Electronic Supplementary Material (ESI) for Nanoscale.

Supporting information

Clustering Triggered Emissive Liquid Crystalline Template for Dual Mode Upconverted and Downconverted Circularly Polarized Luminescence

Sreelakshmi Theeyanchery Nalavadath, Sonia Maniappan, Anannya Mandal, Jatish Kumar*

Department of Chemistry, Indian Institute of Science Education and Research (IISER) Tirupati, Tirupati 517507, India

Email: jatish@iisertirupati.ac.in

Page No. Contents

Materials

All the necessary chemicals for the experiments were purchased from external suppliers and utilized without performing any further purification. Ammonium fluoride (NH_4F), thulium chloride hexahydrate ($TmCl_3.6H_2O$), manganese dichloride tetrahydrate ($MnCl_2{\cdot}4H_2O$), sodium hydroxide (NaOH), and holmium chloride hexahydrate ($HoCl_3.6H_2O$) were purchased from Alfa Aesar. Yttrium chloride hexahydrate ($YCl_3.6H_2O$), ytterbium chloride hexahydrate ($YbCl_3.6H_2O$), cholesteryl benzoate (ChB), and L-pyroglutamic acid (L- PGA) were obtained from Sigma Aldrich.

Characterisation

UV–vis spectra were recorded using an Agilent Cary-3500 UV–vis spectrophotometer. The JASCO 8500 fluorescence spectrophotometer was utilized to perform photoluminescence studies. Upconversion photoluminescence (UC-CPL) of the UCNPs was measured with a 980 nm laser diode (continuous wave (CW), 500 mW) serving as an external excitation source on the fluorescence instrument. Structural analysis of the materials was performed using the Rigaku Smart Lab 9 kW powder X-ray diffractometer (PXRD) with Ni filtered Cu Kα radiation ($\lambda = 0.1542$ nm) at 45 kV and 100 mA, employing a scan rate of 2° per min and a stepping size of 0.02° at room temperature. DRCD measurements were carried out using JASCO J-1500 CD spectrometer. The JASCO CPL 300 spectrometer was employed to measure the excited state chirality. For upconversion CPL measurement, a 980 nm laser diode (700 mW) was connected to the CPL instrument. SEM images for characterizing UCNPs were captured using the FEI Nova Nano SEM- q450. Thermogravimetric analysis was performed using the PerkinElmer TGA 8000. POM imaging of samples was conducted using the Nikon Eclipse LV 100N POL microscope. Lifetime and absolute quantum yield were carried out on Edinburg FLS 1000 instrument. DSC measurements were performed using DSC880 (Mettler Toledo).

Synthesis of upconversion nanoparticles

Synthesis of blue emitting 0.1g L-PGA capped $NaYF_4$/ Yb, Tm:

100 mg of L-PGA was dissolved in 6 mL of milli-Q water and 6 mL of methanol and transferred to a Teflon vial. Sequentially, 200 mg of NaOH, 236.6 mg of $YCl_3.6H_2O$, 77.5 mg of $YbCl_3.6H_2O$, 7.6 mg of $TmCl_3.6H_2O$, and 148.2 mg of NH_4F were dissolved in minimal water and added to the solution in the specified order. The mixture was then allowed to stir for 30 minutes. Subsequently, the container was packed inside a hydrothermal reactor and maintained at 180°C for 10 hours with a ramping rate of 5°C per minute. After completion, the reaction

mixture was allowed to cool down to room temperature. Similar procedures were followed for the synthesis of green-emitting (0.5g L-PGA capped NaYF4/ Yb, Mn, Ho) and red-emitting UCNPs (0.1g L-PGA capped NaYF4/ Yb, Er).[1] The synthesized nanophosphors were precipitated by centrifugation at 8000 rpm for 20 minutes. The UCNPs were washed twice with water and finally with ethanol. The sample was then dried at 60°C overnight.

