Supporting Information for

Pushing up the Size Limit of Metal Chalcogenide Supertetrahedral Nanocluster

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Experimental Section:

Chemicals and Materials. Indium (In, 99.99%, powder), sublimed sulfur (S, 99.9%, powder), zinc acetate dihydrate [$Zn(CH_3COO)_2{\cdot}2H_2O$, 99%, powder], manganese acetate tetrahydrate [$Mn(CH_3COO)_2{\cdot}4H_2O$, 99%, powder], diethylenetriamine (DETA, ≥98%, liquid), 2,6-dimethylmorpholine (DMMP, ≥95%, liquid), 3,5-dimethylpiperidine (DMP, 97%, liquid), deionized water. All analytical grade chemicals employed were commercially available and used without further purification.

Synthesis of OCF-99-ZnInS {$[Zn_4In_{16}S_{33}]\cdot 5.35(H^+\text{-DMP})\cdot 3.02(\text{DMP})\cdot 4.54(NH_4^+)$}. Indium power (140 mg, 1.22 mmol), S power (192 mg, 5.99 mmol), $Zn(CH_3COO)_2{\cdot}2H_2O$ (88 mg, 0.40 mmol), 3,5-dimethylpiperidine (3.0 mL, 22.61 mmol) and deionized water (1.0 mL, 55.56 mmol) were mixed and stirred in a 23 mL Teflon-lined stainless autoclave and stirred for about 0.5 h. The vessels were sealed and heated at 180 °C for 7 days, then was cooled to room temperature naturally. Colorless block crystals were obtained. (Yield: 79 mg, 19% based on Zn). Elemental analysis, {calcd. *wt*%: C, 16.77; N, 4.31; H, 3.63; found: C, 17.01; N, 4.40; H, 4.06}.

Synthesis of OCF-99-MnZnInS. Pale yellow block crystals were obtained according to the similar procedure applied in **OCF-99-ZnInS**: indium power (140 mg, 1.22 mmol), S power (192 mg, 5.99 mmol), $Zn(CH_3COO)_2{\cdot}2H_2O$ (82 mg, 0.37 mmol), $Mn(CH_3COO)_2{\cdot}4H_2O$ (6 mg, 0.024 mmol), 3,5-dimethylpiperidine (3.0 mL, 22.61 mmol) and deionized water (1.0 mL, 55.56 mmol) were mixed and heated at 180°C for 7 days. The molar ratio of Mn : Zn : In was calculated to be 0.54: 3.46 : 16, according to EDS results.

Synthesis of OCF-100-ZnInS {$[Zn_{25}In_{31}S_{82}]\cdot 7.2(2H^+\text{-DETA})\cdot 4.6(H^+\text{-DETA})\cdot(H^+\text{-DMP})\cdot 32H_2O$}. indium power (55 mg, 0.48 mmol), S power (191 mg, 5.97 mmol), $Zn(CH_3COO)_2{\cdot}2H_2O$ (109 mg, 0.50 mmol), 3,5-dimethylpiperidine (3.0 mL, 22.61 mmol) and deionized water (1.0 mL, 55.56 mmol) were mixed and stirred in a 23 mL Teflon lined stainless autoclave, which was followed by magnetically stirring for half an hour. After the vessel was sealed and heated at 180°C for 7 days. Notably, Teflon-lined stainless autoclaves containing DETA (2 mL) and DMMP (2 mL) should be heated at 180 °C in advance, then such pretreated autoclaves were used for the following solvothermal processes. The products were completely taken out of autoclave and then ultrasonically washed by ethanol several times. Finally, pale yellow plate-like crystals were obtained after drying in air. (Yield: 34.8 mg, ~18% based on Zn). Elemental analysis, {calcd. *wt*%: C, 7.473; N, 5.328; H, 2.71; found: C, 7.667; N, 5.237; H, 2.814}. The Zn/In ratio was calculated to be 24.96 : 31.00 according to ICP-MS data.

