Supporting Information for

Upconversion circularly polarized luminescence of cholesteric liquid crystal polymer networks with $NaYF_4$:Yb,Tm UCNPs

Liting Xu, Yi Li, Wei Liu* and Yonggang Yang*

State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials, Jiangsu Engineering Laboratory of Novel Functional Polymeric Materials, Department of Polymer Science and Engineering, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, P. R. China. Email: W. Liu, weiliu@suda.edu.cn; Y. Yang, ygyang@suda.edu.cn.

Experimental Section

Materials and instruments

Compounds NaF, $Y(NO_3)_3\ 6H_2O$, $Yb(NO_3)_3\ 5H_2O$, $Tm(NO_3)_3\ 5H_2O$, citric acid and NaOH were obtained from Aladdin Chemical Co., Ltd (Shanghai, China). Ethylene glycol, dichloromethane, and ethanol (EtOH) were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. LC242 was given by Wuxi Wanli Adhesive Material Co., Ltd. CA-iso was given by Soochiral Sci. & Tec. Co., Ltd. Photoinitiator BDK was purchased from Adamas Chemical Co., Ltd (Shanghai, China), and Irgacure 907 was purchased from Aladdin Chemical Co., Ltd (Shanghai, China). Polyethylene terephthalate (PET) films were purchased from Nanya plastics Co., Ltd (Nantong, China). Absorption-type left- and right-handed circular polarizers (LH- and RH-CP) of the Nitto Brand (model: YPM12) were used. The centrifugation was achieved using a CENCE H1850 centrifugal separator (Zhejiang, China). Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 Advance (Germany) X-ray Powder diffractometer with Cu Kα radiation (λ = 1.54056 Å). Cross-sectional FE-SEM images for CLCN films were obtained using a Hitachi Regulus 8230 operating (Ibaraki Prefecture, Japan) at 5.0 kV. Energy dispersive spectrometer (EDS) elemental mappings for UCNPs were obtained using a Hitachi Regulus8230 operating (Ibaraki Prefecture, Japan) equipped with an Oxford EDS at 15.0 kV. The photopolymerization was conducted using a UV lamp (SVC365NM, 365 nm, 5 W, output power) produced by Ninghai County Forres Electric Appliance Co., Ltd (Zhejiang, China) and a high-pressure Hg lamp (MINHIO 4012-20, 350−450 nm, 1.0 kW, input power) produced by MINHIO Intelligent Equipment Co., Ltd (Shenzhen, China). DRCD spectra were measured using a JASCO 815 spectrometer (Tokyo, Japan). UV−*vis* spectra were measured by a UV−vis−NIR spectrophotometer (UV3600, Shimadzu, Japan). POM images of the target compounds were taken using a Leica Microsystems CMS GmbH fitted with a Linkam LTS420 hot stage. Fluorescence spectra were measured on a steady-state lifetime fluorescence spectrometer FLS1000 (Edinburgh Instrument, UK) equipped with an external 980-nm laser resource (power, 0−2 W).

Synthesis of UCNPs.

The UCNPs were synthesized similarly to the procedure described in previous literature.[S1, S2] A solution of NaF (210.0 mg, 5 mmol) in a mixed solvent of H_2O (5 mL) and ethylene glycol (5 mL) was added slowly into a solution of $Y(NO_3)_3{\cdot}6H_2O$ (306.4 mg, 0.800 mmol), $Yb(NO_3)_3{\cdot}5H_2O$ (89.8 mg, 0.200 mmol), $Tm(NO_3)_3{\cdot}5H_2O$ (4.5 mg, 0.010 mmol), citric acid (2.33 g, 12.1 mmol) and NaOH (0.48 g, 12.1 mmol) in ethylene glycol (10 mL). The mixed solution was stirred for 1 h, then transferred into a stainless-steel Teflon autoclave, sealed and heated at 180 °C for 12 h. After the reaction mixture was naturally cooled

down to room temperature. The resulting precipitate was isolated by centrifugation at a rotator speed of 5000 rpm for 6 min, washed with H_2O and EtOH, and dried in a vacuum to afford UCNPs.

Preparation for free-standing CLCN-UCNP films

According to Table S1, the reactive acrylate compound LC242, photoinitiator BDK, chiral additive CA-*iso*, and UCNPs were added into a solvent mixture of dichloromethane and EtOH. The mixture was sonicated fully. Then the solvent on the surface of a glass slide was evaporated completely at 90 °C for 5 min. The thickness of the liquid layer was controlled using an 11-μm-thick spacer in the middle between two glass slides. After cooling to 65 °C, photopolymerization of the CLC layer was carried out using a 365-nm UV lamp (5.0 W) for 10.0 s. Then free-standing CLCN-UCNPs films were obtained and peeled off from the glass slides with a blade.

