Supporting Information for

Assembly of Supertetrahedral Cluster into Cu-In-S Superlattice via Unprecedented Vertex-Edge Connection Mode

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EXPERIMENTAL SECTION

Materials. Indium powder (In, 99.99%, powder), sublimed sulfur (S, 99.9%, powder), copper iodide (Cul, 99%, powder), 3, 5-dimethylpiperidine (97%, liquid), deionized water. All analytical grade chemicals employed in this study were commercially available and used without further purification.

Synthesis of CIS-27. Indium powder (180 mg), sulfur powder (170 mg), copper iodide (40 mg) were mixed with 3, 5-dimethylpiperidine (1 mL) and deionized water (2 mL) in a 23-mL Teflon lined stainless autoclave and vigorous stir for 15 min. Then the vessel was sealed and heated at 190 °C for 7 days and then taken out from the oven and cooled to room temperature naturally. The yellow tetrahedron crystals were obtained together with indefinite kermesinus powders. The crystals of CIS-27 were selected by hand, washed by ethanol, and then dried in air. And the compound is stable under ambient conditions.

Single crystal X-ray diffraction (SCXRD). The single-crystal X-ray diffraction measurements were performed on Photon II CPAD diffractometer with nitrogen-flow temperature controlled using graphite-monchromated Mo-K α (λ =0.71073 Å) radiation at 120 K. The structure was solved by direct method using SHELXS-2014 and the refinements against all reflections of the compound were performed using SHELXS-2014. The protonated organic amines and water molecules located in the void space of the framework cannot be identified owing to their serious disorder and hence the squeeze subprogram has been performed. To meet the charge balance, four copper atoms are distributed among the 12 possible metal sites on four faces of the supertetrahedral cluster with occupancy of 1/3. Consequently, the occupancy of copper and indium in these sites are constrained as 1/3 and 2/3 in the refinement, respectively. Note that such assignment was consistent with the experimental results (EDS and ICP-AES) with atomic ratio of Cu : In = 5 : 30.

Powder X-ray diffraction (PXRD). PXRD data were collected on a Bruker D2 Phaser X-ray diffractometer using Cu-K α (λ = 1.54056 Å) radiation operated at 30 kV and 10 mA. The patterns were recorded in a slow-scanning mode with 2 θ from 4° to 40° with a scan-rate of 2.4 ° min⁻¹.

Elemental analysis. Energy dispersive spectroscopy (EDS) analysis was obtained on energy dispersive spectroscopy (EDS) detector. The EDS measurement indicates that

Cu/In is 5 : 29.3, being in agreement with the ICP-MS experimental results (Cu/In ration is 4.4 : 30.6), these two results are close to the ratio of Cu : In = 5 : 30. Elemental analysis (EA) of C, H, and N was performed on VARIDEL III elemental analyzer {Calcd. (wt%): C, 13.51; H, 2.781; N, 2.252. Found: C, 11.81; H, 2.601; N, 2.278}.

Thermogravimetric analysis (TGA). TGA data was performed with a Shimadzu TGA-50 system under nitrogen flow. The TG curve was performed by heating the sample from 20 to 800 °C with heating rate of 10°C /min. TG-MS measurement was also performed with a NETZSCH QMS403 system with nitrogen flow. The mass signal of H₂S was monitored. The temperature was set from 40 °C to 500 °C with heating rate of 10°C /min.

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 400-40000 cm⁻¹.

In28-S42	2.377(5)	In2-S2	2.389(5)
In28-S25	2.385(5)	In2-S5	2.445(5)
In28-S47	2.425(5)	In2-S7	2.506(5)
In32-S29	2.519(5)	In32-S51	2.400(5)
Cu1-S15	2.302(5)	Cu1-S25	2.324(5)
Cu1-S21	2.327(5)	Cu1-S23	2.335(5)

 Table S1. Selected bond lengths (Å) for CIS-27.

Table S2. Selected bond angles (°) for CIS-27.

