Supporting Information For

Ligand-partially-protected metal-chalcogenide supertetrahedral clusters

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Supplementary Tables and Figures

Table S1. The structure refinement parameters on **ISC-24**, **ISC-25** and **ISC-26** series.

Compound	ISC-24-MnSnS	ISC-25-MnSnS-SPh	ISC-26-MnSnSeS-SPh	ISC-26-MnSnSeCl-SePh
E. F.	$C_{63}H_{141}Mn_4N_9S_{17}Sn_4$	$C_{60}H_{111}Mn_4N_6S_{17}Sn_4$	$C_{66}H_{116}Mn_4N_6S_5Se_{12}Sn_4$	$C_{66}H_{126}Mn_4N_6Se_{16.57}Cl_{0.43}Sn_4$
F. W.	2303.653	2192.33	2795.98	3022.79
Morphology	block	rhombohedral	rhombohedral	rhombohedral
Crystal system	Cubic	trigonal	trigonal	trigonal
Space group	*P-43n*	*R-3*	*R-3*	*R-3*
Z	6	6	6	6
T/K	120.00	120.00	123.00	120.03
λ/Å	0.71073	0.71073	0.71073	0.71073
a/Å	27.9971(13)	16.1766(5)	16.4718(5)	16.5878(5)
b/Å	27.9971(13)	16.1766(5)	16.4718(5)	16.5878(5)
c/Å	27.9971(13)	62.4767(18)	62.634(2)	62.041(2)
α/°	90	90	90	90
β/°	90	90	90	90
γ/°	90	120	120	120
V/Å^3	21945(3)	14158.7(10)	14717.2(10)	14783.7(10)
D (g/cm^3)	1.396	1.547	1.893	2.037
μ/mm^{-1}	2.111	2.449	6.093	7.662
F(000)	9392.0	6630.0	8052.0	8610.0
Col. refs.	469759	20190	22357	127820
Indep. refs.	3822	4464	5937	6022
GOF on F^2	1.103	1.038	1.046	1.049
R_1, wR_2 ($I>2\sigma(I)$)	0.0349, 0.0790	0.0446, 0.1157	0.0543, 0.1279	0.0502, 0.1172
R_1, wR_2 (all data)	0.0462, 0.0939	0.0531, 0.1255	0.0953, 0.1566	0.0655, 0.1327

Abbreviations: E. F.: Empirical formula; F. W.: Formula Weight.

Table S2. Summary of the existing PP-type metal chalcogenide supertetrahedral cluster. The cases using the same capping reagent but different in sizes or components were omitted for clarity.

Compound name	Cluster formula	Type	Terminating reagent	Ref.
ISC-1	$[Ga_{10}S_{16}(SH)(3,5\text{-}DMP)_3]^{3-}$	A	3,5-dimethylpyridine	1
ISC-2	$[Ga_{10}S_{16}(SH)(3,4\text{-}DMP)_3]^{3-}$	A	3,4-dimethylpyridine	1
ISC-3	$[In_{10}S_{16}(DBN)_4]^{2-}$	A	DBN	1
ISC-9	$[In_{22}Cd_{13}S_{52}(1\text{-}MIM)_4]^{12-}$	A	1-methylimidazole	1
T5-1	$(C_9H_{17}N_2)_{12}[Cu_5In_{30}Se_{52}Cl_3(C_3H_4N_2)]$	A	imidazole	2
IL-InSe-3	$C_{53}H_{99}N_{12}Cl_3In_{10}Se_{16}$	A	1-butyl-2-methylimidazole	3
1c	$[Bmmim]_4[Sn_{10}S_{16}O_4(SMe)_4]$	B	Methyl	4
1a	$[Bmmim]_7[Sn_{10}S_{16}O_4(SBu)_4]Br_3$	B	Butyl	5
ISC-25-MnSnS-SPh	$[Mn_4Sn_4S_{14}(SPh)_3]^{7-}$	C	Phenyl	**This work**
ISC-26-MnSnSeCl-SePh	$[Mn_4Sn_4Se_{12.6}Cl_{0.4}(SePh)_4]^{5.6-}$	C	Phenyl	**This work**
ISC-26-MnSnSeS-SPh	$[Mn_4Sn_4Se_{12}S(SPh)_4]^{6-}$	C	Phenyl	**This work**

Notes: Type A: Nitrogen containing species terminated; Type B, Alkyl group covalently terminated, Type C, Aryl group covalently terminated.

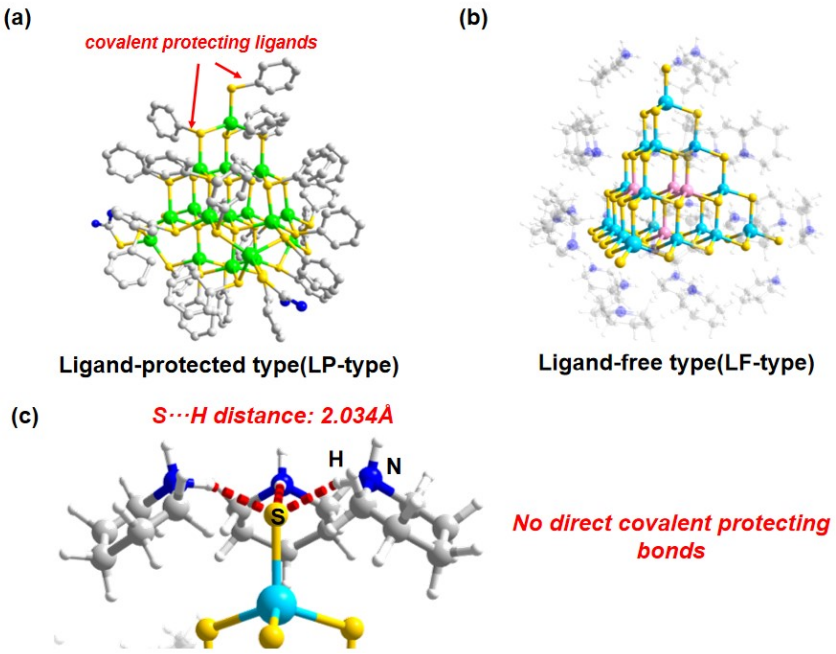

Fig. S1. Typical models of C*n* series clusters (or called: ligand-protected type, LP-type) and T*n* series clusters (or called: ligand-free type, LF-type). (a) LP-type MCSCs, the excess negative charge generated by S^{2-} were neutralized by covalent linked ligands; (b) LF-type MCSCs, the excess negative charge generated by S^{2-} were neutralized by the protonated organic amines (usually called templates in the synthetic process), the counterions were blurred to highlight the cluster; (c) The hydrogen bonds that further stable the isolated clusters. Green, Cd atom; pink, Zn atom; yellow, S atom, respectively.

