Supporting Information of Isolated-Mn^{2+}-like Luminescent Behavior in $CsMnF_3$ Caused by Competing Magnetic Interactions at Cryogenic Temperature

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Supplementary Tables and Table captions:

Table S1. The refined Crystallographic and structure data summary for CMF.

Formula sum	$CsMnF_3$
Crystal system	hexagonal
Space-group	P 6_3/mmc (194)
a (Å)	6.2325
c (Å)	15.1193
a/b	1
b/c	0.4122
c/a	2.4259
Cell volume ($Å^3$)	508.62
Z	6
Rwp (%)	3.58
Rp (%)	2.71
Gof	1.48

Table S2. The atomic coordinates of CMF.

	Atom	Ox.	Site	Wyck.	x/a	y/b	z/c
$CsMnF_3$	Cs1	1	*-6m2*	2b	0	0	0.25
	Cs2	1	*3m.*	4f	0.33333	0.66667	0.0986
	Mn1	2	*-3m.*	2a	0	0	0
	Mn2	2	*3m.*	4f	0.33333	0.66667	0.85
	F1	-1	*mm2*	6h	0.522	0.044	0.25

F2	-1	*.m.*	12k	0.835	0.67	0.078

Table S3. The selected bond distances of CMF.

Bond	Distance (Å)
Mn1-F2	2.136(2)
Mn1-F2	2.136(2)
Mn1-F2	2.136(2)
Mn1-F2	2.136(2)
Mn1-F2	2.136(2)
Mn2-F2	2.118(3)
Mn2-F2	2.118(3)
Mn2-F2	2.118(3)
Mn2-F1	2.173(7)
Mn2-F1	2.173(7)
Mn2-F1	2.173(7)
Mn2-F2	2.118(3)
Mn1-F2	2.136(2)

Table S4. The Mn^{2+}-Mn^{2+} distances and Mn^{2+}-F^{-}-Mn^{2+} angles of CMF.

Species	Distance(Å)	Angle (°)
Mn1-F2-Mn2	4.253(4)	177.41(6)
Mn2-F1-Mn2	3.023(9)	88.14(5)

Table S5. The Mn^{2+}-Mn^{2+} distances and Mn^{2+}-Cl^{-}-Mn^{2+} angles of for CMC.

Species	Distance(Å)	Angle (°)
Mn1-Cl2-Mn2	3.179(7)	77.24(1)
Mn2-Cl1-Mn2	5.025(5)	180

Supplementary Figures and Figure captions:

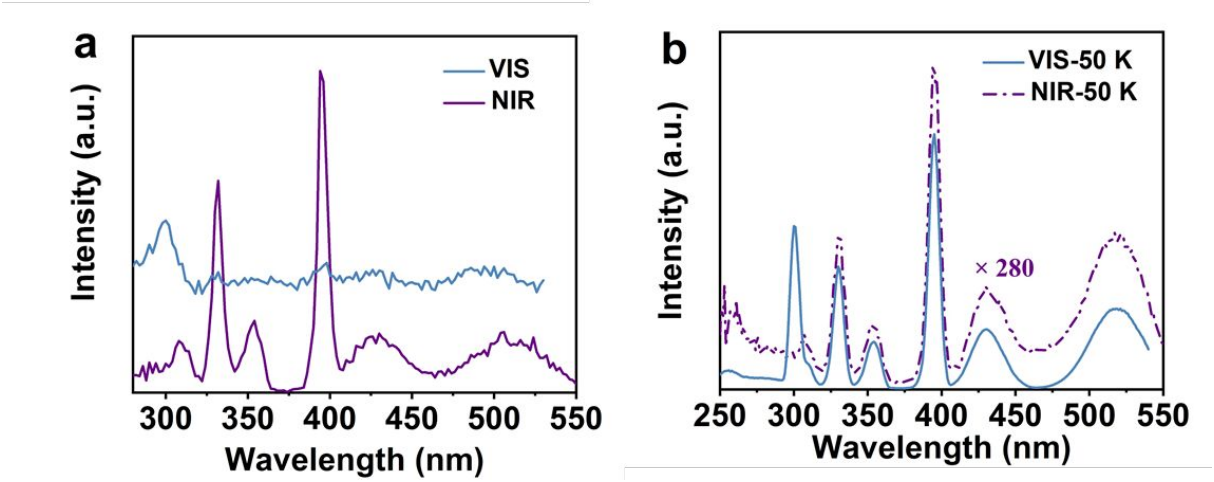

Figure S1. The excitation spectra of CMF at (a) room temperature and (b) 50 K.

