Electronic supporting information

Radiative energy transfer enabling upconverted circularly polarized persistent luminescence for multilevel information encryption

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Characterization

UV-vis spectra, fluorescence spectra and CD spectra were obtained using a Hitachi U-3900, EDINBURGH FS5 and JASCO 1500 spectrometers, respectively. CPL measurements were performed with JASCO CPL-200 spectrometer. POM images were taken by Leica DM2700M upright materials microscope. X-ray diffraction (XRD) analysis was performed on a PANalytical Empyrean X-ray diffractometer (Japan) with Cu Kα radiation (λ=1.5406Å), which was operated at a voltage of 40 kV and a current of 200 mA. TEM images were taken by a FEI Tecnai G2 20 A-TWIN microscope (200 kV). 980 nm (10 W) laser were purchased from Changchun New Industries Optoelectronics Technology Co., Ltd. The photoluminescence signals were collected by a monochromator equipped with charge coupled device (CCD) detector and measured by a spectrometer (Andor Technology, iVac 316), programmable time delayed was controlled by PAG 100 (purchased from Beijing Zolix Instrument Co., Ltd.). Photos were taken by a P30 Huawei with Professional Mode.

Materials

Commercial room-temperature nematic liquid crystal, SLC1717, was purchased from the Chengzhi Yonghua Display Material Co., Ltd. Chiral dopant, R(S)811, was purchased from the TOKYO Chemical Industry Co., Ltd. 1-octadecene (>90%), oleic acid (technical grade 90%) were purchased from Alfa Aesar. Erbium(III) acetate hydrate was purchased from Aladdin. Alkaline earth aluminate monoclinic systems GP ($SrAl_2O_4$: Eu, Dy), BP ($CaAl_2O_4$: Eu, Nd) and sulfide-type hexagonal crystal RP (Y_2O_2S: Eu, Mg, Ti) were purchased from Shenzhen Yao De Sheng Technology Co., Ltd. $YCl_3 \cdot 6H_2O$ (99.99%), $YbCl_3 \cdot 6H_2O$ (99.9%), and $TmCl_3 \cdot 6H_2O$ (99.9%) were purchased from Alfa Aesar. NH_4F (99.99%) were purchased from the Shanghai Aladdin

Biochemical Technology Co., Ltd. Quarter wave plate (400–800 nm) and liner polarizer (400–700 nm) were purchased from Thorlabs.

Synthetic Procedures

Synthesis of OA-modified UCNP-Tm

The OA-coated UCNP-Tm (NaYF4:20% Yb, 1% Tm) were synthesized according to the previously reported method.[4] In a typical procedure, the mixture of 1.38 mg (0.005 mmol) of $TmCl_3 \cdot 6H_2O$, 38.75 mg (0.1 mmol) of $YbCl_3 \cdot 6H_2O$, 119.83 mg (0.395 mmol) of $YCl_3 \cdot 6H_2O$, 6 mL of oleic acid and 10 mL of 1-octadecene was added in a three-neck flask and degassed under N_2 flow for 1 h. After that, it was heated to 160 °C with N_2 flow to remove moisture until a transparent solution was observed, and then cooled down to room temperature. The methanol solution of NH_4F (2.5 mmol, 8 mL) and 2 mL of methanol containing 20 mg NaOH were dropped into the reacted solution, respectively. The mixture was heated to 80 ˚C in a vacuum to remove methanol. Finally, the solution was fast heated to 300 °C and kept for 1 h under N_2 atmosphere, then cooled down to room temperature naturally. Then 30 mL of ethanol was added to precipitate the produces. The samples were collected by centrifugation (5000 rpm, 10 min) and washed with ethanol for three times. The obtained UCNPs were dried in a vacuum at room temperature.

Experimental Method

Fabrication of the Chiral Liquid Crystal Samples. The used LC samples were fabricated by the follow steps. First, 4.7 mg R(S)811, 10 mg SLC1717, 1 mL UCNPs cyclohexane dispersions (5 mg mL^{-1}), and 1 mL phosphors cyclohexane dispersions (3 mg mL^{-1}) were added into a 5 mL centrifuge tube. After that, the resulting solution was sonicated for about 1 min to obtain a uniform solution. Subsequently, the solution was transferred on the slide and then hexane was evaporated

slowly by using hot stage. Finally, the heating mixture was loaded into the liquid crystal cell by capillary action.

Supplementary Figures

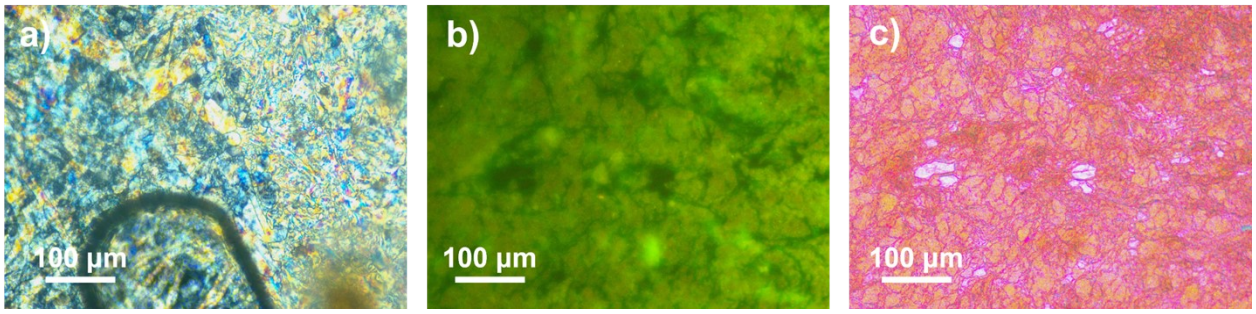

Figure S1 Polarized optical microscopy (POM) images of blue, green, and red phosphors in N*LC under the crossed polarizers

