Supporting Information for

Three new metal chalcogenide open frameworks built through co-assembly and/or hybrid assembly between supertetrahedral T5-InOS and T3-InS nanoclusters

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Experimental Section:

Chemicals and Materials. Indium nitrate hydrate ($In(NO_3)_3·4.5H_2O$, ≥ 99.5%), indium powder (In, 99.99%), thiourea (CH_4N_2S, 99%), sulfide powder (S, ≥ 99.5%), tetrazole (CH_2N_4, 99%), acetonitrile (C_2H_3N, ≥98%), dimethyl formamide (DMF, > 99.5%), (R)-(-)-2-Amino-1-butanol (R-2-AB, 98%), N-Aminoethylpiperazine (AEP, > 99.0%), 1,5-Diazabicyclo[4.3.0]non-5-ene (DBN, 98%), 1,8-diazabicyclo [5,4,0]undec-7-ene (DBU, 99%) and were all used without any further purification.

Synthesis of IS-3: A mixture of In (114 mg, 1 mmol), S (96 mg, 3 mmol), dimethyl formamide (DMF, 2.5mL), (R)-(-)-2-Amino-1-butanol (R-2AB, 1.5 mL) and 1,5-Diazabicyclo[4.3.0]non-5-ene (DBN, 1.5 mL) was stirred in a 23 mL Teflon-lined stainless steel autoclave for half an hour. After the vessel was sealed and heated at 180 °C for 7 days, the autoclave was subsequently cooled to room temperature. A large amount of colorless block crystals was obtained by sonication treatment in ethyl alcohol (yield: >40%, based on In element). The phase purity was identified by powder X-ray diffraction measurements.

Synthesis of IOS-35: A mixture of $In(NO_3)_3·4.5H_2O$ (124mg, 0.325 mmol), thiourea (76 mg, 1 mmol), tetrazole (70 mg, 1 mmol), dimethyl formamide (DMF, 2 mL), AEP (2 mL) and 1,8-diazabicyclo [5.4.0]-7-undecene (DBU, 2 mL) was stirred in a 23 mL Teflon-lined stainless steel autoclave for half an hour. After the vessel was sealed and heated at 150 °C for 10 days, the autoclave was subsequently cooled to room temperature. A small amount of pale-yellow octahedral crystals was obtained by sonication treatment in ethyl alcohol (yield: < 1%, based on In element). The phase purity was identified by powder X-ray diffraction measurements.

Synthesis of IOS-5: A mixture of $In(NO_3)_3·4.5H_2O$ (124mg, 0.325 mmol), thiourea (76 mg, 1 mmol), tetrazole (70 mg, 1 mmol), acetonitrile (1 mL), AEP (1 mL) and 1,8-diazabicyclo [5.4.0]-7-undecene (DBU, 3 mL) was stirred in a 23 mL Teflon-lined stainless steel autoclave for half an hour. After the vessel was sealed and heated at 150 °C for 10 days, the autoclave was subsequently cooled to room temperature. A small amount of pale-yellow octahedral crystals was obtained by sonication treatment in ethyl alcohol (yield: < 1%, based on In element). The phase purity was identified by powder X-ray diffraction measurements.

Single-Crystal X-ray Diffraction Characterization. The single-crystal X-ray diffraction measurements on **IS-3, IOS-35** and **IOS-5** were performed on a Bruker Smart CPAD area diffractometer with nitrogen-flow temperature controller using graphite-monochromated MoKα (λ = 0.71073 Å) radiation at 120 K. The structure was solved by direct method using SHELXS-2014 and the refinement against all reflections of the compound was performed using SHELXL-2014. In these structures, some cations and free solvent molecules were highly disordered and could not be located. The diffuse electron densities resulting from these residual cations and solvent molecules were removed from the data set using the SQUEEZE[1] routine of PLATON and refined further using the data generated. In addition, for IOS-35 and IOS-5, the high angle data (above 1.2 Å resolution) was dominated by noise [I/sigma < 2.0] and was omitted by collecting relatively low resolution for high-quality crystal data.

