Electronic Supplementary Information (ESI) for

Exploring the Effect of Intercluster Torsion Stress on Mn^{2+}-Related Emission from Cluster-Based Layered Metal Chalcogenides

Xiaofan Xu,[a] Dandan Hu,[a] Chaozhuang Xue,[a] Jiaxu Zhang,[a] Dong-Sheng Li,[b] and

Tao Wu*[a]

[a] *College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Jiangsu 215123, China.*

[b] *College of Materials and Chemical Engineering, Hubei Provincial Collaborative Innovation Center for New Energy Microgrid, Key Laboratory of Inorganic Nonmetallic Crystalline and Energy Conversion Materials, China Three Gorges University, Yichang, Hubei 443002, China.*

**Email: wutao@suda.edu.cn*

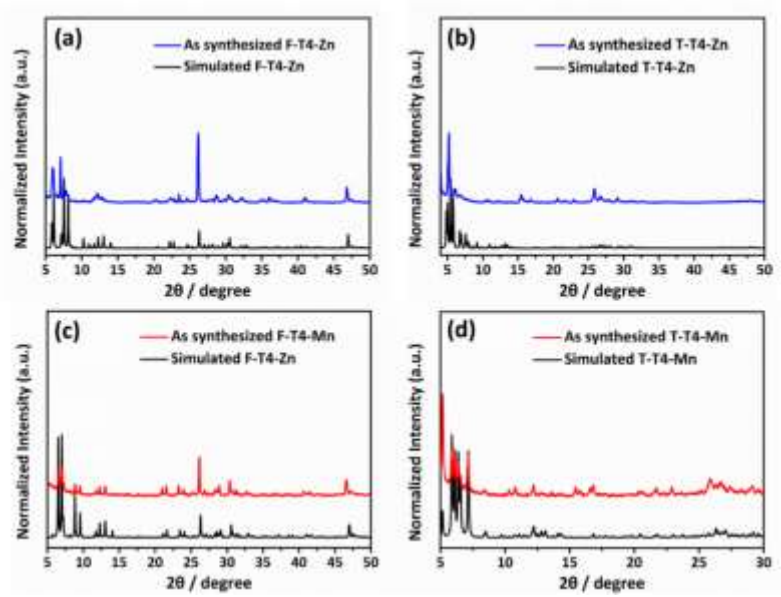


Figure S1. PXRD patterns of F-T4-Zn (a), T-T4-Zn (b), F-T4-Mn (c), and T-T4-Mn (d).

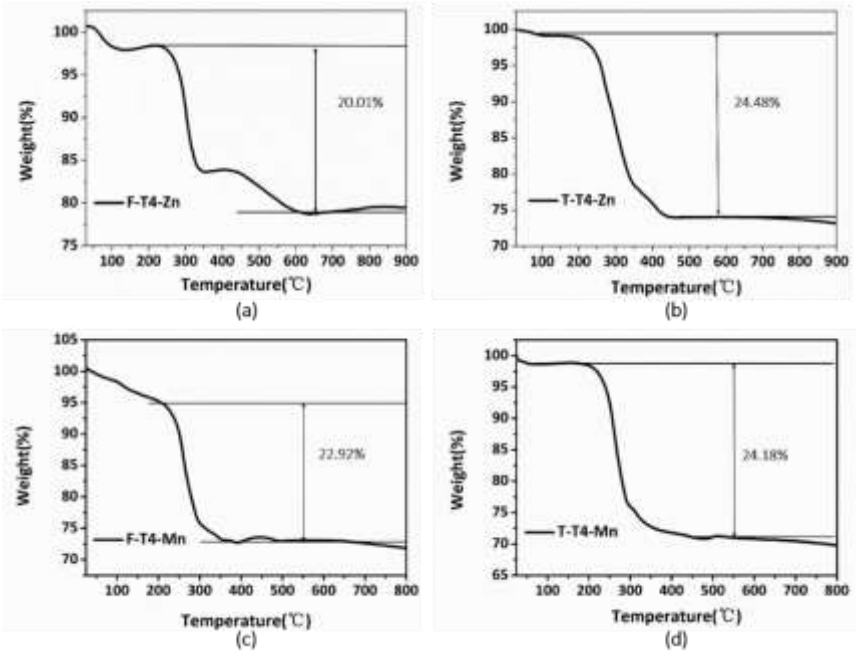


Figure S2. TGA curves of F-T4-Zn (a), T-T4-Zn (b), F-T4-Mn (c) and T-T4-Mn (d). The weight loss of 20.01 % for T-T4-Zn between 200-610 °C could be attributed to the loss of the charge-balanced DMP and AEP molecules (*Calcd.* 20.99%). For T-T4-Zn, about 24.48% weight loss was observed from 200°C to 400 °C, which is attributed to the removal of DMP molecules (*Calcd.* 25.07%). F-T4-Mn undergoes the weight loss about 22.92% from 200°C to 400 °C, corresponding to the removal of TAEA molecules (*Calcd.* 21.31 %). An abrupt weight loss of 24.18% in T-T4-Mn between 200-400 °C is attributed to the carbonization of the DMP molecules (*Calcd.* 25.44 %).

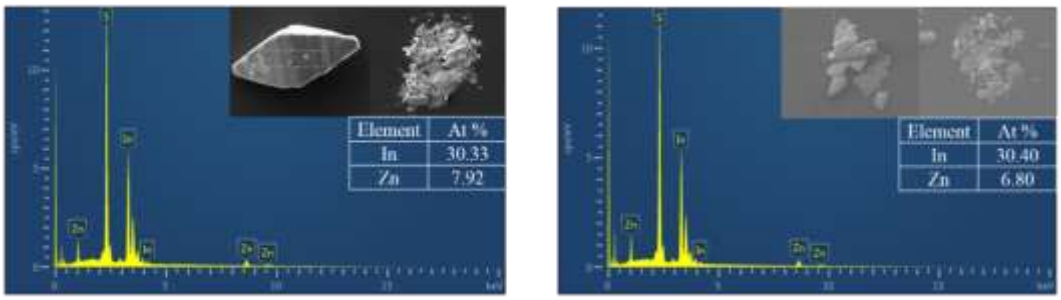


Figure S3. Energy dispersive X-ray spectroscopy (EDS) of F-T4-Zn (left) and T-T4-Zn (right). The insets are SEM images of the as-synthesized crystals.