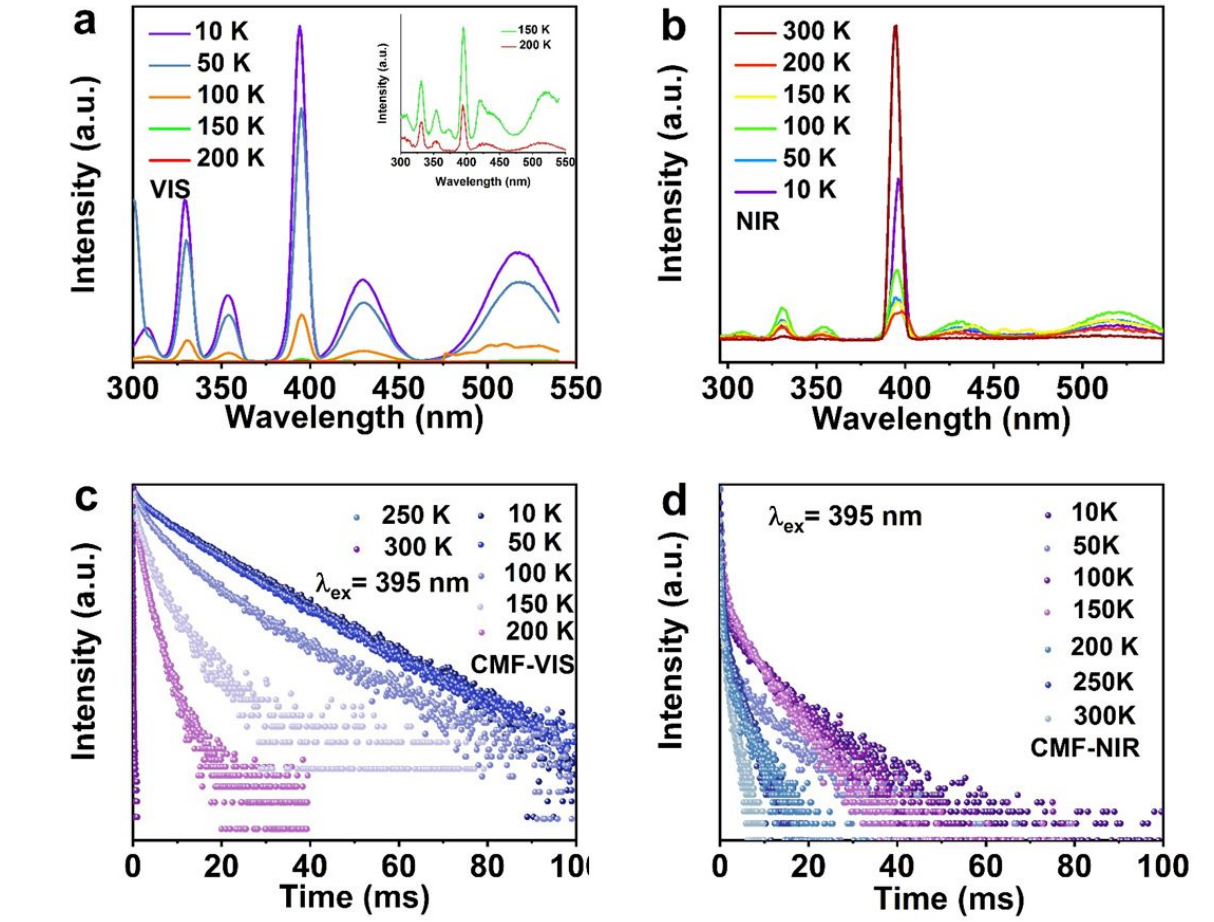

Figure S2. (a-b) The temperature-dependent excitation spectra of CMF. (c-d) The temperature-dependent decay curves of CMF.

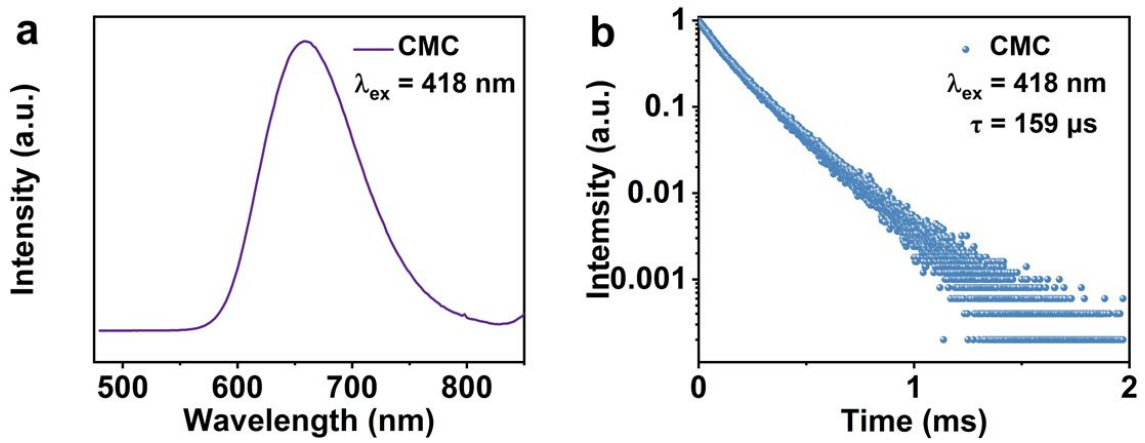

Figure S3. (a) The emission spectrum and (b) the decay curve of CMC at room temperature.