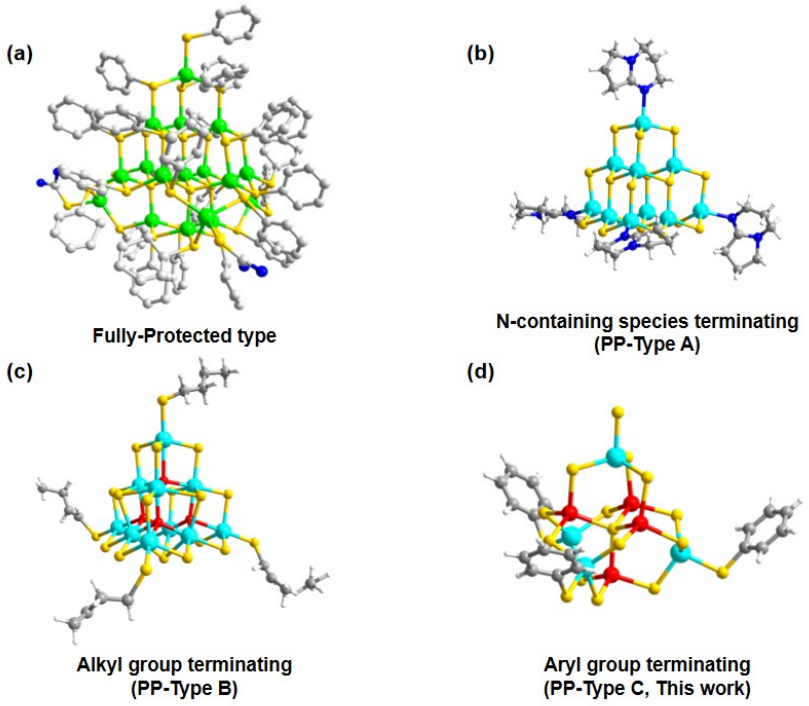

Fig. S2. Summary of the existing types of ligand protected metal chalcogenide supertetrahedral clusters..

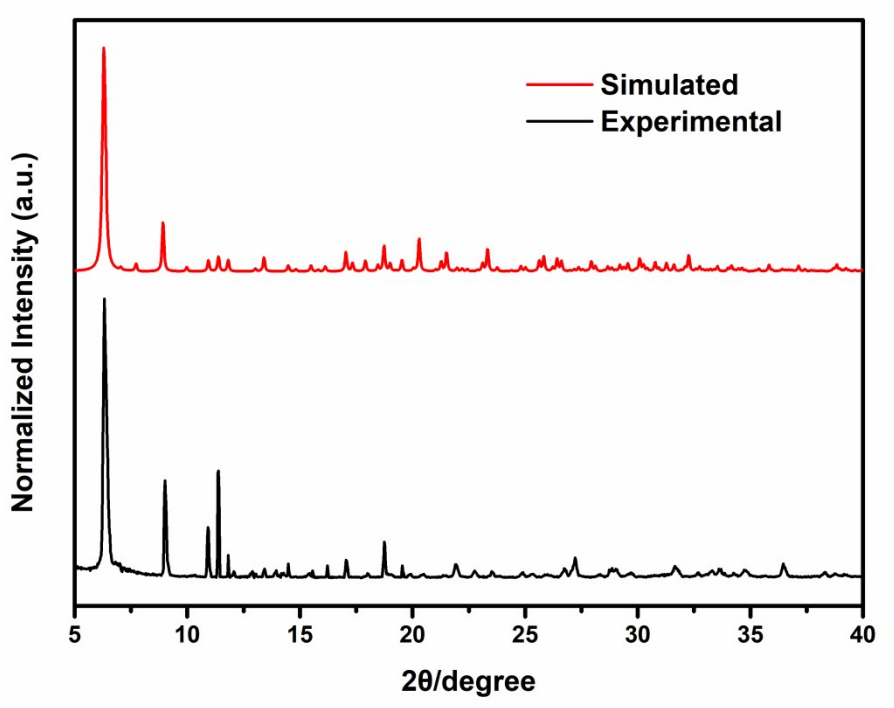

Fig. S3. Powder X-ray diffraction (PXRD) pattern of as-synthesized **ISC-24-MnSnS** and its simulated results.

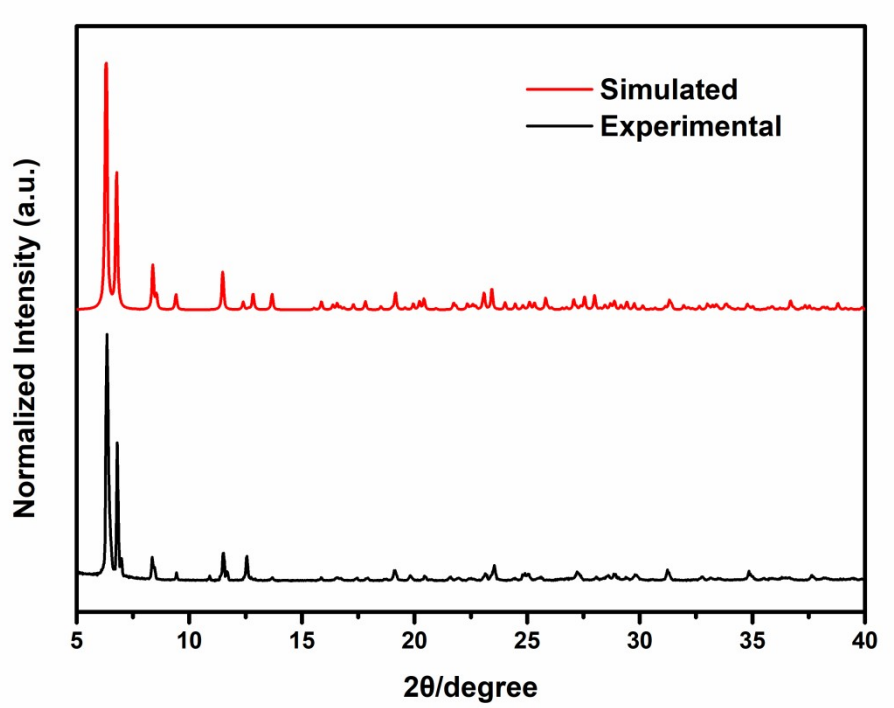

Fig. S4. Powder X-ray diffraction (PXRD) pattern of as-synthesized **ISC-25-MnSnS-SPh** and its simulated results.

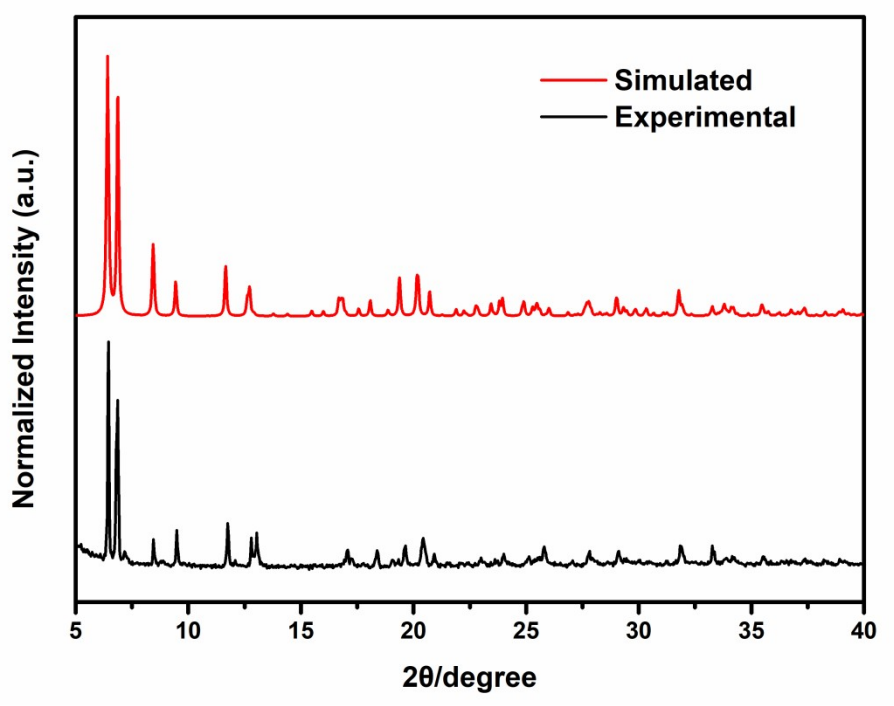

Fig. S5. Powder X-ray diffraction (PXRD) pattern of as-synthesized **ISC-26-MnSnSeCl-SePh** and its simulated results.