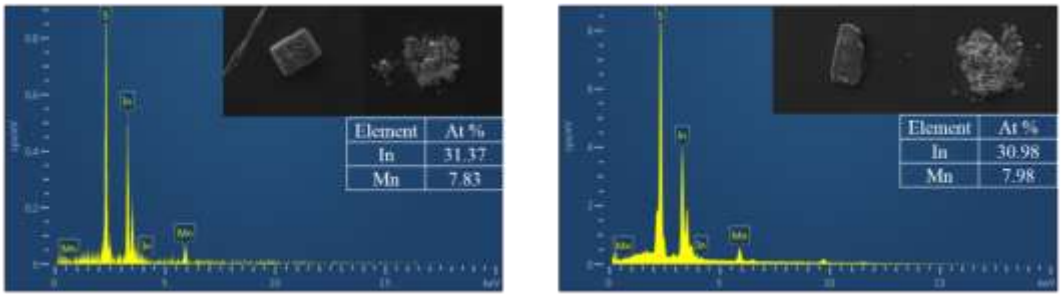


Figure S4. Energy dispersive X-ray spectroscopy (EDS) of F-T4-Mn (left) and T-T4-Mn (right). The insets are SEM images of the as-synthesized crystals.

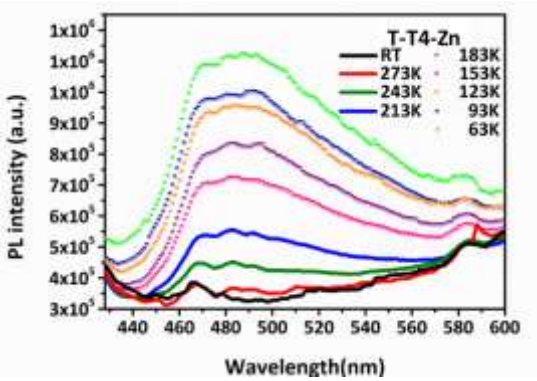


Figure S5. Low-temperature PL spectra of T-T4-Zn.

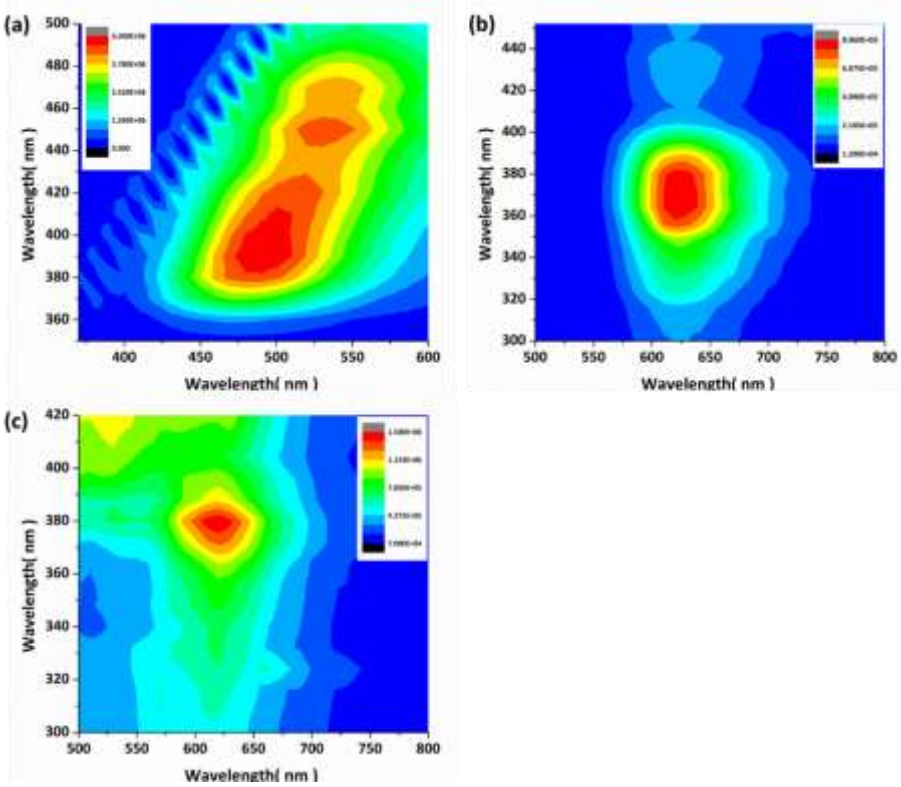


Figure S6. 2D PLE and PL spectra of the F-T4-Zn (a); F-T4-Mn (b) and T-T4-Mn (c).

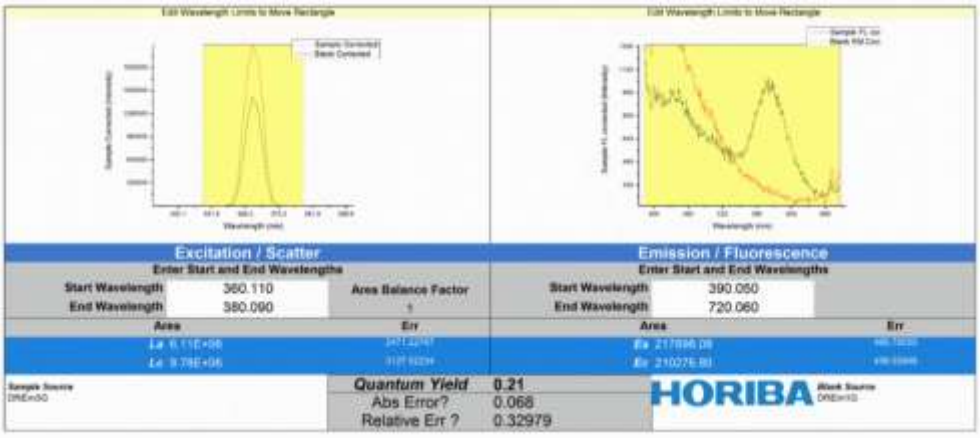


Figure S7. PL quantum yield for F-T4-Mn.

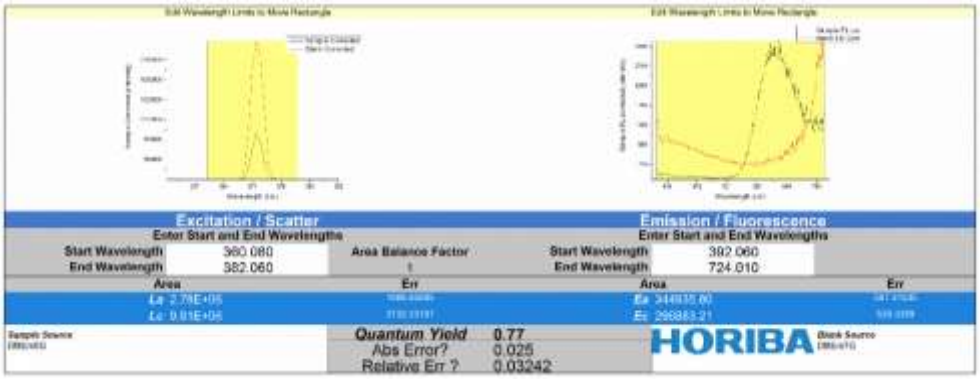


Figure S8. PL quantum yield for T-T4-Mn.