Powder X-ray Diffraction (PXRD) Characterization. PXRD data were collected on a desktop diffractometer (D2 PHASER, Bruker, Germany) using Cu-Kα (λ = 1.54056 Å) radiation operated at 30 kV and 10 mA. The samples were ground into fine powders 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 40 s accumulation time were applied.

Thermogravimetric (TG) Measurement. A Shimadzu TGA-50 thermal analyzer was used to measure the TG curve by heating the sample from room temperature to 800℃ with heating rate of 10 °C/min under N_2 flow.

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}.

UV–Vis Absorption, Steady-State Fluorescence. Single-crystal UV-Vis absorption and Fluorescence of **IS-3, IOS-35** and **IOS-5** were performed through a Craic Technologies micro-spectrophotometer. Single-crystal samples were placed on quartz slides and the data were collected after optimization of the micro-spectrophotometer. Emission spectra were acquired under the excitation of 365 nm light using a mercury lamp with a 400 nm optical filter.

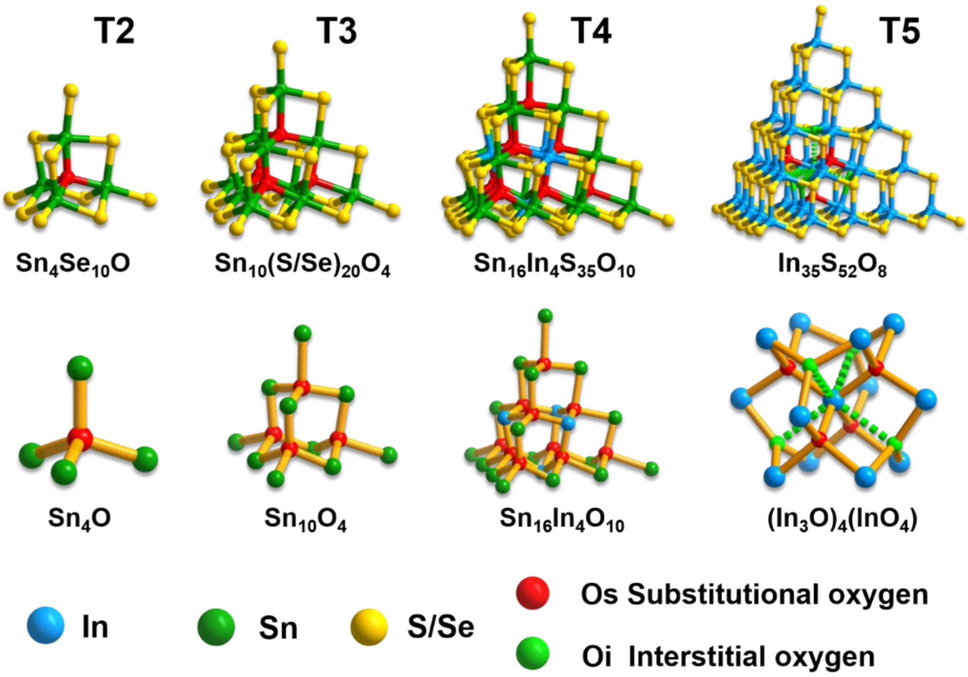

Figure S1. The development of oxy-chalcogenide nanocluster and its cores.

