Supplementary information for:

Sustainable circularly polarized luminescent inks for cryptography

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MATERIALS AND METHODS

Materials

The nematic liquid crystal host E7 (n = 1.747, Tc = 60°C) and the chiral dopants R/S5011 were purchased from Shijiazhuang Yesheng Chemical Technology Co. Ltd. The fluorescent dyes 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl) -4H-pyran (DCM, 95%), coumarin 7 (C7, 98%), and 7-hydroxy-4-(trifluoromethyl) coumarin (CouOH, 98%) were purchased from Sigma-Aldrich. Gelatins and chloroform were purchased from Sinopharm Chemical Reagent Co. Ltd. Polymethyl methacrylate (PMMA, 92%) was purchased from Adamas.

Preparation of CLCs

Firstly, we prepared left-handed and right-handed CLCs by mixing E7 with chiral dopants S5011 and R5011, respectively. Add a series of chiral dopants with weight ratios of 2.32, 2.81, and 3.29 wt% to tune the PBG of CLC to the red, green, and blue regions, respectively. Add red -, green -, or blue-emitting dyes DCM, C7, and CouOH to CLCs with corresponding PBGs at a doping concentration of 1% by weight, respectively. The CLCs-based CPL precursor was obtained by subjecting the nematic liquid crystal, chiral dopant, and dye to ultrasound treatment for 5 minutes and allowing them to stand in an 80 °C drying oven for 12 hours.

Preparation of PMMA solution

Firstly, mix 5 g PMMA with 45 g chloroform and let it stand at 50 °C for 12 hours to obtain a PMMA solution with a weight ratio of 10 wt%.

Preparation of CPLI

Firstly, mix 5 g of PMMA chloroform solution with a concentration of 10% and 0.2 g of CPL precursor. Stir at 50 °C and 500 rpm for 10 minutes, then transfer the mixture to a glass bottle and seal it for storage.

Production of circularly polarized information array

A pneumatic extrusion-type microelectronic printer (MP1100, Prtronic, China) was used for printing. Load CPLI into a 5.0 ml syringe barrel with a nozzle inner diameter of 250 μm. By adjusting the printing speed and pressure, the release of CPLI can be precisely regulated. The pattern can be customized through the drawing software provided by the printer.

We also prepared a large-scale luminescent coating with circular polarization characteristics by spraying CPLI onto a PET substrate using a spray gun pen (S-130, Ningbo SIBONGD Electromechanical Technology Co. Ltd) powered by an air pump (AF18, Ningbo HSENG Pneumatic Machinery Co. Ltd). Firstly, pour CPLI into the reservoir of the spray gun pen and spray it onto the PET substrate with 0.9 bar compressed air. We move the spray gun pen back and forth until the substrate is evenly covered, and then dry it with hot air at 50 °C for 2 min, repeating the above process three to four times. During the spraying process, we maintain a distance of 15 cm

between the spray gun pen and the substrate, without any specific humidity requirements.

Characterizations

The TG-DSC curve and DSC curves were recorded on a thermogravimeter (TA Discovery TGA) and a differential scanning calorimeter (Shimadzu, DSC-60), respectively. CD and CPL spectra were measured on a JASCO J-1500 and JASCO CPL-300 spectrophotometer, respectively. Polarized optical microscopy images were recorded on the material microscope upright at Mshot MP41. The Fourier transform infrared (FTIR) spectrum was measured with an FTIR microscope (Nicolet iN10MX). SEM images were obtained by using a field-emission scanning electron microanalyzer (Zeiss Supra 40 scanning electron microscopes at an acceleration voltage of 1.5 kV). Brightness intensity was performed on brightness meter (Hopoocolor, CX1000). The UV-visible (UV-vis) near-infrared spectrophotometer (Shimadzu 3700 DUV) was used for transmission and UV-vis spectra, Hitachi F-4700 fluorescence spectrophotometer for fluorescence spectra.

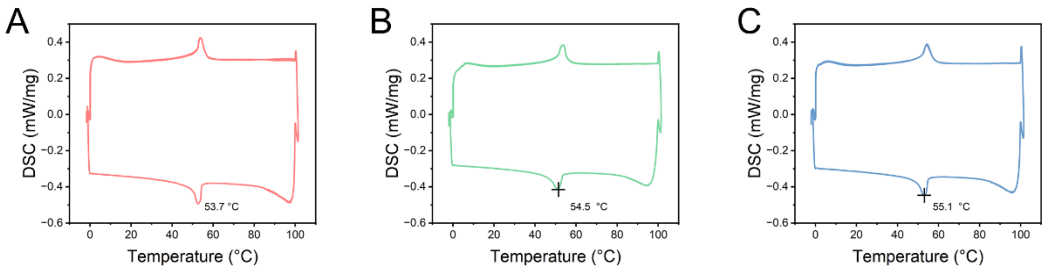

Figure S1. (A-C) DSC curves of heating-cooling cycles of the CLCs with red (A), green (B), and blue (C) emissive between 0-100 °C in a nitrogen atmosphere.