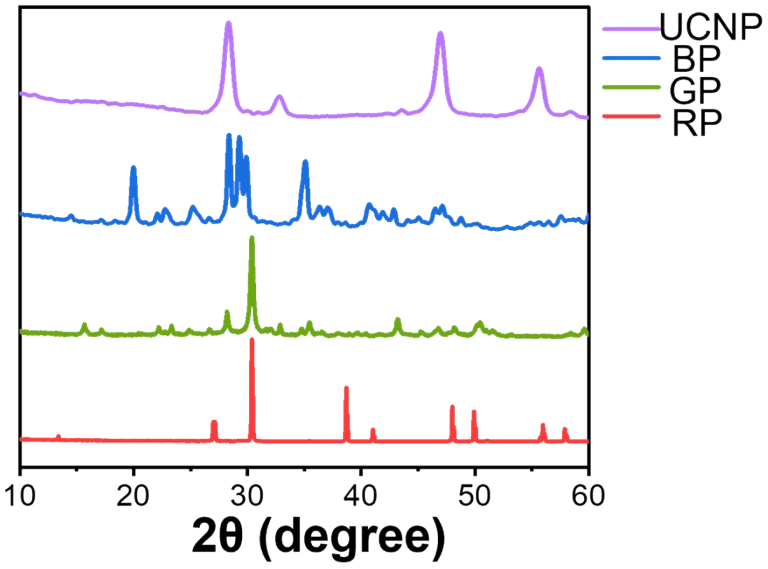

Figure S2 XRD patterns of the UCNPs-Tm, BP (blue phosphors), GP (green phosphors), and RP (red phosphors).

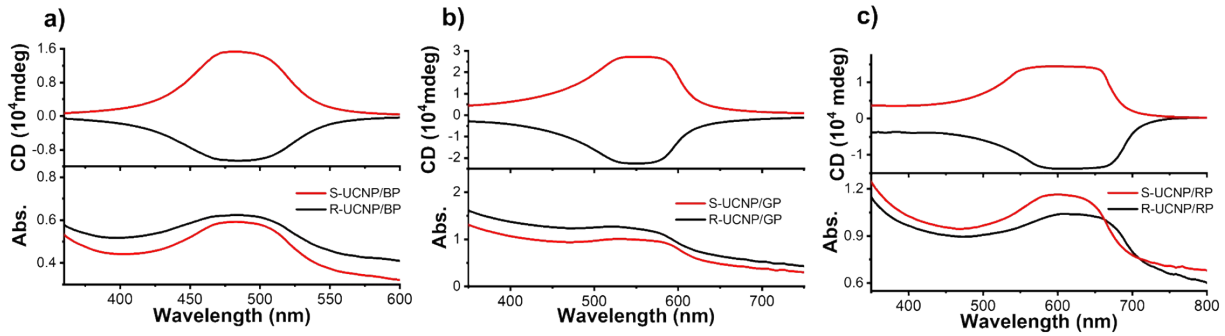

Figure S3 CD and Abs. spectra of a) *R*-/*S*-UCNPs/BP system in N*LC; b) *R*-/*S*-UCNPs/GP system in N*LC; c) *R*-/*S*-UCNPs/RP system in N*LC.

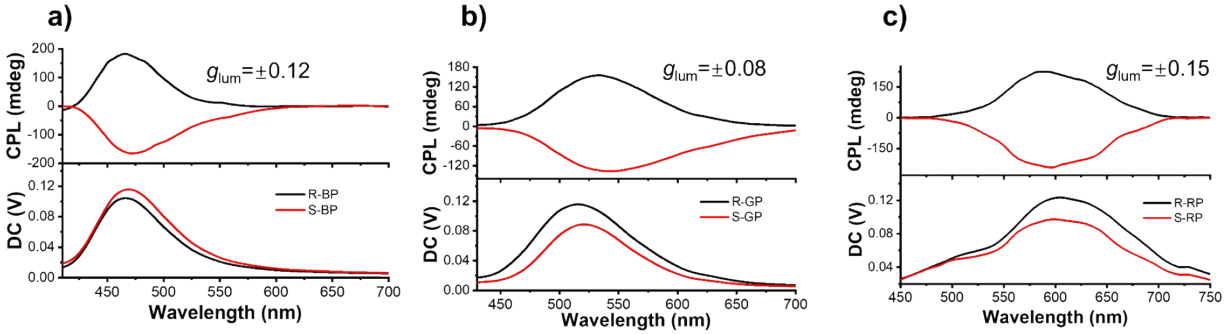

Figure S4 CPL emission and DC spectra of phosphors in N*LC under 365 nm excitation a-c) BP, GP and RP detected by CPL 200.

