Supplementary Material (ESI) for Chemical Communications

Electronic Supporting Information

$(H_2en)_2Cu_8Sn_3S_{12}$: a trigonal CuS_3-Based open-framework sulfide with interesting ion-exchange properties

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1. X-ray crystallography

The intensity data were collected on Bruker Smart APEX II diffractometer equipped with graphite monochromitized Mo *Ka* radiation (λ = 0.71073 Å) at room temperature. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELX97.[1] The hydrogen atoms of ethylenediamine in compound **1** and **1Cs** were not added. The Cs atoms in compound **1Cs** show disorder over several positions. The occupancies of Cs atoms were adjusted manually to refine Cs atoms with reasonable thermal parameters. The disordered diprotonated ethylenediamine cations in both structures were treated with *SQUEEZE,* and the platon.sqf files have been appended to the bottom of the CIFs, respectively.

[1] G. M. Sheldrick, *SHELXS97 and SHELXL97*, University of Göttingen, Germany, **1997**.

2. More structure details

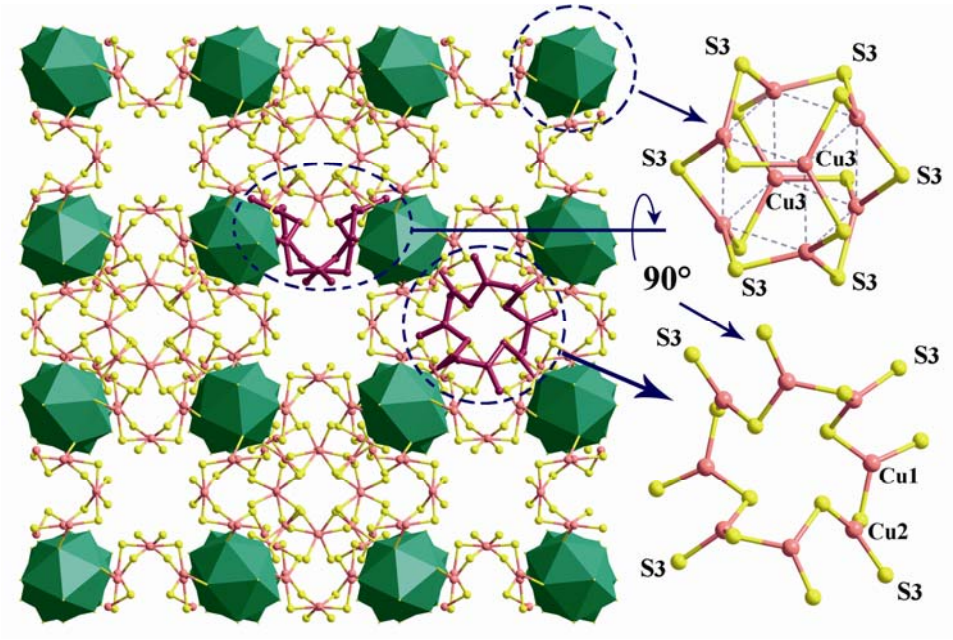

Fig. S1 The trigonal CuS_3-Based framework and its two fundamental building blocks: $[Cu_8S_{12}]^{16-}$ cluster and $[Cu_8S_{16}]^{24-}$ cluster. The $[Cu_8S_{12}]^{16-}$ cluster consists of eight Cu^+ ions (six Cu(4) and two Cu(3)) arrayed as a distorted cube and S^{2-} ions bridging adjacent Cu^+ ions, and it has a icosahedral shape defined by the 12 bridging S^{2-} ions. The $[Cu_8S_{16}]^{24-}$ cluster is formed by alternation of $Cu(1)S_3$ and $Cu(2)S_3$ units, in which only two vertices of all CuS_3 triangle are shared with adjacent CuS_3 triangle.

