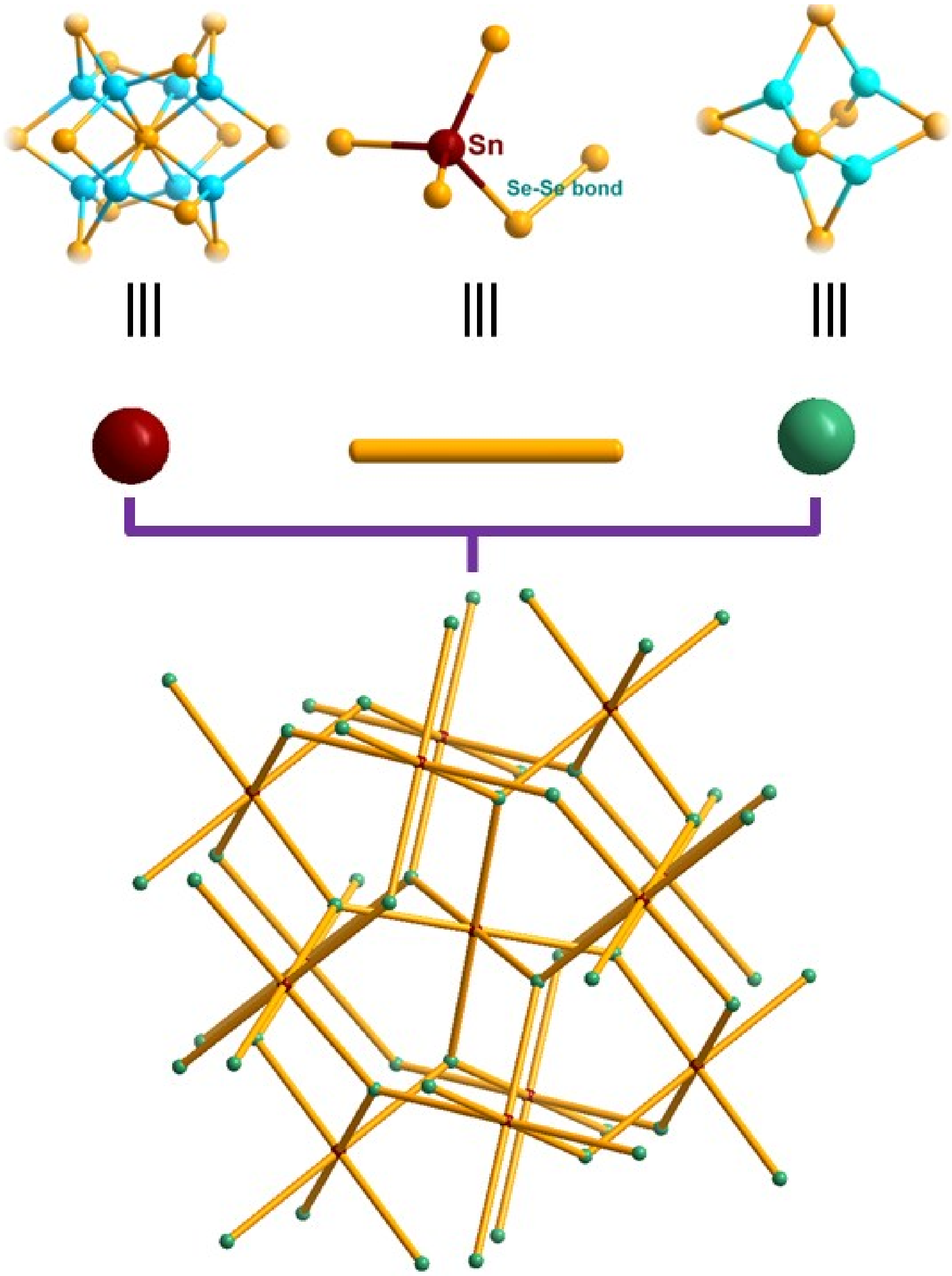

Figure S1. Topological representation of CuSnSe-1. After topological analysis, the structure of CuSnSe-1 can be classified as pry (pyrite) topology with Schläfli symbol of $\{6^{12};8^3\}\{6^3\}_2$ by treating octahedral Cu_4Se_6 and icosahedral Cu_8Se_{13} nanocluster as nodes.