Preparation of the CLCN-UCNPs coated PET film

The CLCN-UCNPs coated PET film was prepared using the CLC mixture LC242/CA-*iso*/UCNPs/Irgacure 907 (w/w/w/w, 90.3/3.7/3.0/3.0). The CLC mixture was dissolved in a mixed solvent of cyclohexane and EA to form a solution with 20 wt% of solid content, and coated on a PET film using a 40 μm Mayer bar for controlling the thickness. After coating, the sample was heated at 120 °C for 5 min to evaporate the solvent. Finally, the film was obtained by curing with a high-pressure Hg lamp (1.0 kW).

Preparation of the PMMA-UCNPs film

The PMMA and UCNPs (w/w, 97.0/3.0) were added into a mixed solvent of dichloromethane and EtOH. After casting the solution onto the surface of a quartz plate, and keeping the coated quartz plate at 90 °C for 5 min, a thin PMMA-UCNPs film was obtained.

Table S1 Summary of UCNPs-based CPL materials with $|g_{lum}|$ values higher than 0.1 in the literature.

UCNPs-based UC-CPL materials	λ_{ex} (nm)	λ_{em} (nm)	g_{lum} values	Ref.	Year	Remarks
CNC/glycerol composite film, G1-U	974	450	–0.156	S3	2019	Humidity control
R811-LC-UCNPs	980	475	+0.3	S4	2020	Using the liquid crystal cell
R811-LC-UCNPs-$CsPbBr_3$	980	495	+1.1	S4	2020	Using the liquid crystal cell
Switch 6/UCNP/SLC1717	980	605	+0.49	S5	2020	Using the liquid crystal cell
$NaGdF_4Yb^{3+},Er^{3+}$@Carbon Dots	980	543	+0.84	S6	2022	Cholesteric nanocellulose film
Composite I	980	523, 542	+1.8	S7	2022	Using the liquid crystal cell
Composite II	980	654	+1.9	S7	2022	Using the liquid crystal cell
UCNPs-on-Meta	980	803, 863, 894	+0.34, +0.84, +0.95	S8	2022	Plasmonic chiral metasurface
S811/UCNPs-1/SLC1717	1532	542	–0.83	S9	2023	Using the liquid crystal cell
R811-SLC1717-UCNPs	980	802	–0.5	S10	2023	Using the liquid crystal cell
S811-SLC1717-UCNPs	980	802	+0.5	S10	2023	Using the liquid crystal cell

Table S2 Mass percentages of compounds in free-standing CLCN-UCNPs films with different concentrations of CA-*iso*.

LC242	UCNPs	BDK	CA-*iso*
93.2	3.0	1.0	2.8
93.1	3.0	1.0	2.9
92.5	3.0	1.0	3.5
92.3	3.0	1.0	3.7
91.8	3.0	1.0	4.2

Table S3 Mass percentages of compounds in CLCN-coated PET films with different concentrations of CA-*iso*.

LC242	Irgacure 907	CA-*iso*
93.9	3.0	3.1
93.4	3.0	3.6
93.2	3.0	3.8
93.0	3.0	4.0
92.8	3.0	4.2
92.5	3.0	4.5

References

S1 J. Wang, Y. Zhao, B. Li, L. Sun and J. Chen, *Mater. Lett.*, 2013, **93**, 297.

S2 R. Rafique, S. H. Baek, L. M. T. Phan, S.-J. Chang, A. R. Gul and T. J. Park, *Mat. Sci. Eng. C*, 2019, **99**, 1067.

S3 W. Li, M. Xu, C. Ma, Y. Liu, J. Zhou, Z. Chen, Y. Wang, H. Yu, J. Li and S. Liu, *ACS Appl. Mater. Interfaces*, 2019, **11**, 23512.

S4 X. Yang, M. Zhou, Y. Wang and P. Duan, *Adv. Mater.*, 2020, **32**, 2000820.

S5 A. Juan, H. Sun, J. Qiao and J. Guo, *Chem. Commun.*, 2020, **56**, 13649.

S6 Y. Dong, H. Zhao, S. Wang, Q. Cheng, S. Liu and Y. Li, *ACS Appl. Mater. Interfaces*, 2022, **14**, 40313.

S7 H. He, J. Wang, K. Li, M. Cen, W. Cai, J. Liu, D. Luo, Y. Q. Lu and Y. J. Liu, *Laser Photonics Rev.*, 2022, **16**, 2200115.

S8 H. He, M. Cen, J. Wang, Y. Xu, J. Liu, W. Cai, D. Kong, K. Li, D. Luo, T. Cao and Y. J. Liu, *ACS Appl. Mater. Interfaces*, 2022, **14**, 53981.