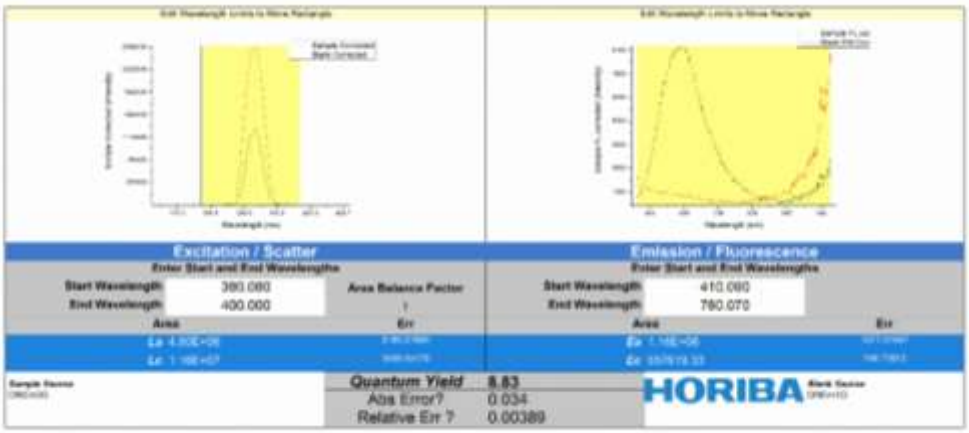


Figure S9. PL quantum yield for F-T4-Zn.

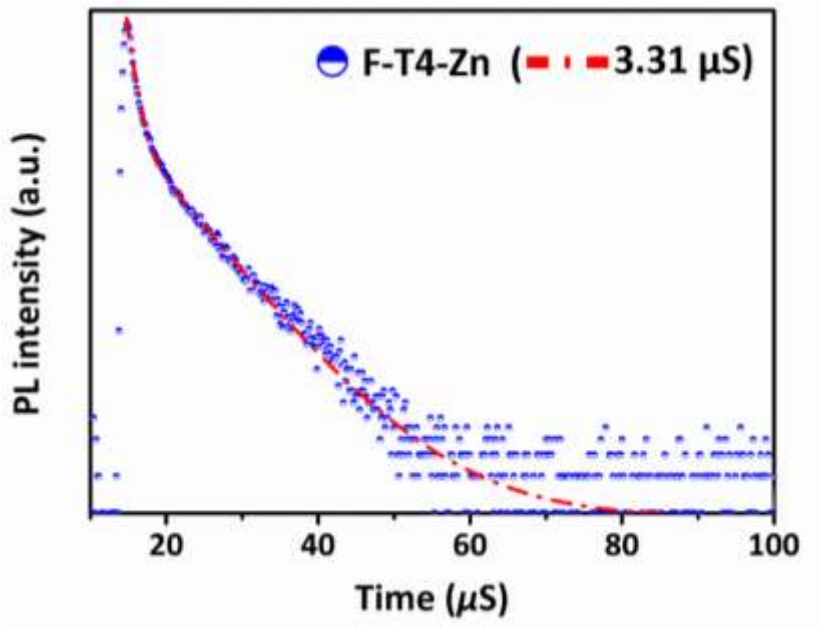


Figure S10. The room-temperature PL decay curves of F-T4-Zn.

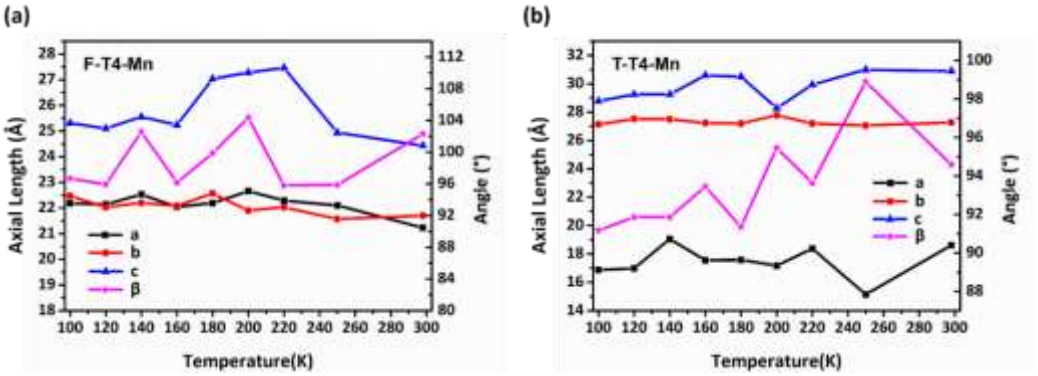
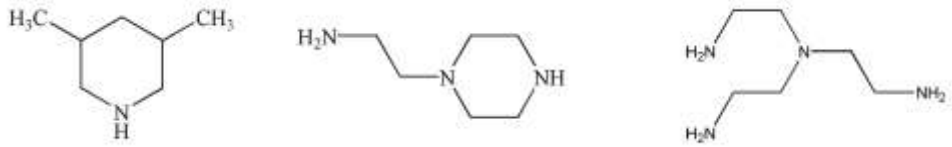


Figure S11. The crystal unit cell parameters of F-T4-Mn and T-T4-Mn at different temperature.



Scheme S1. The structure of template molecules used in this work.

Table S1. Structure refinement parameters on OCF-98-ZnInS, OCF-98-MnInS, OCF-99-ZnInS and OCF-99-MnInS.