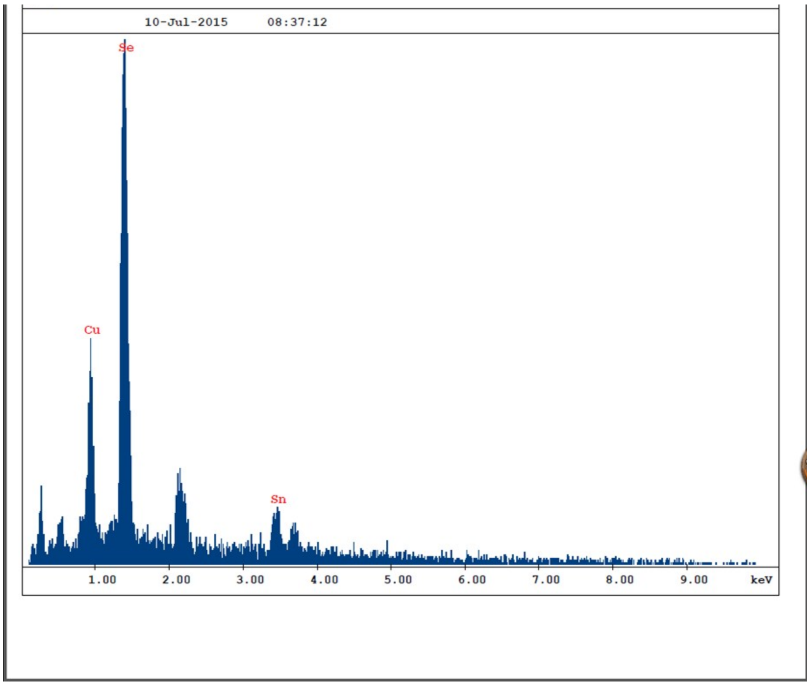

Figure S2. EDS of CuSnSe-1.

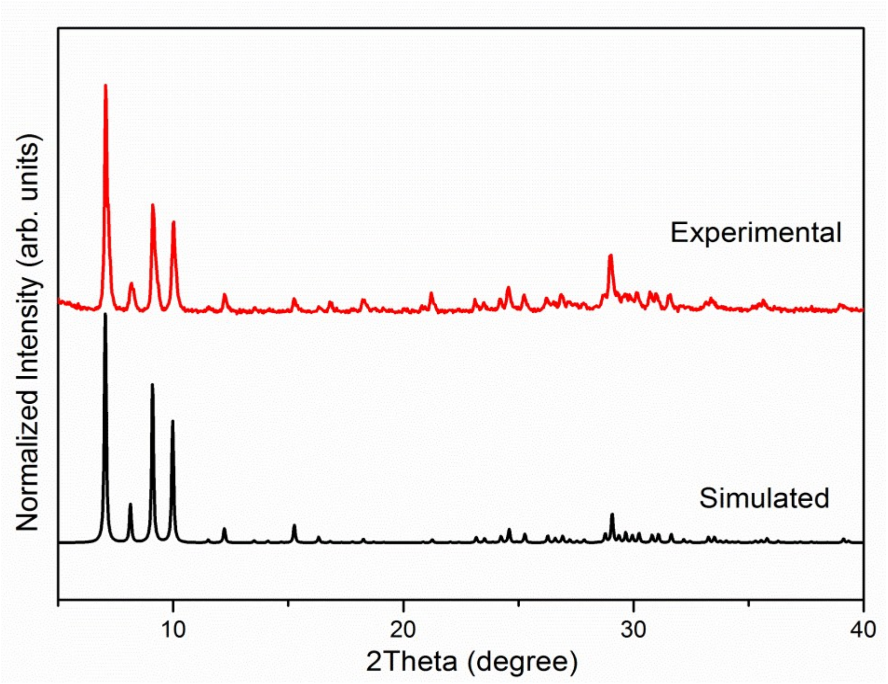

Figure S3. The simulated and experimental XRD patterns of CuSnSe-1.