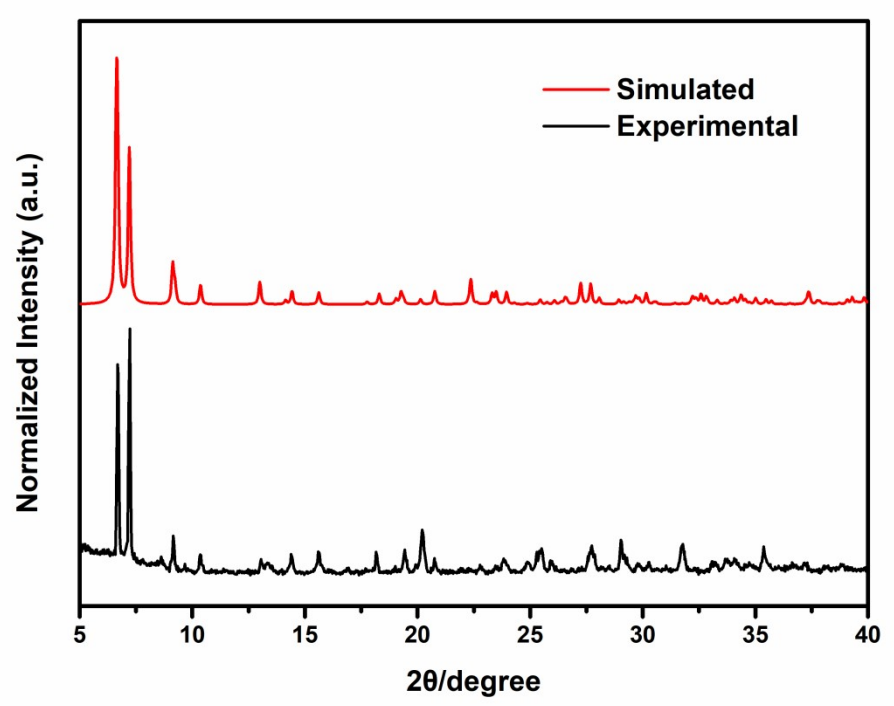

Fig. S6. Powder X-ray diffraction (PXRD) pattern of as-synthesized **ISC-26-MnSnSeS-SPh** and its simulated results.

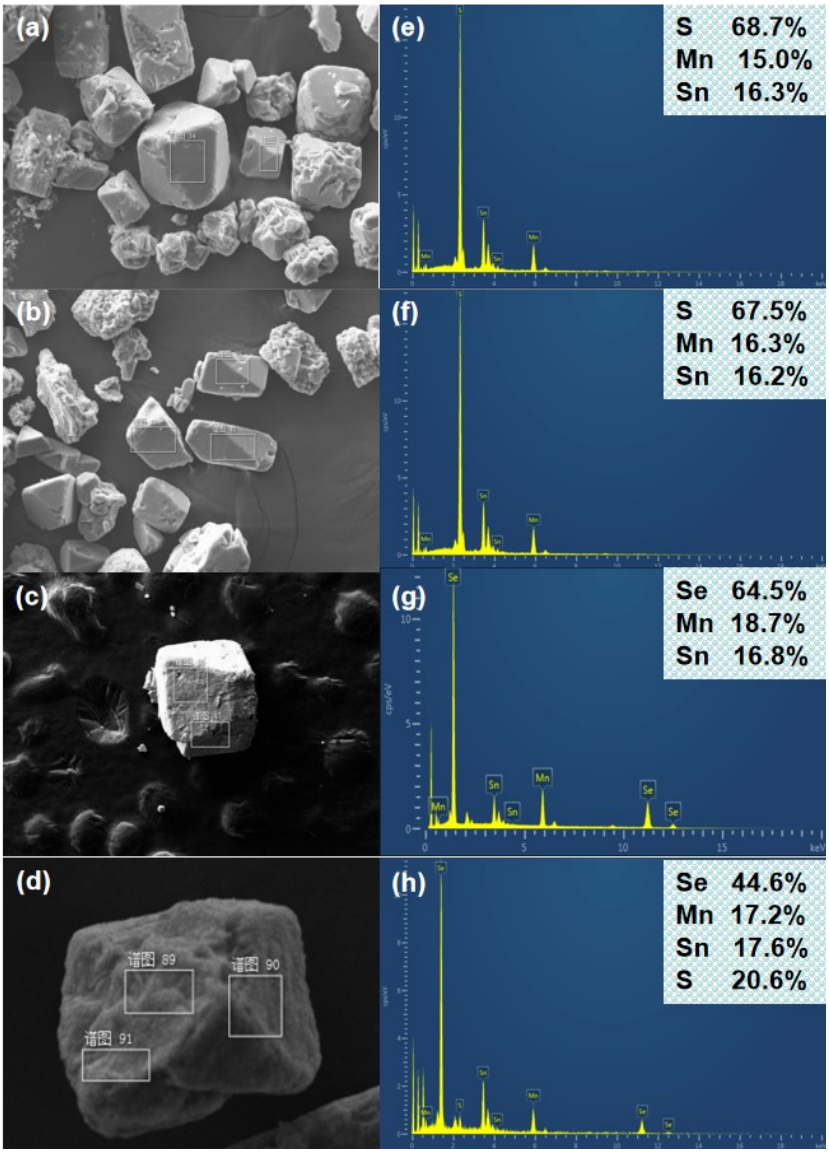

Fig. S7. SEM image (left) and EDS result (right) of **ISC-24-MnSnS** (a & e); **ISC-25-MnSnS-SPh** (b & f); **ISC-26-MnSnSeCl-SePh** (c & g) and **ISC-26-MnSnSeS-SPh** (d & h). According to the molecular formula of the title compounds, the ratio of Mn: Sn: Q (Q represents S or Se) in the **ISC-24**, **ISC-25** and **ISC-26** series structures should be 4:4:17, and the converted atomic percentage should be Mn (16%), Sn (16%), Q (68%), respectively. But the weak signal of Cl in **ISC-26-MnSnSnSeCl-SePh** has been judged as impurity by the instrument, so the test result here should be Mn: Sn: Se=4:4:16, that is, the atomic percentage should be Mn (16%), Sn (16%), Q (68%), respectively. The Cl existence has been further verified by XPS test. All in all, the test results are in good agreement with the fitting results.