Compound	**OCF-98-ZnInS (F-T4-Zn)**	**OCF-98-MnInS (F-T4-Mn)**	**OCF-99-ZnInS (T-T4-Zn)**	**OCF-99-MnInS (T-T4-Mn)**
Empirical formula	$[Zn_4In_{16}S_{33}](C_7H_{16}N)(C_6H_{18}N_3)_3(C_6H_{15}N_3)_{2.54}$	$[Mn_4In_{16}S_{33}](C_6H_{22}N_4)_{2.5}(C_6H_{18}N_4)_{3.2}$	$[Zn_4In_{16}S_{33}](C_7H_{16}N)_{5.36}(C_7H_{15}N)_{3.2}(NH_4)_{4.54}$	$[Mn_4In_{16}S_{33}](C_7H_{16}N)_8(C_7H_{15}N)(NH_4)_2$
Formula weight	3995.9366	3958.5988	4213.1647	4177.9324
CCDC	1843095	---	1574361	1843091
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*C2/c*	*C2/c*	$P2_1/n$	$P2_1/c$
Z	4	---	4	4
a (Å)	21.872(4)	22.10	24.736(4)	17.4022(12)
b (Å)	21.889(4)	22.12	26.149(4)	26.9527(19)
c (Å)	24.682(5)	24.60	26.677(4)	30.407(2)
α (deg.)	90.000	90.000	90.000	90.000
β (deg.)	96.475(7)	96.27	107.650(5)	99.851(2)
γ (deg.)	90.000	90.000	90.000	90.000
V (Å^3)	11741(4)	12025	16442(5)	14051.6(17)
GOF on F^2	1.110	---	1.078	1.047
R_1, wR_2 ($I>2\sigma(I)$)	0.1021, 0.2862	---	0.0579, 0.1639	0.0554, 0.1457
R_1, wR_2 (all data)	0.1120, 0.2999	---	0.0866, 0.1814	0.0626, 0.1520

Table S2. The selected bond lengths (Å) for F-T4-Zn, T-T4-Zn and F-T4-Mn.

F-T4-Zn					
Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
In1	S8	2.406(10)	S1	In3[1]	2.396(10)
In1	S7	2.419(11)	S2	In1[1]	2.516(10)
In1	S18[3]	2.450(11)	S3	In3[1]	2.445(11)
In1	S2[1]	2.516(10)	S4	Zn1[1]	2.295(10)
In2	S8	2.436(10)	S4	Zn2	2.411(11)
In2	S10	2.447(10)	S4	Zn2[1]	2.411(11)
In2	S9	2.460(11)	S5	In2[1]	2.468(10)
In2	S5[1]	2.468(10)	S6	In5	2.417(12)
In3	S1	2.396(10)	S6	In4	2.426(12)
In3	S16[2]	2.400(12)	S7	Zn2	2.348(11)
In3	S3[1]	2.445(11)	S7	In4	2.464(12)
In3	S2	2.471(10)	S9	In7[1]	2.435(11)
In4	S17[3]	2.395(12)	S10	Zn2	2.305(10)
In4	S3	2.517(11)	S10	In6[1]	2.526(11)
In5	S5	2.477(11)	S11	Zn2	2.341(11)
In6	S10[1]	2.526(11)	S11	In5	2.459(12)
In7	S9[1]	2.435(11)	S11	In6	2.508(11)
In7	S15	2.470(12)	S12	In5	2.451(13)
In8	S15	2.400(11)	S12	In7	2.468(13)
In8	S16	2.439(12)	S13	In6	2.392(12)
In8	S18	2.461(11)	S13	In7	2.453(13)
In8	S17	2.474(12)	S14	In6	2.408(11)
Zn1	S4	2.295(10)	S14	In6[1]	2.408(11)
Zn1	S3	2.298(11)	S16	In3[5]	2.400(12)
Zn1	S2	2.333(10)	S17	In4[4]	2.396(12)
Zn1	S5	2.350(11)	S18	In1[4]	2.450(11)

Symmetry: 1, 1-X, +Y, 1/2-Z; 2, -1/2+X, 1/2+Y, +Z; 3, 3/2-X, 1/2+Y, 1/2-Z; 4, 3/2-X, -1/2+Y, 1/2-Z; 5, 1/2+X, -1/2+Y, +Z.

T-T4-Zn					
Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
In01	S31	2.417(3)	In0A	S25	2.424(3)
In01	S7	2.423(3)	In0A	S17	2.479(3)
In01	S13	2.472(3)	In0A	S26	2.483(3)
In01	S16	2.489(3)	In0C	S10	2.415(4)
In1	S10	2.414(4)	In0D	S29[3]	2.425(3)
In1	S32	2.420(3)	In0D	S11	2.429(4)
In1	S17	2.450(3)	In0D	S19	2.436(4)
In1	S18	2.494(3)	In0D	S21	2.444(3)

In02	S20	2.407(4)	In0F	S29	2.414(4)
In02	S19	2.429(3)	In0F	S33	2.451(4)
In02	S12	2.462(3)	In0F	S32	2.454(4)
In02	S22	2.486(3)	In0F	S28	2.468(3)
In2	S1[2]	2.421(4)	Zn1I	S26	2.347(3)
In2	S30	2.436(4)	Zn1I	S22	2.353(3)
In2	S31	2.444(4)	Zn1I	S23	2.353(3)
In2	S24	2.472(4)	S1	In2[1]	2.421(4)
In03	S7	2.420(3)	S1	In0G	2.425(4)
In03	S3	2.423(3)	S2	In08	2.417(4)
In03	S6	2.463(3)	S2	In0G	2.431(4)
In03	S9	2.484(3)	S3	In0G	2.454(4)
In04	S27	2.412(3)	S4	In0C	2.425(3)
In04	S33	2.430(3)	S4	In0G	2.459(4)
In04	S26	2.459(3)	S5	In08	2.412(3)
In04	S18	2.483(3)	S5	In06	2.421(4)
In05	S27	2.419(3)	S6	Zn1H	2.345(3)
In05	S24	2.431(4)	S6	In08	2.474(3)
In05	S16	2.451(3)	S8	Zn1J	2.352(3)
In05	S23	2.472(3)	S8	In0C	2.496(3)
In06	S11	2.431(3)	S9	Zn1K	2.338(3)
In06	S12	2.464(3)	S9	In0C	2.441(3)
In06	S14	2.471(3)	S12	Zn1H	2.357(3)
In07	S20	2.407(3)	S13	Zn1H	2.347(3)
In07	S30	2.431(4)	S18	Zn1K	2.362(3)
In07	S13	2.460(3)	S17	Zn1J	2.349(3)
In07	S23	2.487(3)	S16	Zn1K	2.337(3)
In08	S8	2.486(3)	S15	Zn1K	2.349(3)
In09	S25	2.422(3)	S15	Zn1I	2.353(3)
In09	S21	2.442(3)	S15	Zn1J	2.362(3)
In09	S22	2.462(3)	S15	Zn1H	2.364(3)
In09	S14	2.464(3)	S14	Zn1J	2.335(3)
In0A	S28	2.414(3)	S29	In0D[4]	2.425(3)

Symmetry: 1, -1/2+X, 3/2-Y, -1/2+Z; 2, 1/2+X, 3/2-Y, 1/2+Z; 3, 3/2-X, -1/2+Y, 1/2-Z; 4, 3/2-X, 1/2+Y, 1/2-Z.

