Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Heavy Mn^{2+} doped Near-Infrared Photon Upconversion Luminescence in Fluoride $RbZnF_3:Yb^{3+}, Mn^{2+}$ Guided by Dopant Distribution Simulation

Xinxin Han,[a] Enhai Song,*[a] Shuai Zhang,[a] Shi Ye,[a] Xiaobao Yang[b] and Qinyuan Zhang*[a]

[a]*State Key Laboratory of Luminescent Materials and Devices, Guangdong Provincial Key Laboratory of Fiber Laser Materials and Applied Techniques, School of Materials Science and Engineering, South China University of Technology, Guangzhou 510641, China*

[b]*Department of Physics, South China University of Technology, Guangzhou 510641, China*

*Corresponding author E-mail: msehsong@scut.edu.cn(Enhai Song); qyzhang@scut.edu.cn(Qinyuan Zhang).

Table S1 Number of Mn^{2+}-Mn^{2+} dimer, average Mn^{2+}-Mn^{2+} distance, total energy (*E*) and formation enthalpy (*ΔH)* of three different substitution geometry models for a 3×3×3 supercell of $RbZnF_3$ with two Zn^{2+} replaced by two Mn^{2+} (coverage *x*'=2/27)

Models for *x*=2/27	Number of Mn^{2+}-Mn^{2+} dimer	Average Mn^{2+}-Mn^{2+} distance (Å)	*E* (eV)	*ΔH* (eV)
M1	**1**	**4.1887**	**-564.8166**	**0.0384**
M2	0	5.9238	-564.7370	0.1180
M3	0	7.2551	-564.7356	0.1194

Table S2 Number of Mn^{2+}-Mn^{2+} dimer, average Mn^{2+}-Mn^{2+} distance, total energy (*E*) and formation enthalpy (*ΔH)* of ten different substitution geometry models for a 3×3×3 supercell of $RbZnF_3$ with three Zn^{2+} replaced by three Mn^{2+} (coverage *x*'=3/27)

Models for *x*=3/27	Number of Mn^{2+}-Mn^{2+} dimer	Average Mn^{2+}-Mn^{2+} distance (Å)	*E* (eV)	*ΔH* (eV)
M1	2	5.584993	-569.7340	0.1250
M2	**2**	**4.767087**	**-569.8025**	**0.0565**
M3	1	5.345433	-569.7240	0.1350
M4	1	5.789213	-569.7304	0.1286
M5	1	6.232993	-569.7264	0.1326
M6	0	5.92378	-569.6415	0.2175
M7	0	5.92378	-569.6405	0.2185
M8	0	7.25512	-569.6398	0.2192
M9	0	6.81134	-569.6390	0.2200
M10	0	7.25512	-569.6373	0.2217

Table S3 Number of Mn^{2+}-Mn^{2+} dimer, average Mn^{2+}-Mn^{2+} distance, total energy (*E*) and formation enthalpy (*ΔH)* of thirty-four different substitution geometry models for a 3×3×3 supercell of $RbZnF_3$ with four Zn^{2+} replaced by four Mn^{2+} (coverage *x*'=4/27)

Models for *x*=4/27	Number of Mn^{2+}-Mn^{2+} dimer	Average Mn^{2+}-Mn^{2+} distance (Å)	*E* (eV)	*ΔH* (eV)
M1	4	4.767087	-574.7123	0.14972
M2	3	5.50004	-574.6430	0.21904
M3	**4**	**4.767087**	**-574.8499**	**0.01208**
M4	3	5.05626	-574.7701	0.09192
M5	2	5.345433	-574.6886	0.17339
M6	3	5.05626	-574.7569	0.10509
M7	3	5.27815	-574.7744	0.08761
M8	2	5.567323	-574.6917	0.17031
M9	2	5.567323	-574.6989	0.16313
M10	2	5.789213	-574.6955	0.16652
M11	2	6.011103	-574.6931	0.1689
M12	2	5.345433	-574.6846	0.17739
M13	1	5.634607	-574.6119	0.25014
M14	1	5.856497	-574.6161	0.24592
M15	2	5.789213	-574.7073	0.15474
M16	1	6.078387	-574.6156	0.24642
M17	1	6.078387	-574.6138	0.24818
M18	2	6.011103	-574.7137	0.14834
M19	2	6.011103	-574.7106	0.15138
M20	1	6.078387	-574.6237	0.23834
M21	1	6.300277	-574.6189	0.24311
M22	1	6.078387	-574.6218	0.24025
M23	1	6.300277	-574.6204	0.24159
M24	1	6.522167	-574.6167	0.24529
M25	2	6.232993	-574.7014	0.16064
M26	1	6.522167	-574.6143	0.24766
M27	0	6.14567	-574.5299	0.33215
M28	0	5.92378	-574.5300	0.33205
M29	0	6.14567	-574.5289	0.33308
M30	0	6.36756	-574.5284	0.33362
M31	0	6.58945	-574.5273	0.33469
M32	0	6.36756	-574.5275	0.33451
M33	0	6.58945	-574.5269	0.33506
M34	0	6.58945	-574.5267	0.33528

