# Supporting Information

## Ultrahigh energy transfer efficiency and efficient $Mn^{2+}$ red emission realized by structural confinement in $Ca_9LiMn(PO_4)_7$: $Eu^{2+}$, $Tb^{3+}$ phosphor

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Table S1 Main processing and refinement parameters of CLMP host from the Rietveld Structure Analysis

| Formula | | $Ca_9LiMn(PO_4)_7$ | | | | |
|---|---|---|---|---|---|---|
| Space group | | *R*3*c* (161) - trigonal | | | | |
| Cell parameters | | $a = b = 10.3659(1)$ Å, $c = 37.1503(4)$ Å, $V = 3457.08$ Å$^3$, $Z = 6$ | | | | |
| Reliability factors | | $R_{wp} = 9.06$ %, $R_p = 6.90$ %, $\chi^2 = 2.462$ | | | | |
| Atom | Site | *x* | *y* | *z* | occupancy | *U* (Å$^2$) |
| Ca1 | 18b | 0.71883 | 0.85610 | 0.44341 | 1.0 | 0.0107 |
| Ca2 | 18b | 0.60636 | 0.81241 | 0.24243 | 1.0 | 0.0239 |
| Ca3 | 18b | 0.12123 | 0.27191 | 0.33661 | 1.0 | 0.0302 |
| Li1 | 6a | 0 | 0 | 0.16995 | 1.0 | 0.0269 |
| Mn1 | 6a | 0 | 0 | 0.01325 | 1.0 | 0.0269 |
| P1 | 6a | 0 | 0 | 0.27130 | 1.0 | 0.0984 |
| P2 | 18b | 0.70219 | 0.86909 | 0.14271 | 1.0 | 0.0792 |
| P3 | 18b | 0.65769 | 0.85071 | 0.04449 | 1.0 | 0.0020 |
| O1 | 6a | 0 | 0 | 0.32093 | 1.0 | 0.0298 |
| O2 | 18b | 0.00673 | 0.87212 | 0.25235 | 1.0 | 0.0329 |
| O3 | 18b | 0.69917 | 0.87660 | 0.19032 | 1.0 | 0.0220 |
| O4 | 18b | 0.78096 | 0.79077 | 0.13416 | 1.0 | 0.0156 |
| O5 | 18b | 0.71518 | -0.01091 | 0.12351 | 1.0 | 0.0152 |
| O6 | 18b | 0.52152 | 0.76605 | 0.14018 | 1.0 | 0.0072 |
| O7 | 18b | 0.58857 | 0.96677 | 0.04375 | 1.0 | 0.0270 |
| O8 | 18b | 0.59092 | 0.69978 | 0.06219 | 1.0 | 0.0263 |
| O9 | 18b | 0.81823 | 0.87601 | 0.04182 | 1.0 | 0.0240 |
| O10 | 18b | 0.59138 | 0.82076 | 0.99772 | 1.0 | 0.0238 |

Table S2 Main processing and refinement parameters of CLMP: $0.02Eu^{2+}$ sample from the Rietveld Structure Analysis