T-T4-Mn					
Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
In1	S29[1]	2.425(5)	In11	S13	2.467(5)
In1	S3	2.458(5)	In11	S22	2.408(5)
In1	S1	2.458(5)	In11	S26	2.504(5)
In1	S2	2.466(5)	In11	S25	2.442(5)
In2	S5	2.486(5)	In12	S15	2.474(5)

In2	S6	2.460(5)	In12	S24	2.448(5)
In2	S1	2.413(5)	In12	S27	2.490(5)
In2	S4	2.418(5)	In12	S28	2.411(5)
In3	S5	2.474(5)	In13	S29	2.441(5)
In3	S7	2.415(5)	In13	S16	2.461(5)
In3	S8	2.499(5)	In13	S30	2.441(5)
In3	S2	2.447(5)	In13	S25	2.443(5)
In4	S6	2.476(5)	In14	S26	2.506(5)
In4	S3	2.441(5)	In14	S17	2.447(5)
In4	S8	2.490(5)	In14	S31	2.413(5)
In4	S9	2.417(5)	In14	S30	2.428(5)
In5	S11	2.486(5)	In15	S18	2.513(5)
In5	S12	2.478(5)	In15	S31	2.425(5)
In5	S4	2.418(5)	In15	S27	2.480(5)
In5	S10	2.421(5)	In15	S32	2.431(5)
In6	S13	2.486(5)	In16	S19	2.468(5)
In6	S17	2.493(5)	In16	S33	2.434(5)
In6	S7	2.447(5)	In16	S28	2.461(5)
In6	S16	2.416(5)	In16	S32	2.470(6)
In7	S18	2.495(5)	Mn1	S14	2.417(6)
In7	S15	2.474(5)	Mn1	S18	2.414(5)
In7	S19	2.444(5)	Mn1	S17	2.417(6)
In7	S9	2.407(5)	Mn1	S8	2.430(6)
In8	S20	2.468(5)	Mn2	S11	2.419(5)
In8	S21	2.459(5)	Mn2	S14	2.430(5)
In8	S33[2]	2.449(5)	Mn2	S5	2.427(5)
In8	S10	2.449(5)	Mn2	S13	2.430(6)
In9	S23	2.459(5)	Mn3	S14	2.402(5)
In9	S11	2.496(5)	Mn3	S6	2.418(5)
In9	S22	2.433(5)	Mn3	S12	2.417(6)
In9	S20	2.424(5)	Mn3	S15	2.438(5)
In10	S23	2.481(5)	Mn4	S23	2.425(5)
In10	S12	2.479(5)	Mn4	S14	2.416(5)
In10	S21	2.429(5)	Mn4	S26	2.420(6)
In10	S24	2.429(5)	Mn4	S27	2.421(5)

Symmetry: 1, 1-X, 1/2+Y, 1/2-Z; 2, +X, 1/2-Y, -1/2+Z.

Table S3. The selected bond angles (°) for F-T4-Zn, T-T4-Zn and T-T4-Mn.

F-T4-Zn							
Atom	**Atom**	**Atom**	**Angle/˚**	**Atom**	**Atom**	**Atom**	**Angle/˚**
S8	In1	S7	109.3(4)	S4	Zn1	S3	112.2(4)
S8	In1	$S18^{3}$	105.8(4)	S4	Zn1	S2	112.7(3)
S7	In1	$S18^{3}$	109.6(4)	S3	Zn1	S2	103.9(4)
S8	In1	$S2^{1}$	108.2(3)	S4	Zn1	S5	114.6(5)
S7	In1	$S2^{1}$	112.2(4)	S3	Zn1	S5	106.7(4)
$S18^{3}$	In1	$S2^{1}$	111.6(4)	S2	Zn1	S5	105.9(4)
S8	In2	S10	107.9(3)	S10	Zn2	S11	105.8(4)
S8	In2	S9	107.1(3)	S10	Zn2	S7	105.1(4)
S10	In2	S9	110.8(4)	S11	Zn2	S7	106.3(4)
S8	In2	$S5^{1}$	108.4(4)	S10	Zn2	S4	114.1(3)
S10	In2	$S5^{1}$	112.5(4)	S11	Zn2	S4	114.4(3)
S9	In2	$S5^{1}$	110.0(4)	S7	Zn2	S4	110.5(5)
S1	In3	$S16^{2}$	106.1(4)	$In3^{1}$	S1	In3	104.4(6)
S1	In3	$S3^{1}$	108.8(3)	Zn1	S2	In3	107.9(4)
$S16^{2}$	In3	$S3^{1}$	109.3(4)	Zn1	S2	$In1^{1}$	107.1(4)
S1	In3	S2	108.4(3)	In3	S2	$In1^{1}$	105.0(4)
$S16^{2}$	In3	S2	111.8(4)	Zn1	S3	$In3^{1}$	109.4(4)
$S3^{1}$	In3	S2	112.2(4)	Zn1	S3	In4	107.2(4)
$S17^{3}$	In4	S6	104.3(4)	$In3^{1}$	S3	In4	106.6(4)
$S17^{3}$	In4	S7	111.1(4)	Zn1	S4	$Zn1^{1}$	113.3(8)
S6	In4	S7	110.3(4)	Zn1	S4	Zn2	109.00(15)
$S17^{3}$	In4	S3	110.1(4)	$Zn1^{1}$	S4	Zn2	109.59(15)
S6	In4	S3	110.6(4)	Zn1	S4	$Zn2^{1}$	109.59(15)
S7	In4	S3	110.3(4)	$Zn1^{1}$	S4	$Zn2^{1}$	109.00(15)
S6	In5	S12	104.2(4)	Zn2	S4	$Zn2^{1}$	106.1(7)
S6	In5	S11	108.8(4)	Zn1	S5	$In2^{1}$	107.8(4)
S12	In5	S11	109.7(5)	Zn1	S5	In5	108.2(4)
S6	In5	S5	109.8(4)	$In2^{1}$	S5	In5	106.4(4)
S12	In5	S5	112.6(4)	In5	S6	In4	103.7(4)
S11	In5	S5	111.5(4)	Zn2	S7	In1	108.9(5)
S13	In6	S14	105.1(5)	Zn2	S7	In4	107.2(4)
S13	In6	S11	107.6(4)	In1	S7	In4	108.0(4)
S14	In6	S11	109.8(3)	In1	S8	In2	105.2(4)
S13	In6	$S10^{1}$	114.1(4)	$In7^{1}$	S9	In2	105.8(4)
S14	In6	$S10^{1}$	109.4(3)	Zn2	S10	In2	109.2(4)
S11	In6	$S10^{1}$	110.7(4)	Zn2	S10	$In6^{1}$	108.1(4)
$S9^{1}$	In7	S13	113.1(4)	In2	S10	$In6^{1}$	105.1(4)
$S9^{1}$	In7	S12	113.8(4)	Zn2	S11	In5	108.3(5)
S13	In7	S12	110.0(5)	Zn2	S11	In6	107.3(4)