Table S4 Number of Mn^{2+}-Mn^{2+} dimer, average Mn^{2+}-Mn^{2+} distance, total energy (*E*) and formation enthalpy (*ΔH)* of one hundred and five different substitution geometry models for a 3×3×3 supercell of $RbZnF_3$ with five Zn^{2+} replaced by five Mn^{2+} (coverage *x*'=5/27)

Models for *x*=5/27	Number of Mn^{2+}-Mn^{2+} dimer	Average Mn^{2+}-Mn^{2+} distance (Å)	*E* (eV)	*ΔH* (eV)
M1	4	5.322528	-579.7559	0.10907
M2	6	4.882756	-579.5917	0.27327
M3	5	5.05626	-579.6740	0.19101
M4	4	5.229764	-579.6647	0.20034
M5	5	5.189394	-579.6773	0.18773
M6	5	5.322528	-579.6861	0.17887
M7	4	5.496032	-579.2931	0.57186
M8	4	5.496032	-579.5999	0.26513
M9	4	5.629166	-579.6048	0.26023
M10	4	5.7623	-579.6339	0.23112
M11	4	5.7623	-579.6166	0.24845
M12	3	5.935804	-579.5355	0.32946
M13	3	5.935804	-579.5363	0.32871
M14	3	6.068938	-579.5340	0.33101
M15	4	5.229764	-579.7216	0.14338
M16	**5**	**5.189394**	**-579.8008**	**0.06422**
M17	4	5.496032	-579.7314	0.13357
M18	4	5.7623	-579.7284	0.13659
M19	4	5.229764	-579.7211	0.14391
M20	4	5.362898	-579.7202	0.1448
M21	4	5.496032	-579.7324	0.1326
M22	3	5.536402	-579.6543	0.21073
M23	3	5.669536	-579.6505	0.21453
M24	3	5.80267	-579.6526	0.21239
M25	3	5.536402	-579.6363	0.22872
M26	3	5.669536	-579.6516	0.21343
M27	2	5.709906	-579.5707	0.29427
M28	2	5.84304	-579.5731	0.29186
M29	2	5.84304	-579.5724	0.2926
M30	3	5.80267	-579.6649	0.20007
M31	3	5.536402	-579.6448	0.22021
M32	3	5.669536	-579.6424	0.22261
M33	3	5.80267	-579.6387	0.22627
M34	3	5.935804	-579.6348	0.23022
M35	4	5.496032	-579.7400	0.12501
M36	3	5.80267	-579.6590	0.20604
M37	3	5.669536	-579.6563	0.20874
M38	4	5.629166	-579.7340	0.13098