| Formula | | $Ca_{9-x}LiMn(PO_4)_7$: $xEu^{2+}$ ($x$ = 0.02) | | | | |
|---|---|---|---|---|---|---|
| Space group | | *R*3*c* (161) - trigonal | | | | |
| Cell parameters | | $a = b$ = 10.3733(1) Å, $c$ = 37.1844(3) Å, $V$ = 3465.15 Å$^3$, $Z$ = 6 | | | | |
| Reliability factors | | $R_{wp}$ = 7.36 %, $R_p$ = 5.56 %, $\chi^2$ = 3.251 | | | | |
| Atom | Site | $x$ | $y$ | $z$ | occupancy | $U$ (Å$^2$) |
| Ca1 | 18b | 0.71865 | 0.85429 | 0.44078 | 0.9978 | 0.0217 |
| Eu1 | 18b | 0.71865 | 0.85429 | 0.44078 | 0.0022 | 0.0217 |
| Ca2 | 18b | 0.61096 | 0.82387 | 0.23999 | 0.9978 | 0.0161 |
| Eu2 | 18b | 0.61096 | 0.82387 | 0.23999 | 0.0022 | 0.0161 |
| Ca3 | 18b | 0.13159 | 0.27698 | 0.33432 | 0.9978 | 0.0297 |
| Eu3 | 18b | 0.13159 | 0.27698 | 0.33432 | 0.0022 | 0.0297 |
| Li1 | 6a | 0 | 0 | 0.15018 | 1.0 | 0.0220 |
| Mn1 | 6a | 0 | 0 | 0.00860 | 1.0 | 0.0220 |
| P1 | 6a | 0 | 0 | 0.27323 | 1.0 | 0.0236 |
| P2 | 18b | 0.69189 | 0.86379 | 0.14056 | 1.0 | 0.0236 |
| P3 | 18b | 0.66187 | 0.85301 | 0.03920 | 1.0 | 0.0236 |
| O1 | 6a | 0 | 0 | 0.31724 | 1.0 | 0.0450 |
| O2 | 18b | 0.00215 | 0.85653 | 0.26237 | 1.0 | 0.0450 |
| O3 | 18b | 0.76652 | 0.89686 | 0.18982 | 1.0 | 0.0450 |
| O4 | 18b | 0.73053 | 0.76139 | 0.13285 | 1.0 | 0.0211 |
| O5 | 18b | 0.72199 | -0.01015 | 0.12176 | 1.0 | 0.0211 |
| O6 | 18b | 0.52599 | 0.76372 | 0.14006 | 1.0 | 0.0211 |
| O7 | 18b | 0.59633 | 0.96185 | 0.05021 | 1.0 | 0.0211 |
| O8 | 18b | 0.56944 | 0.70268 | 0.05830 | 1.0 | 0.0211 |
| O9 | 18b | 0.82764 | 0.92176 | 0.04760 | 1.0 | 0.0211 |
| O10 | 18b | 0.62040 | 0.82892 | 1.00133 | 1.0 | 0.0211 |

Table S3 Main processing and refinement parameters of CLMP: $0.02Eu^{2+}$, $0.90Tb^{3+}$ sample from the Rietveld Structure Analysis

| Formula | | $Ca_{9-x-y}LiMn(PO_4)_7$：$xEu^{2+}$, $yTb^{3+}$ ($x$ = 0.02, $y$ = 0.90) | | | | |
|---|---|---|---|---|---|---|
| Space group | | *R*3*c* (161) - trigonal | | | | |
| Cell parameters | | $a = b$ = 10.3836(1) Å, $c$ = 37.1446(6) Å, $V$ = 3468.36 Å$^3$, $Z$ = 6 | | | | |
| Reliability factors | | $R_{wp}$ = 5.07 %, $R_p$ = 3.85 %, $\chi^2$ = 2.463 | | | | |
| Atom | Site | *x* | *y* | *z* | occupancy | *U* (Å$^2$) |
| Ca1 | 18b | 0.72139 | 0.85167 | 0.43354 | 0.89524 | 0.0098 |
| Eu1 | 18b | 0.72139 | 0.85167 | 0.43354 | 0.0022 | 0.0098 |
| Tb1 | 18b | 0.72139 | 0.85167 | 0.43354 | 0.10256 | 0.0098 |
| Ca2 | 18b | 0.62344 | 0.82339 | 0.23244 | 0.89522 | 0.0079 |
| Eu2 | 18b | 0.62344 | 0.82339 | 0.23244 | 0.0022 | 0.0079 |
| Tb2 | 18b | 0.62344 | 0.82339 | 0.23244 | 0.10257 | 0.0079 |
| Ca3 | 18b | 0.12403 | 0.26917 | 0.32642 | 0.90294 | 0.0370 |
| Eu3 | 18b | 0.12403 | 0.26917 | 0.32642 | 0.0022 | 0.0370 |
| Tb3 | 18b | 0.12403 | 0.26917 | 0.32642 | 0.09487 | 0.0370 |
| Li1 | 6a | 0 | 0 | 0.17921 | 1.0 | 0.0667 |
| Mn1 | 6a | 0 | 0 | 0.00053 | 1.0 | 0.0535 |
| P1 | 6a | 0 | 0 | 0.26834 | 1.0 | 0.0149 |
| P2 | 18b | 0.68426 | 0.86326 | 0.13512 | 1.0 | 0.0059 |
| P3 | 18b | 0.64897 | 0.83853 | 0.03216 | 1.0 | 0.0513 |
| O1 | 6a | 0 | 0 | 0.31295 | 1.0 | 0.0063 |
| O2 | 18b | 0.02696 | 0.85624 | 0.24702 | 1.0 | 0.0667 |
| O3 | 18b | 0.74169 | 0.89715 | 0.17277 | 1.0 | 0.0503 |
| O4 | 18b | 0.76641 | 0.76524 | 0.12335 | 1.0 | 0.0347 |
| O5 | 18b | 0.73876 | 0.02208 | 0.11192 | 1.0 | 0.0215 |
| O6 | 18b | 0.52690 | 0.77631 | 0.12578 | 1.0 | 0.0405 |
| O7 | 18b | 0.61116 | 0.95177 | 0.04449 | 1.0 | 0.0010 |
| O8 | 18b | 0.58030 | 0.69209 | 0.05138 | 1.0 | 0.0010 |
| O9 | 18b | 0.83480 | 0.92042 | 0.03861 | 1.0 | 0.0010 |
| O10 | 18b | 0.62659 | 0.83123 | 0.99227 | 1.0 | 0.0010 |