S9[1]	In7	S15	103.7(4)	In5	S11	In6	106.7(4)
S13	In7	S15	108.3(4)	In5	S12	In7	103.3(4)
S12	In7	S15	107.4(4)	In6	S13	In7	105.7(5)
S15	In8	S16	109.4(4)	In6	S14	In6[1]	104.1(7)
S15	In8	S18	103.0(4)	In8	S15	In7	104.3(4)
S16	In8	S18	113.8(4)	In3[5]	S16	In8	106.7(5)
S15	In8	S17	108.5(4)	In4[4]	S17	In8	105.2(5)
S16	In8	S17	110.2(5)	In1[4]	S18	In8	104.3(4)
S18	In8	S17	111.6(4)				

Symmetry: 1, 1-X, +Y, 1/2-Z; 2, -1/2+X, 1/2+Y, +Z; 3, 3/2-X, 1/2+Y, 1/2-Z; 4, 3/2-X, -1/2+Y, 1/2-Z; 5, 1/2+X, -1/2+Y, +Z.

T-T4-Zn							
Atom	**Atom**	**Atom**	**Angle/˚**	**Atom**	**Atom**	**Atom**	**Angle/˚**
S31	In01	S7	105.65(12)	S1	In0G	S3	99.99(13)
S31	In01	S13	109.61(11)	S2	In0G	S3	112.53(14)
S7	In01	S13	109.29(11)	S1	In0G	S4	112.19(13)
S31	In01	S16	110.78(11)	S2	In0G	S4	111.39(14)
S7	In01	S16	108.89(11)	S3	In0G	S4	110.94(13)
S13	In01	S16	112.39(10)	S16	Zn1K	S9	102.96(12)
S10	In1	S32	105.79(12)	S16	Zn1K	S15	115.13(11)
S10	In1	S17	113.89(12)	S9	Zn1K	S15	114.95(11)
S32	In1	S17	111.29(11)	S16	Zn1K	S18	107.70(12)
S10	In1	S18	107.65(12)	S9	Zn1K	S18	107.34(12)
S32	In1	S18	108.32(12)	S15	Zn1K	S18	108.28(11)
S17	In1	S18	109.67(10)	S14	Zn1J	S17	104.48(11)
S20	In02	S19	105.52(12)	S14	Zn1J	S8	108.26(12)
S20	In02	S12	112.58(11)	S17	Zn1J	S8	105.84(12)
S19	In02	S12	109.86(12)	S14	Zn1J	S15	112.80(11)
S20	In02	S22	108.11(11)	S17	Zn1J	S15	114.33(11)
S19	In02	S22	109.31(11)	S8	Zn1J	S15	110.64(11)
S12	In02	S22	111.26(10)	S26	Zn1I	S22	104.57(11)
S1[2]	In2	S30	109.82(14)	S26	Zn1I	S23	105.62(12)
S1[2]	In2	S31	101.55(13)	S22	Zn1I	S23	108.08(12)
S30	In2	S31	113.87(13)	S26	Zn1I	S15	113.98(11)
S1[2]	In2	S24	109.63(12)	S22	Zn1I	S15	112.48(11)
S30	In2	S24	111.53(14)	S23	Zn1I	S15	111.57(11)
S31	In2	S24	109.96(13)	S6	Zn1H	S13	106.15(11)
S7	In03	S3	105.07(12)	S6	Zn1H	S12	105.82(11)
S7	In03	S6	109.66(11)	S13	Zn1H	S12	106.03(11)
S3	In03	S6	108.15(12)	S6	Zn1H	S15	112.43(11)
S7	In03	S9	108.54(11)	S13	Zn1H	S15	112.24(11)
S3	In03	S9	112.46(12)	S12	Zn1H	S15	113.59(11)

S6	In03	S9	112.66(10)	In2[1]	S1	In0G	107.86(14)
S27	In04	S33	104.98(12)	In08	S2	In0G	105.86(14)
S27	In04	S26	113.10(12)	In03	S3	In0G	105.78(13)
S33	In04	S26	112.41(11)	In0C	S4	In0G	107.29(13)
S27	In04	S18	108.96(12)	In08	S5	In06	104.39(12)
S33	In04	S18	108.09(12)	Zn1H	S6	In03	108.19(11)
S26	In04	S18	109.11(10)	Zn1H	S6	In08	108.69(12)
S27	In05	S24	106.01(12)	In03	S6	In08	106.82(11)
S27	In05	S16	111.12(12)	In03	S7	In01	103.60(12)
S24	In05	S16	109.96(12)	Zn1J	S8	In08	107.95(12)
S27	In05	S23	108.91(11)	Zn1J	S8	In0C	109.61(12)
S24	In05	S23	109.51(12)	In08	S8	In0C	108.75(12)
S16	In05	S23	111.20(10)	Zn1K	S9	In0C	106.28(12)
S5	In06	S11	106.06(12)	Zn1K	S9	In03	107.24(12)
S5	In06	S12	111.10(11)	In0C	S9	In03	106.61(12)
S11	In06	S12	110.31(12)	In1	S10	In0C	103.42(12)
S5	In06	S14	108.87(12)	In0D	S11	In06	105.79(13)
S11	In06	S14	108.86(11)	Zn1H	S12	In02	106.54(11)
S12	In06	S14	111.48(10)	Zn1H	S12	In06	106.93(12)
S20	In07	S30	105.35(12)	In02	S12	In06	109.08(12)
S20	In07	S13	110.31(11)	Zn1H	S13	In07	108.95(12)
S30	In07	S13	113.73(12)	Zn1H	S13	In01	108.33(12)
S20	In07	S23	110.00(11)	In07	S13	In01	106.81(11)
S30	In07	S23	107.77(12)	Zn1J	S14	In09	107.78(12)
S13	In07	S23	109.56(10)	Zn1J	S14	In06	108.16(12)
S5	In08	S2	105.93(13)	In09	S14	In06	106.94(12)
S5	In08	S6	109.55(12)	Zn1K	S15	Zn1I	109.62(11)
S2	In08	S6	113.64(12)	Zn1K	S15	Zn1J	110.19(12)
S5	In08	S8	110.58(11)	Zn1I	S15	Zn1J	109.72(11)
S2	In08	S8	107.69(13)	Zn1K	S15	Zn1H	109.12(11)
S6	In08	S8	109.40(10)	Zn1I	S15	Zn1H	109.04(12)
S25	In09	S21	105.56(11)	Zn1J	S15	Zn1H	109.13(11)
S25	In09	S22	109.58(12)	Zn1K	S16	In05	106.75(12)
S21	In09	S22	108.87(11)	Zn1K	S16	In01	107.02(12)
S25	In09	S14	110.16(12)	In05	S16	In01	106.19(12)
S21	In09	S14	110.21(11)	Zn1J	S17	In1	106.09(12)
S22	In09	S14	112.23(10)	Zn1J	S17	In0A	106.81(12)
S28	In0A	S25	105.66(11)	In1	S17	In0A	107.24(12)
S28	In0A	S17	109.90(12)	Zn1K	S18	In04	109.44(12)
S25	In0A	S17	109.36(12)	Zn1K	S18	In1	110.15(13)
S28	In0A	S26	108.17(12)	In04	S18	In1	110.42(12)
S25	In0A	S26	109.76(12)	In02	S19	In0D	105.52(14)
S17	In0A	S26	113.68(10)	In07	S20	In02	104.40(13)