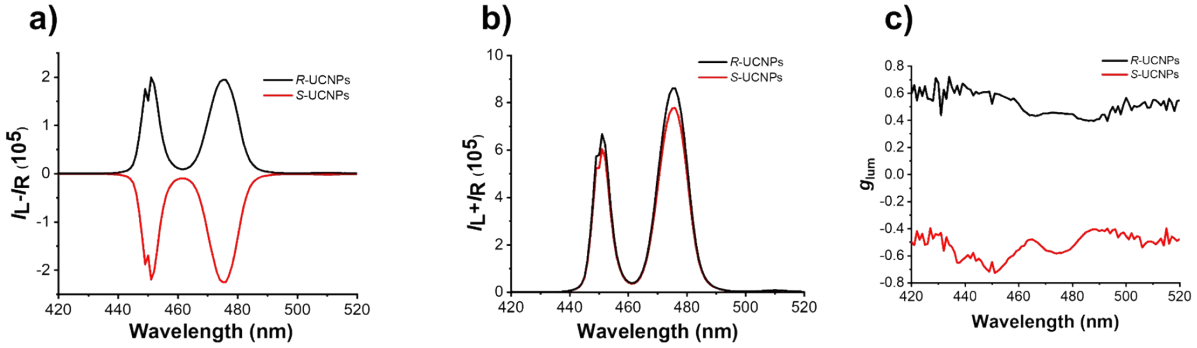

Figure S5 a) Circularly polarized luminescence emission (I_L-I_R) spectra of *R*/*S*-UCNPs in N*LC (excited by laser, λ_{ex} = 980 nm). b) Total luminescence emission (I_L+I_R) spectra of *R*/*S* -UCNPs in N*LC (excited by laser, λ_{ex} = 980 nm). c) The g_{lum} of *R*/*S*-UCNPs in N*LC (excited by laser, λ_{ex} = 980 nm). The samples were UCNPs/LC (wt) = 5:10.

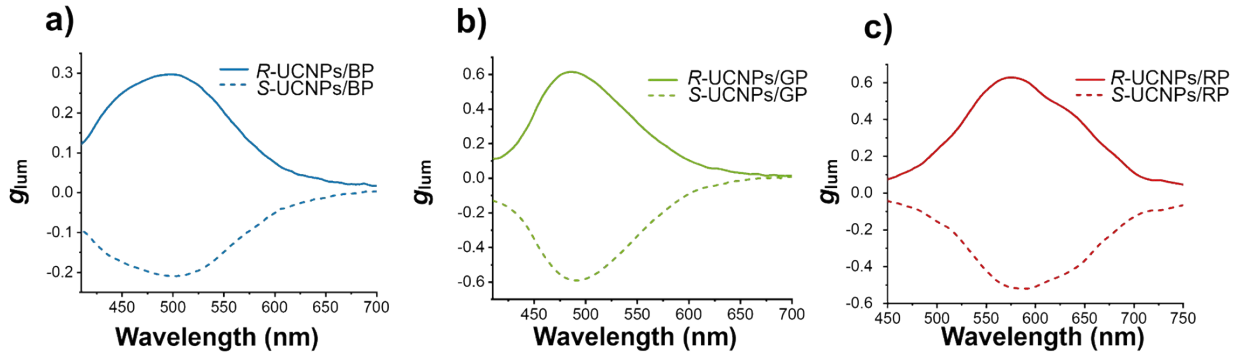

Figure S6 The g_{lum} value of UCNPs/phosphors in N*LC under 365 nm excitation a-c) UCNPs/BP UCNPs/GP and UCNPs/RP detected by CPL 200.