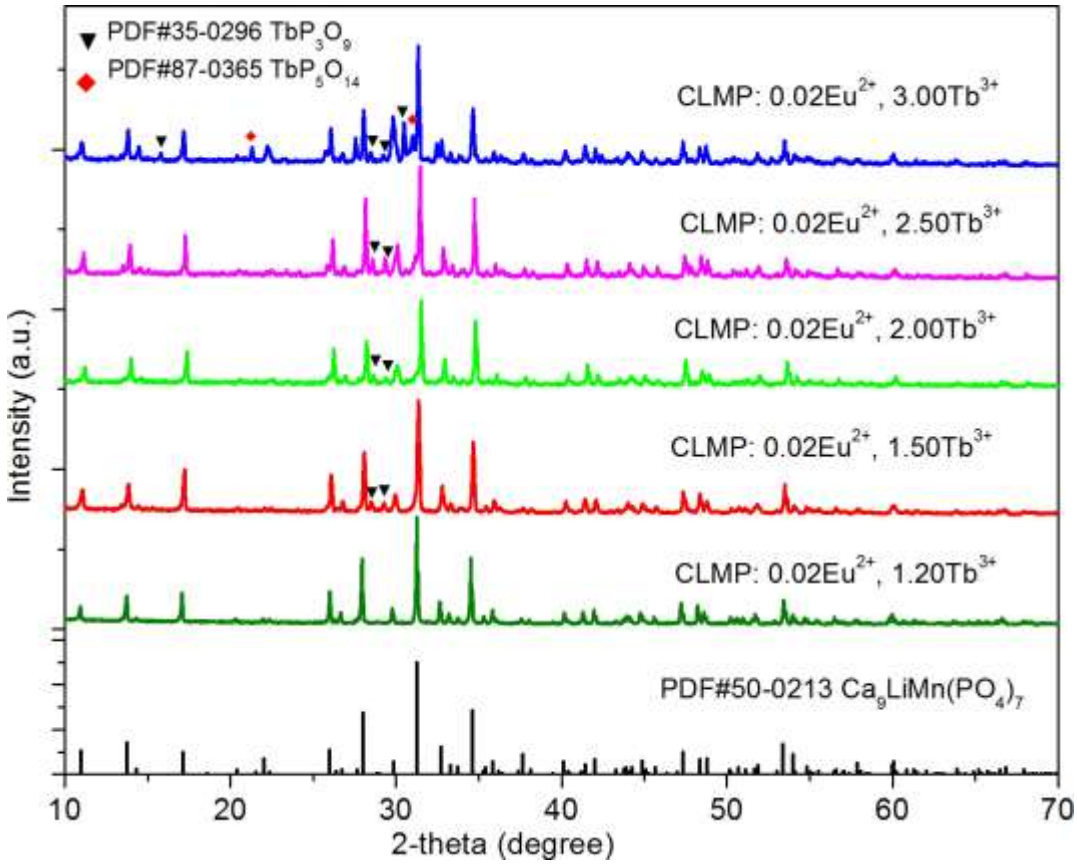


Fig.S1 XRD patterns of CLMP: 0.02$Eu^{2+}$, $y$$Tb^{3+}$ ($y$ = 0~3.0) samples

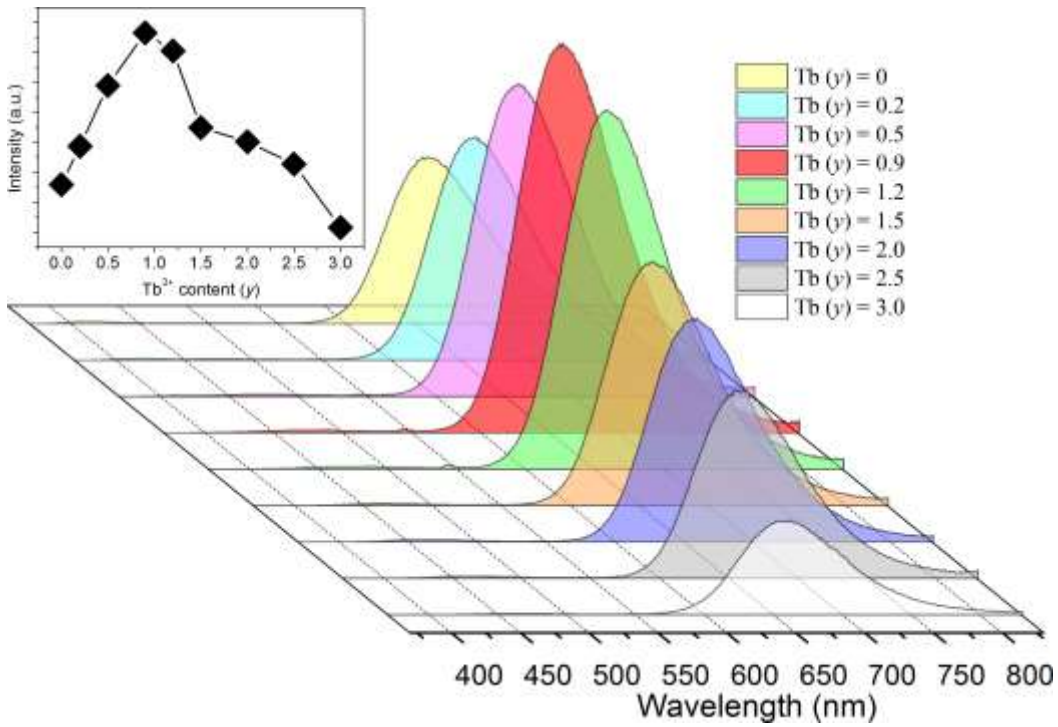


Fig.S2 The PL spectra of CLMP: 