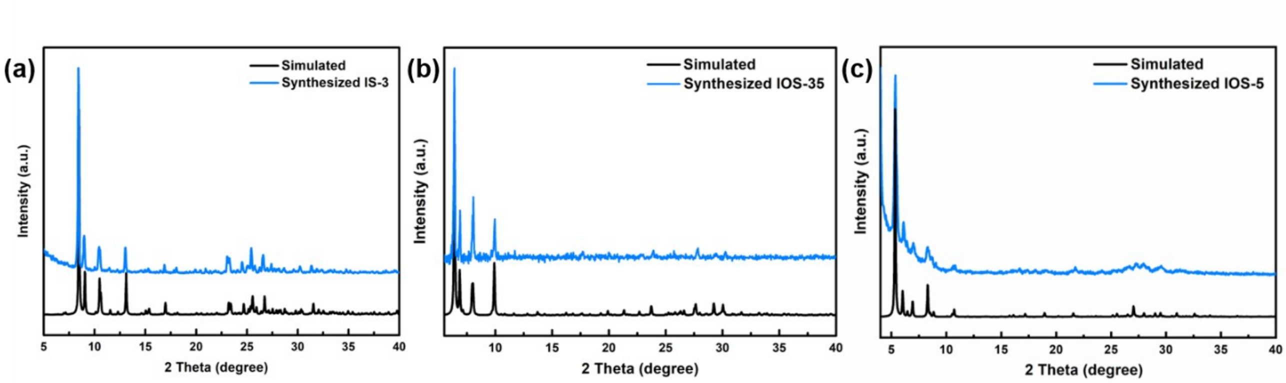

Figure S2. Powder X-ray diffraction (PXRD) pattern of as-synthesized **IS-3**(a), **IOS-35**(b) and **IOS-5** (c) and its simulated one. The curves match well, indicating that the pure phase was obtained.

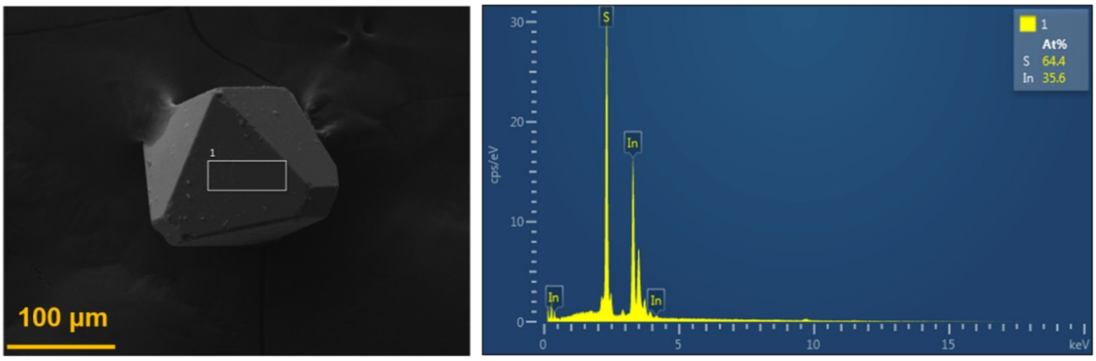

Figure S3. Left: SEM image of as-synthesized **IS-3** crystals. Right: energy dispersive spectroscopy (EDS) of **IOS-3**. (the ratio of In/S *Calcd.*:0.556, *Found*:0.553.)

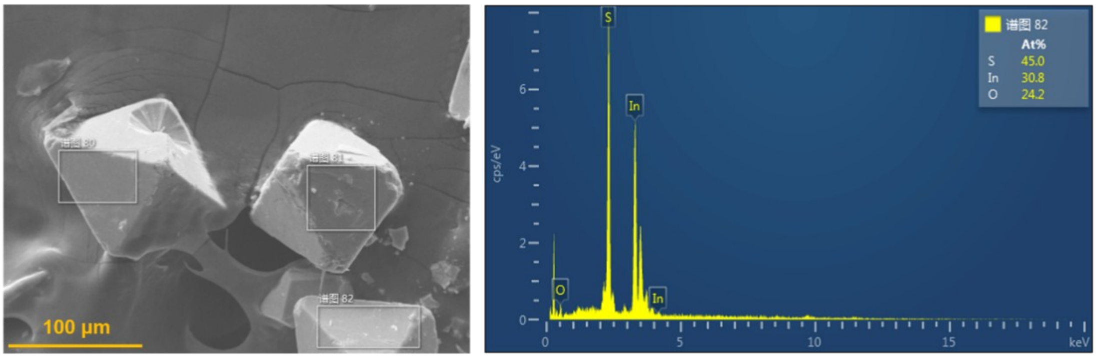

Figure S4. Left: SEM image of as-synthesized **IOS-35** crystals. Right: energy dispersive spectroscopy (EDS) of **IOS-35**. (the ratio of In/S *Calcd.*:0.662, *Found:* 0.684.)