\$3-In1-\$52	100.76(18)	S35-In20-S29	93.39(16)
S3-In1-S2	118.1(2)	S35-In20-S34	112.07(19)
Cu1-S23-In11	110.40(19)	\$34-In20-\$29	124.48(17)
Cu1-S23-In16	110.66(19)	In11-S10-In6	104.08(17)
Cu1-S23-In26	108.14(19)	In11-S10-In5	108.72(19)

CIS-27 Formula $Cu_5In_{30}S_{53}C_{77}N_{11}O_{7.1}H_{190.2}$ Formula weight 6845.67 Crystal morphology Pyramidal Monoclinic Crystal system Ζ 4 Space group Сс T/K 120 <mark>λ/</mark> Å 0.71073 a/ Å 33.4954(18) b/ Å 19.3412(11) *c/* Å 35.425(2) *a/*⁰ 90 **6/**⁰ 115.1467(16) γ/⁰ 90 *V*(Å³) 20775(2) F(000) 12996 *D*(g cm⁻³) 2.189 μ (mm⁻¹) 4.322 Flack Parameter 0.056 (14) Collected reflections 171721 Independent reflections 47051 (*R*_{int}=0.0879) GOF on F^2 1.038 0.0618, 0.1290 $R_1, wR_2(I > 2\sigma(I))$ R_1, wR_2 (all data) 0.1288, 0.1183

 Table S3 Crystal data and refinement results of CIS-27.



Figure S1 Inter-clusters vertex-vertex connection mode by sharing bi-coordinated chalcogenide atom. Such connection mode is the most common in chalcogenide open frameworks. Examples of T2-T2, T3-T3, T4-T4, and T5-T5 can be found in the compound of UCR-21, UCR-7, OCF-5 and UCR-16, respectively. Other examples of this mode between different sized clusters such as T2-T5, T3-T5 are not shown here for clarity.¹⁻⁴



Figure S2 Inter-clusters vertex-vertex connection mode by sharing three-coordinated sulfur atom in UCR-8. UCR-8 is a type of nanocluster superlattice in which each four-connected T4 cluster ($[M_4In_{16}S_{35}]$, M = Fe, Co, Zn, and Cd) alternates with a three-connected sulfur anion to form a rare and yet theoretically important non-centrosymmetric and non-interpenetrating (3,4)-connected net topologically identical to that of the hypothetical cubic carbon nitride type net. ⁵



Figure S3 Inter-clusters vertex-vertex connection mode by sharing polysulfur chain in UCR-18. In UCR-18, T3 clusters are connected at three corners through S²⁻ bridges into a 3connected sheet with 6-rings (six T3 clusters in a ring). These sheets are joined through -S-S-S- bridges into a 3D net.⁶



Figure S4 Inter-clusters vertex-vertex connection mode by sharing four-coordinated sulfur atom in CIS-11.⁷



Figure S5. Inter-clusters edge-edge connection mode by metal complex.⁸



Figure S6. The morphology of crystal CIS-27.



Figure S7. TGA for CIS-27.



Figure S8. TG-MS curves of CIS-27



Figure S9. EDS experiments of pristine and thermally treated samples

Elements	Cu/In	S
Theoretical	35	53
Untreated	35	52.6
Thermally Treated (300 °C)	35	50.2
Thermally Treated (350 °C)	35	44.4

Table S4. Atomic ratios of the EDS experiments. The atomic number of Cu and In in all the samples is set to be 35 for clarity.

To further verify the release of H_2S from **CIS-27** during the second step, we also made EDS experiment of the thermally treated sample. Two batches of sample were thermally treated in tube surface under nitrogen flow with heating rate of 5 °C/min. When the temperature reached 300 °C and 350 °C, the samples were allowed to cool down naturally without further heating. EDS experiments of the samples (see Figure S9 and Tabel S4) indicated the loss of sulfur element, which further confirmed the escape of H_2S during second step.



Figure S10. The FT-IR curve of CIS-27.



Figure S11. 3D structure of CIS-27.

Reference

- 1 N. Zheng, X. Bu, B. Wang and P. Feng, *Science*, 2002, **298**, 2366-2369.
- 2 N. Zheng, X. Bu, H. Vu and P. Feng, Angew. Chem., 2005, 117, 5433-5437.
- 3 T. Wu, X. Wang, X. Bu, X. Zhao, L. Wang and P. Feng, *Angew. Chem.*, 2009, **121**, 7340 7343.
- 4 X. Bu, N. Zheng, Y. Li and P. Feng, J. Am. Chem. Soc., 2002, **124**, 12646-12647.
- 5 X. Bu, N. Zheng, Y. Li and P. Feng, J. Am. Chem. Soc., 2003, **125**, 6024-6025.
- 6 N. Zheng, X. Bu and P. Feng, J. Am. Chem. Soc., 2003, **125**, 1138-1139.
- 7 L. Wang, T. Wu, F. Zuo, X. Zhao, X. Bu, J. Wu and P. Feng, J. Am. Chem. Soc., 2010, 132, 3283-3285.
- 8 Y.-H. Wang, M.-H. Zhang, Y.-M. Yan, G.-Q. Bian, Q.-Y. Zhu and J. Dai, *Inorg. Chem.*, 2010, **49**, 9731-9733.