Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supporting Information for

Tin-oxychalcogenide supertetrahedral clusters maintained in an MTN zeolite-analog arrangement by Coulombic interactions

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Section S1: General Methods

Chemicals: *n*-Butyltin trichloride (*n*-butyl$SnCl_3$, 98%, liquid), *n*-butyl alcohol (99.5%, liquid), 1,5-Diazabicyclo[4.3.0]non-5-ene (DBN, 99%, liquid), thiourea (99%, solid), SeO_2 (99%, solid), 1,4-diaminobutane (DBA, 98%, liquid), 1-butyl-2,3-dimethylimidazolium chloride ([BMMIm]Cl, 99%, solid), Dimethyl sulfoxide (DMSO, 99.5%, liquid) were all used as supplied without further purification.

Instrumentation: Energy dispersive spectroscopy (EDS) analysis was performed on scanning electron microscope (SEM) equipped with Oxford INCA system. Elemental analysis (EA) was carried out on a Vario EL-Cube. Inductively coupled plasma optical emission spectroscopy (ICP–OES) was performed on an Ultima-2 spectrometer. The powder X-ray diffraction (PXRD) data of the samples were collected on a Rigaku Mini Flex II diffractometer using Cu Kα radiation (λ = 1.54056 Å) under ambient conditions. The UV–Vis diffuse reflection spectroscopy (DRS) data were recorded at room temperature using a powder sample with $BaSO_4$ as a standard (100% reflectance) on a PerkinElmer Lamda-950 UV spectrophotometer and scanned at 250-800 nm. Thermo gravimetric analysis (TGA) was carried out on a Mettler Toledo TGA/SDTA 851e analyzer in air atmosphere with a heating rate of 10 °C min^{-1} from 25 to 800 °C. Fourier transform infrared (FT–IR) spectra were acquired using KBr pellets on a Nicolet Magna 750 FT–IR spectrometer over a range 400-4000 cm^{-1}. The gas adsorption measurements were performed on a Micromeritics ASAP 2020 surface area and pore size analyzer. Electrospray ionization mass spectrometry (ESI–MS) data were collected on a DECAX- 30000 LCQ Deca XP instrument. Fluorescence was recorded on an Edinburgh FLS980 fluorescent photometer.

Single Crystal Characterization: The single crystal X-ray diffraction measurement was performed on ROD, Synergy Custom system, HyPix diffractometer with micro-focus metaljet Kα (λ = 1.34050 Å) radiation at 100 K. The structure was solved by direct method and refined by full-matrix least-squares on F^2 using the olex2.[1] All the non-hydrogen atoms are refined anisotropically. Contributions to scattering due to disordered solvent molecules were removed using the SQUEEZE routine of PLATON.[2]

Structures were then refined again using the data generated.

Photoelectric Response: Fluorine-doped tin oxide (FTO) glasses were cleaned by sonication in the acetone for half an hour and then dried at 60 °C over night in an oven. Then the dry and clean FTO glasses were used as the working electrodes. 5 mg sample was dispersed in the 0.5 ml solvent (T3-SnOS-MTN in DMF and T3-SnOSe-MTN in CH_3OH) and sonicated for 1 hour to get slurry. The conductive tape was used to adhere to part of FTO glasses to leave a circle with an area of 0.25 cm^2 for the slurry and then dried at room temperature naturally. The photocurrent measurements were performed in the cell equipped with three electrodes in the presence of 0.2 M Na_2SO_4 solution. A 300W Xe lamp (Beijing perfectlight, PLS-SXE300c) with a 420 nm cut-off filter was prepared for the photocurrent tests.