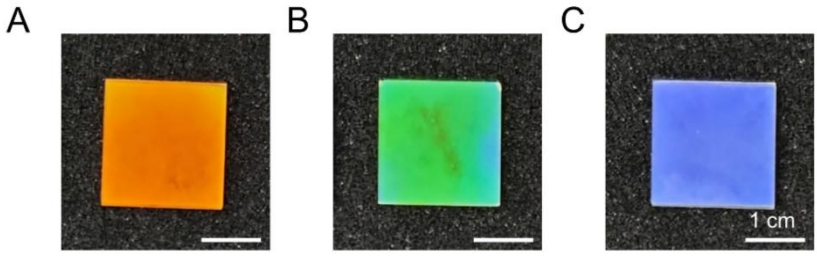

Figure S2. (A-C) Photographs of CLCs encapsulated in cells, using 1.0 wt% dye content in the system with R5011/E7 weight ratios of 0.02/0.98 to 0.035/0.965, respectively. Scale bars: 1 cm.

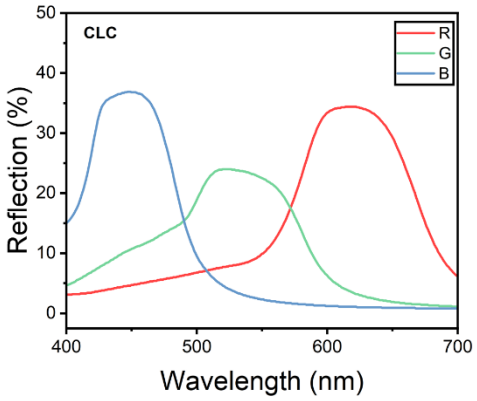

Figure S3. Reflection spectra of the CLCs, using 1.0 wt% dye content in the system with R5011/E7 weight ratios of 0.0232/0.9768, 0.0281/0.9719, 0.0329/0.9671, respectively.

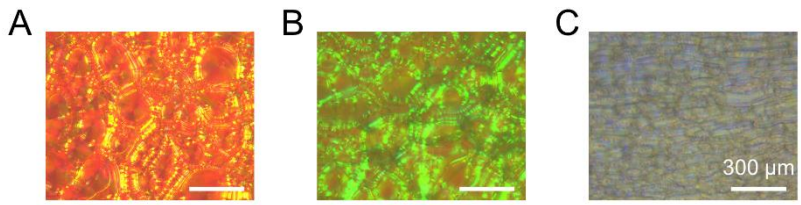

Figure S4. (A-C) The POM images of CLCs with R5011/E7 weight ratios of 0.0232/0.9768, 0.0281/0.9719, 0.0329/0.9671, respectively. Scale bars: 300 μm.

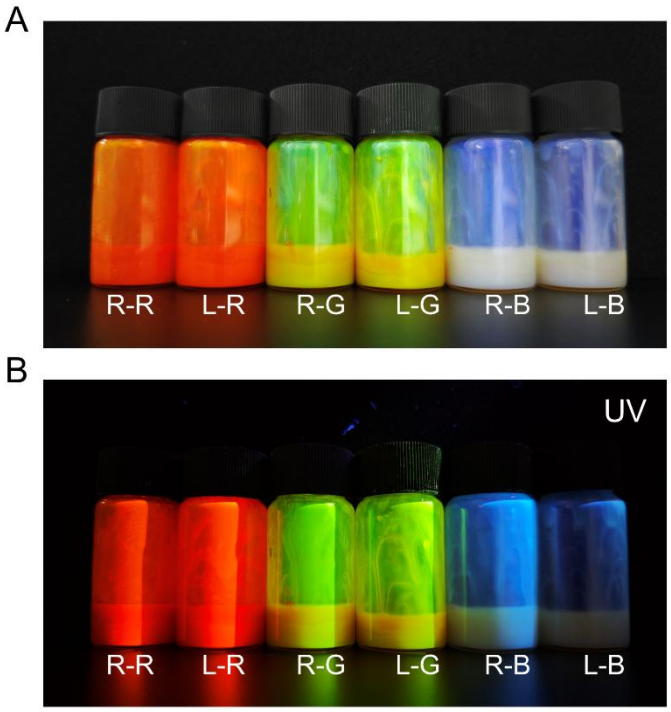

Figure S5. (A and B) Photographs of CLCs with left- and right-handed red emissive, with left- and right-handed green emissive, with left- and right-handed blue emissive under natural light (A) and UV excitation (B), respectively.

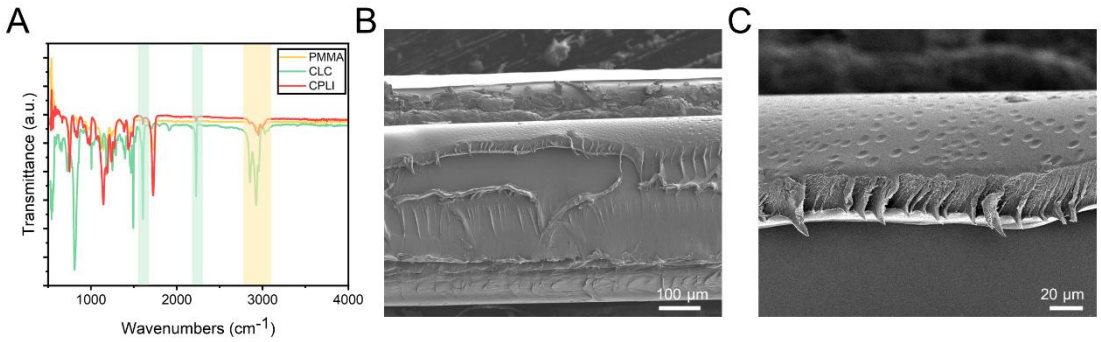

Figure S6. (A) FTIR spectra of the CLCs, polymer, and film made from CPLI. (B and C) The morphologies of the film were observed by cross-sectional SEM.