S9 C. Jiang, Y. Shi, X. Yang, T. Zhao, J. Zhou, X. Jin, Y. Zhang and P. Duan, *Adv. Opt. Mater.*, 2023, **11**, 2300001.

S10 X. Yang, X. Jin, A. Zheng and P. Duan, *ACS Nano*, 2023, **17**, 2661.

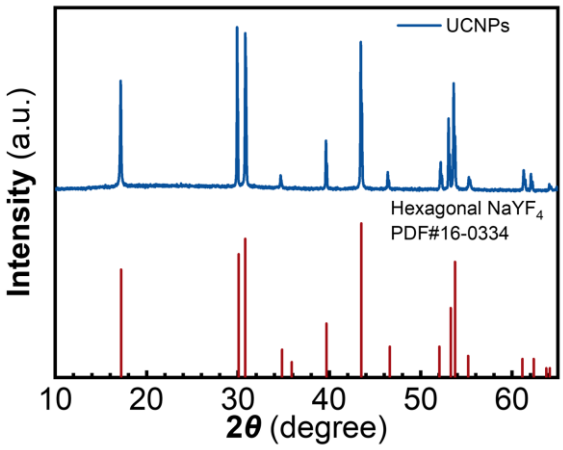

Fig. S1 PXRD pattern of UCNPs and the standard card of hexagonal phase $NaYF_4$ (Joint Committee on Powder Diffraction Standards, JCPDS-16-0334).

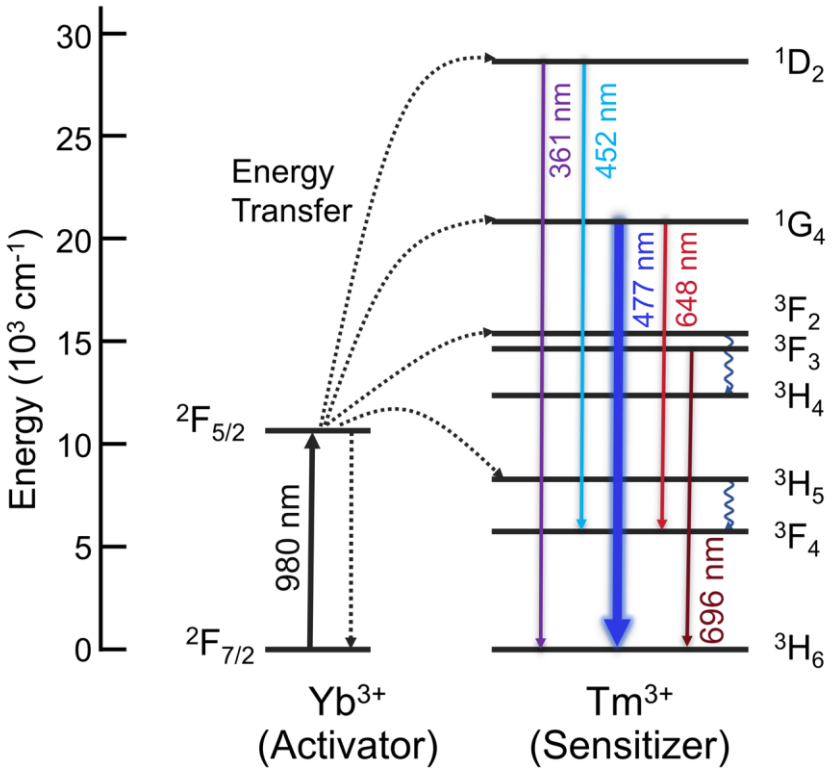

Fig. S2 Energy-level diagrams and proposed UCL energy transfer pathways of $NaYF_4$:Yb,Tm UCNPs.