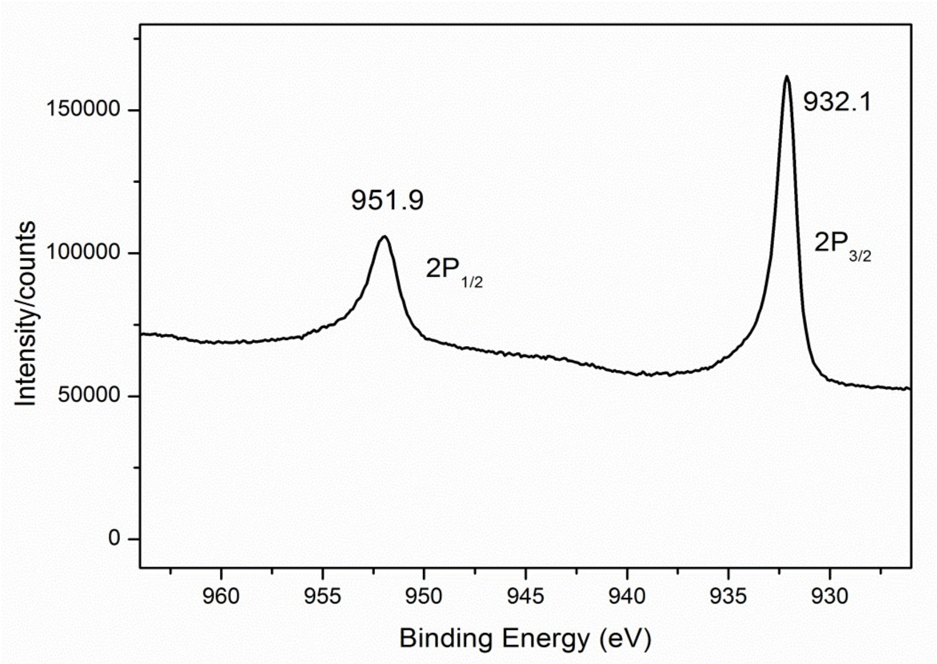

Figure S4. XPS analysis of CuSnSe-1.