Figure S7. POM image of film in reflection mode. Scale bar, 10 µm.

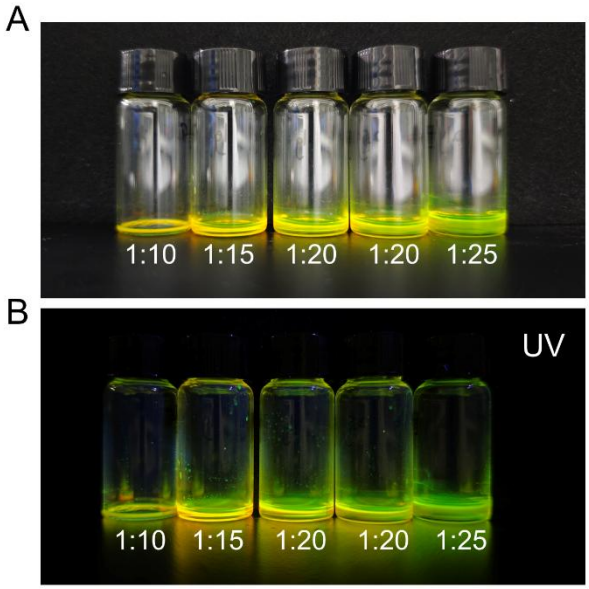

Figure S8. (A and B) Photographs of the CPLI with the different weight ratios of CLCs and PMMA solution (10 wt% in chloroform) under natural light (A) and under ultraviolet light (B).

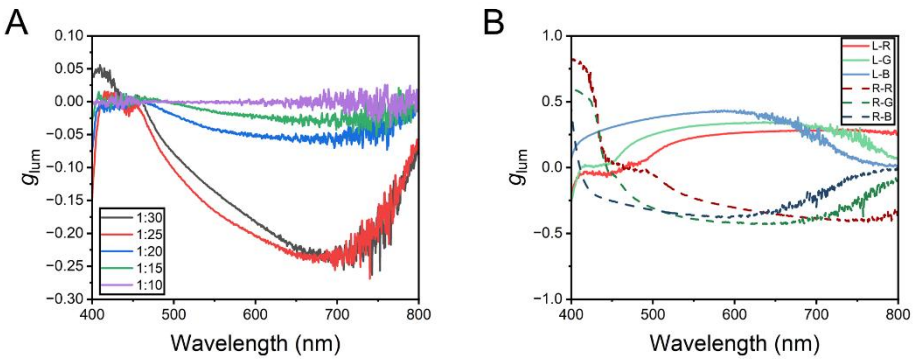

Figure S9. (A) The g_{lum} values of green-emissive films prepared from corresponding inks with different weight ratios of CLCs and PMMA solution (10 wt% in chloroform). (B) The g_{lum} values of red-, green-, and blue-emissive films prepared from corresponding inks.

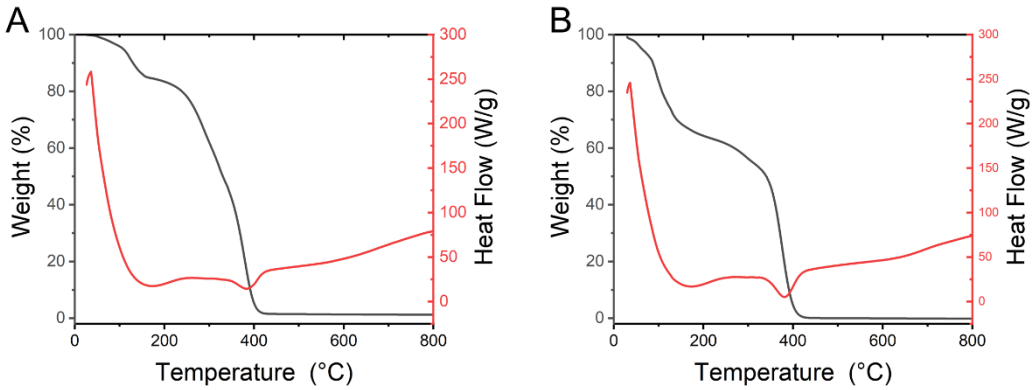

Figure S10. (A and B) Thermogravimetry–differential scanning calorimetry (TG-DSC) curves of the CPLI (A) and corresponding films (B) between 30-800 °C in a nitrogen atmosphere.