Preparation of ChB film and UCNP incorporated ChB film

The preparation of ChB films involved melting approximately 25 mg of the ChB material on a glass substrate until it reached 186 °C at a rate of 2.5 °C per minute. Subsequently, it was cooled to 160 °C (within the cholesteric range) at the same rate and then rapidly cooled to room temperature. For the fabrication of UCNP-ChB composite films, ChB and UCNPs were combined in the required weight percentages: 20 wt% for blue, 40 wt% for green, and 20 wt% for red-emitting UCNPs. The mixture was thoroughly ground and homogenized before being placed on the glass substrate to undergo multiple heating-cooling cycles.

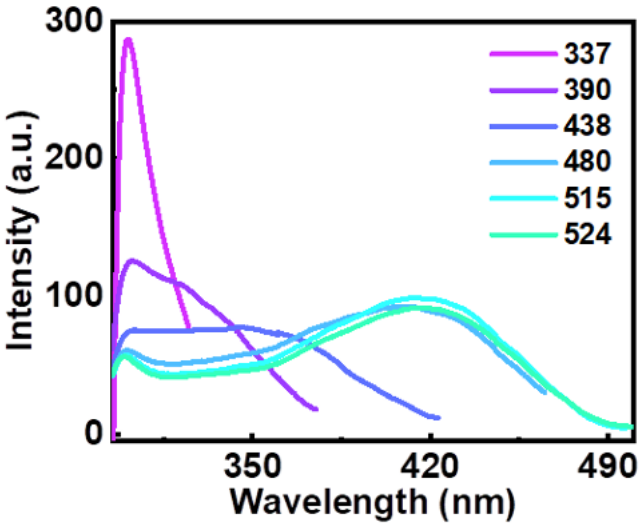

Fig. S1 Excitation spectra of 0.1 M ChB in THF solution.