Synthesis of OCF-100-MnZnInS. Yellow plate-like crystals were obtained by the similar procedure applied in **OCF-100-ZnInS**: indium power (55 mg, 0.48 mmol), S power (191 mg, 5.96 mmol), $Zn(CH_3COO)_2{\cdot}2H_2O$ (101 mg, 0.46 mmol), $Mn(CH_3COO)_2{\cdot}4H_2O$ (9mg, 0.037mmol), 3,5-dimethylpiperidine (3.0 mL, 22.61 mmol) and deionized water (1.0 mL, 55.56 mmol) were mixed and heated at 180 °C for 6 days. The molar ration of Mn : Zn : In was calculated to be 1.06: 23.94 : 31 according to EDS results.

Single-Crystal X-Ray Diffraction (SCXRD) Characterization. The single-crystal X-ray diffraction measurements on **OCF-99 and OCF-100** were performed on a Bruker Smart CPAD area diffractometer with nitrogen-flow temperature controller using graphite-monochromated Mo-*K*α (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. The CCDC number is 1574361 for OCF-99-ZnInS, 1573898 for OCF-100-ZnInS.

Powder X-Ray Diffraction (PXRD) Characterization. PXRD data were collected on a desktop diffractometer (D2 PHASER, Bruker, Germany) using Cu-*K*α (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 (EA). 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. Elemental analysis of C, H, and N was performed on VARIDEL III elemental analyzer. Inductively coupled plasma mass spectrometer (ICP-MS) analysis was conducted on Thermofisher Scientific iCAPQ.

Thermogravimetric Analysis (TGA). A Shimadzu TGA-50 thermal analyzer was used to measure the TG curve by heating the sample from room temperature to 800 ^{o}C with the heating rate of 5 $^{o}C \cdot min^{-1}$ under N_2 flow.

UV-Vis Absorption. Room-temperature solid-state UV-Vis diffusion reflectance spectra of crystal samples were measured on a SHIMADZU UV-3600 UV-Vis-NIR spectrophotometer coupled with an integrating sphere by using $BaSO_4$ powder as the reflectance reference. The absorption spectra were calculated from reflectance spectra by using the Kubelka-Munk function: $F(R)=\alpha/S=(1-R)^2/2R$, where R, α, and S are the reflection, the absorption and the scattering coefficient, respectively.

PL and Photoluminescence Excitation (PLE) Spectra. PL and photoluminescence excitation (PLE) spectra were recorded by an HORIBA scientific Fluorolog-3 steady state and time-resolved fluorescence spectrophotometer equipped with a 450 W xenon lamp. PL decays were recorded using an HORIBA scientific Fluorolog-3 steady state fluorimeter with a time-correlated single-photon counting (TCSPC) spectrometer and a pulsed xenon lamp as the excitation source. Low temperature PL spectra were recorded on a HORIBA scientific Fluorolog-3 spectrophotometer with a low temperature accessory.

Table S1. Summary on the composition, size, atom number of S and Zn sites with different coordination number in the isolated T*n*-ZnS NCs.