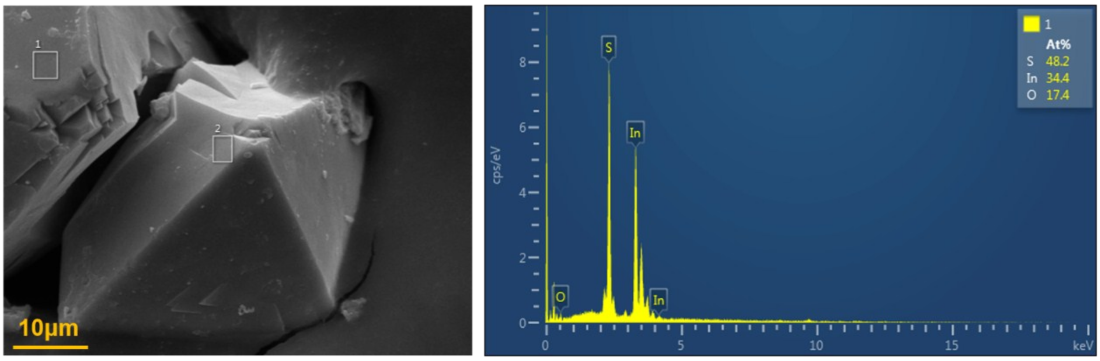

Figure S5. Left: SEM image of as-synthesized **IOS-5** crystals. Right: energy dispersive spectroscopy (EDS) of **IOS-5**. (the ratio of In/S *Calcd.*:0.7, *Found:* 0.714.)

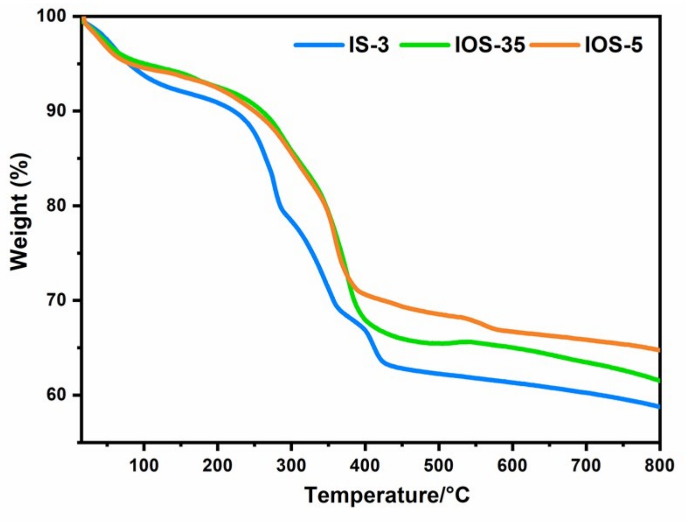

Figure S6. Thermal gravimetric analysis (TGA) of **IS-3**, **IOS-35** and **IOS-5**.

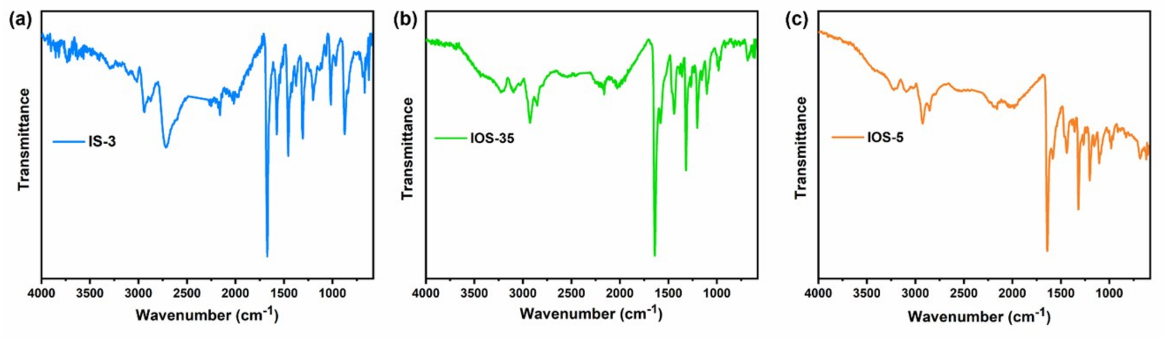

Figure S7. FT-IR spectra of **IS-3**(a), **IOS-35**(b) and **IOS-5**(c).