S10	In0C	S4	106.40(12)	In09	S21	In0D	106.78(12)
S10	In0C	S9	112.95(12)	Zn1I	S22	In09	108.01(12)
S4	In0C	S9	108.91(12)	Zn1I	S22	In02	107.56(11)
S10	In0C	S8	107.69(11)	In09	S22	In02	107.15(12)
S4	In0C	S8	109.66(12)	Zn1I	S23	In05	109.44(12)
S9	In0C	S8	111.10(10)	Zn1I	S23	In07	107.43(12)
S29[3]	In0D	S11	105.45(14)	In05	S23	In07	108.99(11)
S29[3]	In0D	S19	105.38(14)	In05	S24	In2	106.32(13)
S11	In0D	S19	117.00(13)	In09	S25	In0A	102.16(12)
S29[3]	In0D	S21	109.74(11)	Zn1I	S26	In04	106.49(12)
S11	In0D	S21	109.34(13)	Zn1I	S26	In0A	106.95(12)
S19	In0D	S21	109.65(13)	In04	S26	In0A	107.59(12)
S29	In0F	S33	110.42(14)	In04	S27	In05	103.50(12)
S29	In0F	S32	113.20(14)	In0A	S28	In0F	106.72(13)
S33	In0F	S32	111.39(12)	In0F	S29	In0D[4]	106.82(14)
S29	In0F	S28	96.95(12)	In07	S30	In2	105.15(14)
S33	In0F	S28	112.54(13)	In01	S31	In2	106.46(13)
S32	In0F	S28	111.61(13)	In1	S32	In0F	106.40(13)
S1	In0G	S2	109.30(14)	In04	S33	In0F	105.42(13)

Symmetry: 1, -1/2+X, 3/2-Y, -1/2+Z; 2, 1/2+X, 3/2-Y, 1/2+Z; 3, 3/2-X, -1/2+Y, 1/2-Z; 4, 3/2-X, 1/2+Y, 1/2-Z.

T-T4-Mn							
Atom	**Atom**	**Atom**	**Angle/˚**	**Atom**	**Atom**	**Atom**	**Angle/˚**
S29[1]	In1	S3	100.08(16)	S33	In16	S19	108.14(17)
S29[1]	In1	S1	106.06(17)	S33	In16	S28	99.73(17)
S29[1]	In1	S2	115.89(17)	S33	In16	S32	111.82(17)
S3	In1	S2	108.68(17)	S28	In16	S19	113.42(18)
S1	In1	S3	117.48(17)	S28	In16	S32	112.42(19)
S1	In1	S2	108.76(18)	S14	Mn1	S17	116.33(19)
S6	In2	S5	113.20(16)	S14	Mn1	S8	112.6(2)
S1	In2	S5	110.08(17)	S18	Mn1	S14	106.94(19)
S1	In2	S6	107.78(17)	S18	Mn1	S17	108.1(2)
S1	In2	S4	105.72(18)	S18	Mn1	S8	108.97(19)
S4	In2	S5	107.12(18)	S17	Mn1	S8	103.6(2)
S4	In2	S6	112.68(18)	S11	Mn2	S14	110.32(19)
S5	In3	S8	113.56(17)	S11	Mn2	S5	108.90(19)
S7	In3	S5	109.20(17)	S11	Mn2	S13	107.91(19)
S7	In3	S8	109.75(18)	S5	Mn2	S14	110.61(19)
S7	In3	S2	107.95(18)	S5	Mn2	S13	107.1(2)
S2	In3	S5	107.61(18)	S13	Mn2	S14	111.92(19)
S2	In3	S8	108.59(17)	S14	Mn3	S6	112.2(2)
S6	In4	S8	112.58(17)	S14	Mn3	S12	112.5(2)