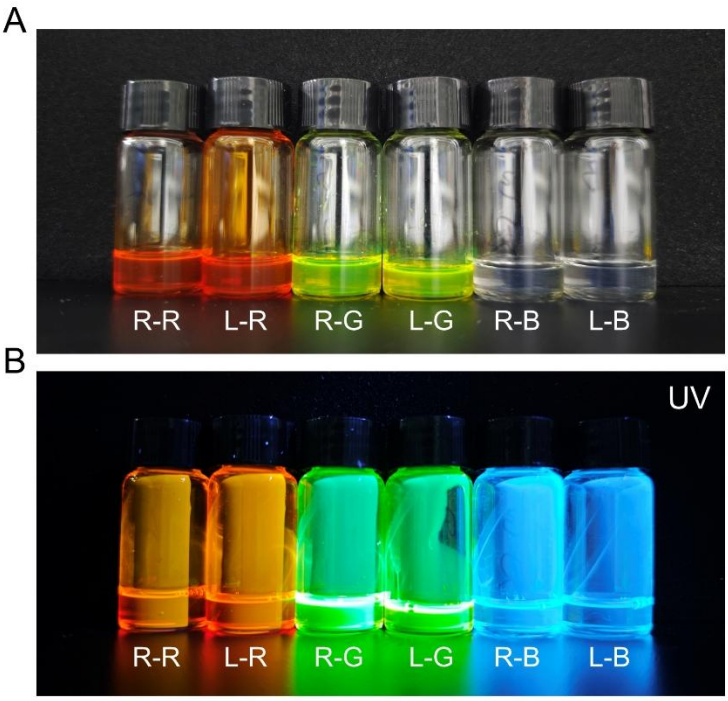

Figure S11. (A and B) Photographs of CPLI with left- and right-handed red emissive, with left- and right-handed green emissive, with left- and right-handed blue emissive under natural light (A) and UV excitation (B), respectively.

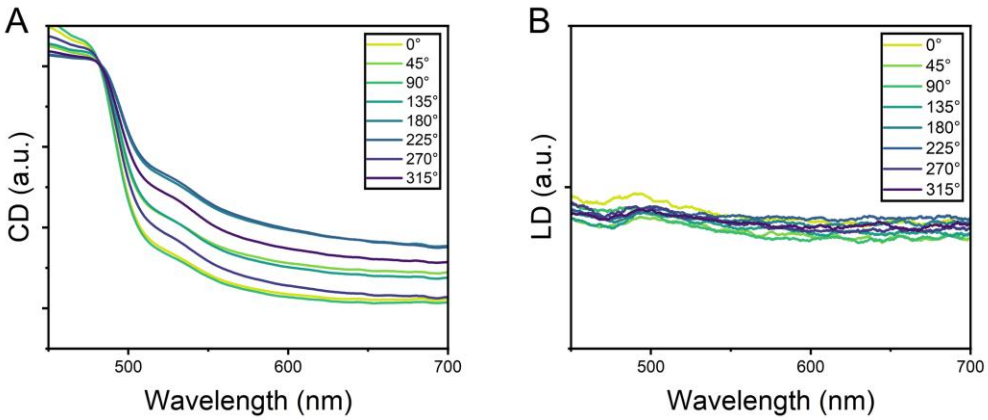

Figure S12. (A and B) CD and LD spectra of film, which are obtained by rotating the sample every 45° in a plane perpendicular to the direction of the optical path for 8 times.

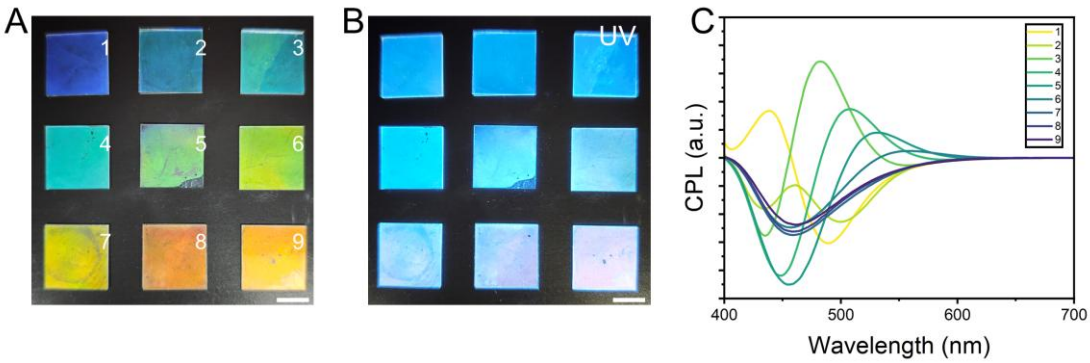

Figure S13. (A and B) CLCs with a continuous PBG from blue to red (A), where the luminescent element is blue (B). Scale bars, 1 cm. (C) CPL spectra with increasing mismatch between PBG and emission wavelength.