M39	3	5.935804	-579.6543	0.21074
M40	3	5.80267	-579.6512	0.21377
M41	3	6.068938	-579.6501	0.21493
M42	2	5.84304	-579.5784	0.28658
M43	3	5.80267	-579.6715	0.19349
M44	2	5.84304	-579.5736	0.29138
M45	2	5.976174	-579.5760	0.28902
M46	3	5.935804	-579.6673	0.19766
M47	3	5.669536	-579.6532	0.21176
M48	2	5.976174	-579.5774	0.28759
M49	2	5.976174	-579.5752	0.28976
M50	2	5.976174	-579.5705	0.29446
M51	2	6.109308	-579.5727	0.29228
M52	2	6.109308	-579.5718	0.2932
M53	3	5.80267	-579.6717	0.19332
M54	2	6.109308	-579.5766	0.28842
M55	3	5.669536	-579.6680	0.19701
M56	2	5.976174	-579.5816	0.28341
M57	2	6.242442	-579.5749	0.29009
M58	2	6.109308	-579.5760	0.28896
M59	3	6.068938	-579.6645	0.20054
M60	3	5.935804	-579.6616	0.20339
M61	2	6.242442	-579.2607	0.6043
M62	2	6.242442	-579.5722	0.29276
M63	2	6.202072	-579.5722	0.29276
M64	2	5.576772	-579.5697	0.29528
M65	2	5.84304	-579.5726	0.29242
M66	1	5.88341	-579.4988	0.3662
M67	1	6.016544	-579.4963	0.36873
M68	2	5.84304	-579.5856	0.27936
M69	1	6.149678	-579.4946	0.37039
M70	1	6.016544	-579.4957	0.36926
M71	2	5.84304	-579.5912	0.27385
M72	2	5.976174	-579.5879	0.27707
M73	1	6.149678	-579.4997	0.36531
M74	1	6.149678	-579.4985	0.36654
M75	1	6.016544	-579.5021	0.36293
M76	1	6.149678	-579.4986	0.36642
M77	1	6.282812	-579.4975	0.3675
M78	1	6.149678	-579.4958	0.36917
M79	2	6.109308	-579.5921	0.27293
M80	2	6.242442	-579.5868	0.27821
M81	2	6.109308	-579.5823	0.28267
M82	2	6.109308	-579.5910	0.27401

M83	2	6.109308	-579.5916	0.27345
M84	1	6.282812	-579.4959	0.36911
M85	1	6.282812	-579.4956	0.36944
M86	2	6.109308	-579.5768	0.2882
M87	2	6.109308	-579.5988	0.26625
M88	2	6.375576	-579.5895	0.27551
M89	2	6.242442	-579.5928	0.27218
M90	2	6.242442	-579.5913	0.27373
M91	1	6.149678	-579.5052	0.35982
M92	1	6.415946	-579.4992	0.36579
M93	1	6.415946	-579.4971	0.36787
M94	1	6.282812	-579.5023	0.36268
M95	1	6.415946	-579.4998	0.36517
M96	2	6.375576	-579.5815	0.28353
M97	0	6.190048	-579.4125	0.4525
M98	0	6.190048	-579.4131	0.45189
M99	0	6.190048	-579.4137	0.45133
M100	0	6.323182	-579.4128	0.45217
M101	0	6.323182	-579.4121	0.45286
M102	0	6.456316	-579.4087	0.45634
M103	0	6.456316	-579.4096	0.4554
M104	0	6.456316	-579.4092	0.45585
M105	0	6.456316	-579.4071	0.45791

Table S5 Rietveld refinement data for $RbZnF_3$

Formula	$RbZnF_3$
space group	$Pm\bar{3}m$
a=b=c (Å)	4.11248(6)
$\alpha=\beta=\gamma$ (°)	90
Z	1
V ($Å^3$)	69.5525(18)
R_{wp} (%)	7.02
R_p (%)	5.32
χ^2	4.365

Note: The refinements are stable and give low R-factors.

Table S6 The fitting parameters of the Mn K-edge EXAFS curves in $RbMnF_3$

Chemical bond	CN (Coordination number)	R (Å)	σ^2(Å^2) (Debye Waller Factor)	ΔE_0 (eV) (Edge-energy shift)
Mn-F	6.2	2.160	0.0077	-7.9
Mn-Rb	8.2	3.733	0.0162	-7.9
Mn-Mn	6.2	4.418	0.0019	-7.9

Error bounds of the structural parameters were estimated as CN±15%; R±1%; σ^2±20%;ΔE_0±20%. Mn K-edge fitting range: K-space range: 3.5-10.5; R-space range: 1.1-4.5 Å.

Table S7 The fitting parameters of the Mn K-edge EXAFS curves in $RbZnF_3$: 20%Mn^{2+}

Chemical bond	CN (Coordination number)	R (Å)	σ^2(Å^2) (Debye Waller Factor)	ΔE_0 (eV) (Edge-energy shift)
Mn-F	5.8	2.152	0.0064	-8.2
Mn-Rb	7.8	3.680	0.0153	-8.2
Mn-Mn/Zn	5.8	4.370	0.0012	-8.2

Error bounds of the structural parameters were estimated as CN±15%; R±1%; σ^2±20%;ΔE_0±20%. Mn K-edge fitting range: K-space range: 3.5-10.5; R-space range: 1.1-4.5 Å.