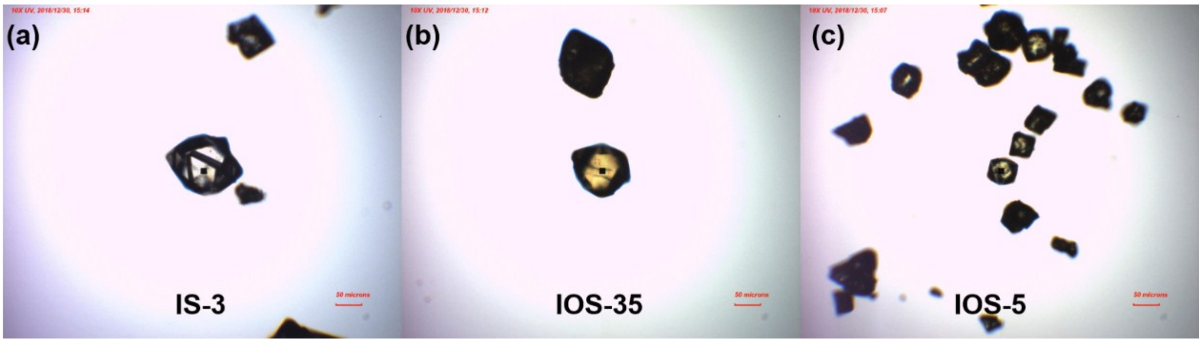

Figure S8. The selected crystals are detected in single-crystal UV-Vis spectra measurement for **IS-3** (a), **IOS-35** (b) and **IOS-5** (c).

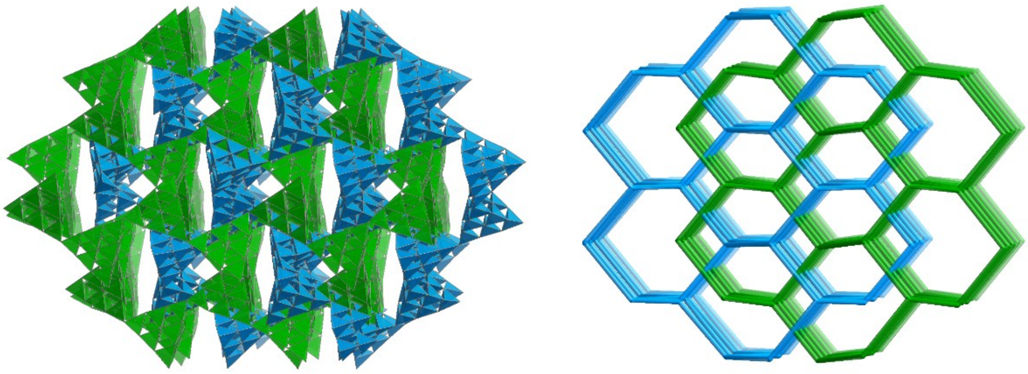

Figure S9. Two-interpenetrating sublattices and diamond-type topology of **IS-3**.

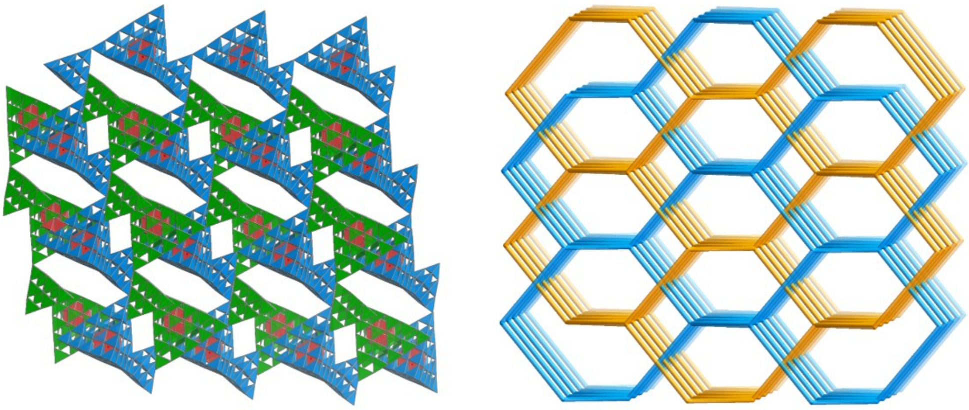

Figure S10. Two-interpenetrating sublattices and diamond-type topology of **IOS-35**.