T*n*	Compositions	Edge Length (nm)	S Coordination				Zn Coordination			
			4 (core)	3 (face)	2 (edge)	1 (vertex)	4 (core)	4 (face)	4 (edge)	4 (corner)
T*n*	**$[Zn_{n(n+1)(n+2)/6}S_{(n+1)(n+2)(n+3)/6}]^{(n+1)(n+2)-}$**	**~ 0.4n**	**(n-3)(n-2)(n-1)/6**	**2(n-2)(n-1)**	**6(n-1)**	**4**	**(n-4)(n-3)(n-2)/6**	**2(n-3)(n-2)**	**6(n-2)**	**4**
T2	$[Zn_4S_{10}]^{12-}$	~ 0.8	0	0	6	4	0	0	0	4
T3	$[Zn_{10}S_{20}]^{20-}$	~ 1.2	0	4	12	4	0	0	6	4
T4	$[Zn_{20}S_{35}]^{30-}$	~ 1.6	1	12	18	4	0	4	12	4
T5	$[Zn_{35}S_{56}]^{42-}$	~ 2.0	4	24	24	4	1	12	18	4
T6	**$[Zn_{56}S_{84}]^{56-}$**	**~ 2.4**	**10**	**40**	**30**	**4**	**4**	**24**	**24**	**4**
T7	$[Zn_{84}S_{120}]^{72-}$	~ 2.8	20	60	36	4	10	40	30	4
T8	$[Zn_{120}S_{165}]^{90-}$	~ 3.2	35	84	42	4	20	60	36	4
T9	$[Zn_{165}S_{220}]^{110-}$	~ 4.0	56	112	48	4	35	84	42	4
T10	$[Zn_{220}S_{286}]^{132-}$	~ 4.4	84	144	54	4	56	112	48	4

Table S2. Summary on the composition, size, atom numbers of S and M sites with different coordination number in the optimal isolated ternary T*n*-ZnInS NCs with all edge and corner metal sites occupied by In atoms.

T*n*	Compositions	S Coordination					Zn Coordination		In Coordination			Ref.
		4 (core)	3 (core)	3 (face)	2 (edge)	1 (vertex)	4 (core)	4 (face)	4 (face)	4 (edge)	4 (corner)	
T*n*	**$[Zn_{(n+8)(n-3)(n-2)/6}In_{(6n-8)}S_{(n+1)(n+2)(n+3)/6}]$**	**(n-3)(n-2)(n-1)/6**	**-**	**2(n-2)(n-1)**	**6(n-1)**	**4**	**(n-4)(n-3)(n-2)/6**	**2(n-3)(n-2)**	**-**	**6(n-2)**	**4**	
T2	$[In_4S_{10}]^{8-}$	0	-	0	6	4	0	0	-	0	4	[1]
T3	$[In_{10}S_{20}]^{10-}$	0	-	4	12	4	0	0	-	6	4	[2]
T4	**$[Zn_4In_{16}S_{35}]^{14-}$**	**1**	**-**	**12**	**18**	**4**	**0**	**4**	**-**	**12**	**4**	**[3] & [this work]**
T5	$[Zn_{13}In_{22}S_{56}]^{20-}$	4	-	24	24	4	1	12	-	18	4	[4]
T6	**$[Zn_{28}In_{28}S_{84}]^{28-}$**	**10**	**-**	**40**	**30**	**4**	**4**	**24**	**-**	**24**	**4**	NA
	$[Zn_{25}In_{31}S_{84}]^{25-}$ (real case)	**10**	**-**	**40**	**30**	**4**	**4**	**21**	**3**	**24**	**4**	**[This work]**
T7	$[Zn_{50}In_{34}S_{120}]^{38-}$	20	-	60	36	4	10	40		30	4	NA
T8	$[Zn_{80}In_{40}S_{165}]^{50-}$	35	-	84	42	4	20	60		36	4	NA
T9	$[Zn_{119}In_{46}S_{220}]^{64-}$	56	-	112	48	4	35	84		42	4	NA
T10	$[Zn_{168}In_{52}S_{286}]^{80-}$	84	-	144	54	4	56	112		48	4	NA

Table S3. Structure refinement parameters on **OCF-99-ZnInS** and **OCF-100-ZnInS**.

Compound	**OCF-99-ZnInS**	**OCF-100-ZnInS**
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$C2/c$
Z	4	8
a (Å)	24.736(4)	32.738(4)
b (Å)	26.149(4)	32.738(4)
c (Å)	26.677(4)	27.371(3)
α (deg.)	90.000	90.000
β (deg.)	107.650(5)	119.826(3)
γ (deg.)	90.000	90.000
V (Å^3)	16442(5)	25448(6)
GOF on F^2	1.078	1.070
R_1, wR_2 ($I > 2\sigma(I)$)	0.0579, 0.1639	0.1039, 0.3667
R_1, wR_2 (all data)	0.0866, 0.1814	0.1716, 0.4151

Table S4. Summary on M–S bond length for tetrahedrally-coordinated metal ions.