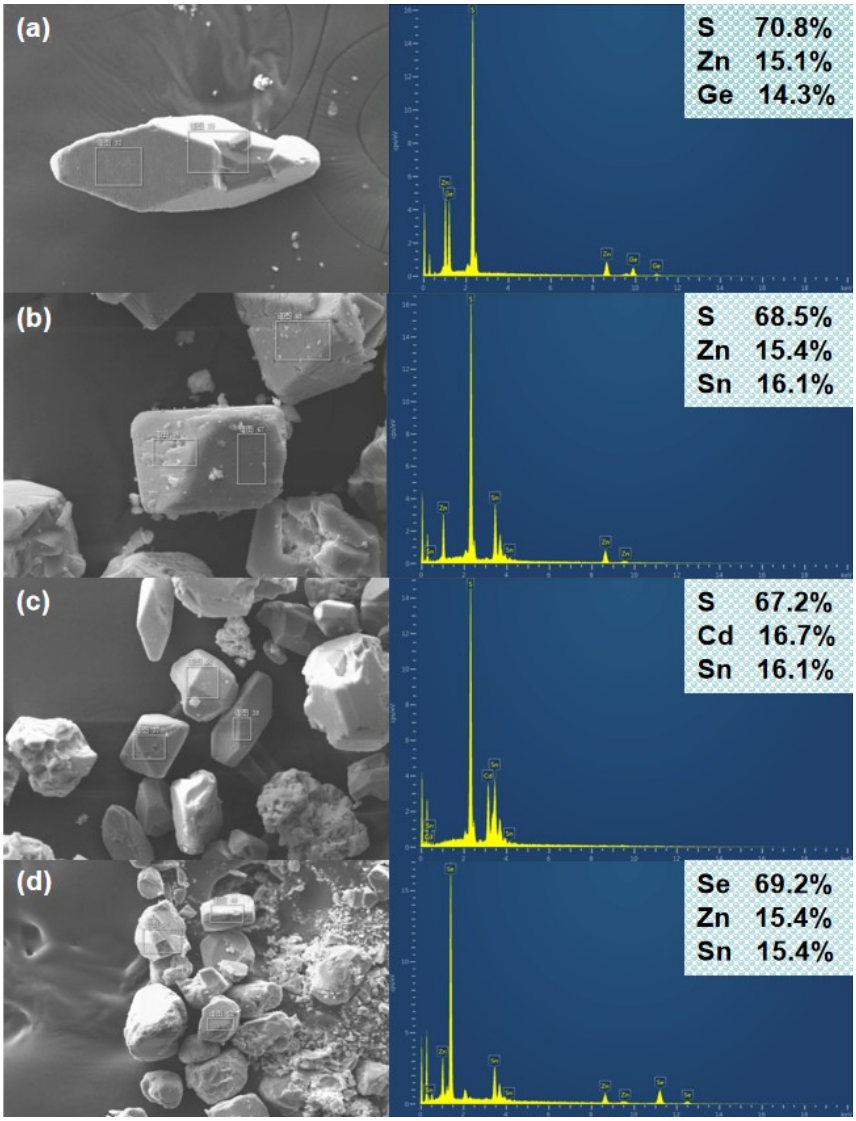

Fig. S8. SEM image (left) and EDS results (right) of **ISC-25** or **ISC-26** series with different components. According to the molecule formula of the title compounds, the ratio of Mn: Sn: Q (Q represents S or Se) in the **ISC-25** or **ISC-26** series structures should be 4:4:17, and the converted atomic percentage should be Mn (16%), Sn (16%), Q (68%), respectively. The above test results are in good agreement with the fitting results.

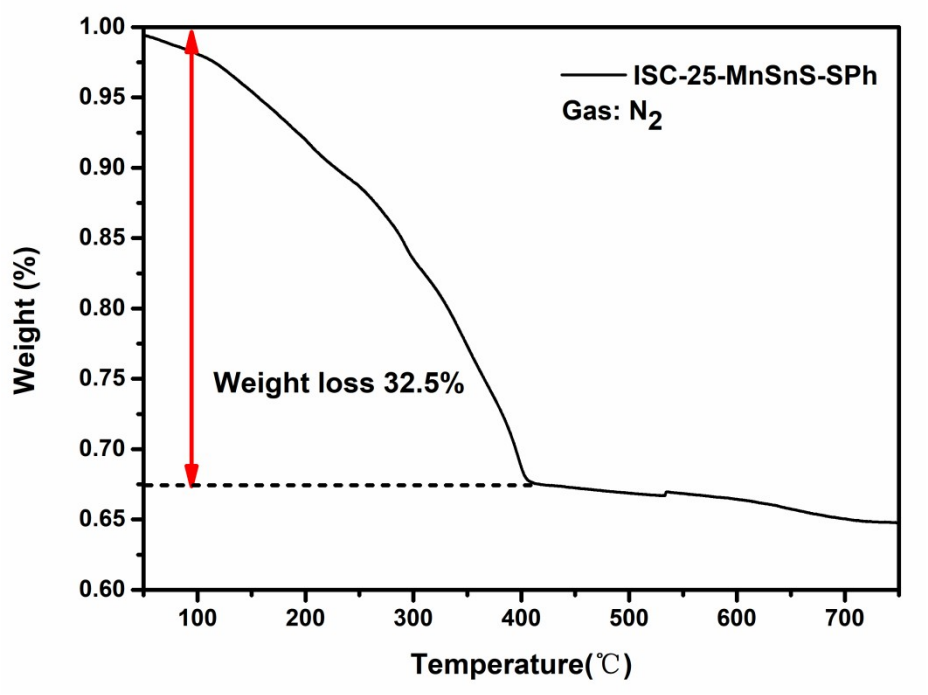

Fig. S9. TGA curves of **ISC-25-MnSnS-SPh**. **ISC-25-MnSnS-SPh** undergoes the total step weight loss about 32.5% from room temperature to 400℃, which is in good agreement with the calculated value from the SCXRD analysis, corresponding to the loss of the organic components (Calcd. 33.62%).