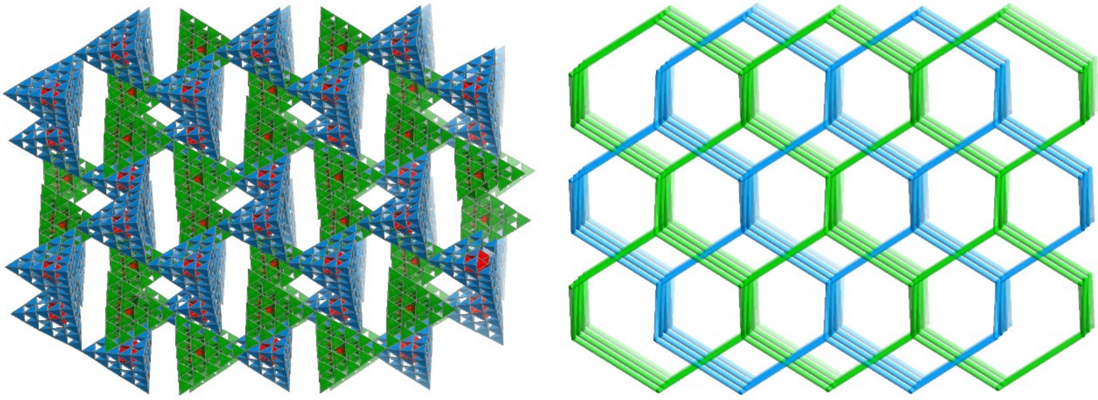

Figure S11. Two-interpenetrating sublattices and diamond-type topology of **IOS-5**.

Table S1. Summary of T*n* cluster-based metal-chalcogenide hybrid structures.

Compound	SBUs	Formula	Topology Type
T2-PseudoT3	T2-(o-T3)	$[Ga_{6.40}Sn_{21.60}S_{52}O_8]^{14.4-}$	PtS
OCF-42	T2-T4	$[(Ga_xGe_{4-x}Se_8)\ (Zn_4Ga_{16}Se_{33})]^{(10+X)-}$	$[8^8.8^8.8^8.8^8.8^2.8^2]\ [4.8^{11}.6^2.8^2.6^2.8^5]$
CIS-52	T2-T5	$[Cu_5In_{33}GeS_{63}]^{18-}$	HCB
UCR-19	T3-T4	$[Zn_4Ga_{26}S_{51}]^{16-}$	D.D.
UCR-15	T3-(coreless-T5)	$[In_{44}S_{72}]^{12-}$	D.D.
IOS-35	T3-(o-T5)	$[In_{45}S_{68}O_8]^{17-}$	D.D.
OCF-45	T4-(coreless-T5)	$[Mn_{11}In_{43}S_{87}]^{23-}$	S.D.

D.D. = double diamond; S.D. = single diamond

Table S2. Crystal data and structure refinement parameters for **IS-3**, **IOS-35** and **IOS-5**.

Compound	IS-3	IOS-35	IOS-5
Crystal system	tetragonal	tetragonal	tetragonal
Space group	$P4_3$	$I4_1/a$	$I4_1/acd$
Z	4	4	2
a (Å)	27.6229(5)	25.7476(19)	29.477(3)
b (Å)	27.6229(5)	25.7476(19)	29.477(3)
c (Å)	31.8781(6)	42.271(4)	54.456(6)
α (deg.)	90	90	90
β (deg.)	90	90	90
γ (deg.)	90	90	90
V (Å^3)	24323.8(10)	28023(5)	47317(11)
GOF on F^2	0.869	1.040	1.032
R_1, wR_2 (I>2σ(I))	0.0454, 0.0829	0.0432, 0.1244	0.0569, 0.1540
R_1, wR_2 (all data)	0.0715, 0.0918	0.0601, 0.1352	0.0923, 0.1849

Reference

1. P. van der Sluis, A. L. Spek, *Acta Crystallogr., Sect. A: Found. Crystallogr.* 1990, **46**, 194-201.