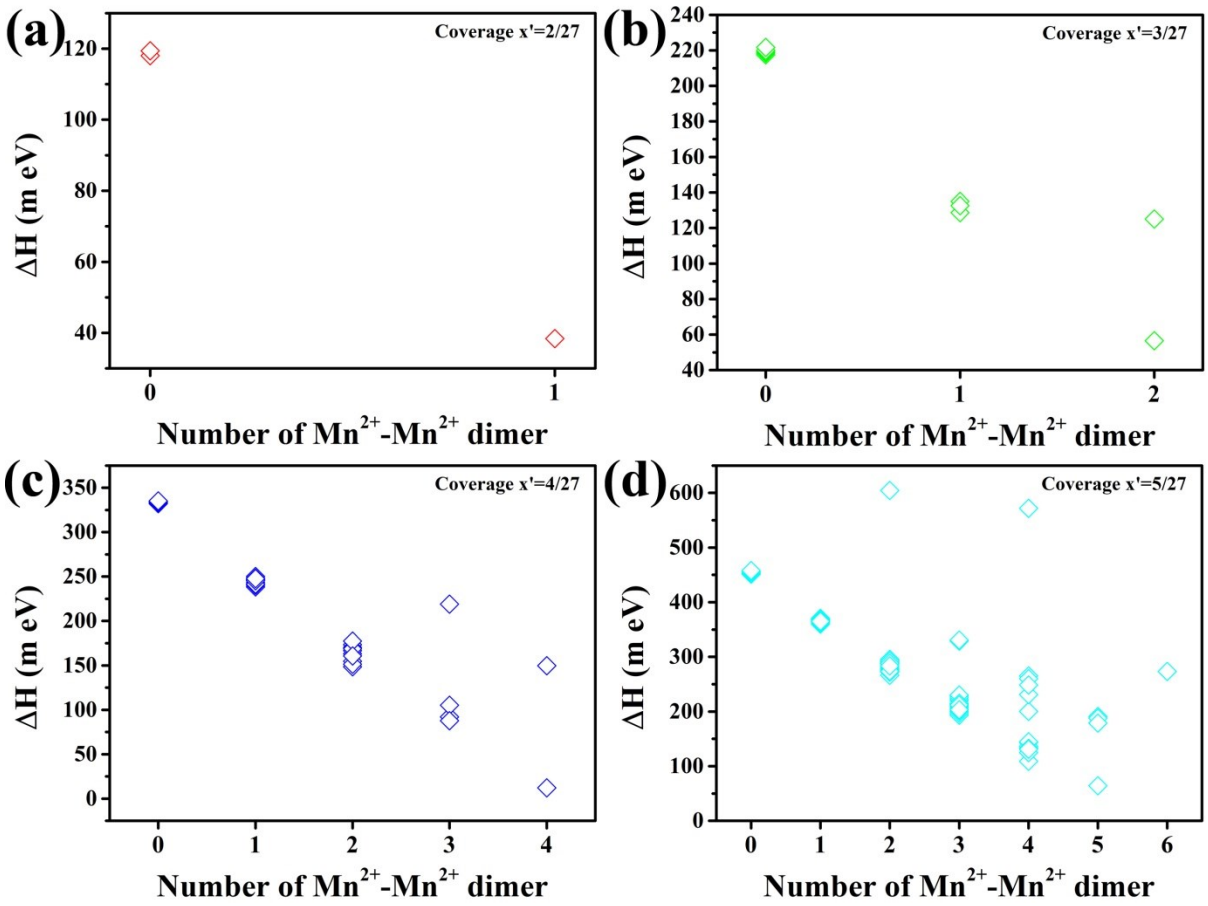

Fig. S1 The dependence of formation enthalpy (*ΔH*) on the number of Mn^{2+}-Mn^{2+} dimer for a certain Mn^{2+} coverage *x*' in a 3×3×3 $RbZnF_3$ supercell: (a) *x*'=2/27, (b) *x*'=3/27, (c) *x*'=4/27, (d) *x*'=5/27.