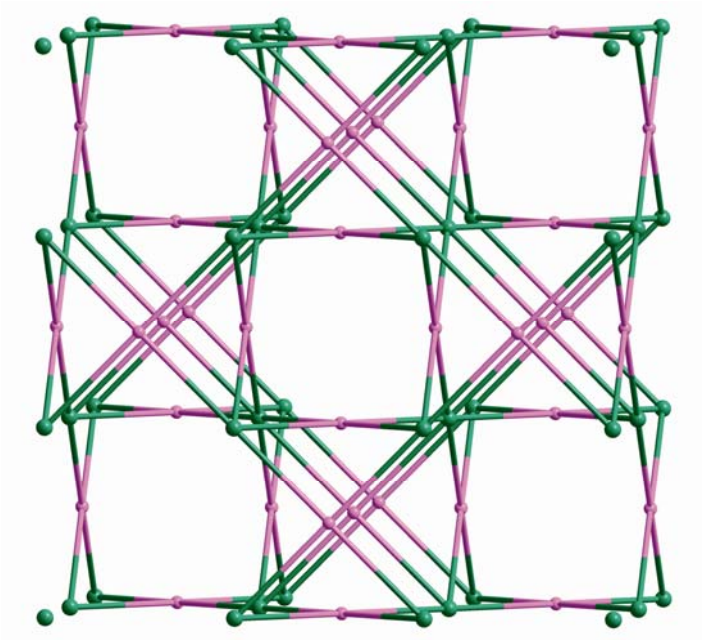

Fig. S2 The schematic representation of the complicated connectivity between clusters in the Cu-S framework. The balls represent $[Cu_8S_{12}]^{16-}$(green) and $[Cu_8S_{16}]^{24-}$(pink) clusters, which are in hexagonal and tetragonal coordination environment, respectively.

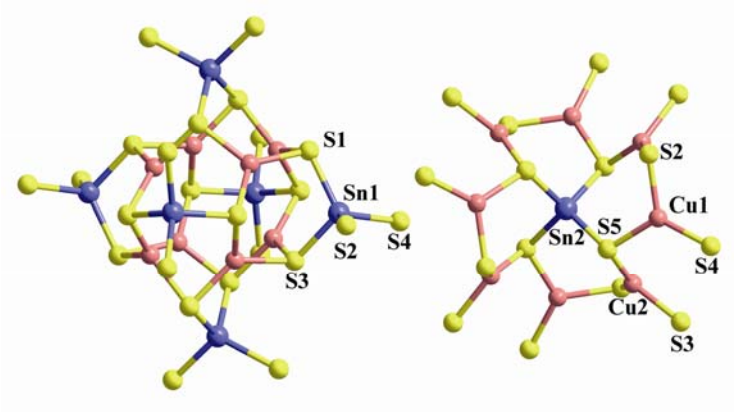

Fig. S3 Local coordination environment of Sn(1) and Sn(2).

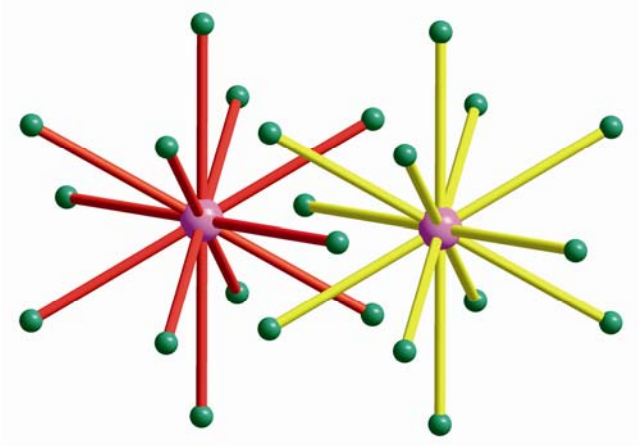

Fig. S4 Schematic representation of the two interpenetrating channel systems along <110> in **1**.

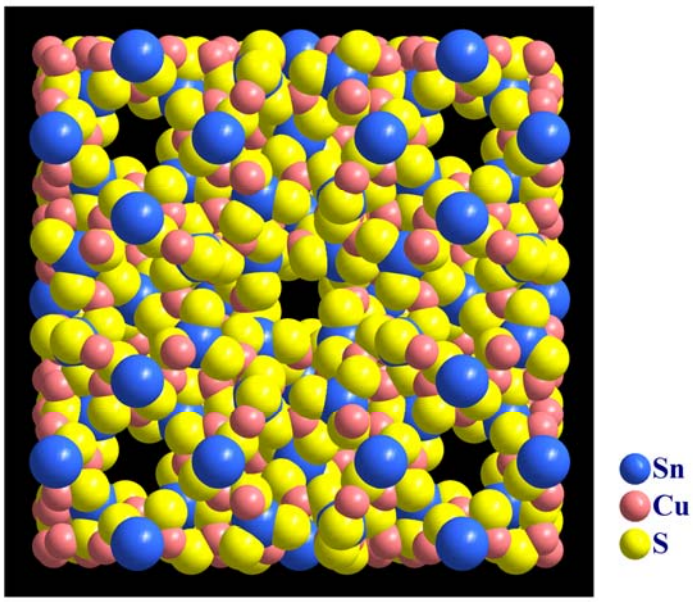

Fig. S5 CPK mode of framework structure of **1** along <100> direction.

