Electronic supplementary information

Realizing an impressive red-emitting $Ca_9MnNa(PO_4)_7$ phosphor through dual function based on disturbing structural confinement and energy transfer

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Table S1. Structural Rietveld refinement parameters and crystallographic data of the CMNPO sample.

Formula	CMNPO
Space group	R3c
a(Å)	10.3923
b(Å)	10.3923
c(Å)	37.1362
α(°)	90
β(°)	90
γ(°)	120
Z	6
V(Å^3)	3473.33
Rp(%)	4.65
Rwp(%)	6.11
χ^2	2.842

Table S2. Final refined atomic coordinates, sites and thermal parameters of CMNPO phosphor

Atom	Site	X	Y	Z	Frac.	U_{iso} X 100
Ca1	18b	0.73303	0.85893	0.43364	1.000	0.80
Ca2	18b	0.62387	0.82039	0.232	1.000	0.1
Ca3	18b	0.12014	0.26089	0.3255	1.000	0.8
Na	6a	0.00000	0.00000	0.1784	1.000	3.3
Mn	6a	0.00000	0.00000	0.00341	1.000	0.6
P1	6a	0.00000	0.00000	0.26607	1.000	1.8
P2	18b	0.69304	0.86457	0.13644	1.000	0.6
P3	18b	0.65492	0.84615	0.03375	1.000	1.0
O1	6a	0.00000	0.00000	0.30726	1.000	0.3
O2	18b	0.00755	0.85941	0.25409	1.000	0.3
O3	18b	0.7607	0.92582	0.17703	1.000	0.3
O4	18b	0.75419	0.75993	0.12506	1.000	0.3
O5	18b	0.74109	0.00507	0.11387	1.000	0.3
O6	18b	0.51205	0.77936	0.12373	1.000	0.3
O7	18b	0.62245	0.99817	0.04078	1.000	0.3
O8	18b	0.5751	0.69467	0.05355	1.000	0.3
O9	18b	0.82822	0.89652	0.03613	1.000	0.3
O10	18b	0.62987	0.84358	0.99232	1.000	0.3

Table S3. Structural Rietveld refinement parameters and crystallographic data of the CMNPO:0.05Eu^{2+} sample.

Formula	CMNPO:0.05Eu^{2+}
Space group	R3c
a(Å)	10.3956
b(Å)	10.3956
c(Å)	37.1523
α(°)	90
β(°)	90
γ(°)	120
Z	6
V($Å^3$)	3477.09
Rp(%)	3.78
Rwp(%)	4.95
χ^2	1.912

Table S4. Final refined atomic coordinates, sites and thermal parameters of CMNPO:0.05Eu^{2+} phosphor

Atom	Site	X	Y	Z	Frac.	U_{iso} X 100
Ca1	18b	0.72612	0.85494	0.43272	1.000	0.8
Ca2	18b	0.61666	0.82459	0.23204	1.000	0.1
Ca3	18b	0.11947	0.26423	0.32529	1.000	0.8
Na	6a	0.00000	0.00000	0.18545	1.000	3.3
Mn	6a	0.00000	0.00000	0.00040	0.9480	0.6
Eu	6a	0.00000	0.00000	0.00040	0.0520	0.6
P1	6a	0.00000	0.00000	0.26649	1.000	1.8
P2	18b	0.69191	0.86224	0.13548	1.000	0.6
P3	18b	0.65831	0.84594	0.03206	1.000	1.0
O1	6a	0.00000	0.00000	0.31792	1.000	0.3
O2	18b	0.01070	0.86430	0.25190	1.000	0.3
O3	18b	0.75110	0.92850	0.17460	1.000	0.3
O4	18b	0.76500	0.77400	0.12200	1.000	0.3
O5	18b	0.72900	0.00460	0.11260	1.000	0.3
O6	18b	0.52050	0.77100	0.13140	1.000	0.3
O7	18b	0.60800	0.95700	0.04560	1.000	0.3
O8	18b	0.56980	0.69210	0.05250	1.000	0.3
O9	18b	0.81585	0.92277	0.04233	1.000	0.3
O10	18b	0.63584	0.83326	0.99233	1.000	0.3

Table S5. The CIE coordinates, CCT, Ra and luminous efficiency (LE) of LED1-4.

LED	CIE coordinates		CCT (K)	Ra	LE (lm/W)
	x	y			
LED-1	0.5517	0.2921	1400	48	15.58
LED-2	0.3472	0.3309	4956	80.5	32
LED-3	0.3299	0.3317	4642	83.4	27.89
LED-4	0.3451	0.3902	5105	64.9	26.5

Note: Under our present experimental conditions, even the combination method (LED-4) of commercially available white LEDs devices has lower luminous efficiency. It is worth pointing out that lower luminous efficiency can be improved by optimizing the processing conditions and controlling the particle size, morphology, and crystallinity of the phosphor. But through comparison, we can conclude that the pronounced warmer tone of the emitting light was observed owing to the incremental red light component in the emission spectrum of LED-3. The CCT decrease from 5105 K to 4642 K and the Ra value was greatly improved, with no significant reduction in luminous efficiency.