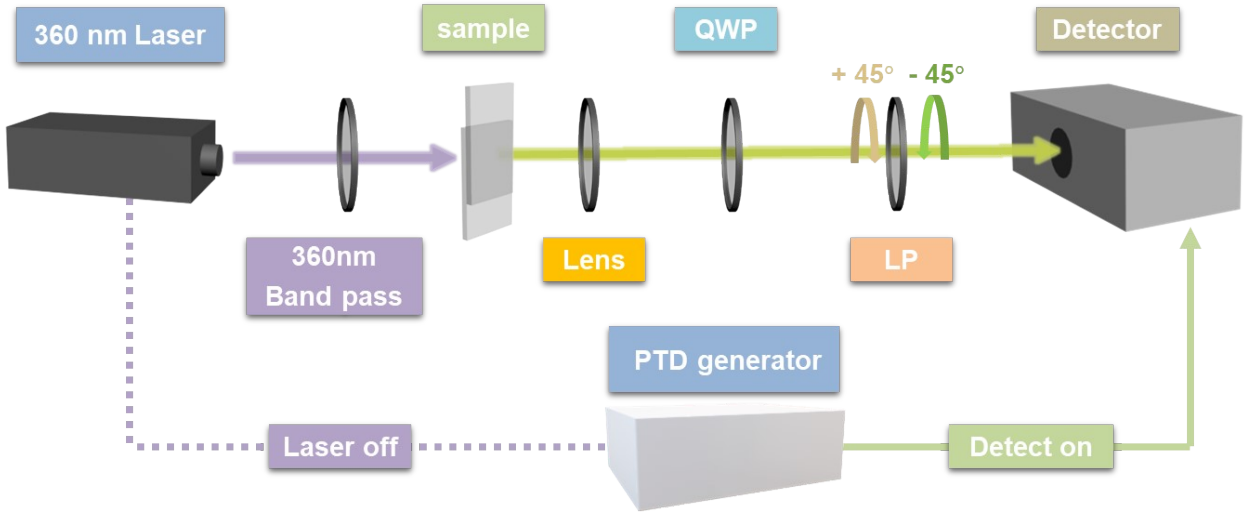

Figure S7 Schematic representation of real-time CPPL detection optical test platform. Programmable time-delay generator can cease excited light while activating the detector. QWP and LP represented achromatic quarter-wave plate (400 nm-800 nm) and linear polarizer (400 nm-700 nm).

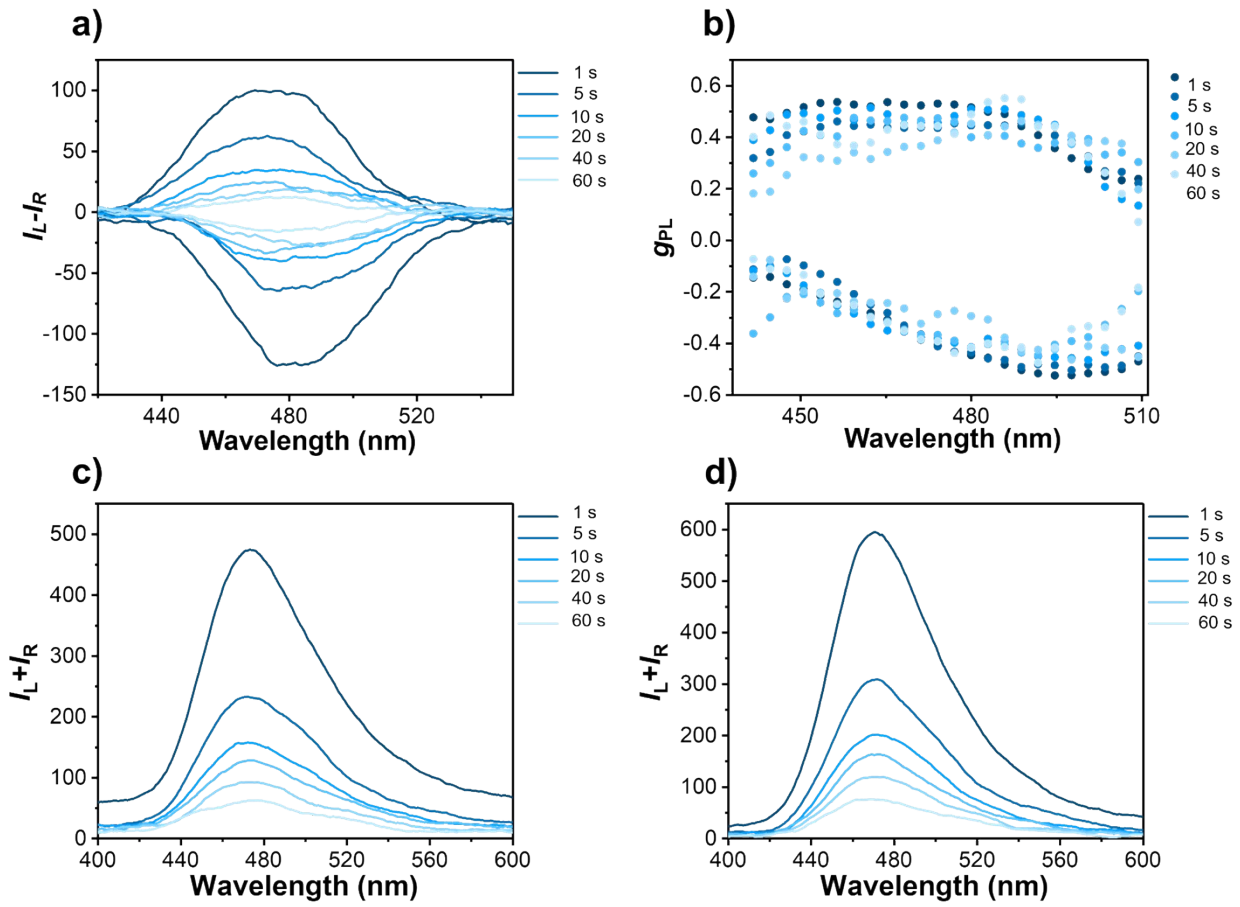

Figure S8 a) Time-resolved circularly polarized persistent luminescence emission (I_L-I_R) spectra of UCNPs/BP in N*LC within 60 s (excited by laser, λ_{ex} = 360 nm). b) The g_{PL} of UCNPs/BP in N*LC within 60 s (excited by laser, λ_{ex} = 360 nm). c) Time-resolved total persistent luminescence emission (I_L+I_R) spectra of *R*-UCNPs/BP in N*LC within 60 s (excited by laser, λ_{ex} = 360 nm). d) Time-resolved total persistent luminescence emission (I_L+I_R) spectra of *S*-UCNPs/BP in N*LC within 60 s (excited by laser, λ_{ex} = 360 nm).The samples were UCNPs/BP (wt) = 4:3.

