









**Fig. 3** (a) The tendency of CPL dissymmetry factor  $g_{lum}$  with different weight ratios of S1/SLC1717 ( $\lambda_{ex} = 360$  nm). (b) CPL spectra of 10 wt% R(S)1 in SLC1717. R1 induced SLC1717 to a right-handed N\*LC, S1 induced SLC1717 to a left-handed N\*LC ( $\lambda_{ex} = 360$  nm,  $|g_{lum}| = 0.2$ ). (c) S1 in solution has the opposite  $g_{lum}$  value in the liquid crystal. The blue square represents the  $g_{lum}$  of S1 in toluene solution ( $[S1] = 10^{-5}$  M); the red square represents the  $g_{lum}$  of 10 wt% S1 in the liquid crystal. The values of  $g_{lum}$  in all emission ranges with intensity were almost the same. (d) POM image of a chiral liquid crystal. The weight ratio of S1/SLC1717 was 10 wt%.

a positive CPL signal indicates a right-handed chiral liquid crystal while a negative CPL signal means a left-handed chiral liquid crystal. Thus, it can be clearly clarified that chiral emitter R1 will induce the nematic liquid crystal to a right-handed N\*LC while the addition of S1 to SLC1717 will result in a left-handed N\*LC.<sup>54</sup> It should be noted that the direction of the CPL signal in the liquid crystal was opposite to the one in toluene solution, which leads to the opposite value of  $g_{lum}$  (Fig. 3c). This could be explained as follows. The CPL activity in solution should be due to the intrinsic chiral emission property of the chiral emitter R(S)1. However, after dispersing into the nematic liquid crystal, the final CPL sign is decided by the handedness of the induced N\*LC. We have also checked the polarizing optical microscope images of S1 in SLC1717 (Fig. 3d). The typical fingerprint texture proved that the N\*LC had been induced successfully by the chiral emitter. In addition, we prepared the sample S1/SLC1717 with various mixing ratios from 5 to 30 wt% to measure the X-ray diffraction (XRD) (see the ESI, Fig. S8†). The results indicated that all mixing ratios showed similar diffraction patterns to those of the original nematic liquid crystal SLC1717. There was no obvious crystallization diffraction peak even at the high mixing ratio of 30 wt%, which indicated that the dopant S1 could well disperse into the liquid crystal matrix. Differential scanning calorimetry (DSC) revealed that the clearing point of SLC1717 showed a slight decline when blending with the chiral emitter (see the ESI, Fig. S9†).

### Upconverted circularly polarized luminescence in a chiral liquid crystal

The most interesting result in this work is that UC-CPL could be significantly amplified in a liquid crystal. Similarly, we have also

checked the influence of different weight ratios of the acceptor in a liquid crystal on the UC-CPL. The upconverted  $g_{lum}$  exhibited the same tendency between promoted and upconverted CPL (Fig. 4a), while the sample with 10 wt% mixing ratio showed the highest upconverted  $g_{lum}$  value. As expected, a mirror-image UC-CPL signal was observed under excitation by a 532 nm green laser (Fig. 4b). It should be emphasized that the UC-CPL signal was consistent with the CPL in the liquid crystal, which indicated that the upconverted emission followed the regulation of a N\*LC. With increasing the excitation intensity of the incident light, the UC-CPL increased. However, after converting to the  $g_{lum}$  value, the intensity was almost the same in all emission ranges (Fig. 4c). Compared with the  $g_{lum}$  of UC-CPL in dilute toluene solution,  $g_{lum}$  in the liquid crystal was one order of magnitude higher (Fig. 4d). These results indicated that whether it is promoted CPL or upconverted CPL, the optical properties of N\*LC play a critical role in determining the emission properties.