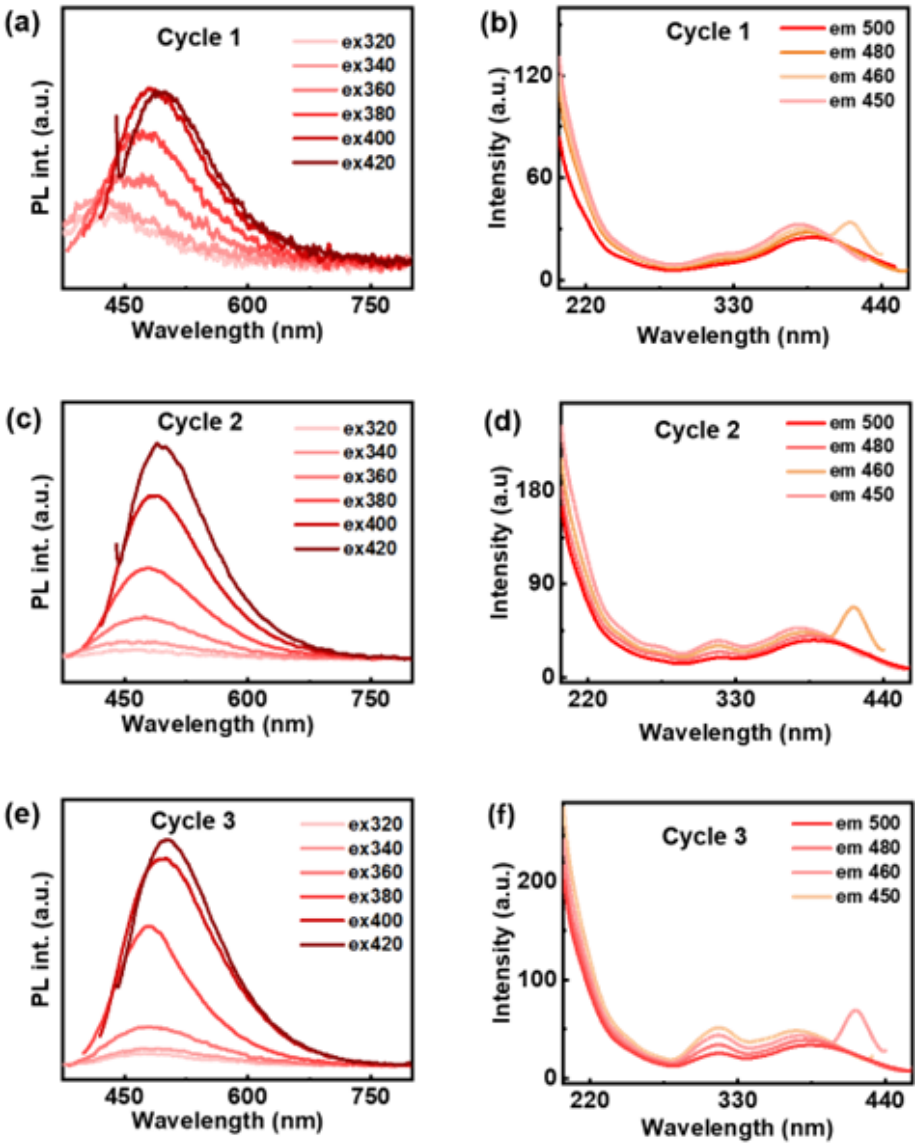

Fig. S2 (a,c,e) Excitation-dependent emission and (b,d,f) excitation spectra corresponding to various emission peaks after (a,b) one, (c,d) two and (e,f) three cycles of heating-cooling.

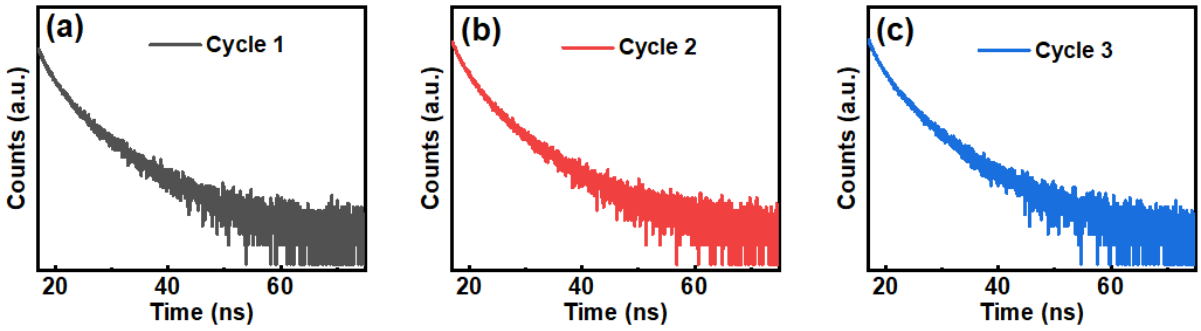

Fig. S3 Lifetime measurements of ChB alone after each thermal cycle at 416 nm excitation. (a) first cycle, (b) second cycle, (c) third cycle.