Compound Name	Zn-(μ_4-S)	Ref.	Compound Name	Mn-(μ_4-S)	Ref.	Compound Name	In-(μ_4-S)	Ref.
ZnS (sphalerite)	2.345	ICSD (code 60378)	**MnS (sphalerite)**	2.421	ICSD (code 76205)	**In_2S_3**	2.439-2.481	ICSD (code 23844)
ZnS (wurtzite)	2.349	COD (code 1011196)	**MnS (wurtzite)**	2.438	ICSD (code 44765)			

Compound Name	NC Type	In-(μ_2-S) (edge)	In-(μ_3-S) (face)	In-(μ_3-S') (core)	□-(μ_3-S') (core)	Ref.
UCR-7	T3-InS	2.352-2.605	2.453-2.545	–	–	[5]
UCR-15-InS	T5-InS	2.391-2.455	2.475-2.526	2.453-2.473	2.201	[6]

Compound Name	NC Type	Zn-(μ_3-S) (face)	Zn-(μ_4-S) (core)	(Zn/In)-(μ_4-S) (core)	In-(μ_2-S) (edge)	In-(μ_3-S) (face)	Ref.
UCR-8-ZnInS	T4-ZnInS	2.356-2.363	2.398	–	2.407-2.455	2.464-2.499	[7]
OCF-99-ZnInS	T4-ZnInS	2.314-2.381	2.306-2.401	–	2.395-2.497	2.432-2.507	This work
OCF-100-ZnInS	T6-ZnInS	**(Zn/In)-(μ_3-S) (face)** 2.284-2.430	2.300-2.369	2.339-2.424	2.398-2.498	2.417-2.537	This work
Compound Name	**NC Type**	**Mn-(μ_3-S) (face)**	**Mn-(μ_4-S) (core)**	**(Mn/In)-(μ_4-S) (core)**	**In-(μ_2-S) (edge)**	**In-(μ_3-S) (face)**	**Ref.**
OCF-44-MnInS	T4-MnInS	2.388-2.467	2.374-2.435	–	2.399-2.497	2.460-2.518	unpublished
OCF-40-MnGaSnS	T4-MnGaSnS	2.391	2.363	–	–	–	[8]