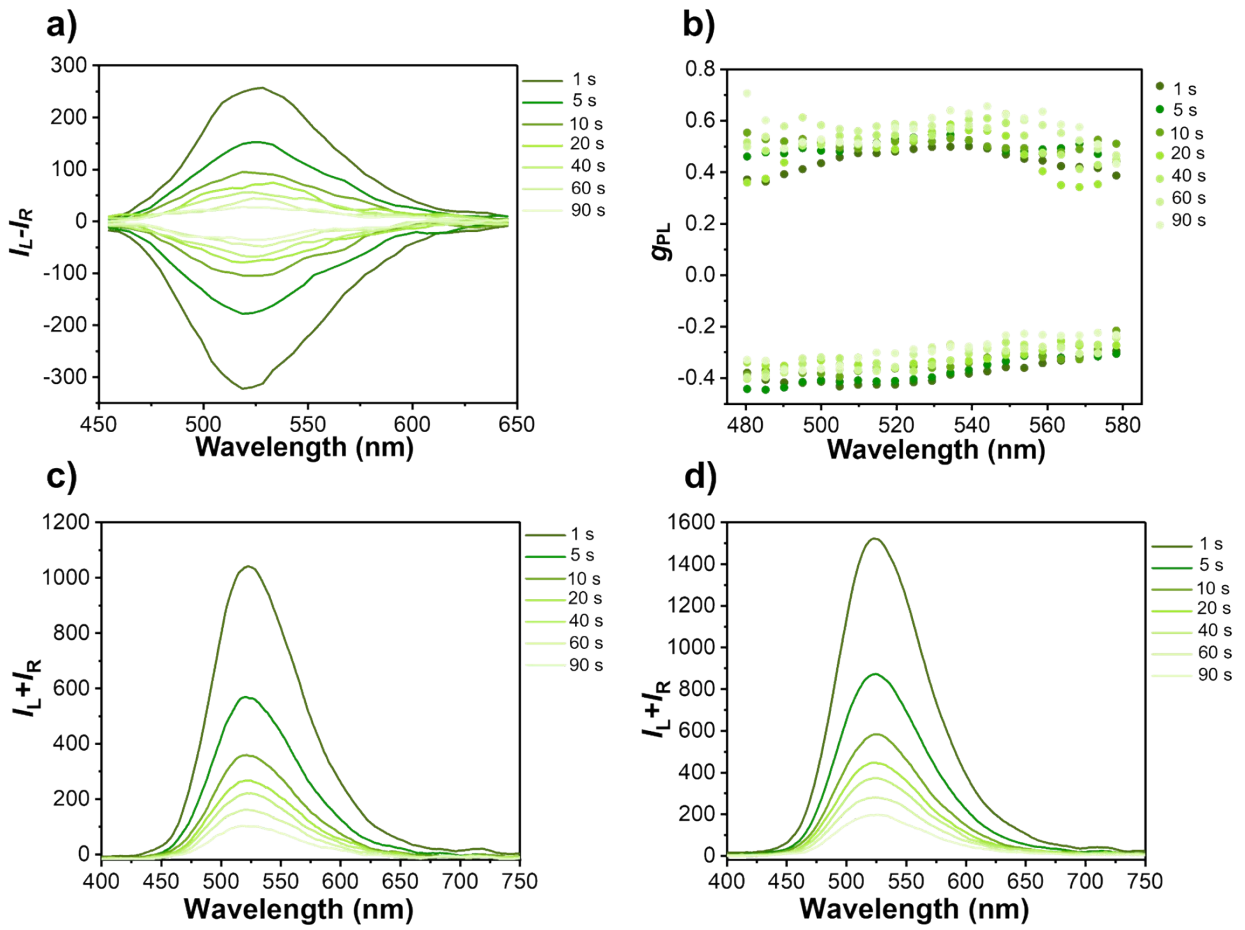

Figure S9 a) Time-resolved circularly polarized persistent luminescence emission (I_L-I_R) spectra of UCNPs/GP in N*LC within 90 s (excited by laser, λ_{ex} = 360 nm). b) The g_{PL} of UCNPs/GP in N*LC within 90 s (excited by laser, λ_{ex} = 360 nm). c) Time-resolved total persistent luminescence emission (I_L+I_R) spectra of *R*-UCNPs/GP in N*LC within 90 s (excited by laser, λ_{ex} = 360 nm). d) Time-resolved total persistent luminescence emission (I_L+I_R) spectra of *S*-UCNPs/GP in N*LC within 90 s (excited by laser, λ_{ex} = 360 nm).The samples were UCNPs/GP (wt) = 5:3.