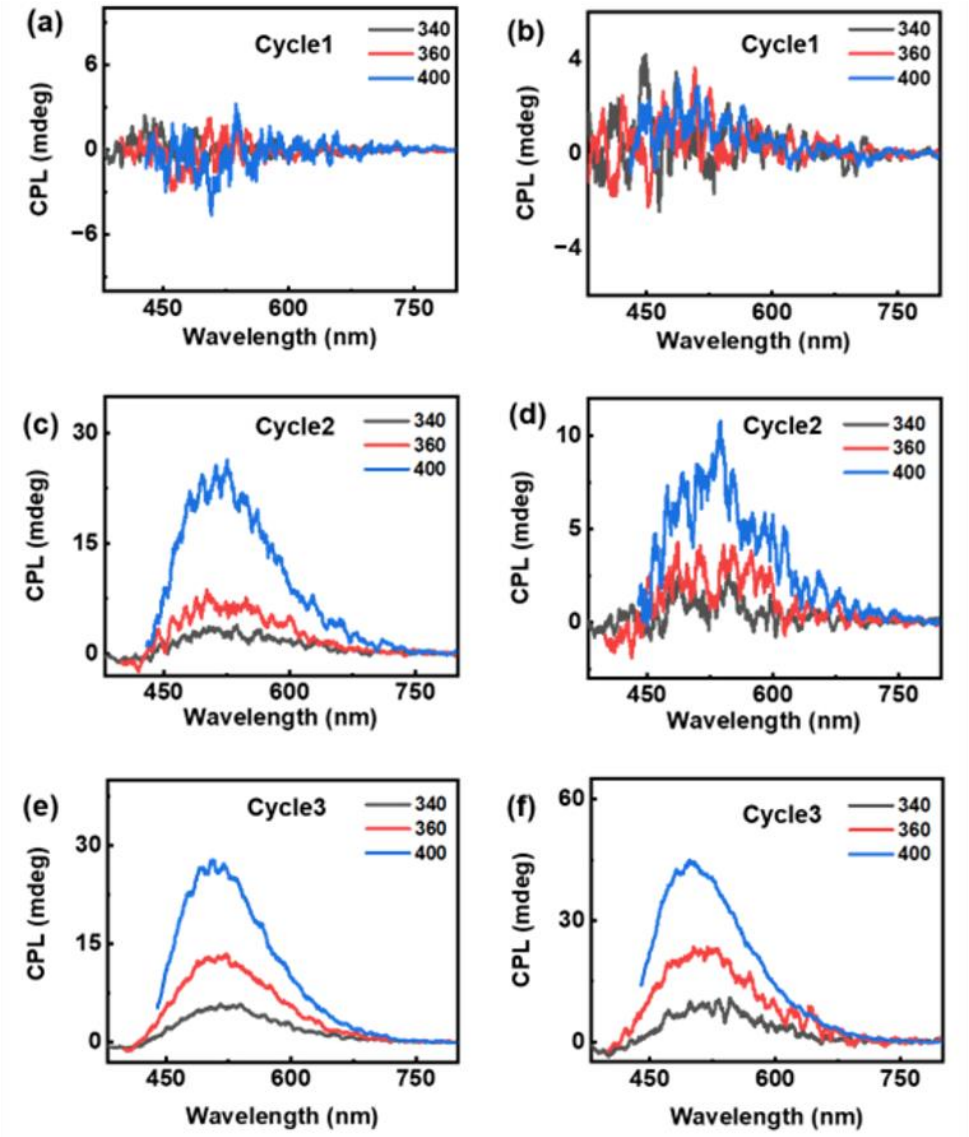

Fig. S4 CPL spectra of ChB under different excitation wavelengths. (a,c,e) CPL spectra after (a) first, (c) second and (e) third heating-cooling cycle of ChB, for the light source directly hitting on the sample and (b,d,f) the corresponding spectra for (b) first, (d) second and (f) third cycle after flipping the film.

Table S1. g_{lum} values of ChB for multiple heating-cooling cycles.

Sample \ Excitation	340 nm	360 nm	400 nm	416 nm
Cycle 1	----	----	----	----
Cycle 2	2.8×10^{-2}	3×10^{-2}	3.1×10^{-2}	3.2×10^{-2}
Cycle 3	5×10^{-2}	5.5×10^{-2}	8.3×10^{-2}	8.6×10^{-2}

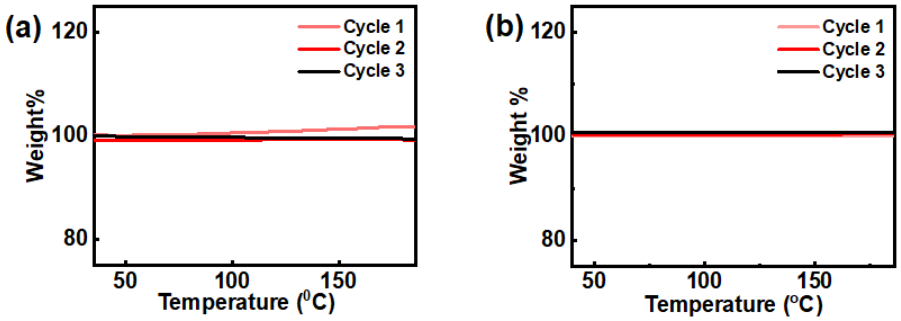

Fig. S5 TGA traces of ChB undergoing three cycles of heating-cooling, (a) under N_2 atmosphere, and (b) in real gas atmosphere.