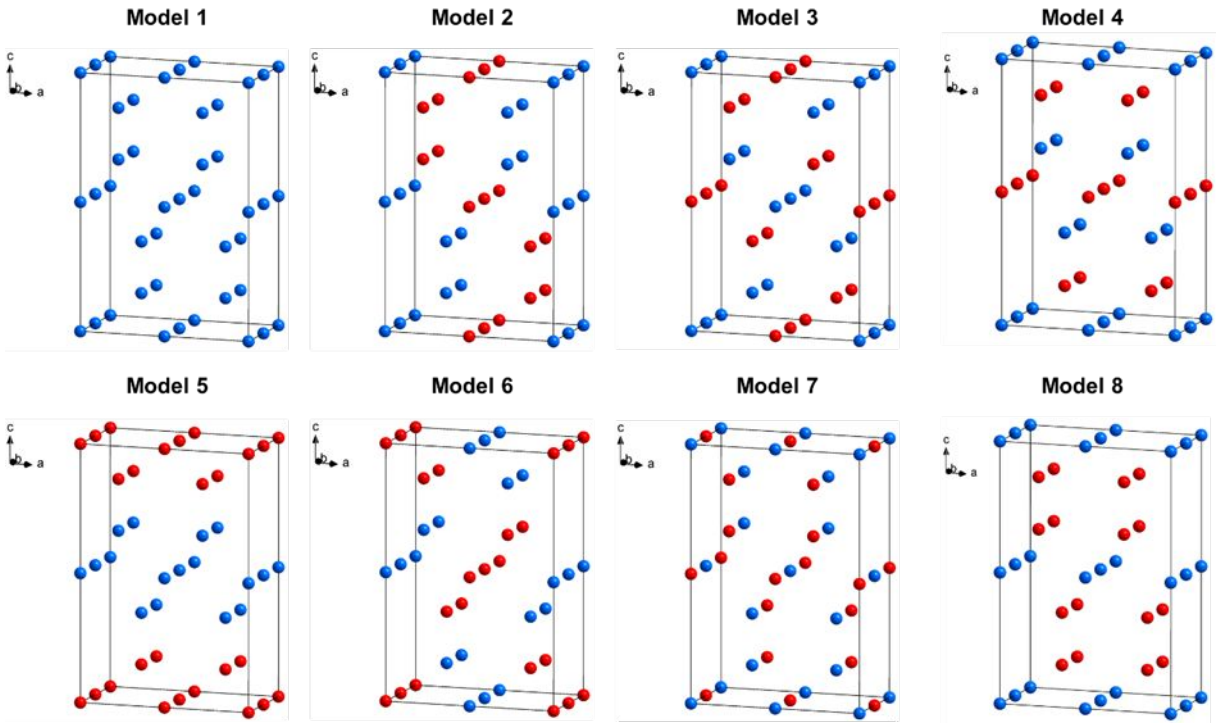

Figure S4. The hypothetic models of Mn^{2+} ion with magnetic moment in CMF. (The red and blue solid spheres denote the opposite magnetic moment directions.)