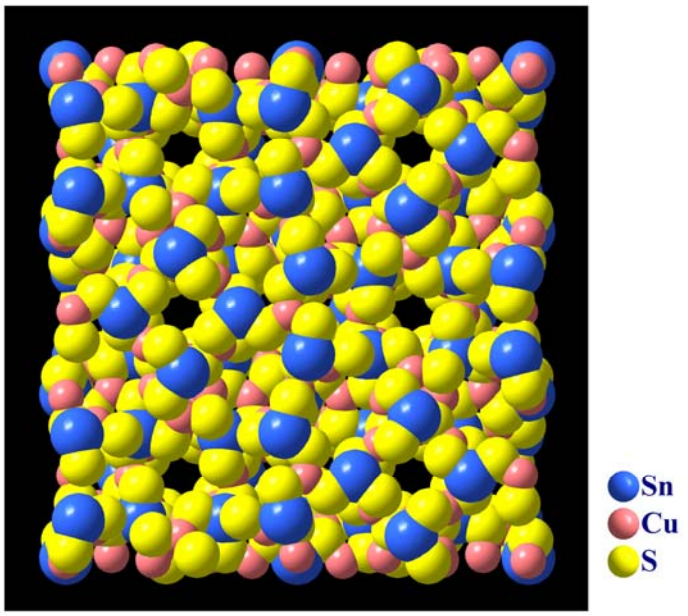

Fig. S6 CPK mode of the framework structure of **1** along <110> direction.

3. General Procedures

All reagents were purchased from commercial sources and were used without further purification. EDS analyses were performed using JSM-5600LV. Elemental analyses were carried out on a Vario-EL analyzer. Thermogravimetric analysis (TGA) of the compound **1** and its ion-exchanged products were carried out by Metter Toledo Star under a flow of nitrogen (40 mL/min) from 25 to 550℃ at heating rate of 10℃/min. Powder X-ray diffraction (XRD) were obtained using a Shimadzu XRD-6000 diffractometer with Cu*K*α radiation (λ = 1.5418 Å). The data were collected at room temperature with a step size of 0.02° and the operating power was 40 kV/20 mA. The UV-vis spectra were measured at room temperature using JASCO V-570UV/VIS/NIR double-beam, double monochromator spectrophotometer, and wavelength range from 200 nm to 800 nm.

3.1 Ion-exchange experiment

(a) Ion-exchange experiments with polycrystalline of 1:

A Typical ion-exchange experiment with alkali cation M (M = Na^+, K^+, Rb^+ and Cs^+) was as follows: 0.040g Polycrystalline of compound **1**(about 0.02 ~ 0.05 mm in dimension) were added to a 40 mL NaCl water solution (0.2 M) of in a Teflon lining(50 mL), the mixture was kept at 60 °C and stirred with mechanical agitator (speed: about 400 r/min) for 12 h. The exchanged products were isolated by filtration, washed several times with deionized water and ethanol then dried in air. Similar ion-exchange routes were then used for K^+, Rb^+ and Cs^+ respectively.

(b) Cs^+ ion-exchange experiment with single crystals of 1:

Several single crystals of **1** (about 0.2 ~ 0.3 mm in dimension) were selected and added to a 40 mL CsCl water solution (0.2 M) in a Teflon lining(50 mL), the solution was kept at 60 °C and stirred with mechanical agitator(speed: about 150 r/min) for 12 h. The exchanged products were isolated by filtration, washed several times with deionized water and ethanol then dried in air.

3.2 EDS and Elemental analyses

Table S1. EDS and Elemental analyses of **1** and its ion-exchanged products.