0.02$Eu^{2+}$, $y$$Tb^{3+}$ ($y$ = 0~3.0) samples under 365 nm excitation

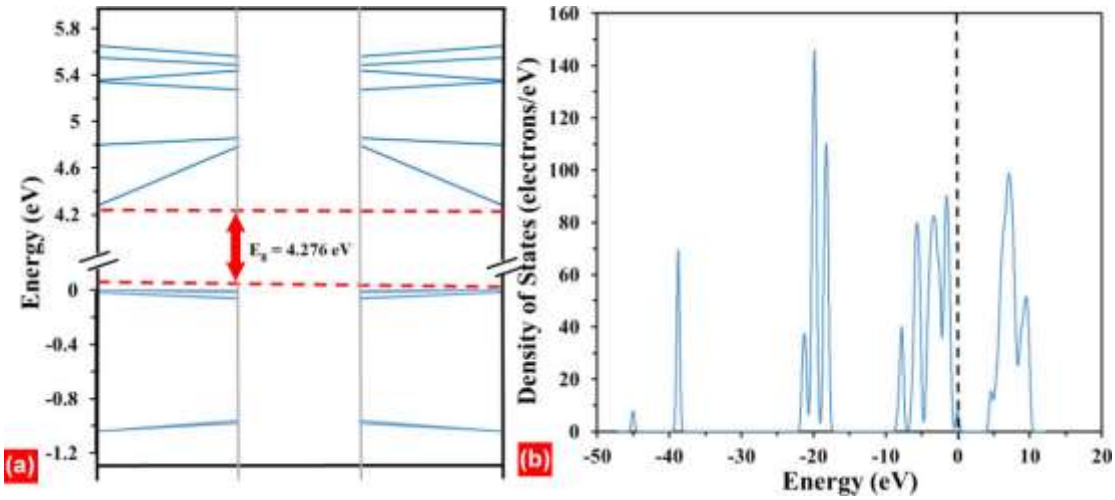


Fig.S3 The electronic band structure and the density of states (DOS) of $Ca_9LiMn(PO_4)_7$ host