Section S2: Synthetic Procedures

Synthesis of T3-SnOS-MTN. *n*-butylSnCl$_3$ (0.1 mL), thiourea (3 mmol), DBN (1 mL), *n*-butyl alcohol (3 mL), were mixed in a 23-mL Teflon-lined stainless autoclave and stirred for 10 minutes. Then the vessel was sealed and heated at 140 °C for 7 days. Colorless or pale-yellow octahedral crystals (yield: 70 mg, ca. 41% base on *n*-butylSnCl$_3$) with pure phase were obtained by filtration after being washed with DMF and acetone for several times. Experimental EA date: C 23.78%, H 3.85%, N 6.19%, S 19.83%; calculated EA date: C 23.75%, H 3.68%, N 7.92%, S 18.13%. Experimental ICP data: Sn 42.12%; calculated ICP date: Sn: 41.95%. IR: *v* (cm^{-1}) = 3430(w), 3197(w), 3108(w), 2955(m), 2874(w), 2778(w), 2041(w), 1674(s), 1592(w), 1454(w), 1419(w), 1377(w), 1307(m), 1207(w), 1124(w), 1066(w), 575(m), 459(w).

Synthesis of T3-SnOSe-MTN. *n*-butylSnCl$_3$ (0.1 mL), SeO$_2$ (2 mmol), DBA (0.8 mL), [BMMIm]Cl (4 mmol), DMSO (0.2 mL), were mixed in a 23-mL Teflon-lined stainless autoclave and stirred for 20 minutes. Then the vessel was sealed and heated at 120 °C for 15 days. Orange octahedral crystals (yield: 17 mg) with pure phase were obtained by filtration after being washed with ethanol for several times. Experimental EA date: C 16.77%, H 2.86%, N 3.55%, S 0.76%; calculated EA date: C: 16.01%, H: 2.96%, N: 4.87%; S: 0.93%; Experimental ICP date: Sn 31.12%, Se 36.21%; calculated ICP date: Sn: 34.41%, Se: 36.62%. IR: *v* (cm^{-1}) = 3122(w), 2913(m), 2860(m), 1575(w), 1525(w), 1448(m), 1372(w), 1237(w), 1184(w), 1128(w), 1035(w), 950(w), 856(w), 726(m), 649(m), 548(s).

Section S3: Crystallographic Data

Table S1 Lattice parameters of T3-SnOX-MTN (X = S/Se) by SCXRD

Compound Name	T3-SnOS-MTN	T3-SnOSe-MTN
a/ Å	74.1412(3)	76.479(4)
b/ Å	74.1412(3)	76.676(4)
c/ Å	74.1412(3)	76.396(4)
α/°	90	89.848(5)
β/°	90	89.829(5)
γ/°	90	89.763(5)
Volume /Å^3	407548 (3)	447985 (40)

Table S2 Crystallographic data of T3-SnOS-MTN

Empirical Formula	$H_8O_8S_{16}Sn_{10}$
Formula Weight	1836.217
Temperature/K	77
Crystal System	cubic
Space Group	*Fd-3m*
a/Å	74.1412(3)
b/Å	74.1412(3)
c/Å	74.1412(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	407548(6)
Z	136
ρ_{calc}/g cm^{-3}	1.013
μ/mm^{-1}	12.687
F(000)	113770.9
Crystal Size/mm^3	0.4 × 0.35 × 0.35
Radiation	GaKα (λ = 1.3405)
2ϑ Range for Data Collection/°	6.22 to 79.96
Index Ranges	-82 ≤ *h* ≤ 38, -90 ≤ *k* ≤ 53, -48 ≤ *l* ≤ 72
Reflections Collected	111223
Independent Reflections	8546 [R_{int} = 0.0309, R_{sigma} = 0.0234]
Data/Restraints/Parameters	8546/0/266
Goodness-of-Fit on F^2	0.925
Final *R* Indexes [*I* >= 2σ (*I*)]	R_1 = 0.0556, wR_2 = 0.1903
Final *R* Indexes [all data]	R_1 = 0.0645, wR_2 = 0.2022
Largest Diff. Peak/Hole / e Å^{-3}	0.74/-0.72

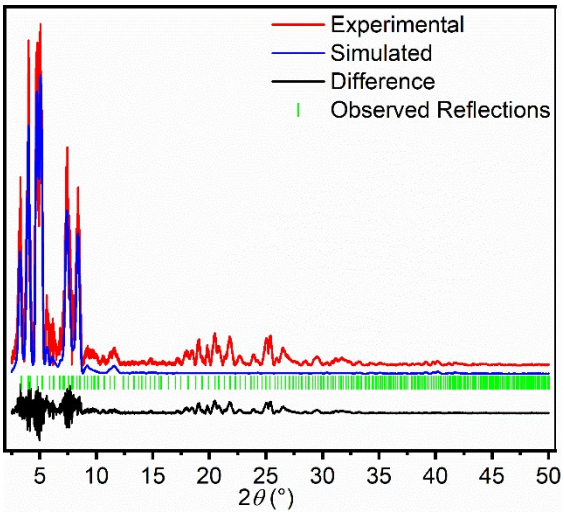

Fig. S1 Experimental and simulated PXRD patterns of T3-SnOSe-MTN after Pawley refinement. The reflection positions are represented by the green bars.