Although the mechanism of photon upconversion amplified circularly polarized luminescence in dilute solution is not clear, the development of various approaches to further promote the level of upconverted circularly polarized luminescence is ongoing. The present liquid crystal system offers unprecedented opportunities for the efficient TTA-based upconversion, circularly polarized emission and upconverted circularly polarized emission. The use of room-temperature liquid crystals allows exploring the luminescence and chiroptical properties in the liquid crystal phase. The orientation of chiral acceptor molecules in the N\*LC enables highly efficient triplet energy transfer and migration which might facilitate the TTA-UC. This



**Fig. 4** (a) The tendency of UC-CPL dissymmetry factor  $g_{lum}$  with different weight ratios of acceptor in the liquid crystal (PtOEP/S1 = 1 mol%,  $\lambda_{ex} = 532$  nm). (b) UC-CPL spectra of 10 wt% R(S)1 in SLC1717 with 1 mol% PtOEP,  $|g_{lum}|$  was nearly 0.04 ( $\lambda_{ex} = 532$  nm). (c) UC-CPL spectra of 10 wt% S1 with different incident power densities of a 532 nm laser in a liquid crystal. The arrow indicates the spectral changes with increasing incident power density from 15.3 to 31.6  $W\ cm^{-2}$ . The corresponding  $g_{lum}$  value was almost the same as the emission value. (d) UC-CPL dissymmetry factor  $g_{lum}$  versus wavelength. The black square represents R(S)1/PtOEP in toluene solution ( $[R(S)1] = 10^{-5}$  M,  $\lambda_{ex} = 532$  nm); the red square represents R(S)1/PtOEP in SLC1717 (R(S)1/SLC1717 = 10 wt%,  $\lambda_{ex} = 532$  nm).



will be a better complement to the system of triplet energy migration-based photon upconversion (TEM-UC) which has been extensively demonstrated by Kimizuka *et al.*<sup>55</sup>

In addition, the well-ordered chiral acceptor–acceptor arrangements would facilitate the chiral emission and upconverted chiral emission in this kind of liquid crystal phase. Thus, the integration of a chiral nematic liquid crystal amplifying CPL with TTA-based photon upconversion thus renovates the field of CPL-active functional materials and TTA-UC.

## Conclusions

In conclusion, the significance of the present study is three-fold. First, by adding the chiral acceptor molecule R(S)1 and the sensitizer PtOEP into the nematic liquid crystal, highly efficient TTA-UC could be observed in the N\*LC. Moreover, efficient triplet energy diffusion and long migration length were calculated in the liquid crystal for the first time. Second, the N\*LC induced by the chiral emitter exhibited good promoted CPL, while the corresponding dissymmetry factor  $g_{lum}$  was amplified by three orders of magnitude to  $10^{-1}$  compared with the solution state. Third, significant amplification of UC-CPL could be observed in this N\*LC system. Upconverted dissymmetry factor showed one order amplification. This work will promote the design and fabrication of chiroptical materials with not only better UC-CPL emission but also rational emission efficiency for more practical application.

## Materials and methods

### Materials

The commercial room-temperature nematic liquid crystal, SLC1717, was bought from the Chengzhi Yonghua Display Material Co., Ltd. Pt(II)octaethyl porphyrin (PtOEP) was bought from Frontier Scientific, Inc. Rhodamine B was bought from Acros Organics.

### Instrumentation

UV-vis spectra were recorded on a Hitachi U-3900 spectrophotometer. Fluorescence spectra were measured on an F-4500 fluorescence spectrophotometer. CD and CPL spectra were measured on JASCO J-1500 and JASCO CPL-200 spectrophotometers, respectively. Lifetime measurements were recorded on the spectrometer using time-correlated single photon counting (TCSPC). Upconverted emission spectra were recorded on a Zolix Omin- $\lambda$ 500i monochromator with a photomultiplier tube PMTH-R 928 using an external excitation source. POM images were recorded on a Leica DM2700M upright materials microscope. Upconverted CPL spectra were recorded on a JASCO CPL-200 spectrophotometer with an external excitation source, a 532 nm semiconductor laser. DSC spectra were recorded on a PerkinElmer Diamond TG/DTA. XRD spectra were measured on a Panalytical Empyrean. Quantum yield was measured on an Edinburg FLS-980 fluorescence spectrometer with a calibrated integrating sphere.