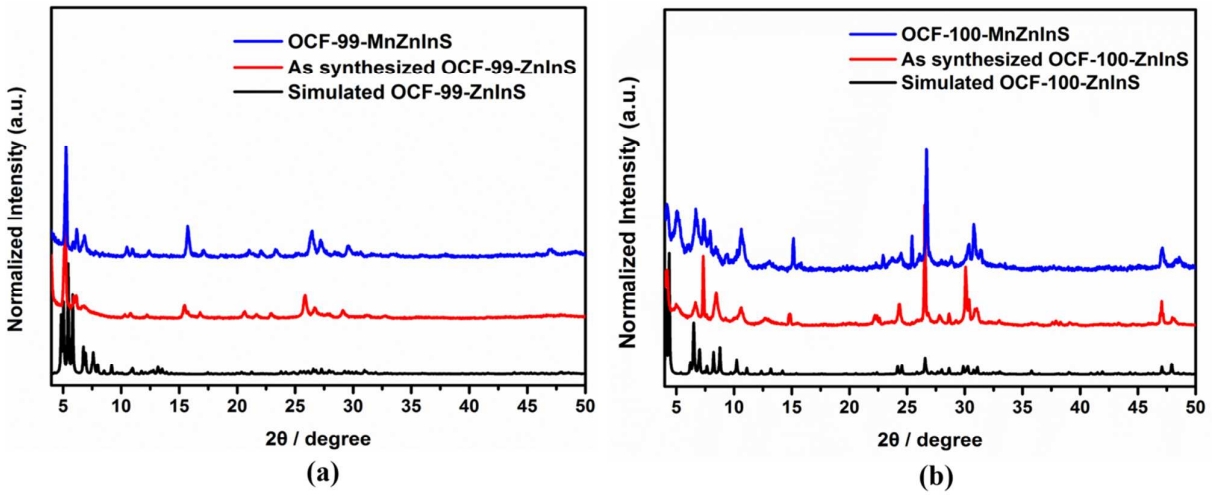

Figure S1. PXRD patterns of **OCF-99-ZnInS**, **OCF-100-ZnInS** and their Mn-doped samples.

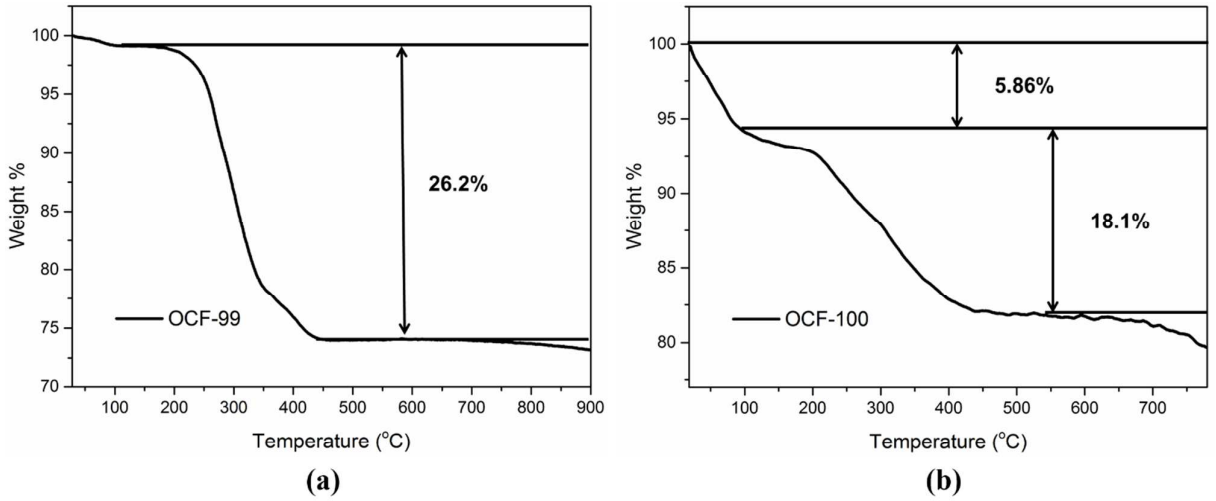

Figure S2. TGA curve of **OCF-99** (a) and **OCF-100** (b). The initial gradual weight loss of 5.86% between 20-100ºC could be attributed to loss of moisture adsorbed on **OCF-100**. An abrupt weight loss of 26.2 % in **OCF-99** and 18.1% in **OCF-100** between 200-400°C is attributed to the carbonization of template molecules.