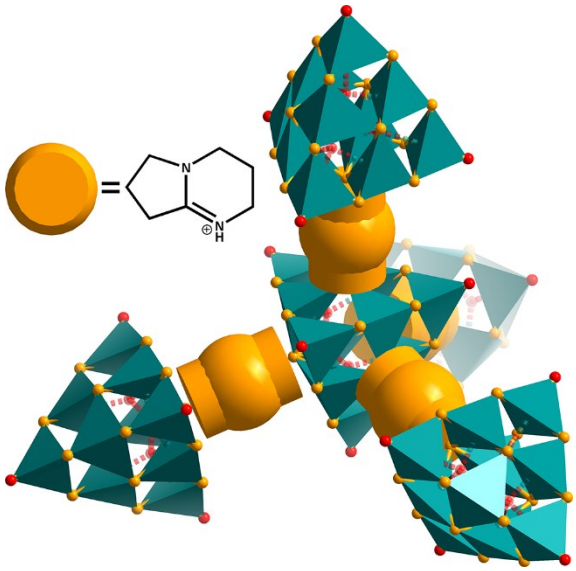

Fig. S2 The linkage mode between oxido-filled-T3 $\{Sn_{10}O_8S_{16}\}$ clusters, each of which connects to four neighbors via the Coulombic interactions with the protonated organic amine templates of H^+DBN.

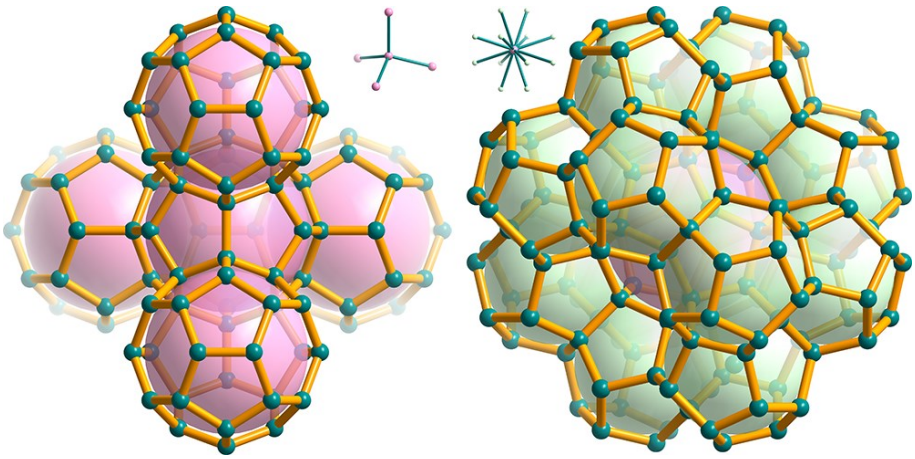

Fig. S3 Each cage-A ($6^4 5^{12}$) surrounded by 4 cage-A ($6^4 5^{12}$) and 12 cage-B (5^{12}) in T3-SnOS-MTN.

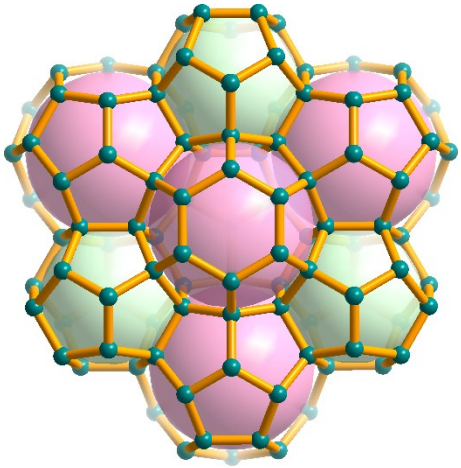

Fig. S4 The $\{Sn_{10}O_8S_{16}\}^{8-}$ anions are scattered in 3D space in an MTN zeotype in which each cluster is treated as a node.