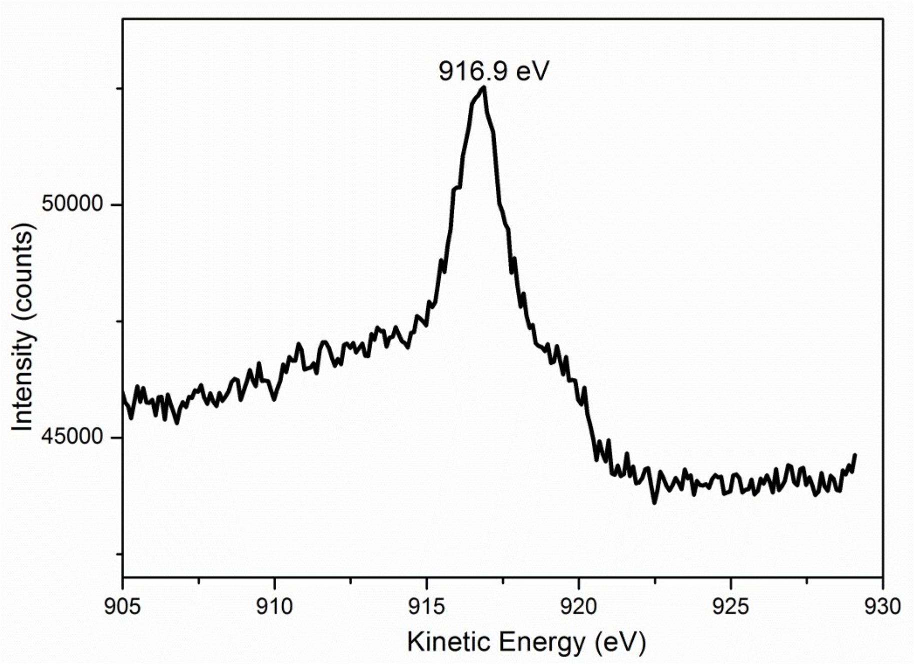

Figure S5 Auger electron spectrum of Cu LM2

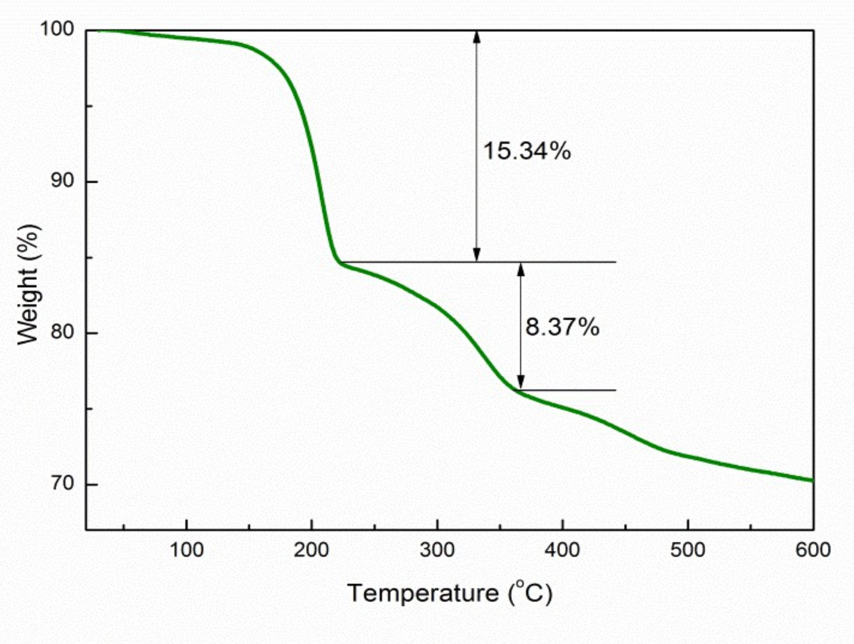

Figure S6. TGA for CuSnSe-1.

Thermogravimetric analysis indicated that CuSnSe-1 undergoes the first step weight loss about 15.34 % from room temperature to 220 °C and second step of weight loss of 8.37% from 220 °C to 370 °C, respectively (Figure S4). These results are in good agreement with the calculated values from the SCXRD analysis, corresponding to the removal of piperidine (Calcd. 16.90%) and hydrogen selenide (8.03%).

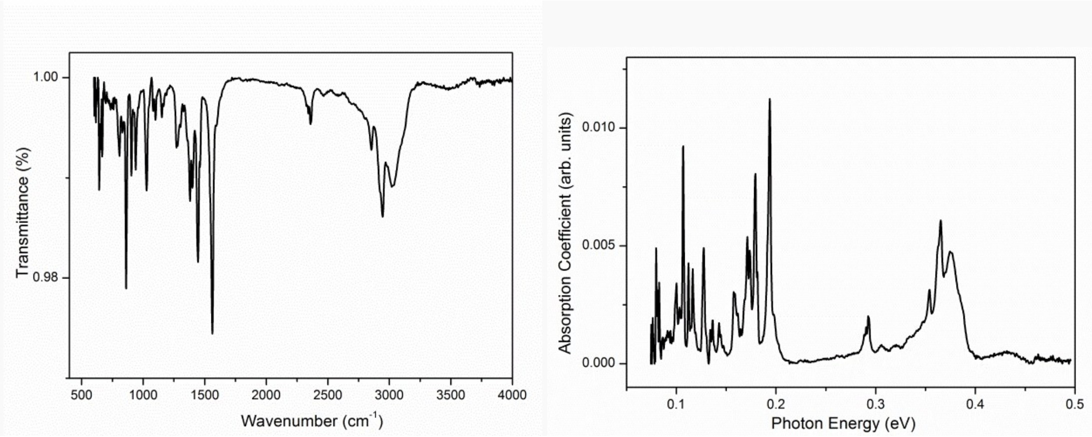

Figure S7 Transmission and absorption modes of FT-IR curves with germanium crystal as the reference