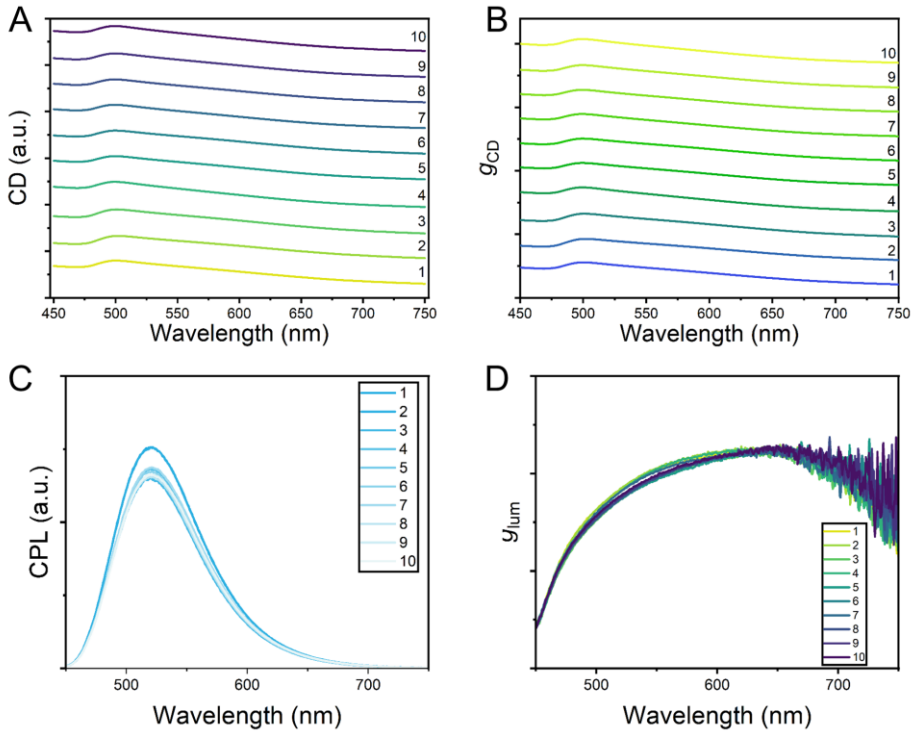

Figure S14. (A to D) CD spectra (A) and CPL spectra (C) at different positions on the film and corresponding g_{CD} (B) and g_{lum} (D).

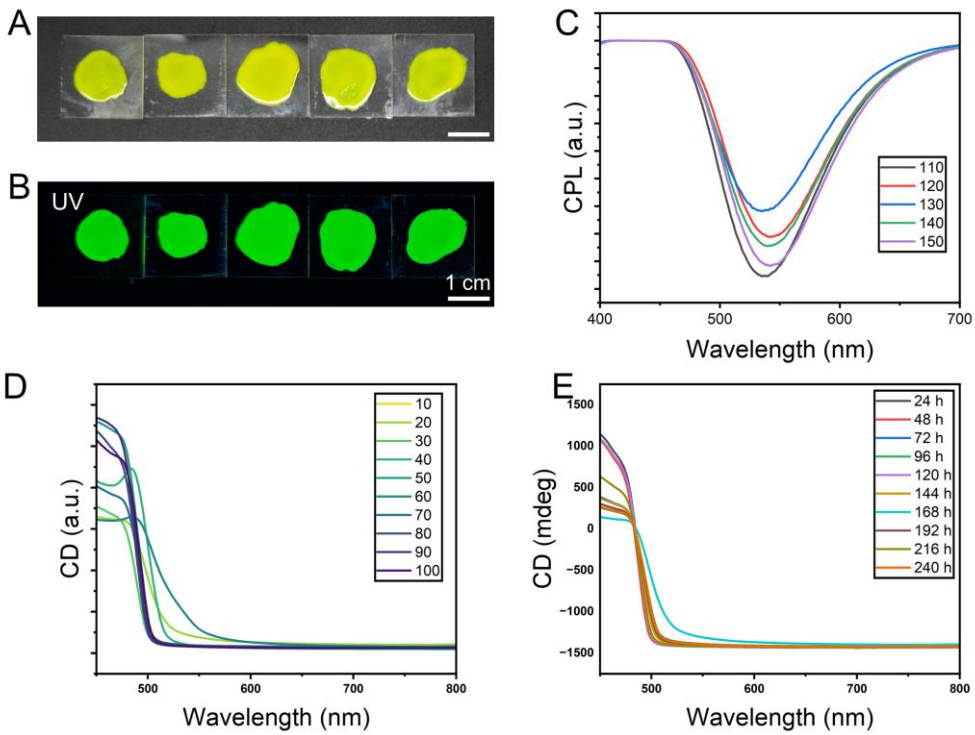

Figure S15. (A and B) Photographs of green-emissive films over 100 recycling cycles. Scale bars, 1 cm. (C) CPL spectra of green-emissive films in recycling. (D and E) CD spectra of green-emissive films during recycling cycles (D) and long-term storage (E).

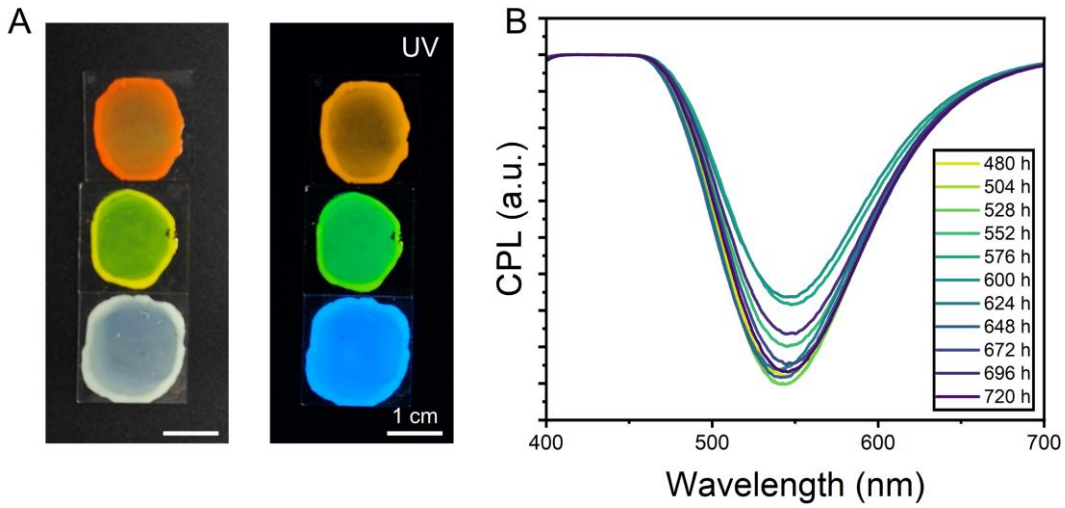

Figure S16. (A) Photographs of the luminous films after exposure in air for over 30 days. Observed under natural light (right), under UV irradiation (left). Scale bars, 1 cm. (B) CPL spectra of films after long-time storage.