Section S4: Fourier-Transform Infrared (FT–IR) Spectroscopy and Thermogravimetric Analysis (TGA)

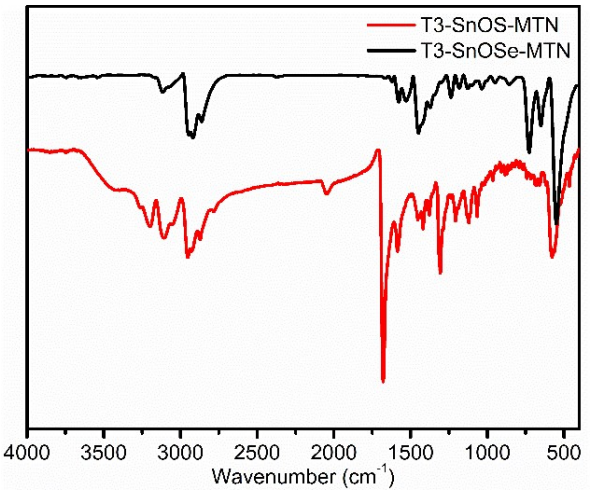

Fig. S5 The FT–IR spectra of samples of T3-SnOX-MTN (X = S/Se).

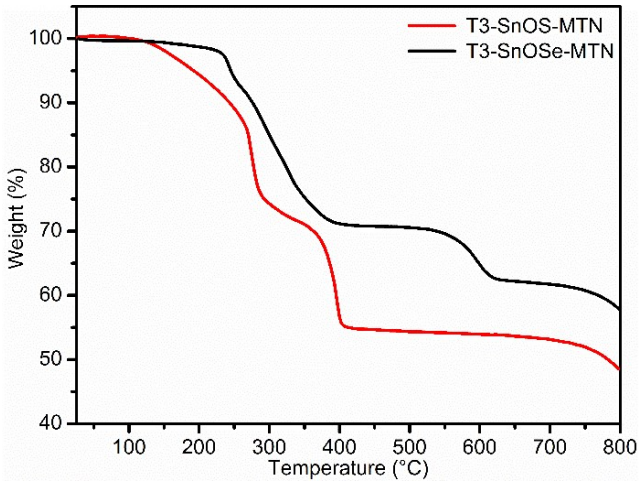

Fig. S6 The TGA curves of samples of T3-SnOX-MTN (X = S/Se).

Section S5: Scanning Electron Microscopy (SEM) and X-ray Energy Dispersive Spectroscopy (EDS)

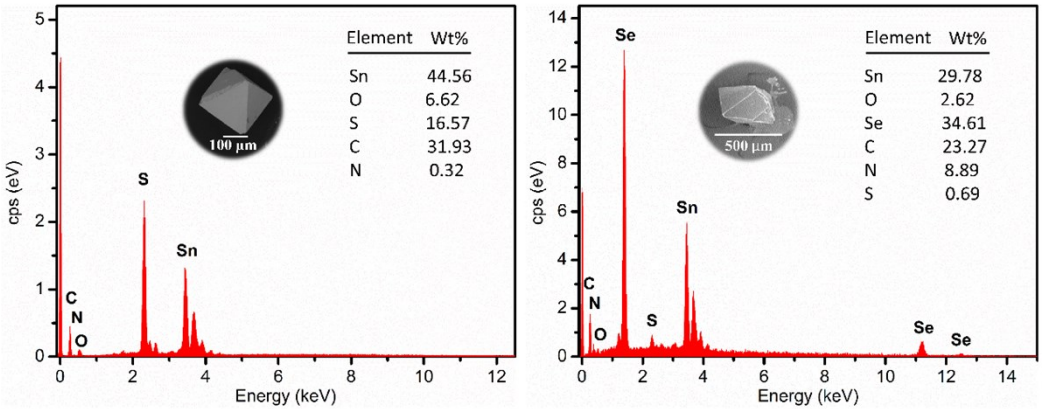

Fig. S7 The SEM images and EDS spectra of T3-SnOS-MTN (left) and T3-SnOSe-MTN (right). For T3-SnOSe-MTN, trace amount of S could be attributed to the presence of guest molecule of DMSO.