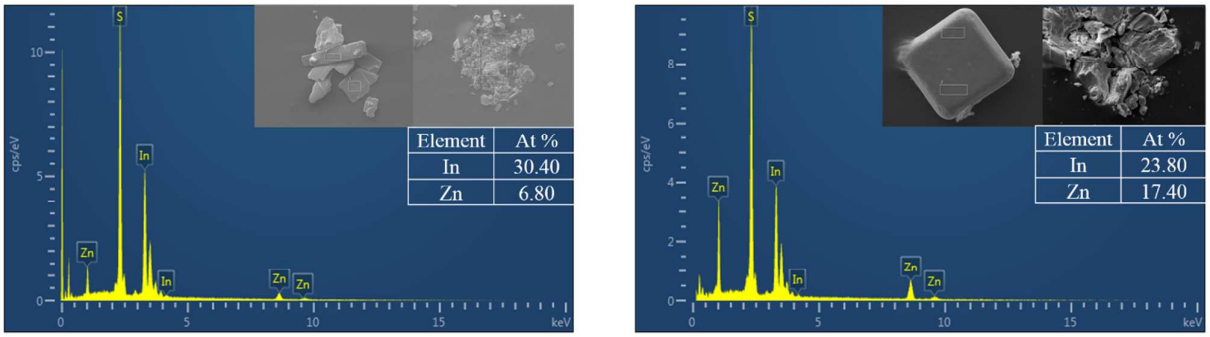

Figure S3. Energy dispersive spectroscopy (EDS) of **OCF-99-ZnInS** (left) and **OCF-100-ZnInS** (right). Inserts are the SEM images of as-synthesized crystals.

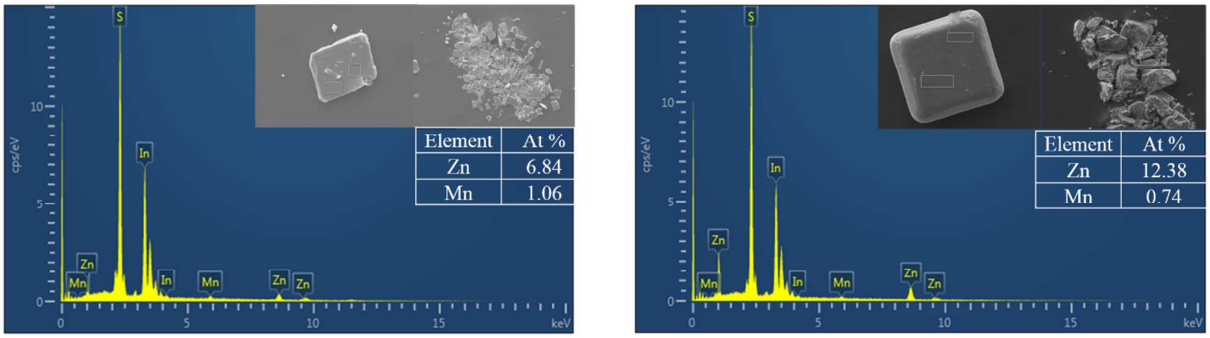

Figure S4. Energy dispersive spectroscopy (EDS) of **OCF-99-MnZnInS** (left) and **OCF-100-MnZnInS** (right). Inserts are the SEM images of as-synthesized crystals.

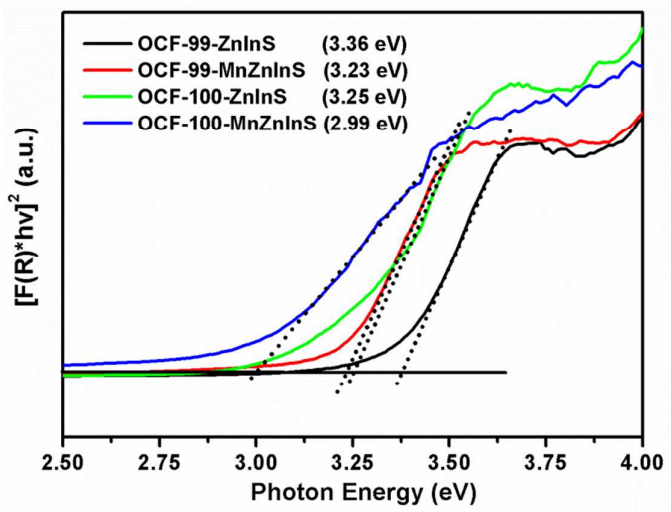

Figure S5. Tauc plot of solid samples derived from UV-Vis DRS.