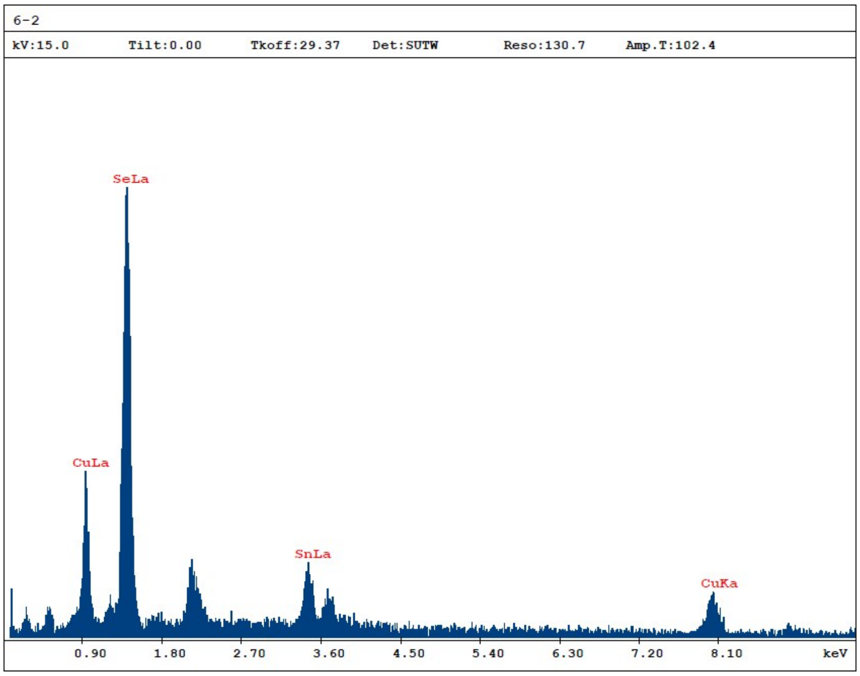

Figure S8. EDS of Cs$^+$-exchanged CuSnSe-1. CsL peak around 4.3 KeV (L) was not observed.

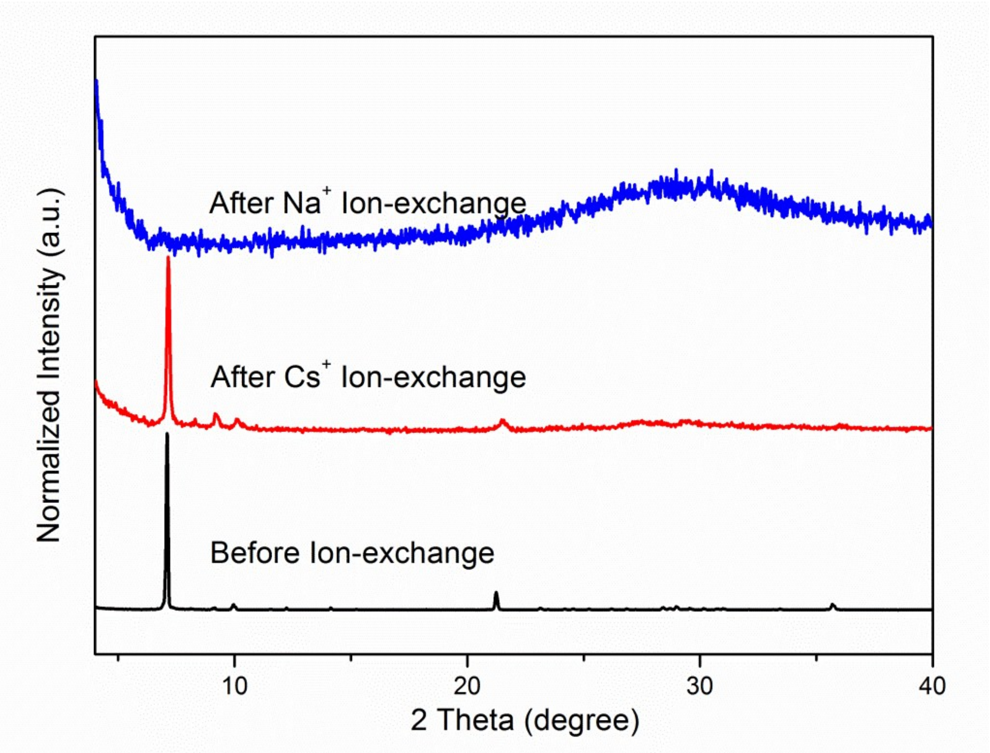

Figure S9. XRD patterns of CuSnSe-1 samples before and after ion-exchange.

Figure S10. Suspension of CuSnSe-1 in NaCl aqueous solution after ion exchange at 60 ^{o}C.

The ion-exchange experiment was performed at a mild temperature of 60 ^{o}C in NaCl or CsCl aqueous solution. Na^+ exchange in sodium chloride aqueous solution resulted in the collapse of the structure, as evidenced by the brick-red suspension (Figure S10) and PXRD (Figure S9). Although the framework remained intact after Cs^+ ion-exchange (Figure S9) and the results of CHN element analysis demonstrated some loss of the guest amines, EDS measurement didn't evidence the existence of Cs^+, which indicates that Cs^+ ion exchange is not successful, either.