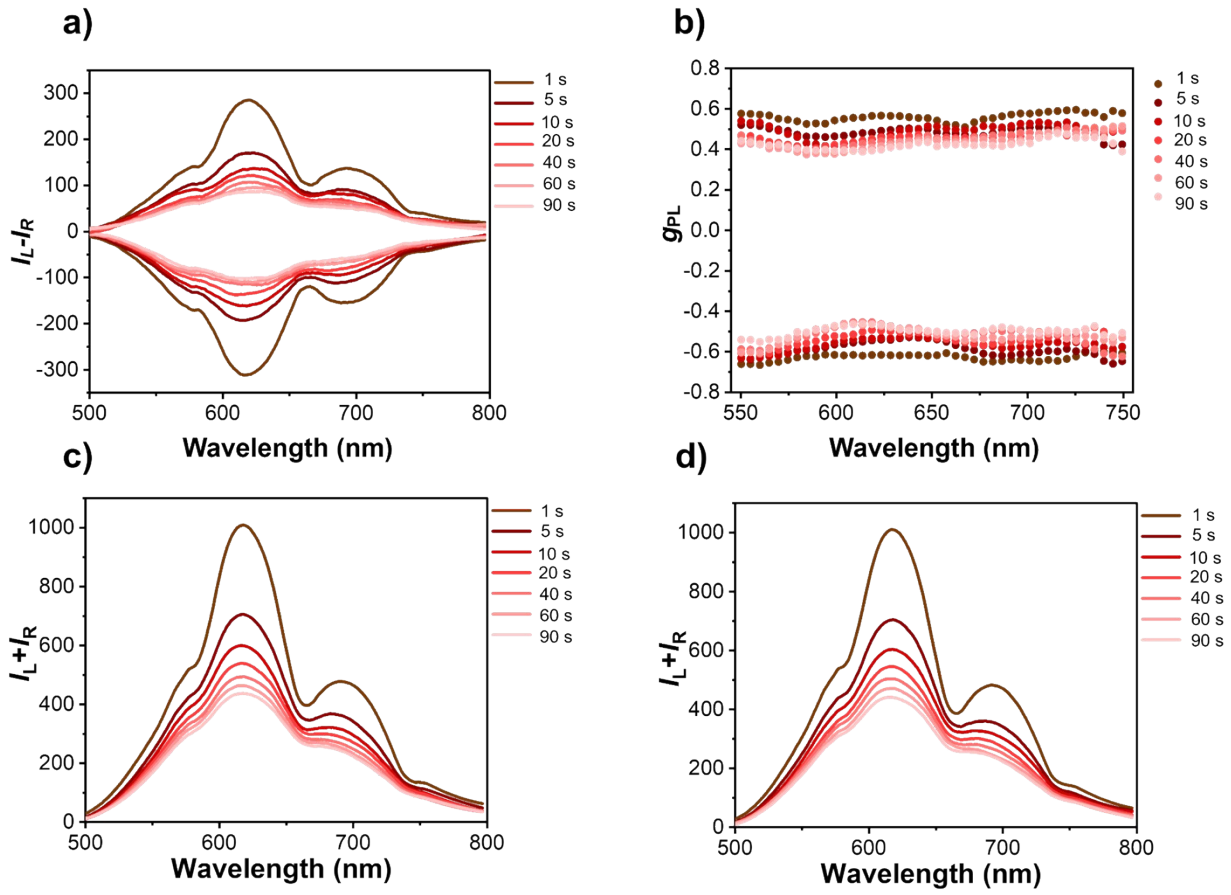

Figure S10 a) Time-resolved circularly polarized persistent luminescence emission (I_L-I_R) spectra of UCNPs/RP in N*LC within 90 s (excited by laser, λ_{ex} = 360 nm). b) The g_{PL} of UCNPs/RP in N*LC within 90 s (excited by laser, λ_{ex} = 360 nm). c) Time-resolved total persistent luminescence emission (I_L+I_R) spectra of *R*-UCNPs/RP in N*LC within 90 s (excited by laser, λ_{ex} = 360 nm). d) Time-resolved total persistent luminescence emission (I_L+I_R) spectra of *S*-UCNPs/RP in N*LC within 90 s (excited by laser, λ_{ex} = 360 nm).The samples were UCNPs/RP (wt) = 5:3.