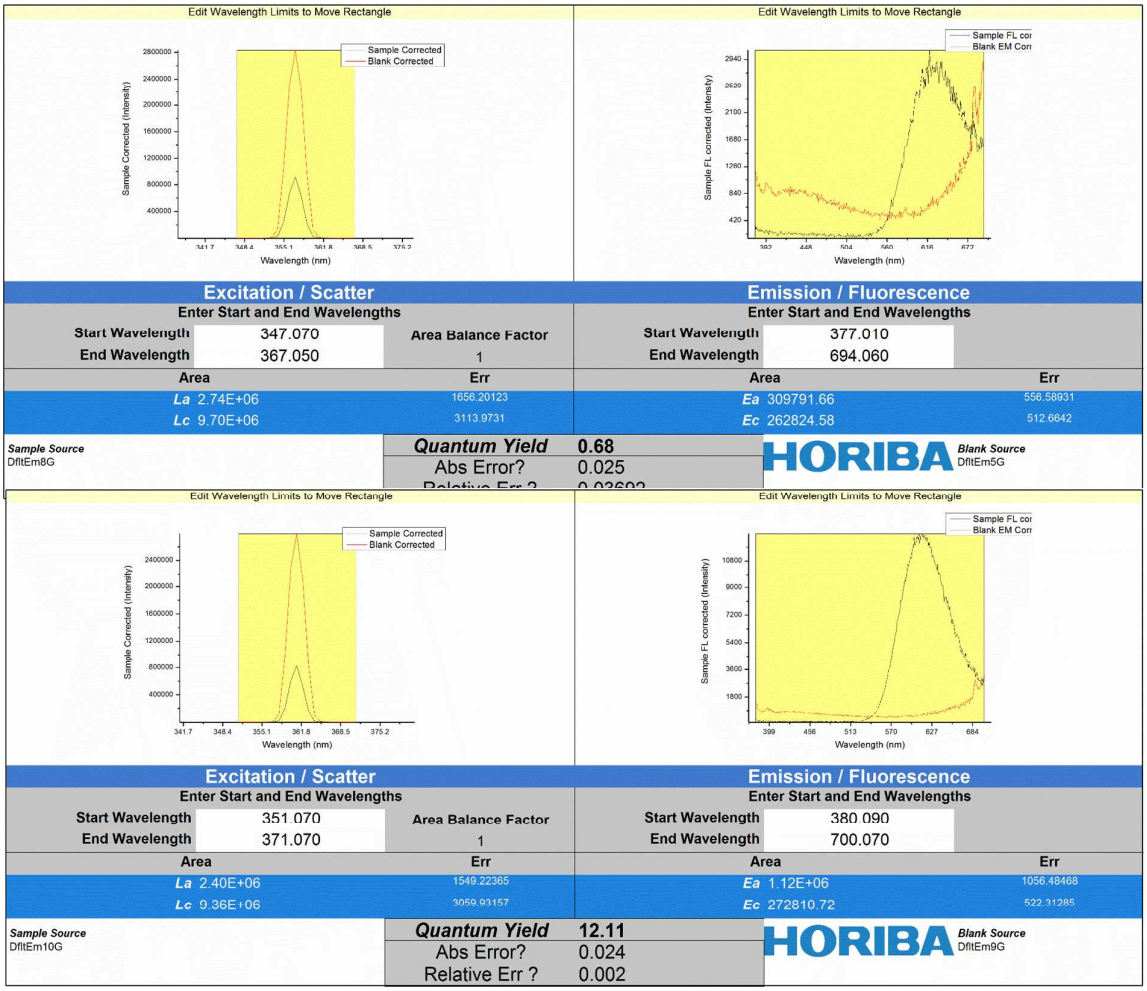

Figure S6. PL quantum yield for **OCF-99-MnZnInS** (top) and **OCF-100-MnZnInS** (down).

References:

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