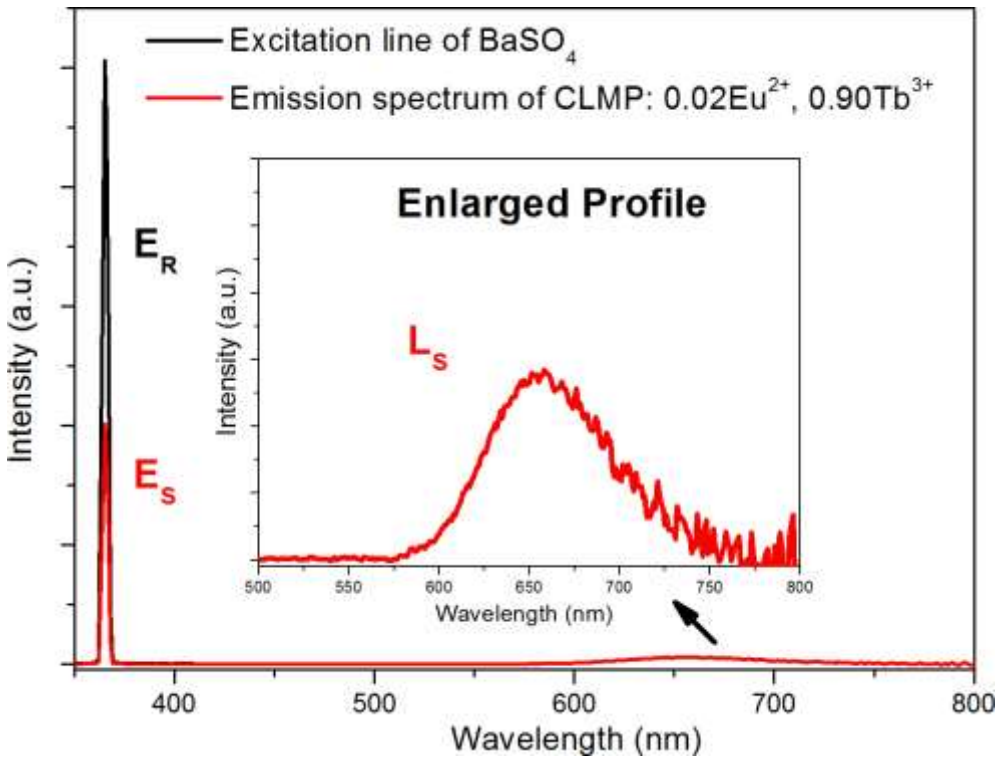


Fig.S4 Excitation lines of $BaSO_4$ and CLMP: $0.02Eu^{2+}$, $0.90Tb^{3+}$, and the emission spectrum of CLMP: $0.02Eu^{2+}$, $0.90Tb^{3+}$ collected by using an integrating sphere. The inset shows a magnification of the emission spectrum of CLMP: $0.02Eu^{2+}$, $0.90Tb^{3+}$.