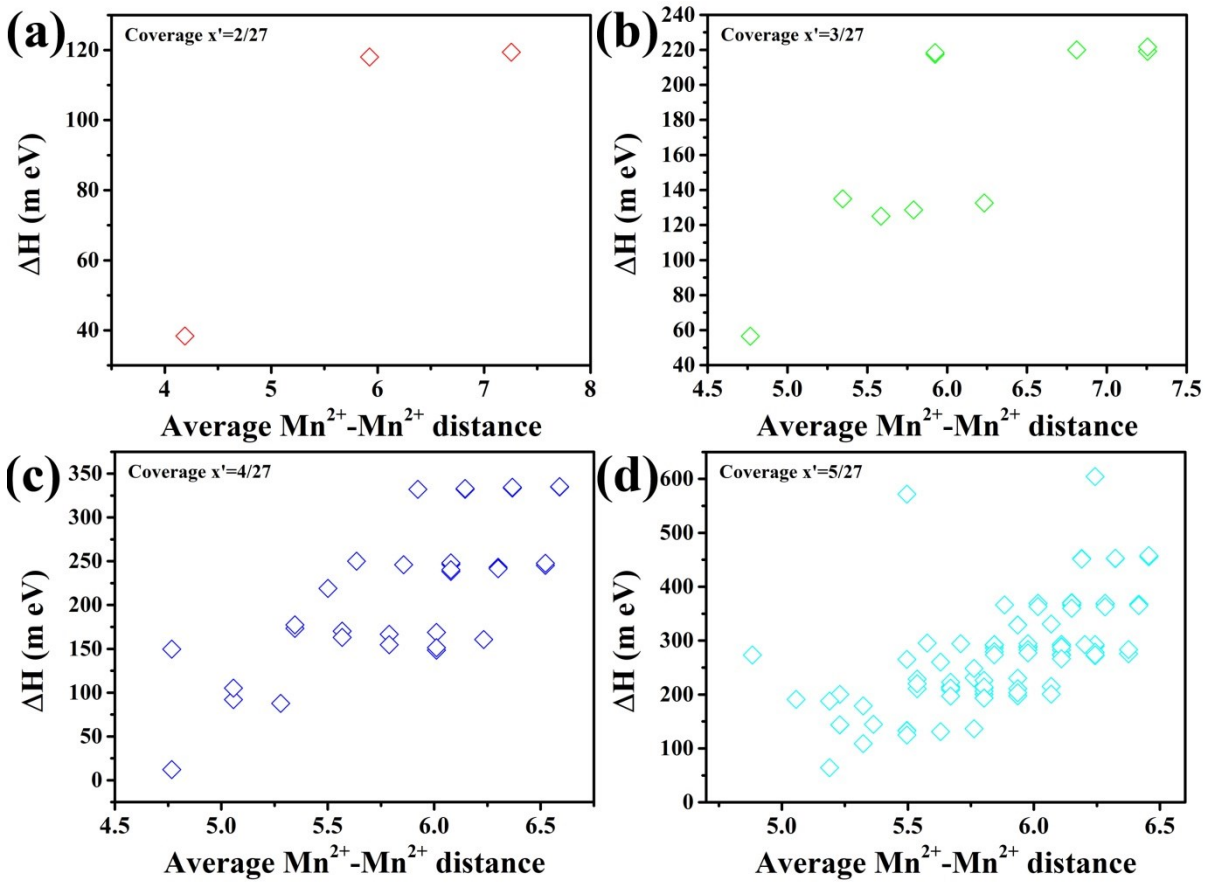

Fig. S2 The dependence of formation enthalpy (*ΔH*) on the average Mn^{2+}-Mn^{2+} distance for a certain Mn^{2+} coverage *x*' in a 3×3×3 $RbZnF_3$ supercell: (a) *x*'=2/27, (b) *x*'=3/27, (c) *x*'=4/27, (d) *x*'=5/27.