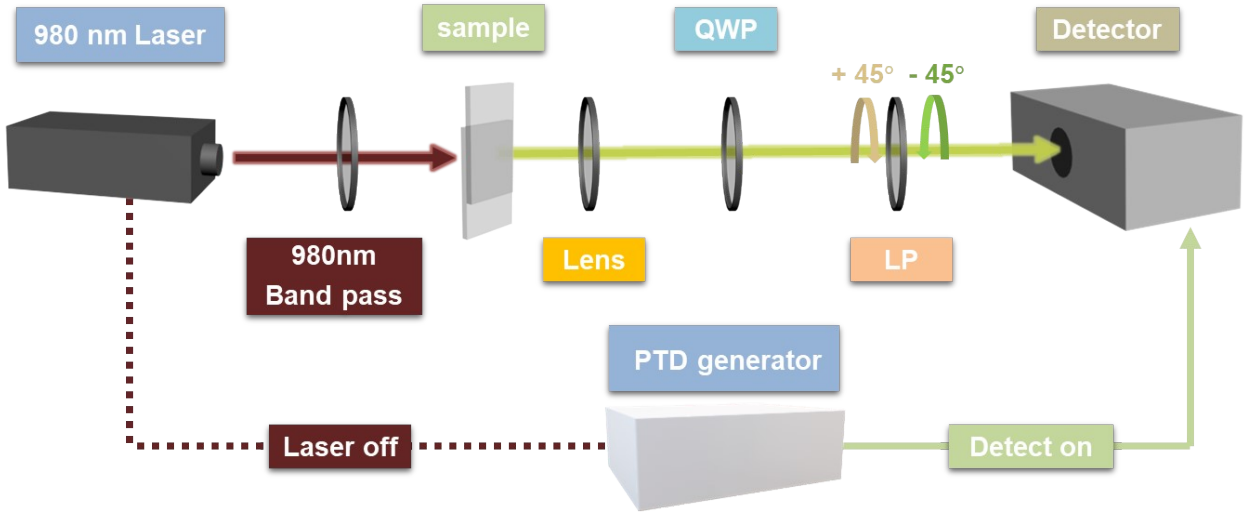

Figure S11 Schematic representation of real-time UC-CPPL detection optical test platform. Programmable time-delay generator can cease excited light while activating the detector. QWP and LP represented achromatic quarter-wave plate (400 nm-800 nm) and linear polarizer (400 nm-700 nm).

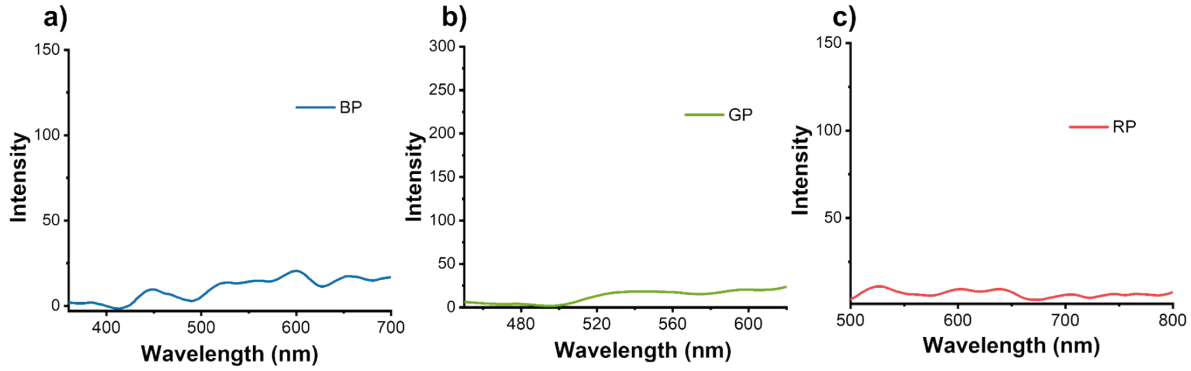

Figure S12 the phosphorescence intensity of RGB phosphors in N*LC under the excited of laser 980nm a-c) BP, GP and RP.

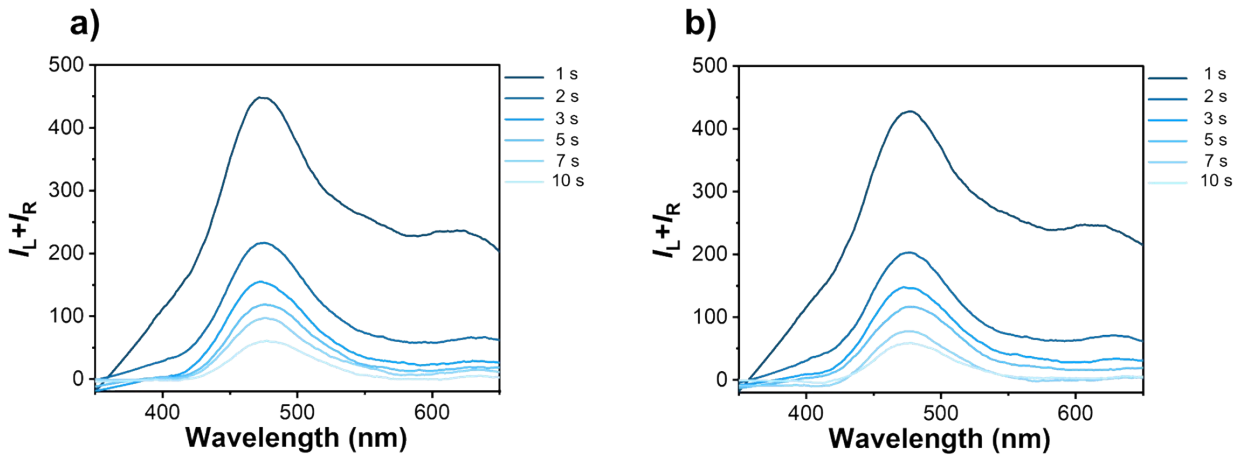

Figure S13 a) Time-resolved total persistent luminescence emission (I_L+I_R) spectra of *R*-UCNPs/BP in N*LC within 10 s (excited by laser, λ_{ex} = 980 nm). d) Time-resolved total persistent luminescence emission (I_L+I_R) spectra of *S*-UCNPs/BP in N*LC within 10 s (excited by laser, λ_{ex} = 980 nm).The samples were UCNPs/BP = 4:3 (wt).