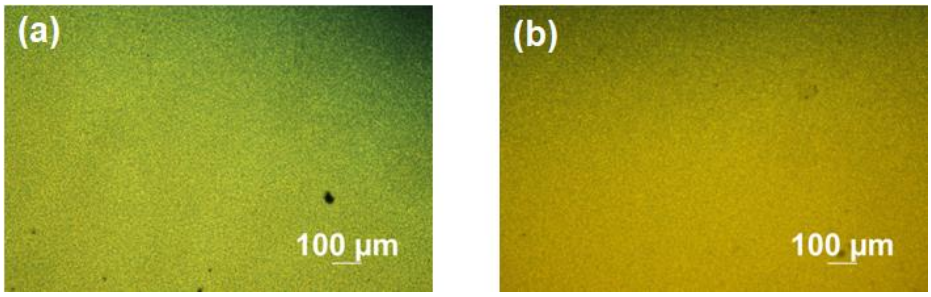

Fig. S6 POM images for different thermal cycles of ChB; Image captured after (a) second heating-cooling cycle and (b) third heating-cooling cycle.

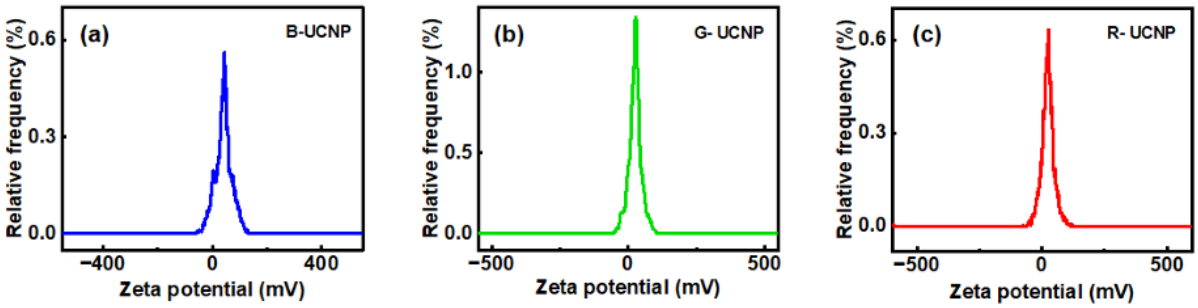

Fig. S7 Zeta potential graph of L-PGA capped blue ($NaYF_4$/Yb,Tm), green ($NaYF_4$/Yb,Mn,Ho) and red ($NaYF_4$/Yb,Er,Mn) emitting UCNPs**.**

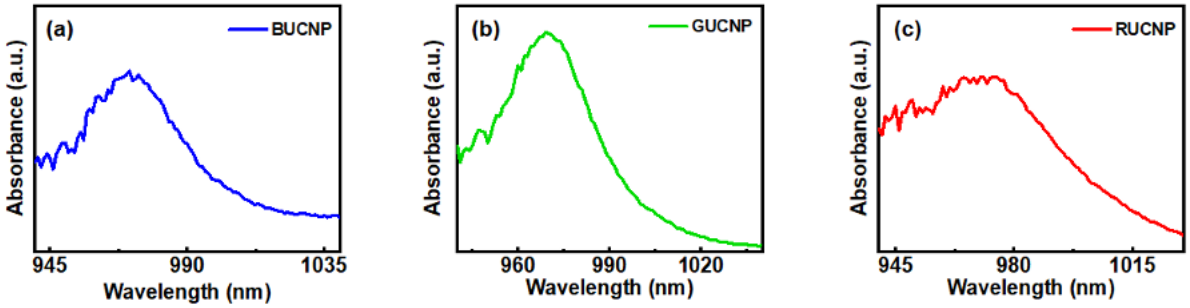

Fig. S8 Absorption spectra of L-PGA capped blue ($NaYF_4$/Yb,Tm), green ($NaYF_4$/Yb,Mn,Ho) and red ($NaYF_4$/Yb,Er,Mn) emitting UCNPs**.**