Section S6: Electrospray Ionization Mass Spectrometry (ESI–MS)

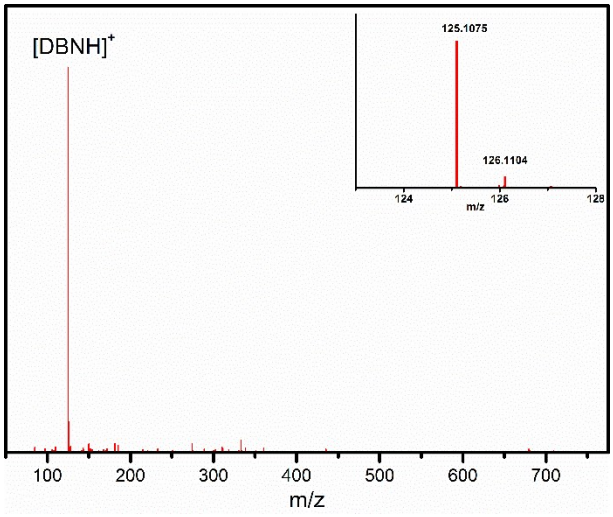

Fig. S8 The positive-mode ESI-MS spectrum of T3-SnOS-MTN in CH_3CN. The main peak at 125.1075 can be assignable to species of H^+DBA (i.e., $[C_7H_{13}N_2]^+$).

Section S7: Gas Sorption (BET)

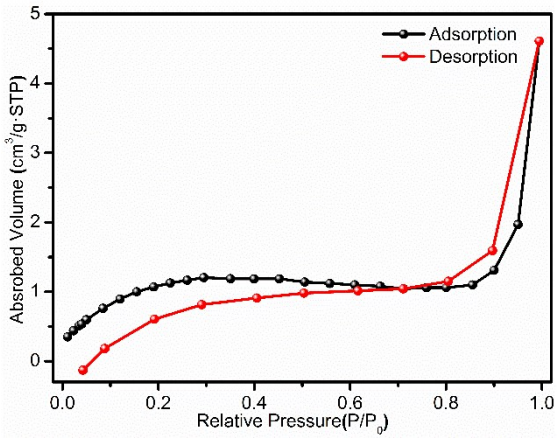

Fig. S9 The N_2 adsorption-desorption isotherms of T3-SnOS-MTN at 77 K.

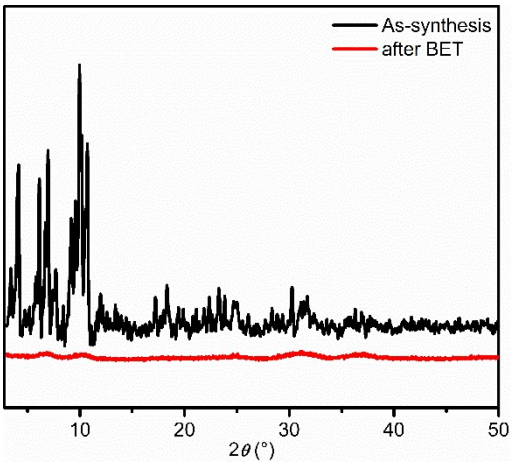

Fig. S10 The PXRD patterns of T3-SnOS-MTN as-synthesis and after the BET testing.

Section S8: Photoluminescence (PL)

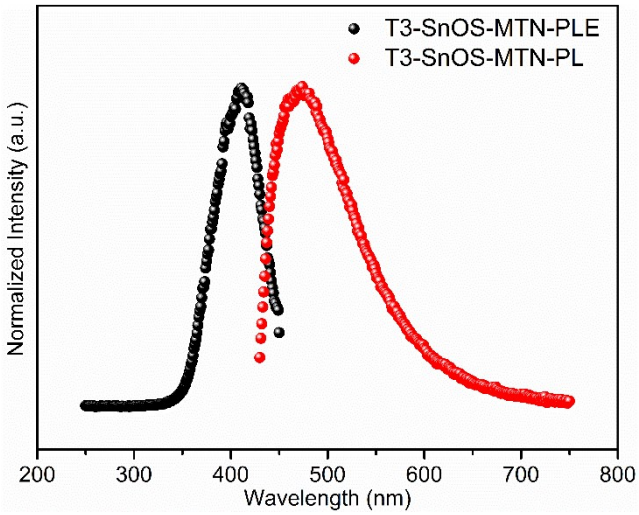

Fig. S11 The photoluminescence spectra of T3-SnOS-MTN.