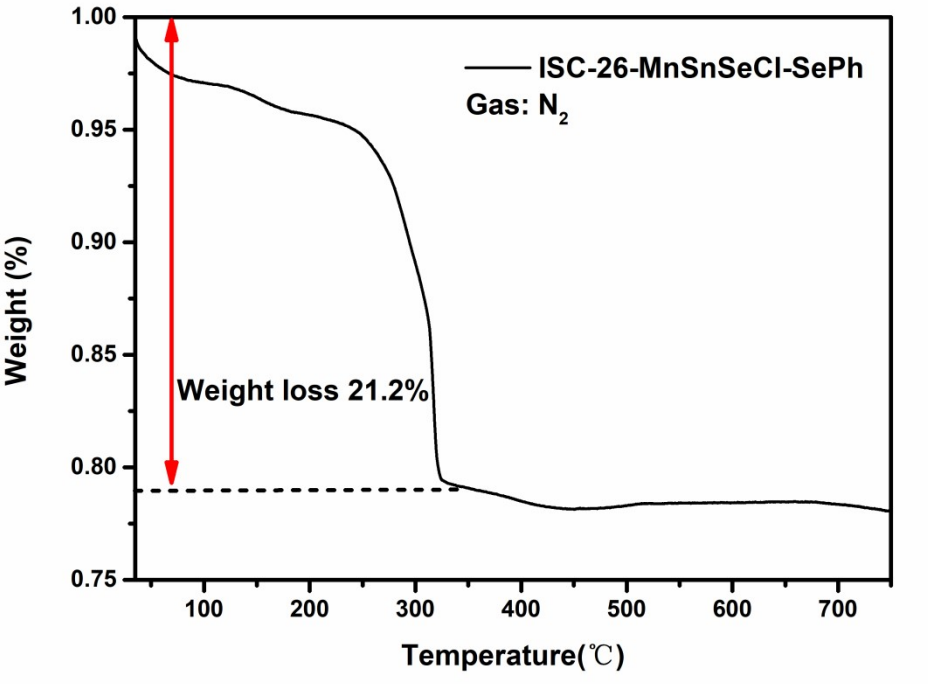

Fig. S10. TGA curves of **ISC-26-MnSnSeCl-SePh**. **ISC-26-MnSnSeCl-SePh** undergoes the total step weight loss about 21.2% from room temperature to 350℃, which is in good agreement with the calculated value from the SCXRD analysis, corresponding to the loss of the organic components (Calcd. 22.51%).

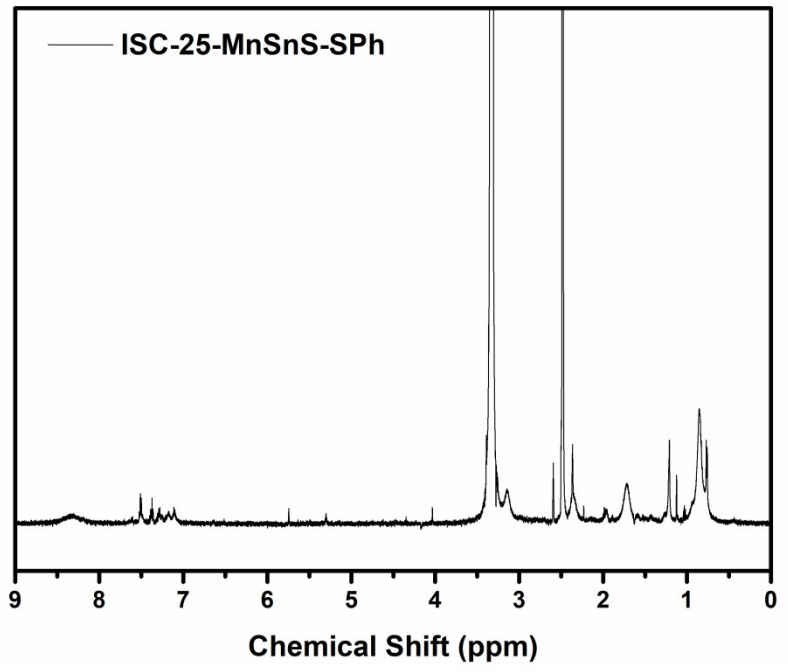

Fig. S11. ^{1}H-NMR spectrum for **ISC-25-MnSnS-SPh**. The two strong signal at 2.5 ppm and 3.3 ppm are inferred to d^{6}-DMSO and H_2O, respectively. The signals at chemical shift between 7-8 ppm confirmed the existence of benzene species, while the signals at 8-9 ppm can be determined as N-H···S hydrogen bonds between the protonated 3,5-DMP and the cluster.

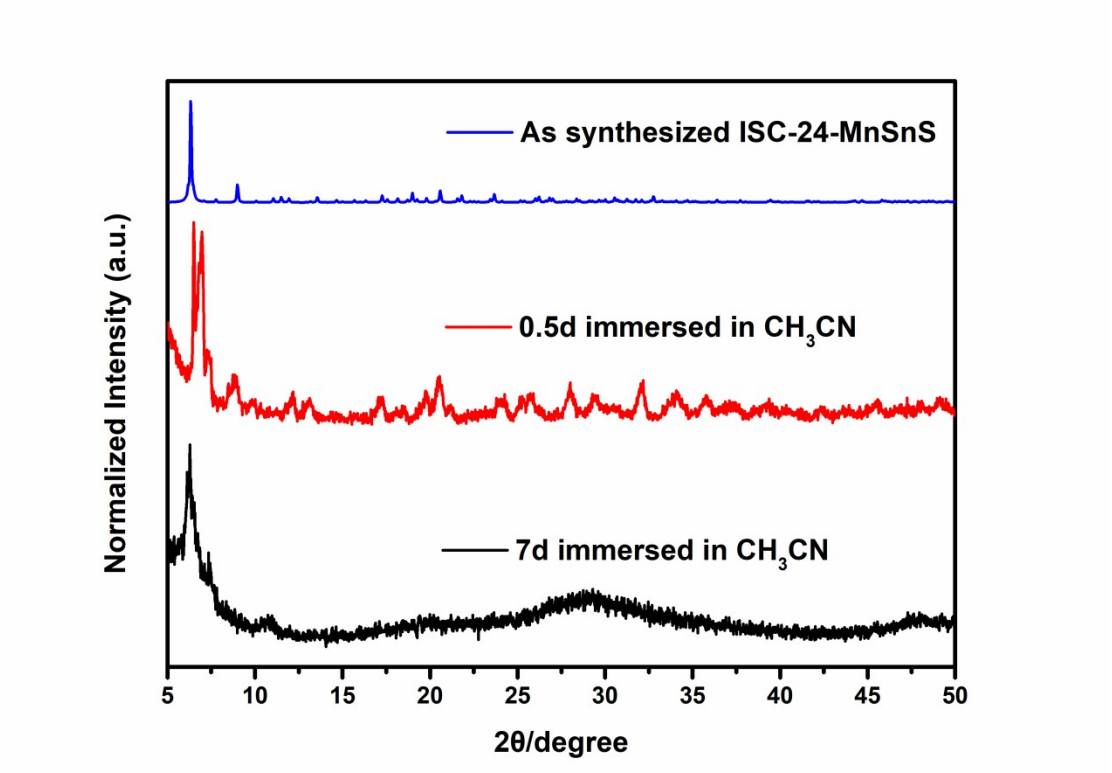

Fig. S12. Chemical stability test of **ISC-24-MnSnS**. The crystals were immersed acetonitrile (MeCN) for 0.5 or 7 days, and then the solvent was removed and the crystals were dried for further testing.