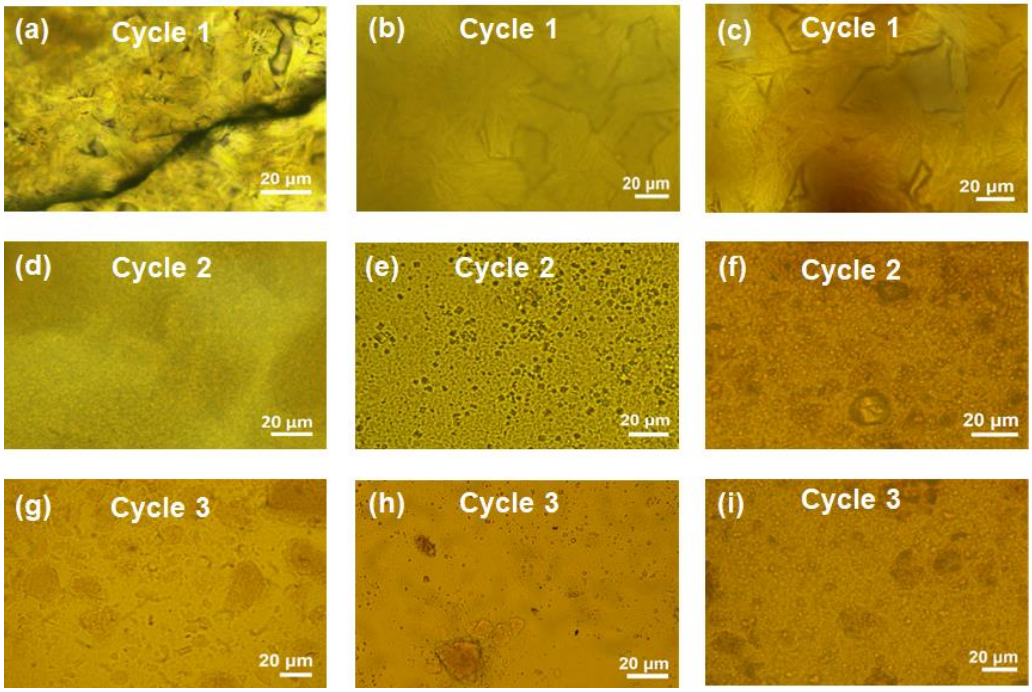

Fig. S9 POM images of (a,d,g) $NaYF_4$/Yb,Tm, (b,e,h) $NaYF_4$/Yb,Mn,Ho and (c,f,i) $NaYF_4$/Yb,Er,Mn incorporated ChB for the (a,b,c) first, (d,e,f) second and (g,h,i) third heating-cooling cycles.

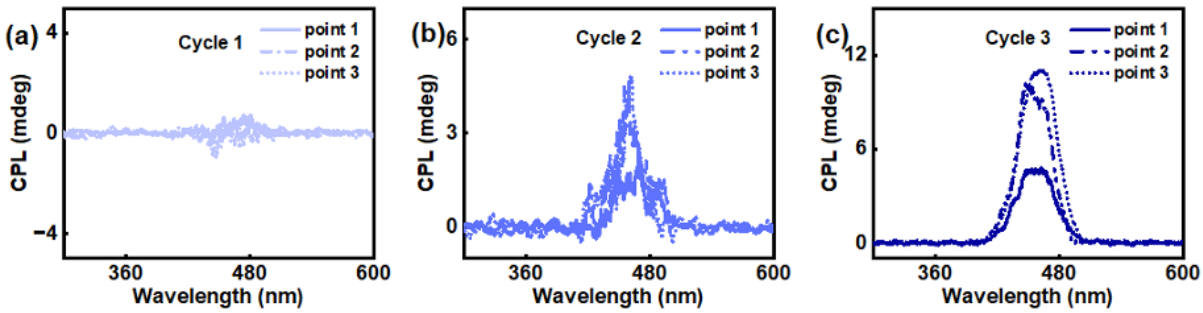

Fig. S10 CPL spectra of ChB-$NaYF_4$/Yb,Tm composite films at 980 nm excitation across different cycles of heating-cooling from different points.