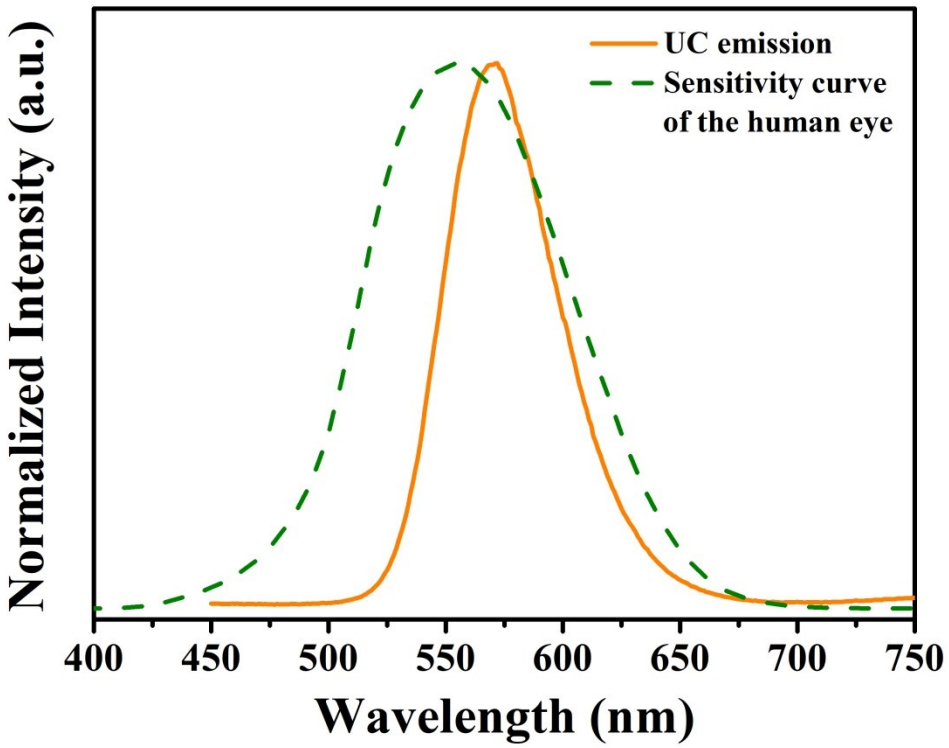

Fig. S3 UC emission spectra of $RbZnF_3$:0.5%Yb^{3+}, 5%Mn^{2+} upon excitation with a 980 nm LD and the sensitivity curve of the human eye (dashed line).

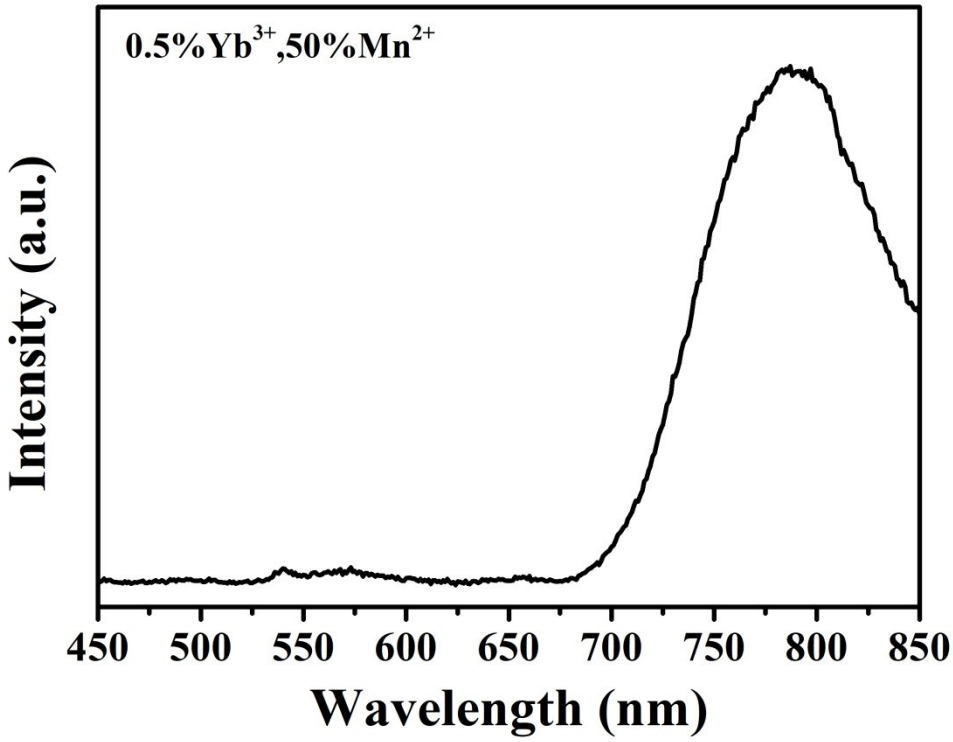

Fig. S4 UC emission spectra of $RbZnF_3$: 0.5%Yb^{3+}, 50%Mn^{2+} upon excitation of 980 nm laser.