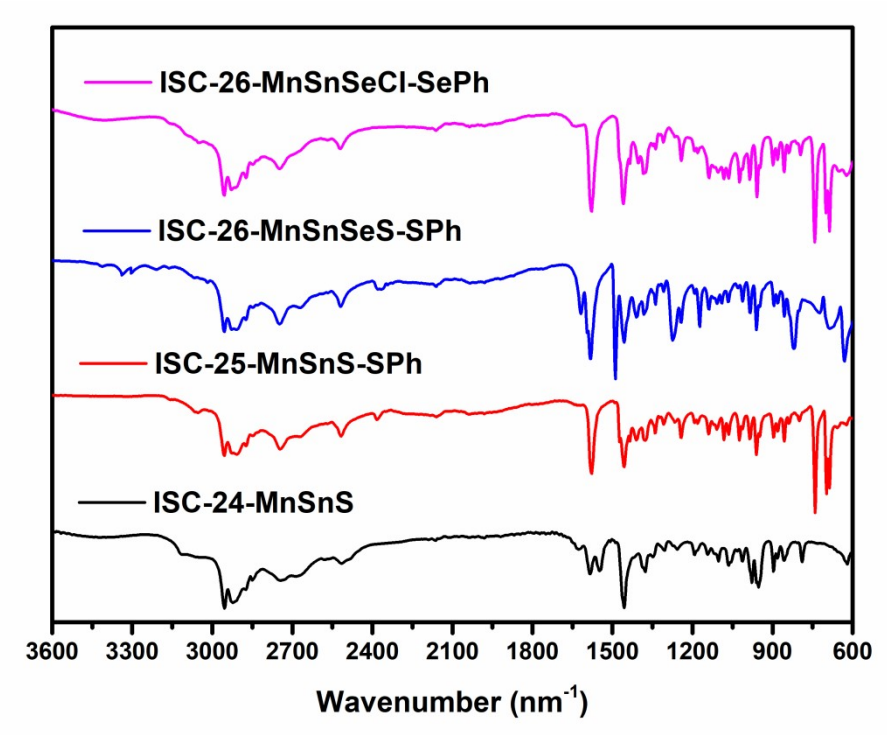

Fig. S13. FT-IR spectra of **ISC-24**, **ISC-25** and **ISC-26** series compounds.

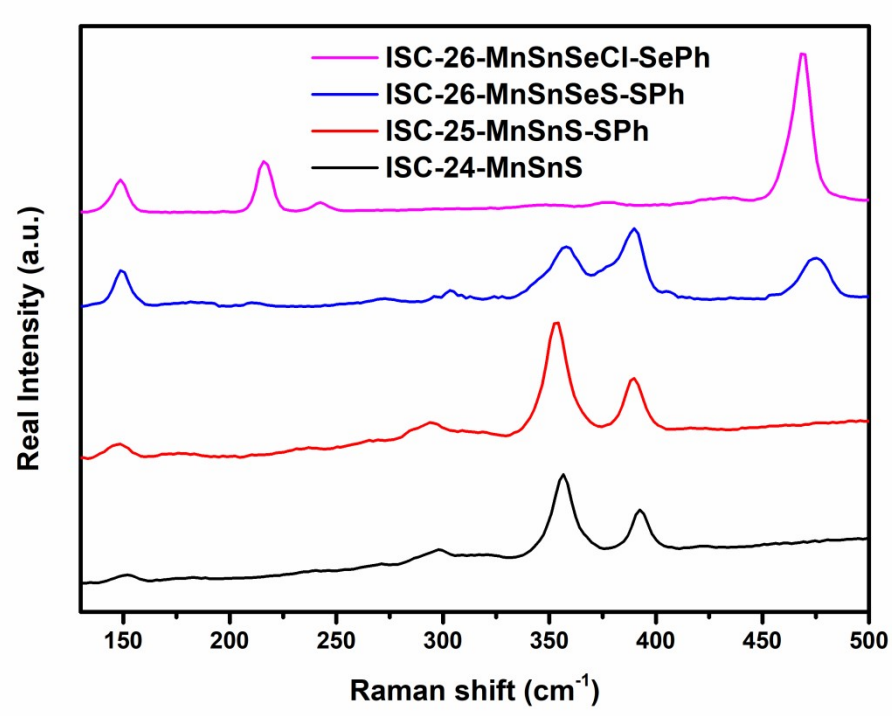

Fig. S14. Raman spectra of **ISC-24**, **ISC-25** and **ISC-26** series compounds.

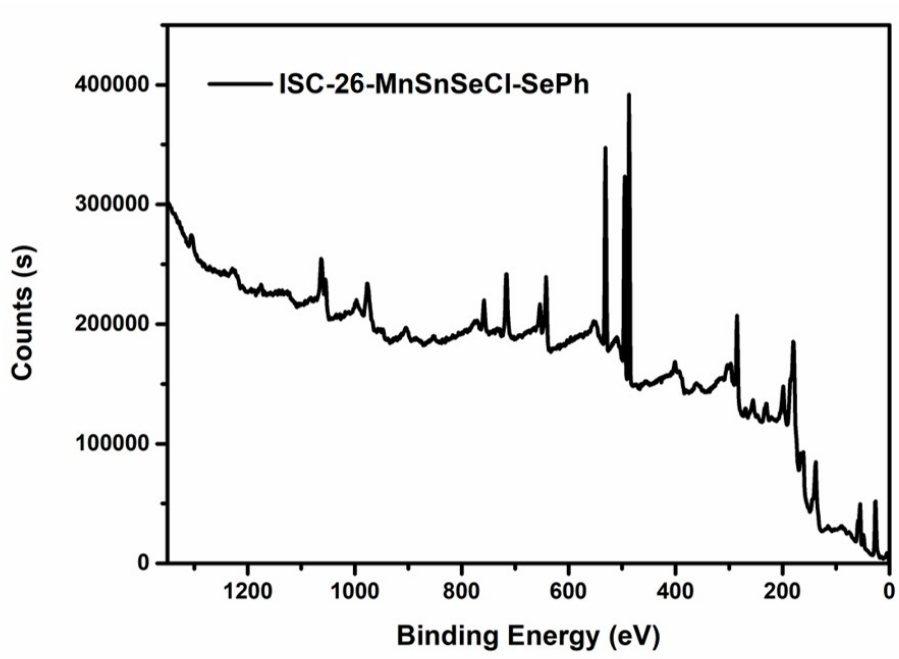

Fig. S15. XPS spectra of **ISC-26-MnSnSeCl-SePh**.

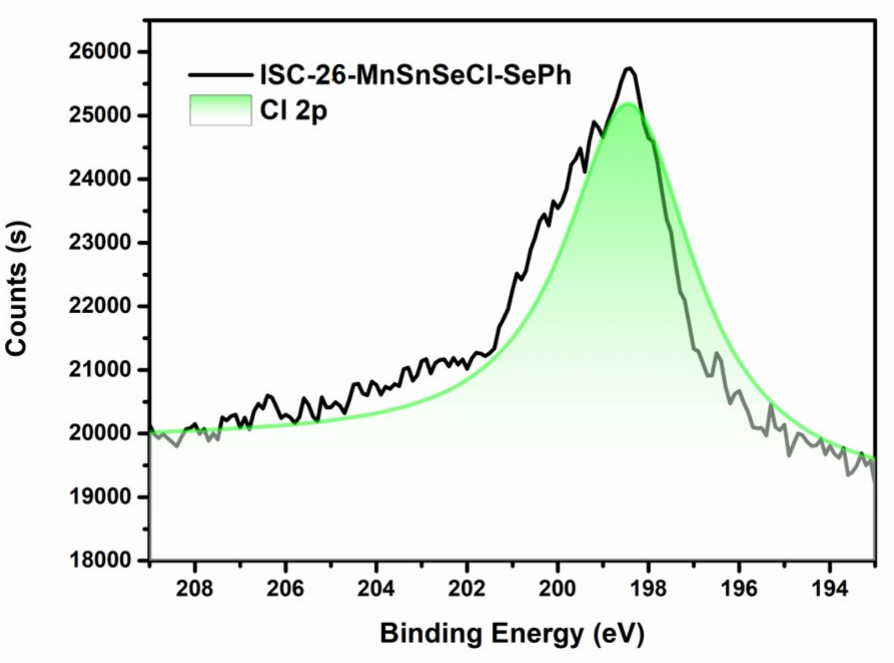

Fig. S16. High-resolution XPS spectra of Cl 2p in **ISC-26-MnSnSeCl-SePh**.