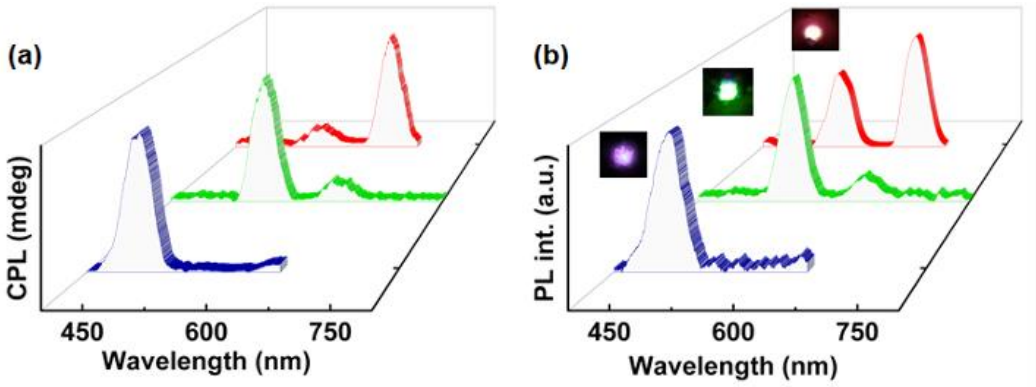

Fig. S11 (a) CPL and (b) PL of flipped ChB-UCNP composite films after third thermal cycle: blue ($NaYF_4$/Yb,Tm), green ($NaYF_4$/Yb,Mn,Ho) and red ($NaYF_4$/Yb,Er,Mn). Inset shows the photographs of films irradiated with 980 nm laser.

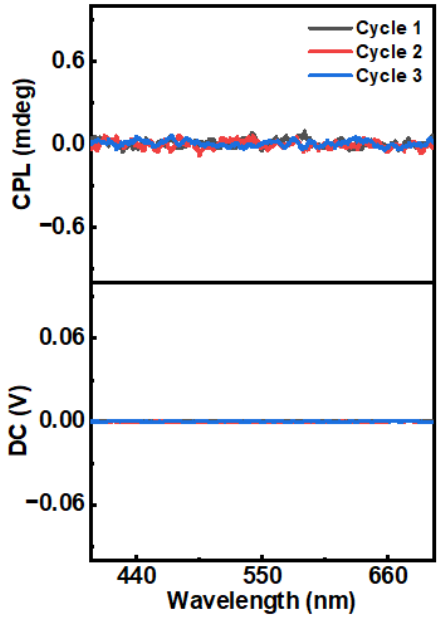

Fig. S12 CPL of ChB film upon 980 nm excitation.

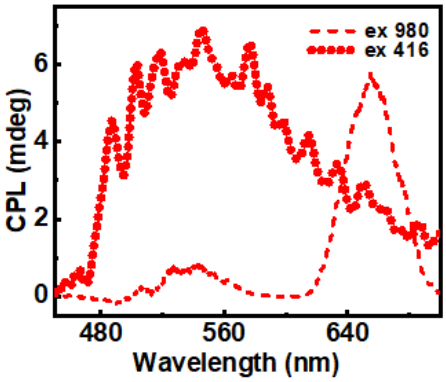

Fig. S13 Upconversion (dashed trace) and downconversion (dotted trace) CPL from red emitting $NaYF_4$/Yb,Er,Mn UCNP incorporated ChB film.

References

1. K. L. Reddy, J.P. Mathew, E. Shiby, and J. Kumar, 2021, *J. Phys. Chem. C*, 2021, **125**, 26263-26273