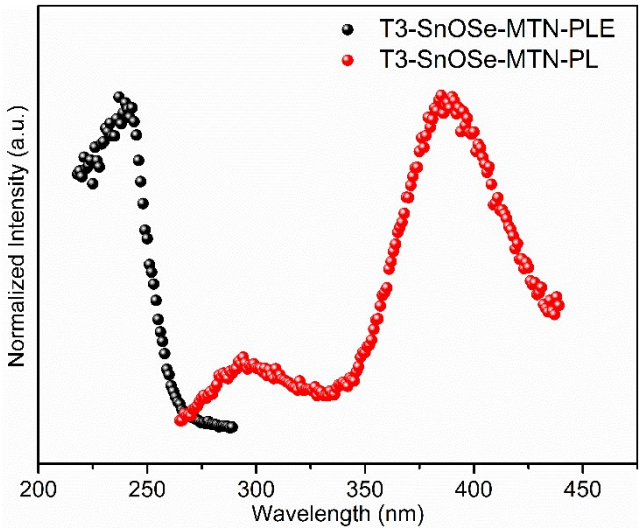

Fig. S12 The photoluminescence spectra of T3-SnOSe-MTN.

Section S9: Proton Conduction

Impedance Analysis. The sample was put into a home-made mold with a radius of 0.2 cm to get circular pellet, whose thickness was measured by a Vernier caliper. Then silver colloid were smeared on both sides of the pellet for fixing copper wires. The proton conductive capacities were performed on a Zahner (IM6) electrochemical impedance spectrometer, over sweeping from 0.1 Hz to 10 MHz, under varying relative humidity. The proton conductivity was calculated by using the following equation

$$\sigma = l/SR$$

where σ is the conductivity (S cm^{-1}). l is the thickness (cm) of the pellet, S is the cross-sectional area (cm^{-2}) of the pellet, R is the bulk resistance (Ω). The activation energy (E_a) was calculated from the following equation

$$\ln \sigma T = \ln\sigma_0 - E_a/KT$$

where σ is the conductivity (S cm^{-1}), K is the Boltzmann constant (eV/K) and T is the temperature (K)

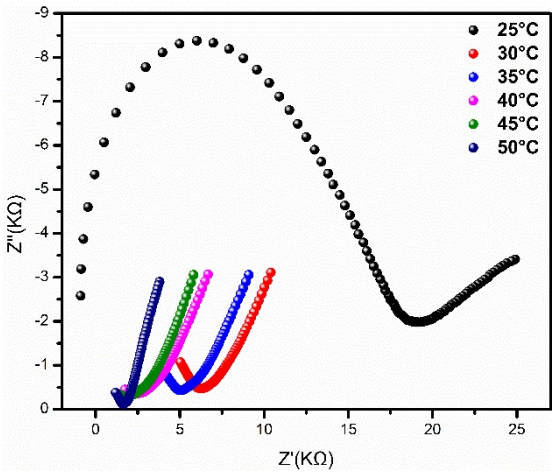

Fig. S13 Nyquist plots of the pelleted sample of T3-SnOS-MTN at different temperatures under 98% RH.

Section S10: References

1 (a) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst*, 2009, **42**, 339-341; (b) G. Sheldrick, *Acta Cryst*, 2015, **C71**, 3-8; (c) L. J. Bourhis, O. V. Dolomanov, R. J. Gildea, J. A. K. Howard and H. Puschmann, *Acta Cryst*, 2015, **A71**, 59-75.

2 P. van der Sluis and A. L. Spek, *Acta Cryst*, 1990, **A46**, 194-201.