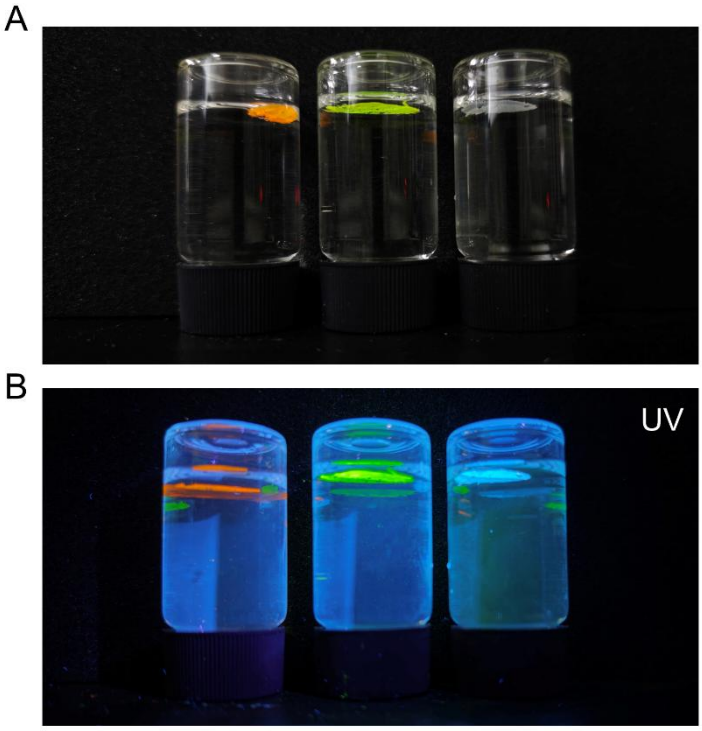

Figure S17. (A and B) Photographs of the luminous films after exposure in water for 7 days. Observed under natural light (A), under UV irradiation (B).

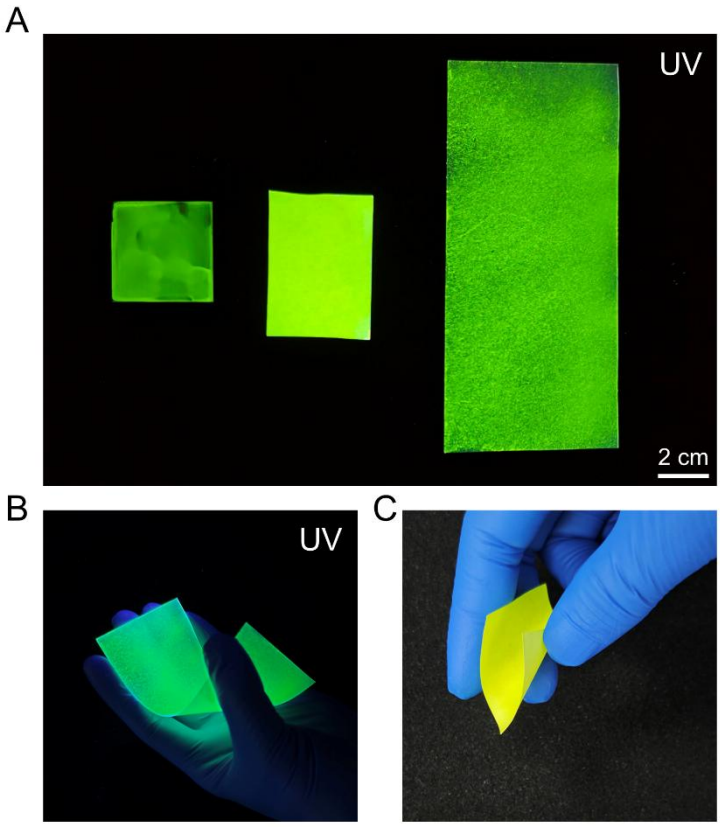

Figure S18. (A) Photographs of films on different substrates under UV: rigid glass plate, flexible paper, and flexible PET plate. (B and C) Photographs demonstrating the flexibility of films on flexible substrates.