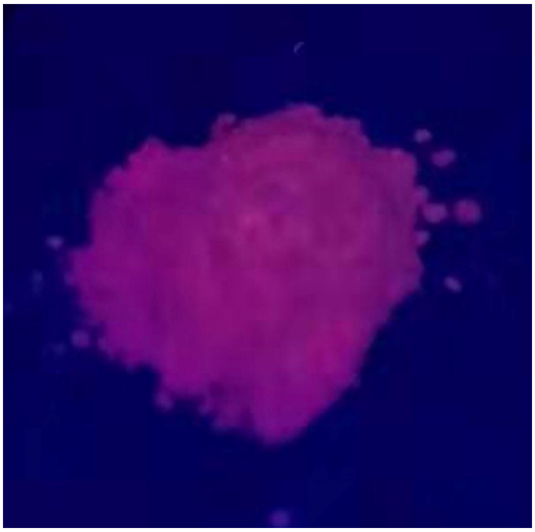

Figure S1. The luminescent photograph of $Ca_9MnNa(PO_4)_7$ phosphor.

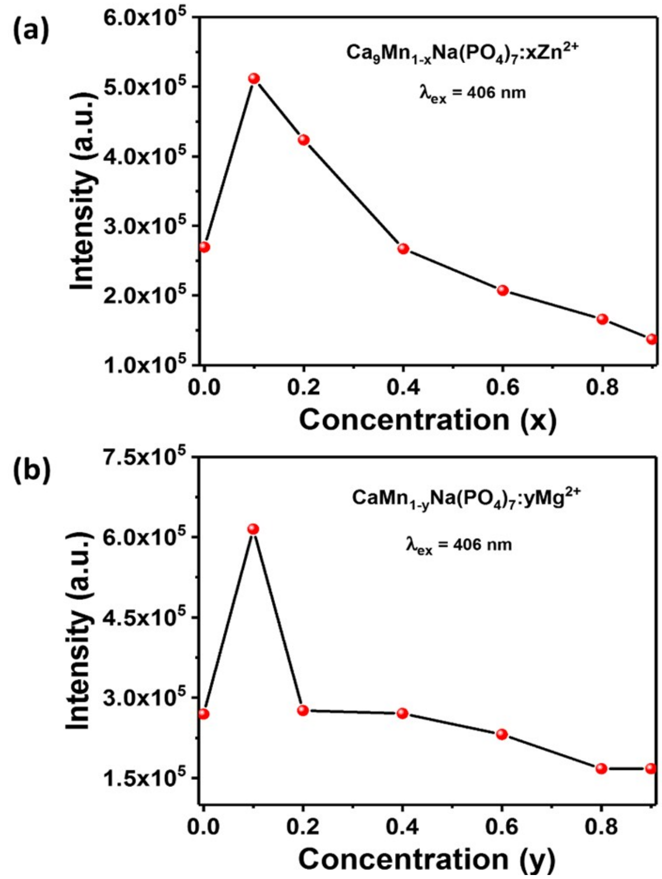

Figure S2. The line diagram of the concentration-dependent luminescence intensity of CMNPO:xZn^{2+} (a) and CMNPO:yMg^{2+} (b) phosphors.

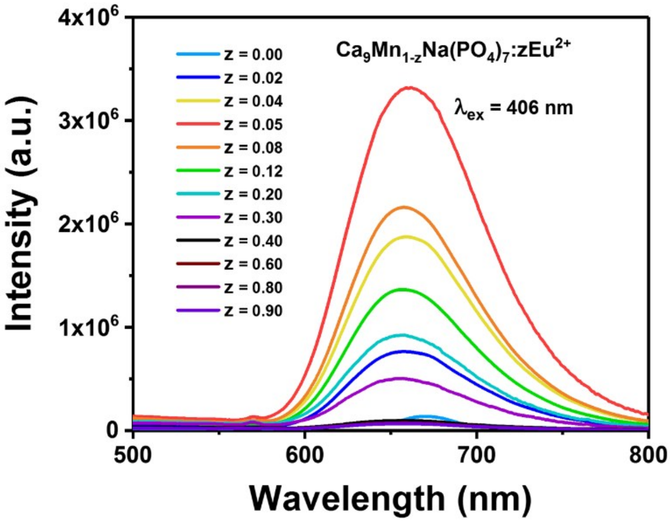

Figure S3. Concentration-dependent emission spectra of $Ca_9Mn_{1-z}Na(PO_4)_7$:zEu^{2+} phosphor.