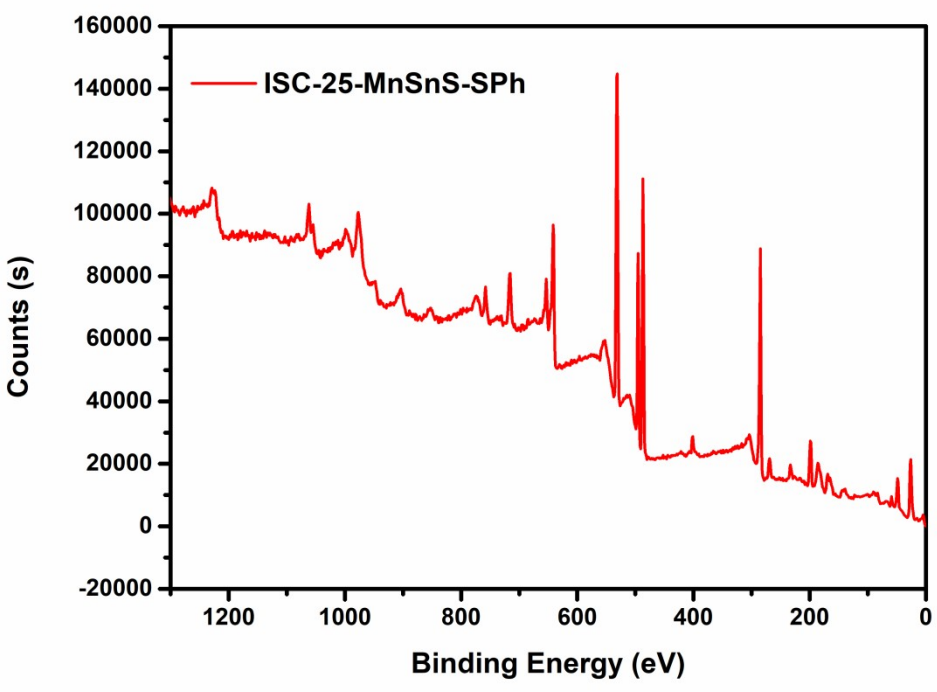

Fig. S17. XPS spectra of **ISC-25-MnSnS-SPh.**

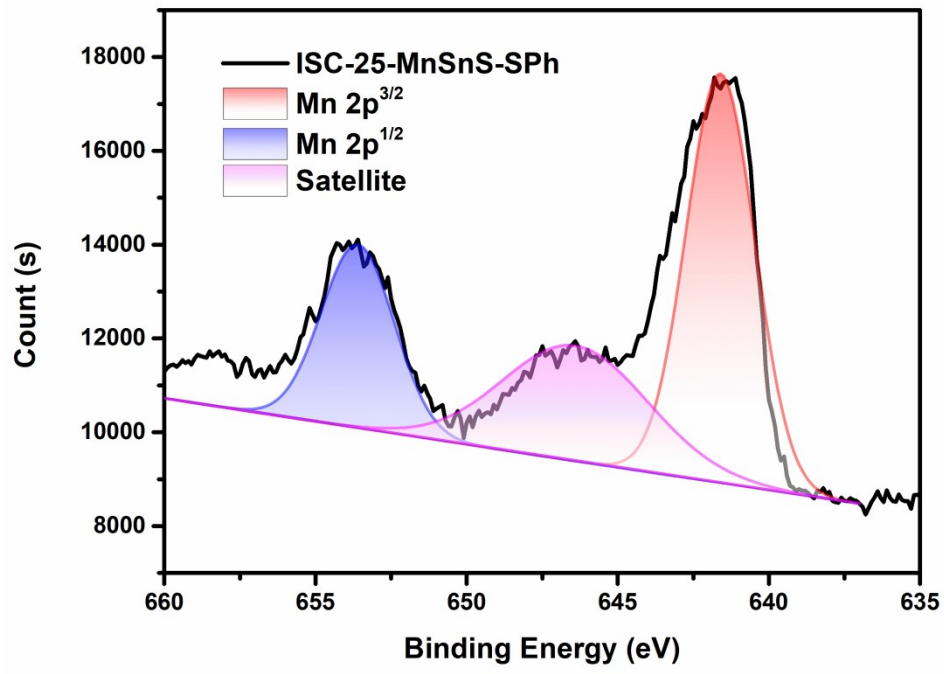

Fig. S18. High-resolution XPS spectra of Mn 2p in **ISC-25-MnSnS-SPh.**

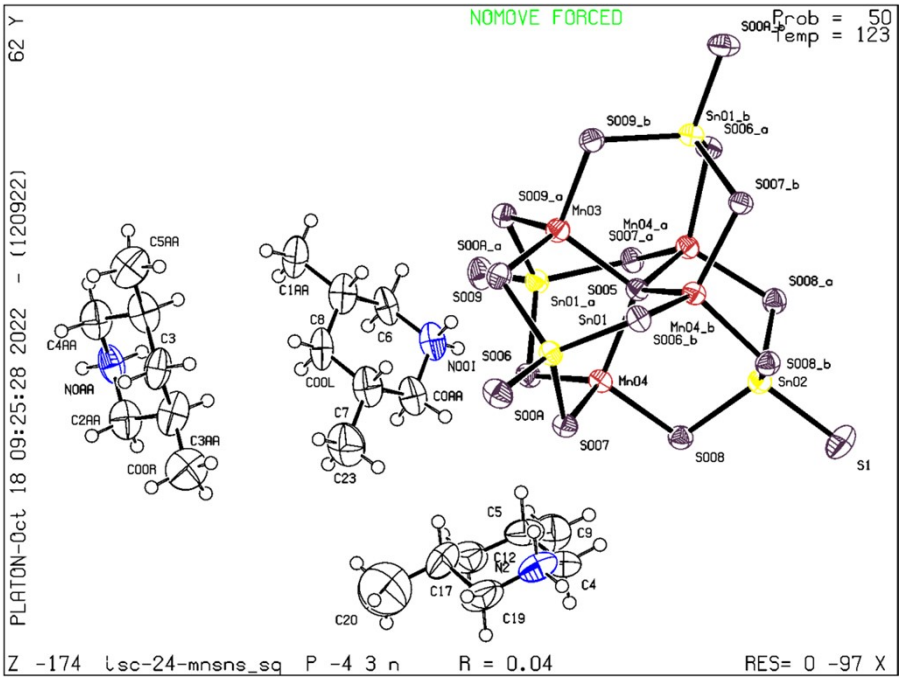

Fig. S19. Ellipsoid plot of **ISC-24-MnSnS.**

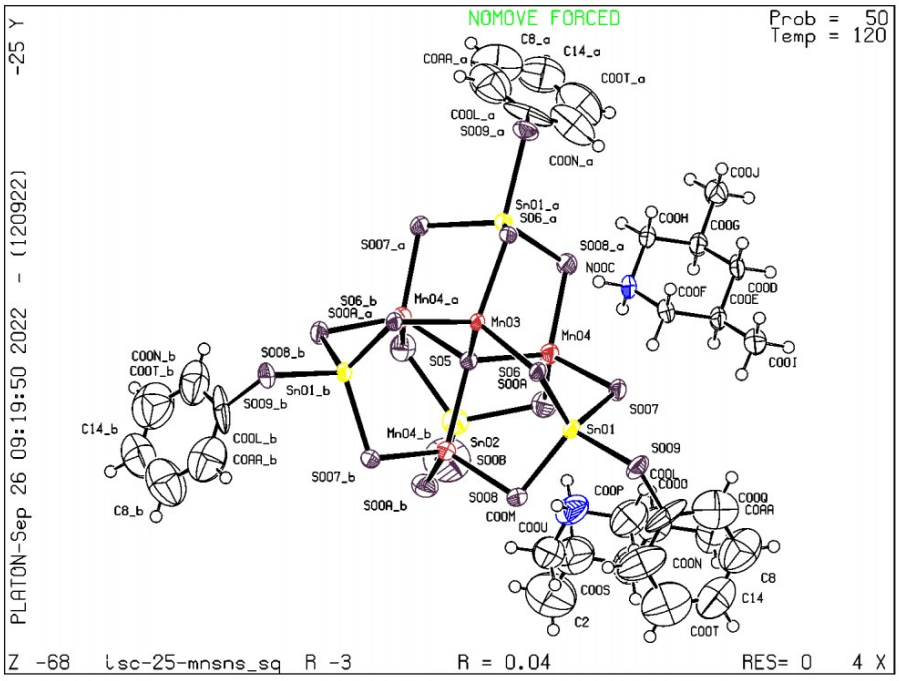

Fig. S20. Ellipsoid plot of **ISC-25-MnSnS-SPh.**

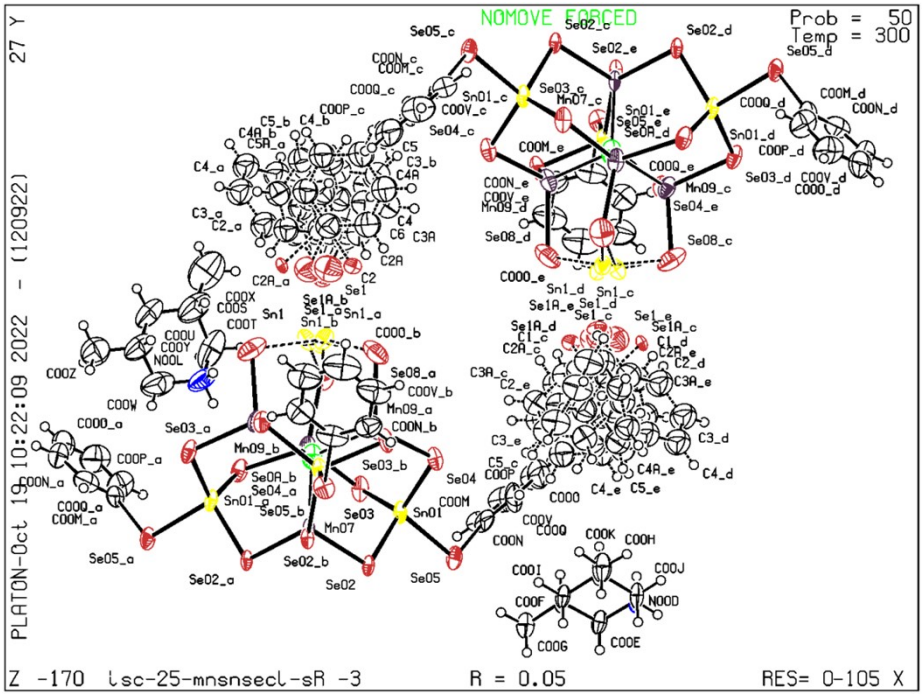

Fig. S21. Ellipsoid plot of **ISC-26-MnSnSeCl-SePh**.

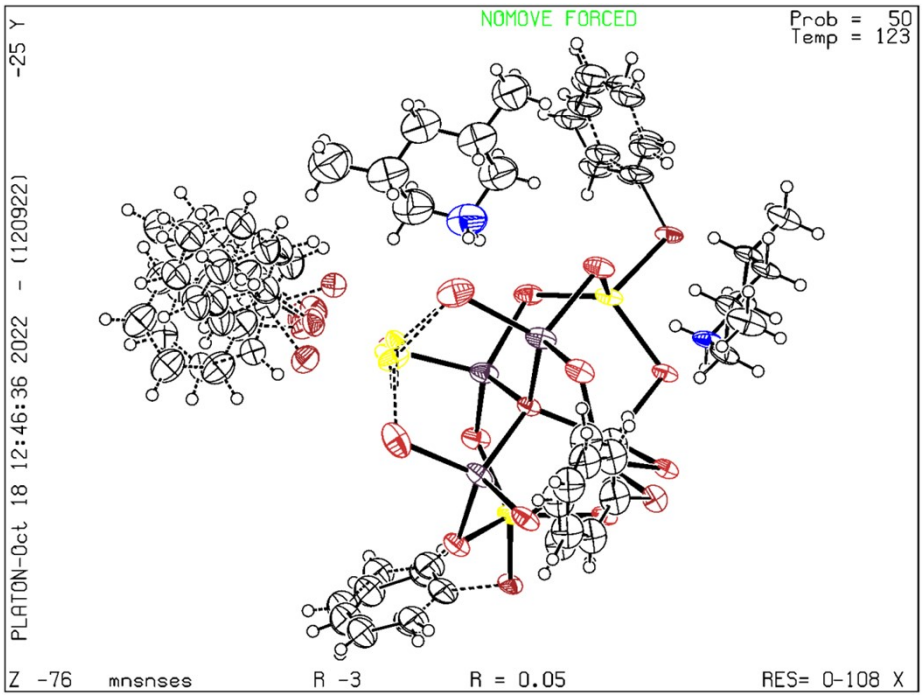

Fig. S22. Ellipsoid plot of **ISC-26-MnSnSeS-SPh**.

References

1. Wu, T.; Bu, X.; Liao, P.; Wang, L.; Zheng, S. T.; Ma, R. & Feng, P., Superbase Route to Supertetrahedral Chalcogenide Clusters. *J. Am. Chem. Soc.* **2012**, *134*, 3619-3622.
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5. Peters, B.; Stuhrmann, G.; Mack, F.; Weigend, F. & Dehnen, S., Highly Soluble Supertetrahedra upon Selective Partial Butylation of Chalcogenido Metalate Clusters in Ionic Liquids. *Angew. Chem. Int. Ed.* **2021**, *60*, 17622-17628.