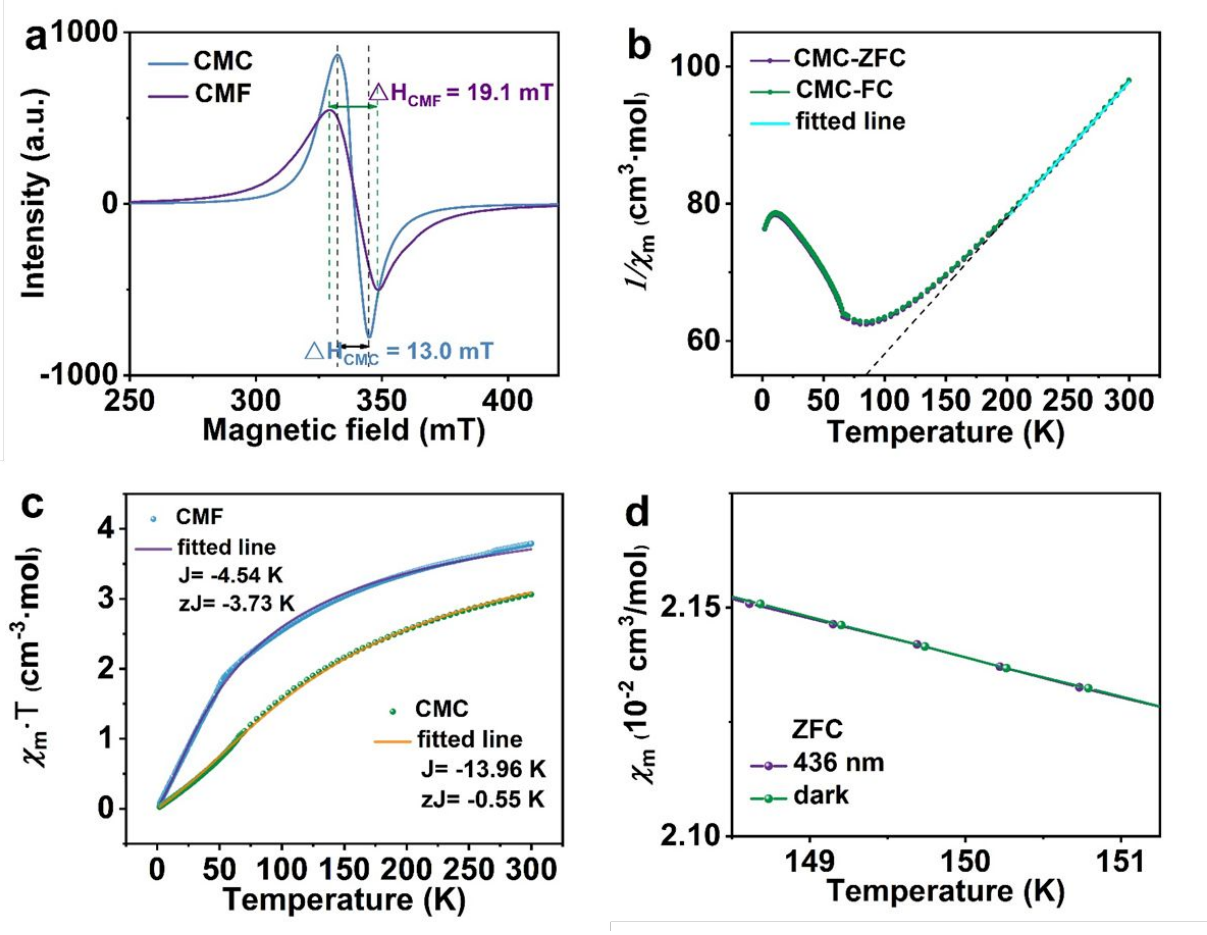

Figure S5. (a) The EPR spectra of CMF and CMC at 130 K. (b) The temperature-dependent inverse of magnetic susceptibility of CMC measures under ZFC and FC mode. (c) Plots of $\chi_m T$ versus T from 2 to 300 K of CMF and CMC. The orange and purple lines across $\chi_m T$ are the fitted lines using the molecular-field theory. (d) The partial photomagnetization curve of CMF.

Here, the magnetic coupling constant J can be estimated using Equation S1-3 given by appropriate isotropic Heisenberg Hamiltonian.[1-2] The molecular-field theory (Equation S3) to fit the plots of $\chi_m T$ versus T from 2 to 300 K of CMF and CMC. (Figure S5c, orange and purple lines.)

$$\chi_{chain} = \frac{2Ng^2\beta^2S(S+1)}{3kT}\frac{(1-u)}{(1+u)} \qquad \text{(S1)}$$

$$u = -coth\frac{JS(S+1)}{kT} + \frac{kT}{JS(S+1)} \qquad \text{(S2)}$$

$$\chi = \frac{\chi_{chain}}{1-(zJ/Ng^2\beta^2)\chi_{chain}} \qquad \text{(S3)}$$

Where, *N, g, k*, and β are the Avogadro constant, the Lande factor, the Boltzmann constant, and the Bohr magneton. *J* and *zJ* are the magnetic coupling constants of the intra- and inter-chain. To obtain a reasonable result, the *S* and *g* are set to 5/2 and 2.05, respectively.

References

(1) Wang, X. Y.; Li, B. L.; Zhu, X.; Gao, S. Extended Networks of Co^{2+} and Mn^{2+} Bridged by NCS^{-}/N^{3-} Anions and Flexible Long Spacers: Syntheses, Structures, and Magnetic Properties. *Eur. J. Inorg. Chem.* **2005,** *16* (8), 3277-3286.

(2) Kahn, O. Molecular magnetism, VCH. *Publishers Inc., New York* **1993**, p251-286.