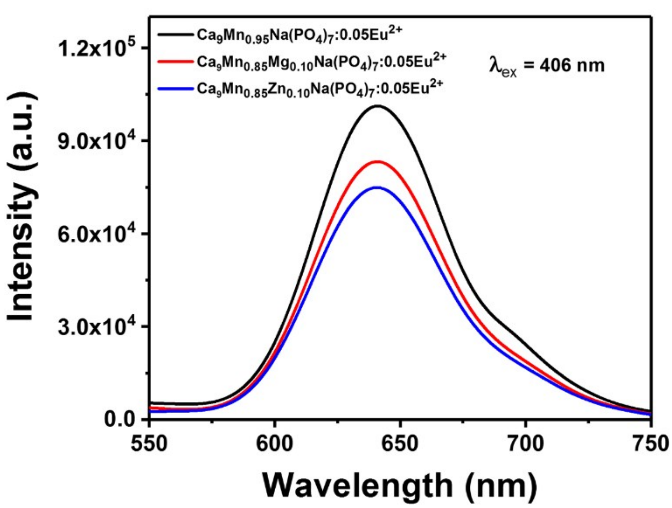

Figure S4. The PL spectra of $Ca_9Mn_{0.95}Na(PO_4)_7$:$0.05Eu^{2+}$, $Ca_9Mn_{0.85}Mg_{0.10}Na(PO_4)_7$:$0.05Eu^{2+}$, $Ca_9Mn_{0.85}Zn_{0.10}Na(PO_4)_7$:$0.05Eu^{2+}$ phosphor.

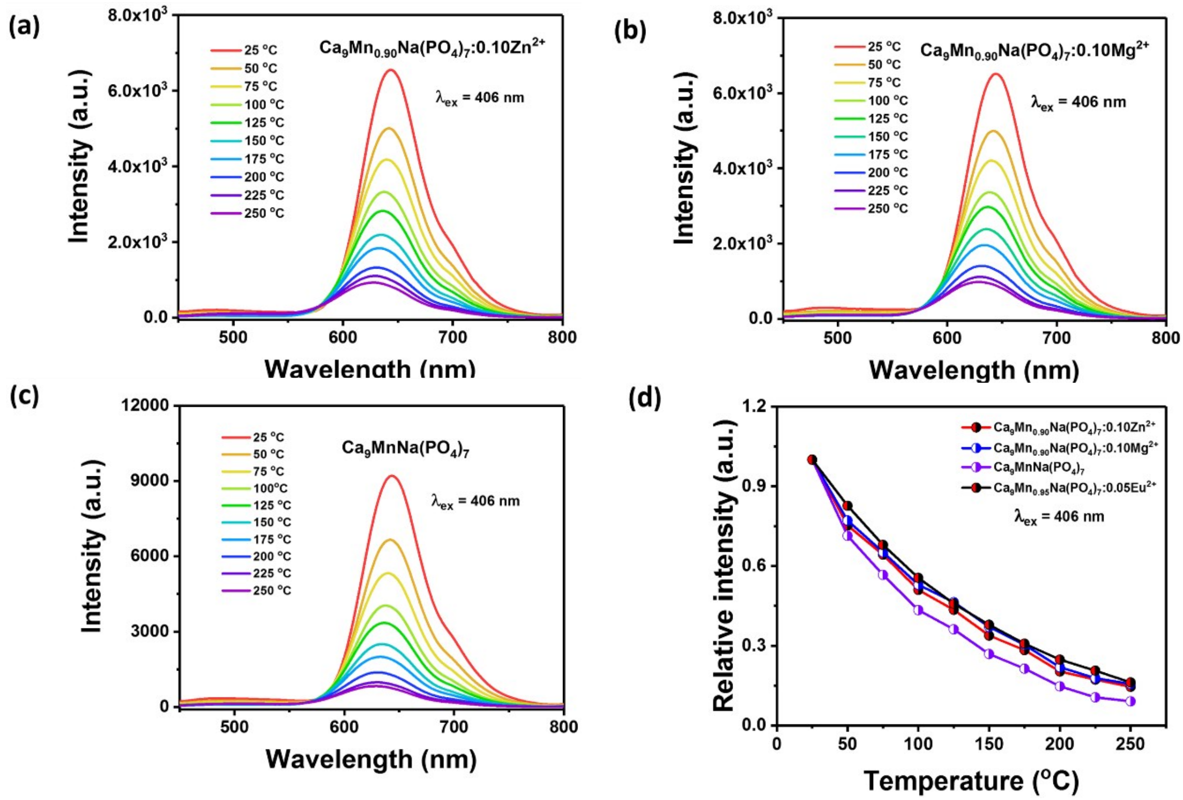

Fig. S5 The temperature-dependent PL spectra of $Ca_9Mn_{0.90}Na(PO_4)_7$:$0.10Zn^{2+}$ (a), $Ca_9Mn_{0.90}Na(PO_4)_7$:$0.10Mg^{2+}$ (b), $Ca_9MnNa(PO_4)_7$ (c) phosphor. The dot-line chart of the temperature-dependent luminescence intensity of Zn^{2+}/Mg^{2+}/Eu^{2+} doped and undoped phosphors (d).