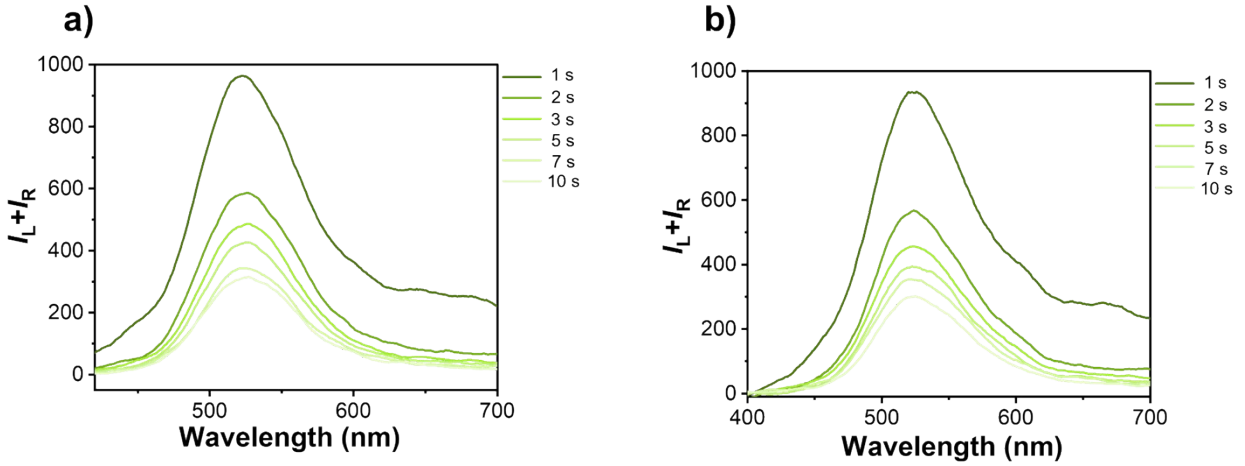

Figure S14 a) Time-resolved total persistent luminescence emission (I_L+I_R) spectra of *R*-UCNPs/GP in N*LC within 10 s (excited by laser, λ_{ex} = 980 nm). d) Time-resolved total persistent luminescence emission (I_L+I_R) spectra of *S*-UCNPs/GP in N*LC within 10 s (excited by laser, λ_{ex} = 980 nm).The samples were UCNPs/BP = 5:3 (wt).

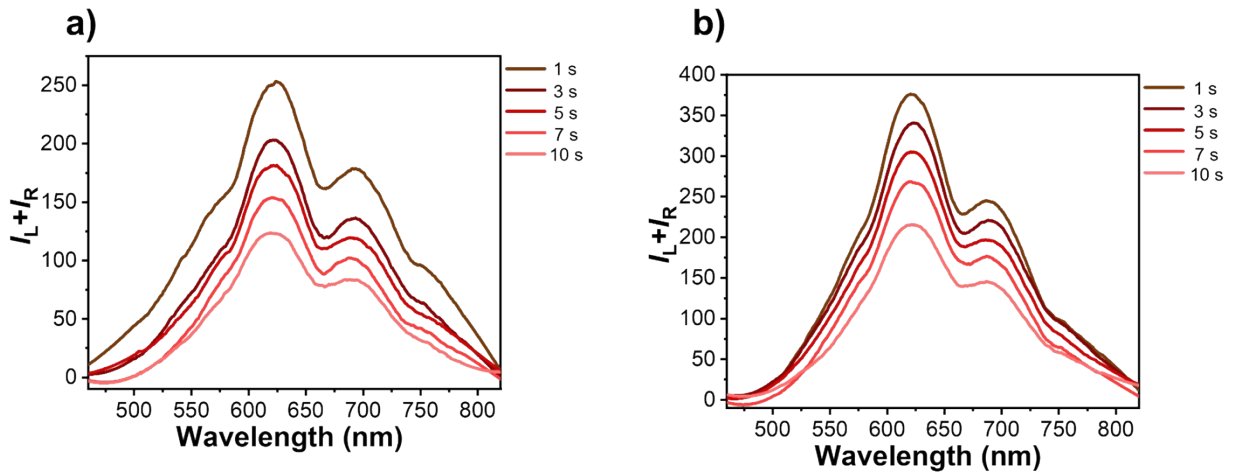

Fig. S15 a) Time-resolved total persistent luminescence emission (I_L+I_R) spectra of *R*-UCNPs/RP in N*LC within 10 s (excited by laser, λ_{ex} = 980 nm). d) Time-resolved total persistent luminescence emission (I_L+I_R) spectra of *S*-UCNPs/RP in N*LC within 10 s (excited by laser, λ_{ex} = 980 nm).The samples were UCNPs/BP = 5:3 (wt).