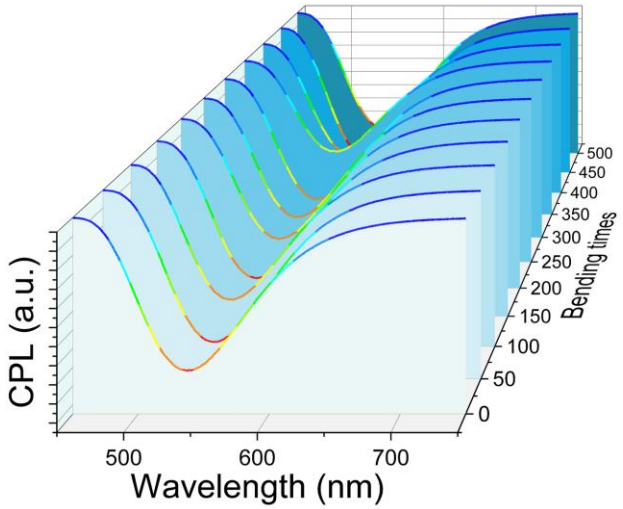

Figure S19. CPL intensity of the bent CPL films under bending cycling.

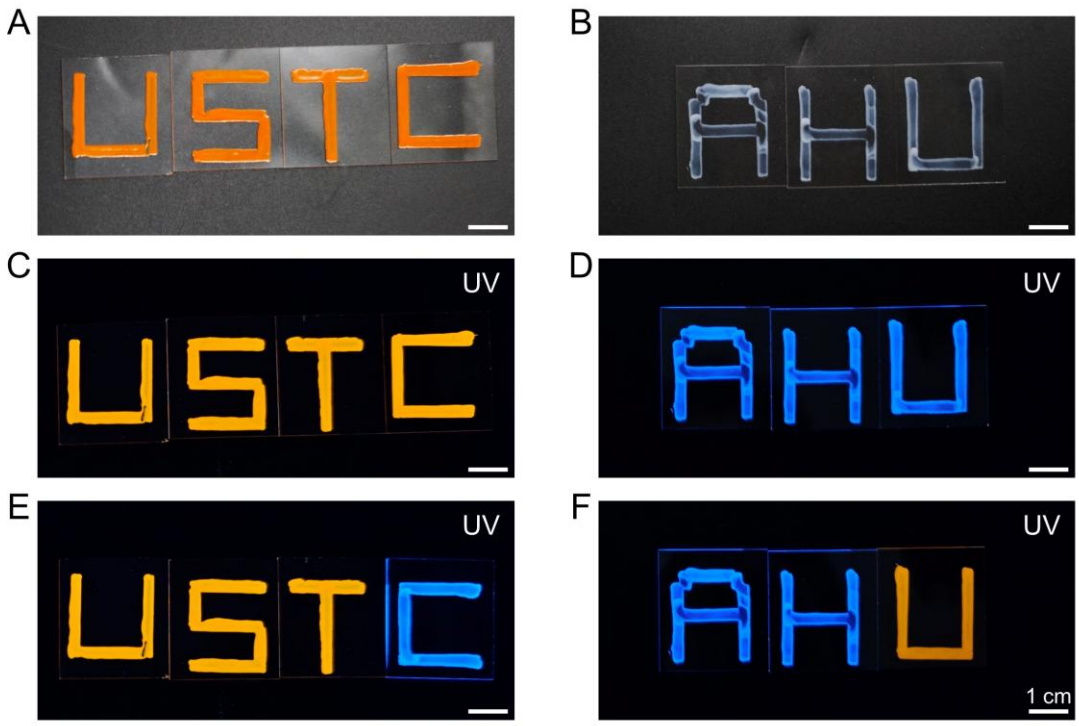

Figure S20. (A, B) Patterns printed from different CPLI. (C-F) Photographs of patterns observed under UV irradiation (C, D), and partial exchange (E, F). Scale bars, 1 cm.

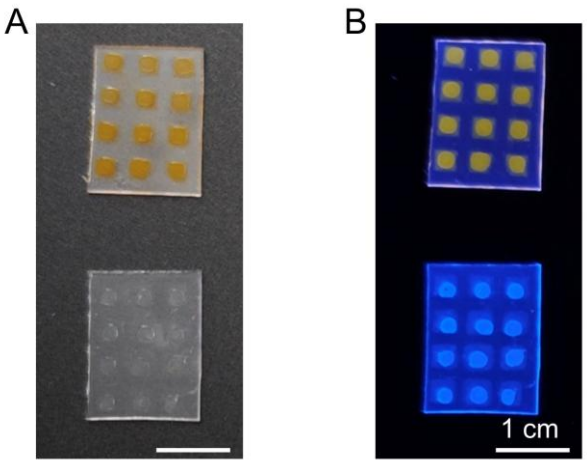

Figure S21. (A and B) Photographs of arrays obtained by screen printing CPLI on PET substrate. Observed under natural light (A) and under UV irradiation (B). Scale bars, 1 cm.

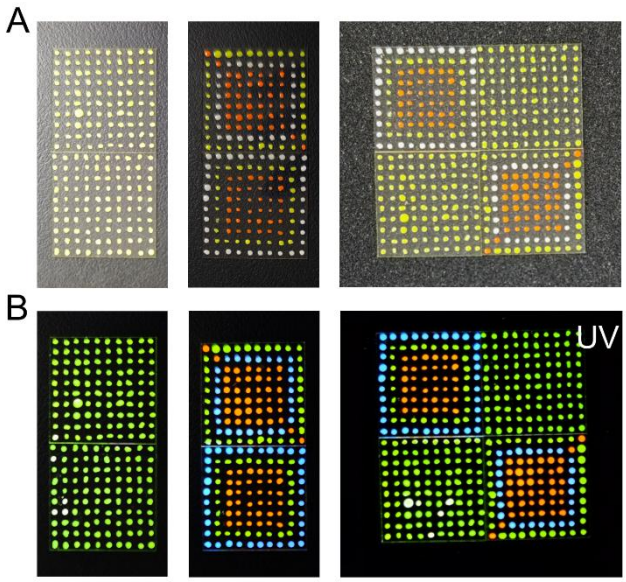

Figure S22. (A and B) Photographs of arrays obtained by manual coating left- and right-handed inks with RGB emissions on glass plate. Observed under natural light (A), under UV irradiation (B). Encryption area, 4×4 cm.