Exchange Cations	EDS results	N, H, C, S analyses (%)	Estimated formulae	Exchange yield (%)	Band-gap energy (eV)
$(H_2en)_2Cu_8Sn_3S_{12}$	$Cu_{7.8}Sn_{3.1}S_{12.0}$	N 4.01, C 3.65, H 1.49, S 27.92 (N 4.08, C 3.50, H 1.46, S 27.98)	$(H_2en)_2Cu_8Sn_3S_{12}$	/	2.05
Na^+	$Na_{1.1}Cu_{8.0}Sn_{3.2}S_{12.2}$	N 2.85, C 2.47, H 1.32 (N 3.00, C 2.57, H 1.36)	$Na_{1.0}(H_2en)_{1.5}Cu_8Sn_3S_{12}•2H_2O$	25	2.00
K^+	$K_{1.6}Cu_{8.2}Sn_{3.1}S_{11.8}$	N 2.38, C 2.19, H 1.17 (N 2.37, C 2.03, H 1.26)	$K_{1.56}(H_2en)_{1.22}Cu_8Sn_3S_{12}•3H_2O$	39	1.80
Rb^+	$Rb_{1.7}Cu_{7.9}Sn_{3.2}S_{12.1}$	N 2.44, C 2.14, H 1.19 (N 2.38, C2.04, H 1.25)	$Rb_{1.44}(H_2en)_{1.28}Cu_8Sn_3S_{12}•3H_2O$	36	1.95
Cs^+	$Cs_{1.6}Cu_{8.2}Sn_{3.0}S_{12.3}$	N 2.34, C 2.05, H 1.06 (N 2.35, C 2.01, H 1.09)	$Cs_{1.40}(H_2en)_{1.30}Cu_8Sn_3S_{12}•2H_2O$	35	1.70

3.3 Powder XRD

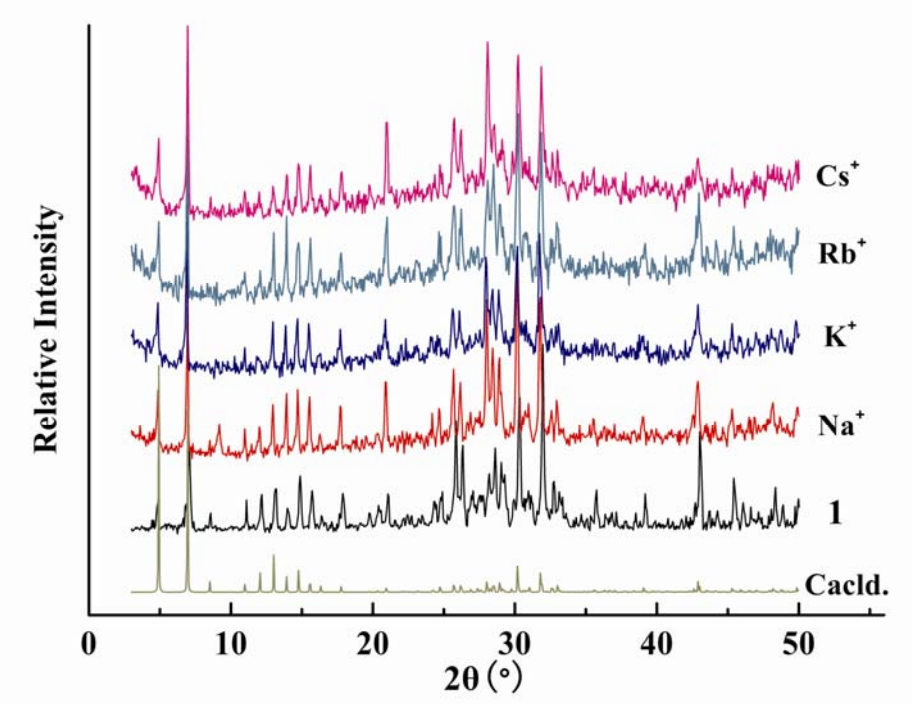

Fig. S7 The PXRD patterns of the compound $(H_2en)_2Cu_8Sn_3S_{12}$**(1)**, Na^+, K^+, Rb^+ and Cs^+ ions-exchanged products and the simulated PXRD pattern calculated from single crystal X-ray data of **1**.