S3	In4	S6	110.50(16)	S14	Mn3	S15	114.0(2)
S3	In4	S8	105.69(17)	S6	Mn3	S15	105.73(19)
S9	In4	S6	111.81(17)	S12	Mn3	S6	105.6(2)
S9	In4	S3	106.62(17)	S12	Mn3	S15	106.06(19)
S9	In4	S8	109.29(18)	S14	Mn4	S23	112.8(2)
S12	In5	S11	111.08(17)	S14	Mn4	S26	106.2(2)
S4	In5	S11	108.22(18)	S14	Mn4	S27	116.3(2)
S4	In5	S12	109.78(18)	S26	Mn4	S23	110.4(2)
S4	In5	S10	107.62(18)	S26	Mn4	S27	108.2(2)
S10	In5	S11	105.78(18)	S27	Mn4	S23	102.9(2)
S10	In5	S12	114.10(18)	In2	S1	In1	105.99(19)
S13	In6	S17	115.63(17)	In3	S2	In1	107.62(19)
S7	In6	S13	111.88(17)	In4	S3	In1	105.80(17)
S7	In6	S17	107.17(17)	In5	S4	In2	107.0(2)
S16	In6	S13	102.37(18)	In3	S5	In2	107.15(18)
S16	In6	S17	109.65(18)	Mn2	S5	In2	106.86(19)
S16	In6	S7	110.05(17)	Mn2	S5	In3	108.5(2)
S15	In7	S18	109.71(16)	In2	S6	In4	110.07(19)
S19	In7	S18	102.26(17)	Mn3	S6	In2	106.53(19)
S19	In7	S15	117.45(17)	Mn3	S6	In4	106.26(19)
S9	In7	S18	110.31(18)	In3	S7	In6	104.37(18)
S9	In7	S15	109.57(18)	In4	S8	In3	108.09(19)
S9	In7	S19	107.25(17)	Mn1	S8	In4	106.5(2)
S21	In8	S20	113.98(17)	Mn1	S8	In3	105.85(19)
$S33^2$	In8	S20	111.15(17)	In7	S9	In4	106.26(18)
$S33^2$	In8	S21	100.11(16)	In5	S10	In8	104.40(19)
S10	In8	S20	109.36(18)	In5	S11	In9	109.95(18)
S10	In8	S21	112.51(18)	Mn2	S11	In9	107.48(19)
S10	In8	$S33^2$	109.40(18)	Mn2	S11	In5	108.17(19)
S23	In9	S11	112.65(16)	In5	S12	In10	106.67(19)
S22	In9	S23	111.12(18)	Mn3	S12	In10	105.5(2)
S22	In9	S11	108.97(18)	Mn3	S12	In5	108.8(2)
S20	In9	S23	108.57(17)	In11	S13	In6	109.78(19)
S20	In9	S11	106.80(17)	Mn2	S13	In6	105.95(19)
S20	In9	S22	108.56(17)	Mn2	S13	In11	107.1(2)
S12	In10	S23	115.56(17)	Mn4	S14	Mn2	110.3(2)
S21	In10	S23	113.49(17)	Mn4	S14	Mn1	108.8(2)
S21	In10	S12	104.42(18)	Mn3	S14	Mn4	108.6(2)
S24	In10	S23	105.59(18)	Mn3	S14	Mn2	110.0(2)
S24	In10	S12	111.97(18)	Mn3	S14	Mn1	109.8(2)
S24	In10	S21	105.51(18)	Mn1	S14	Mn2	109.3(2)
S13	In11	S26	107.90(16)	In7	S15	In12	104.88(19)
S22	In11	S13	110.56(18)	Mn3	S15	In7	106.9(2)

S22	In11	S26	112.31(18)	Mn3	S15	In12	107.14(19)
S22	In11	S25	105.90(18)	In6	S16	In13	109.3(2)
S25	In11	S13	115.01(18)	In14	S17	In6	107.44(19)
S25	In11	S26	105.14(17)	Mn1	S17	In14	103.4(2)
S15	In12	S27	116.60(17)	Mn1	S17	In6	105.33(19)
S24	In12	S15	109.96(18)	In7	S18	In15	111.31(19)
S24	In12	S27	102.94(19)	Mn1	S18	In7	110.0(2)
S28	In12	S15	107.27(18)	Mn1	S18	In15	111.7(2)
S28	In12	S24	107.85(18)	In7	S19	In16	105.28(18)
S28	In12	S27	111.90(18)	In9	S20	In8	107.58(19)
S29	In13	S16	99.44(17)	In10	S21	In8	105.20(18)
S29	In13	S30	109.31(17)	In11	S22	In9	106.34(18)
S29	In13	S25	110.22(17)	In9	S23	In10	106.70(19)
S30	In13	S16	111.64(18)	Mn4	S23	In9	106.68(19)
S30	In13	S25	112.03(19)	Mn4	S23	In10	105.80(19)
S25	In13	S16	113.47(18)	In10	S24	In12	106.6(2)
S17	In14	S26	110.64(17)	In11	S25	In13	103.24(19)
S31	In14	S26	106.55(17)	In11	S26	In14	112.13(19)
S31	In14	S17	115.02(17)	Mn4	S26	In14	112.01(19)
S31	In14	S30	106.27(18)	Mn4	S26	In11	109.03(19)
S30	In14	S26	107.05(17)	In15	S27	In12	106.57(19)
S30	In14	S17	110.88(18)	Mn4	S27	In15	103.6(2)
S31	In15	S18	105.60(17)	Mn4	S27	In12	107.0(2)
S31	In15	S27	116.74(18)	In12	S28	In16	104.94(19)
S31	In15	S32	106.91(18)	$In1^{3}$	S29	In13	105.14(18)
S27	In15	S18	109.01(17)	In14	S30	In13	106.0(2)
S32	In15	S18	112.67(17)	In14	S31	In15	105.80(19)
S32	In15	S27	106.09(19)	In15	S32	In16	105.1(2)
S19	In16	S32	110.78(19)	In16	S33	$In8^{4}$	104.86(19)

Symmetry: 1, 1-X, 1/2+Y, 1/2-Z; 2, +X, 1/2-Y, -1/2+Z; 3, 1-X, -1/2+Y, 1/2-Z; 4, +X, 1/2-Y, 1/2+Z.

Table S4. PL lifetime of F-T4-Zn, F-T4-Mn and T-T4-Mn at room temperature.

	Excitation (nm)	Emission (nm)	CHISQ	A_1(%)	τ_1(μs)	A_2(%)	τ_2(μs)	A_3(%)	τ_3(μs)	AVG (μs)
F-T4-Zn	390	503	0.85	4.91	10.37	42.55	5.52	52.54	0.86	3.31
F-T4-Mn	370	618	1.54	48.31	1.35	51.69	7.52	-	-	4.63
T-T4-Mn	372	628	0.90	3.60	30.75	38.97	14.43	57.43	22.41	19.60

Table S5. The crystal unit cell parameters for F-T4-Mn and T-T4-Mn at different temperature.

F-T4-MnInS				
Temperature	**Crystal data**			
(K)	**a (Å)**	**b (Å)**	**c (Å)**	***β*** **(°)**
100	22.18	22.47	25.31	96.67
120	22.14	22.03	25.10	95.93
140	22.53	22.20	25.55	102.57
160	22.04	22.08	25.24	96.18
180	22.19	22.57	27.03	99.88
200	22.66	21.90	27.28	104.35
220	22.29	22.03	27.46	95.81
250	22.10	21.57	24.94	95.88
298	18.23	21.70	24.43	102.30

T-T4-MnInS				
Temperature	**Crystal data**			
(K)	**a (Å)**	**b (Å)**	**c (Å)**	***β*** **(°)**
100	16.87	27.14	28.78	91.17
120	16.98	27.52	29.25	91.86
140	19.05	27.50	29.25	91.86
160	17.55	27.23	30.59	93.45
180	17.58	27.20	30.50	91.36
200	17.17	27.78	28.28	95.46
220	18.37	27.20	29.93	93.63
250	15.14	27.05	30.99	98.90