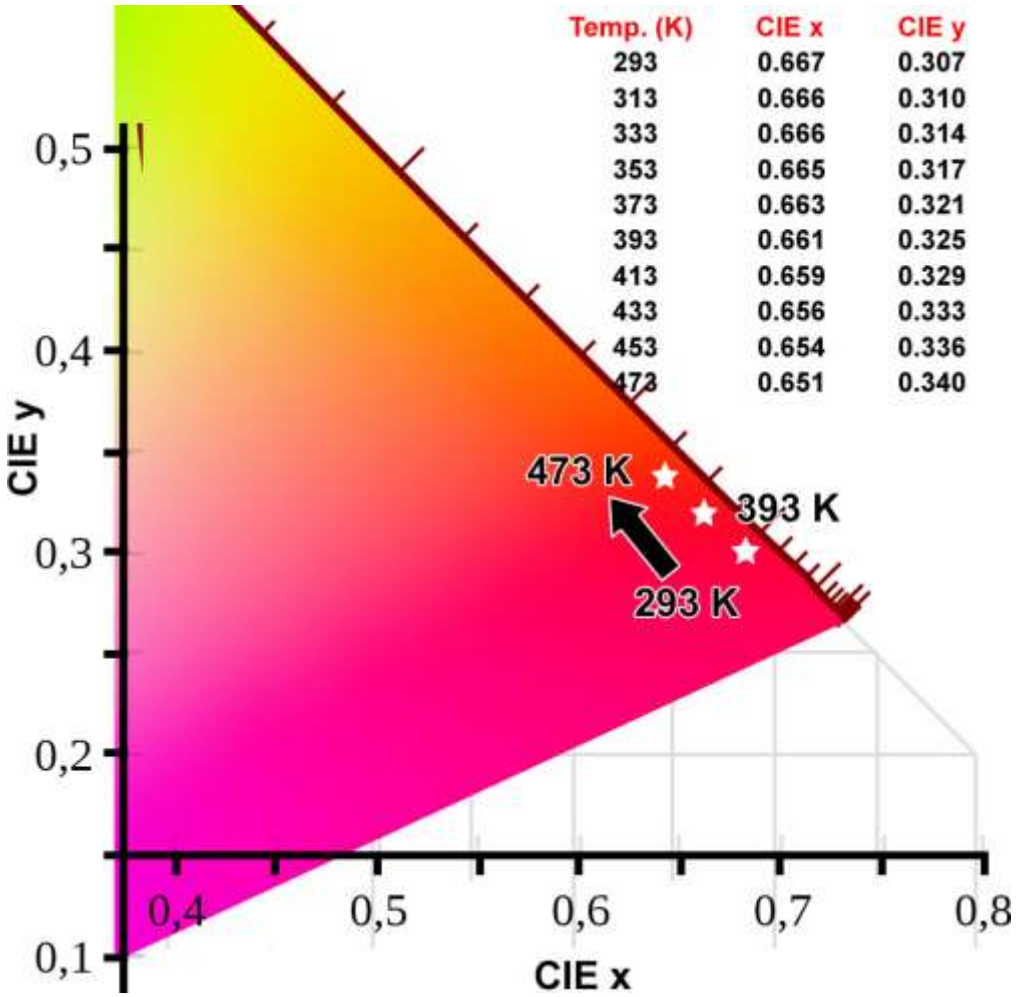


Fig.S5 Temperature-dependent CIE coordinates variation of CLMP: $0.02Eu^{2+}$, $0.90Tb^{3+}$

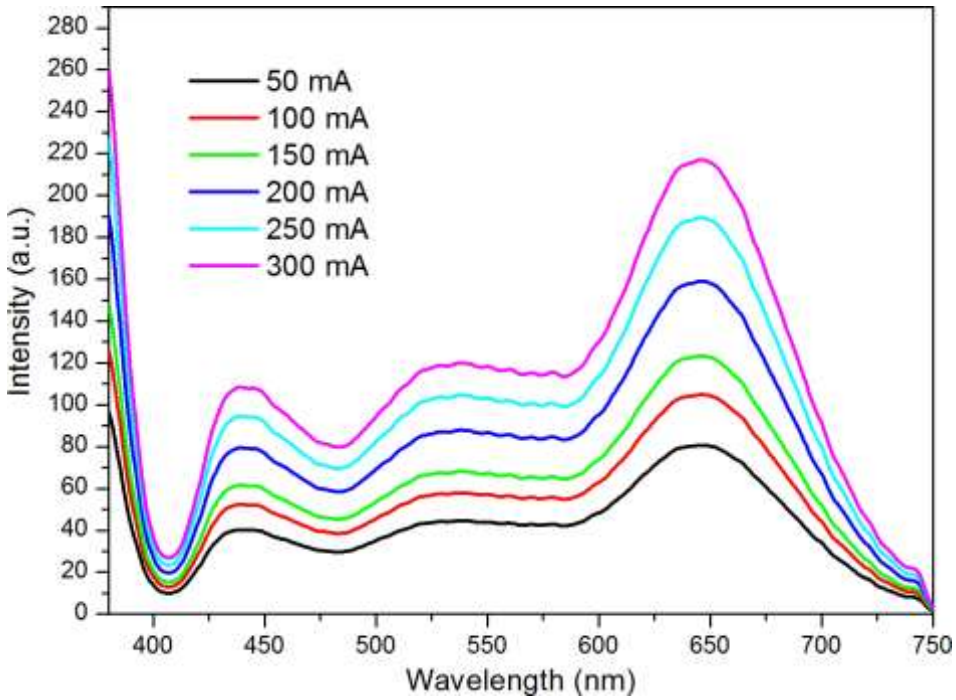


Fig.S6 The EL spectra of white LEDs device at 50~300 mA driving currents