3.4 UV/vis spectra

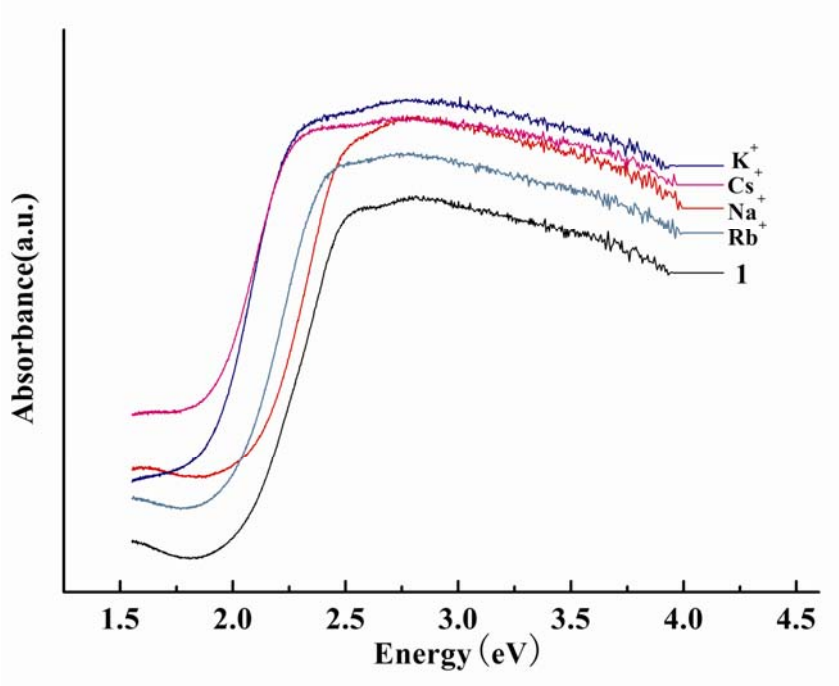

Fig. S8 Solid state UV/vis spectra for $(H_2en)_2Cu_8Sn_3S_{12}$ (**1**) and the Na^+, K^+, Rb^+ and Cs^+ ion-exchanged products, respectively.

3.5 TGA

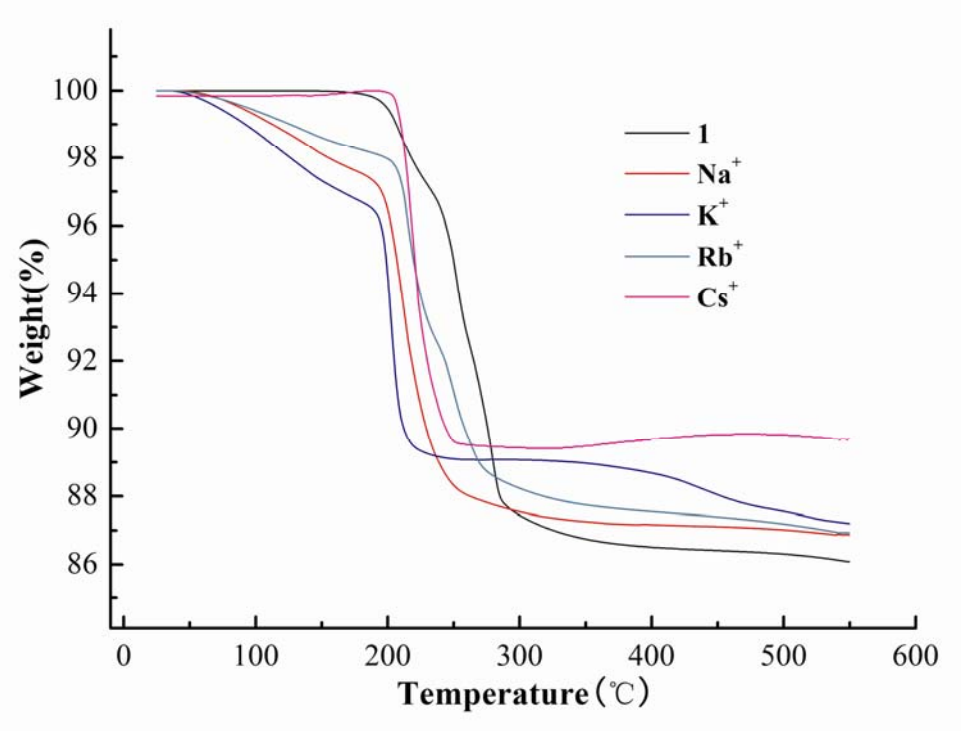

Fig. S9 TGA curves of $(H_2en)_2Cu_8Sn_3S_{12}$(**1**) and the ion-exchange products show respective weight losses in the temperature range 25–550℃ and are mostly due to the losses of the absorbed water, the unexchanged diprotonated ethylenediamine and a small quantity S.

Table S2. TGA data of $(H_2en)_2Cu_8Sn_3S_{12}$ (**1**), and the ions-exchanged products

Exchange Cations	**Experimental** weight losse	**Calculated** weight losses
$(H_2en)_2Cu_8Sn_3S_{12}$	13.5%	13.7%
Na^+	2.5%+10.5%	12.6%
K^+	3.5%+7.5%	11.7%
Rb^+	2.0%+10.0%	11.5%
Cs^+	10.5%	10.2%