### Characterization and methods

The sample used to investigate the UV-vis and fluorescence spectra, lifetime, upconversion emission and UC-CPL was fabricated by the following method. Firstly, 1 mg S1 and 9 mg SLC1717 were added into a 1 mL centrifuge tube, and then mixed with 1 mL toluene. After that, the resulting solution was sonicated for about 1 min to obtain a good solution. Finally, 400  $\mu$ L of the solution was transferred into a quartz cell and toluene was evaporated slowly using a vacuum pump. The thin chiral nematic liquid crystal film was generated in the inner face of the quartz cell. It should be noted that evaporation of toluene should be carried out at an appropriate velocity, otherwise the generated chiral nematic liquid crystal will not be uniform. The chiral nematic liquid crystal containing the PtOEP was fabricated in the same way, 10.6  $\mu$ L PtOEP ( $10^{-3}$  M) should be added with 1 mg S1. The UV-vis spectra were recorded from 200 nm to 800 nm. Emission spectra were recorded with an excitation wavelength of 360 nm. The samples were excited with an incidence angle of  $45^\circ$  to the quartz cell surface and the fluorescence was detected along the normal. Time-resolved upconverted emission spectra were measured with an excitation wavelength of 532 nm laser and detected at 470 nm. The upconverted lifetimes have been fitted with a single exponential decay. Spectra of UC emission and UC-CPL were measured with the excitation wavelength of a 532 nm laser. The semiconductor laser used in our experiment was bought from Changchun New Industries Optoelectronics Technology Co., Ltd. The bandwidth was  $< 0.2$  nm, Gaussian beam in spatial mode TEM<sub>00</sub>, with a polarization ratio of 1 : 100, the polarization direction being horizontal. The sample used for CPL spectra was fabricated by the following method. Firstly, 2 mg S1 and 18 mg SLC1717 were dissolved in 1 mL toluene. After drying the toluene, N\*LC was added into the liquid crystal cell. CPL spectra were recorded with the excitation wavelength of a 360 nm Xe-lamp. The sample used for CD spectra and POM measurement was prepared by the following method. 1 mg S1 and 9 mg SLC1717 were dissolved in 1 mL toluene. Subsequently, the resulting solution was sonicated for about 1 min to obtain a solution. 50  $\mu$ L of the solution was transferred to a 0.1 mm quartz cell and the solvent was evaporated. CD spectra were recorded from 200 nm to 800 nm. By casting the solution on a quartz plate, uniform film could be formed after evaporating the solvent. The film sample could be used for POM measurement and XRD measurement.

### Determination of TTA-UC quantum yield by a relative method

The upconverted emission quantum efficiency was determined relative to a standard according to the following equation:

$$\Phi_{UC} = 2\Phi_{std} \left( \frac{A_{std}}{A_{UC}} \right) \left( \frac{I_{UC}}{I_{std}} \right) \left( \frac{\eta_{UC}}{\eta_{std}} \right)^2$$

where  $\Phi$ ,  $A$ ,  $I$  and  $\eta$  represent the quantum yield, intensity of absorbance at 532 nm, integrated photoluminescence spectral profile, and refractive index of the solvents used as a standard, respectively. The subscripts UC and std denote the parameters of the upconversion and standard systems. Since the standard and the UC dyes are doped in the same liquid crystal, the



refractive indices are the same. Therefore, under our experimental conditions, the upconverted emission quantum efficiency  $\Phi_{UC}$  could be calculated using the equation. For the UC system, the weight ratio of S1/SLC1717 was 10 wt%, the molar ratio of PtOEP/S1 was 1%. For the standard system, the concentration of Rhodamine B was the same as the concentration of PtOEP. The UC system was tested from 400 nm to 530 nm, and the standard system was tested from 540 nm to 750 nm. The UC quantum yield was determined relative to a standard, Rhodamine B in SLC1717 ( $\Phi_{std} = 0.441$ ) under 532 nm excitation. The result of upconverted emission quantum efficiency was the mean value for parallel testing three times.

## Conflicts of interest

There are no conflicts to declare.

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