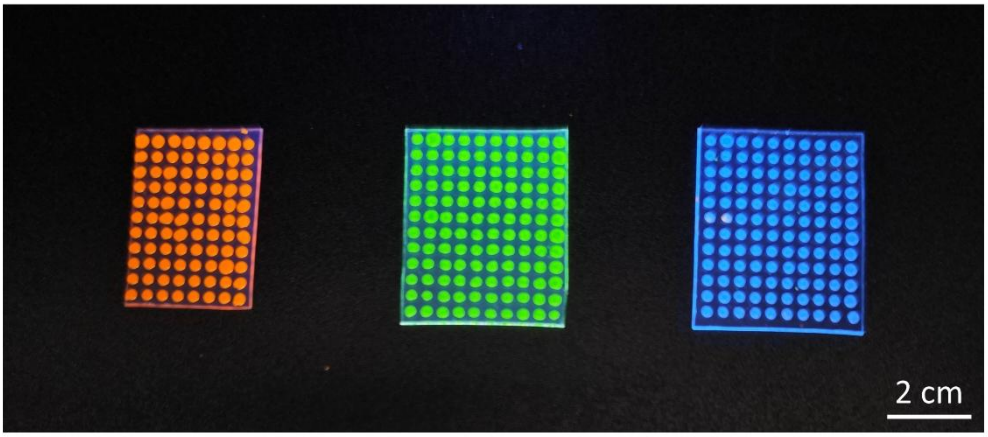

Figure S23. Photographs of arrays obtained by a printer. Observed under UV irradiation. Scale bar, 2 cm.

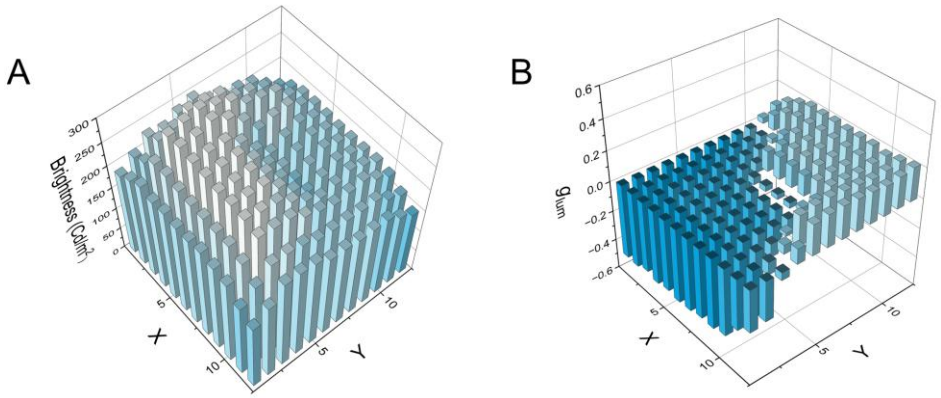

Figure S24. (A) The Encrypting optical differential information of the CPL array is read without polarizers. (B) Circular polarization differential encryption information, referring to the calculation formula of g_{lum}.

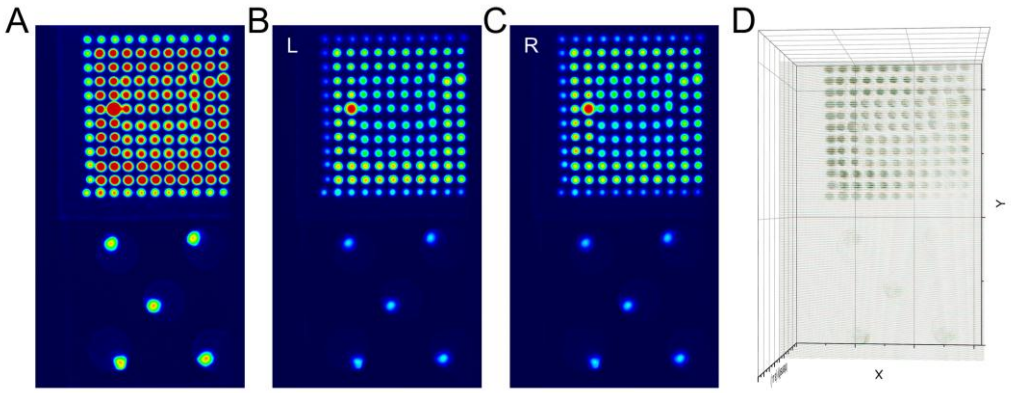

Figure S25. (A-C) Photoluminescence brightness of patterns obtained by alternately printing left- and right-handed inks with RGB emissions on glass plate. Without (A) and with different polarizers (B, C). (D) Through polarization differential imaging, the interference of the five non-polarized emission points is basically eliminated.