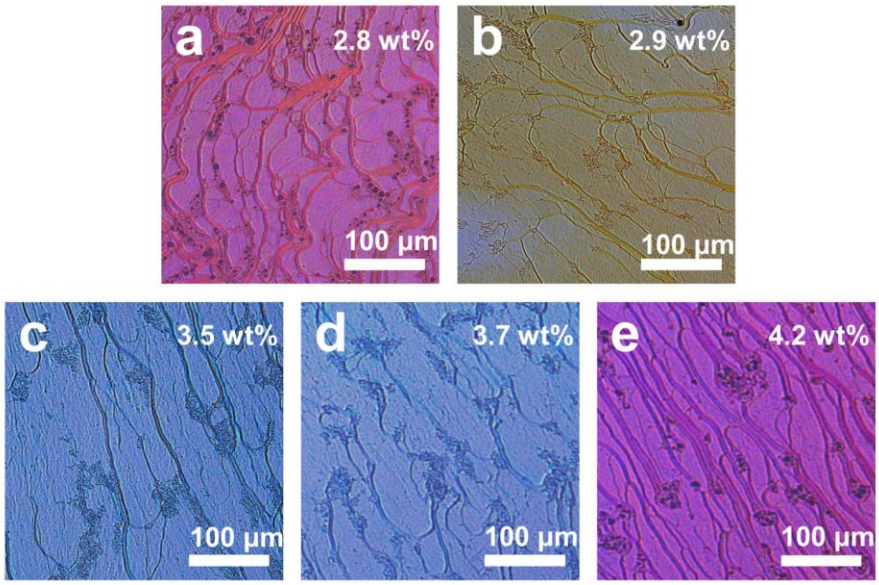

Fig. S3 POM images of UCNPs-CLC mixtures at different concentrations of CA-*iso* at 85 ℃: (a) 2.8 wt%, (b) 2.9 wt%, (c) 3.5 wt%, (d) 3.7 wt% and (e) 4.2 wt%.

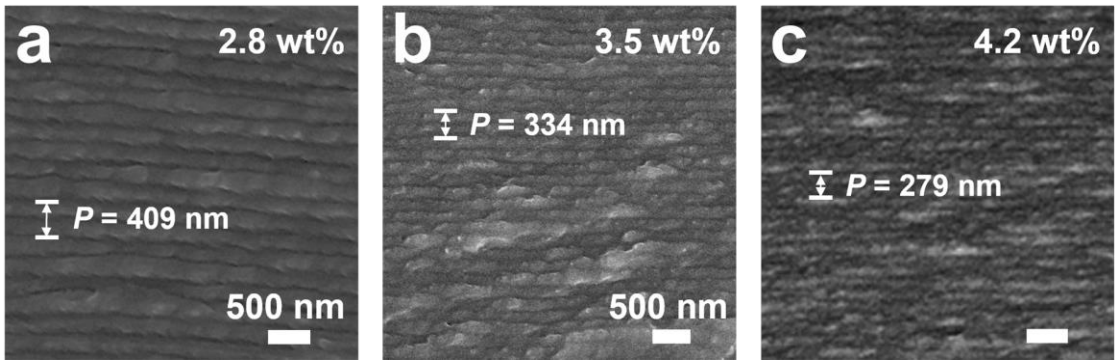

Fig. S4 Cross-sectional FE-SEM images of free-standing CLCN-UCNPs films with different concentrations of CA-*iso*: (a) 2.8, (b) 3.5, and (c) 4.2 wt%.

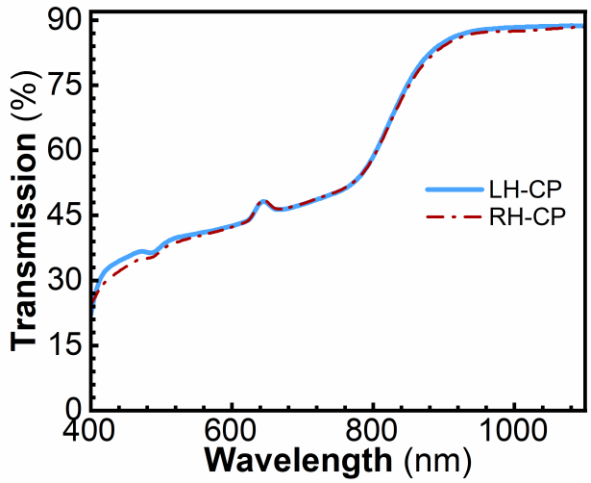

Fig. S5 UV−*vis* spectra of left- and right-handed circular polarizers.

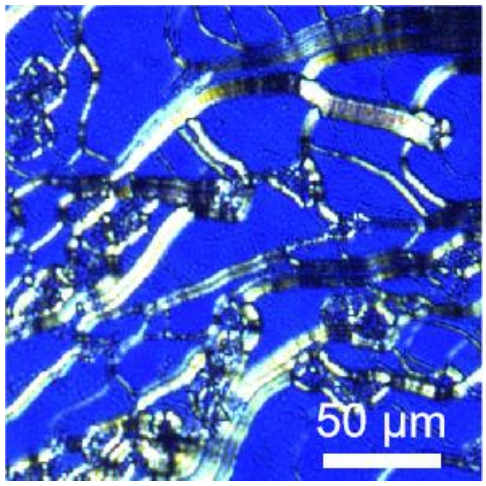

Fig. S6 POM image of the LC242/CA-*iso*/UCNPs/Irgacure 907 (w/w/w/w, 90.3/3.7/3.0/3.0) mixture at 85 °C.

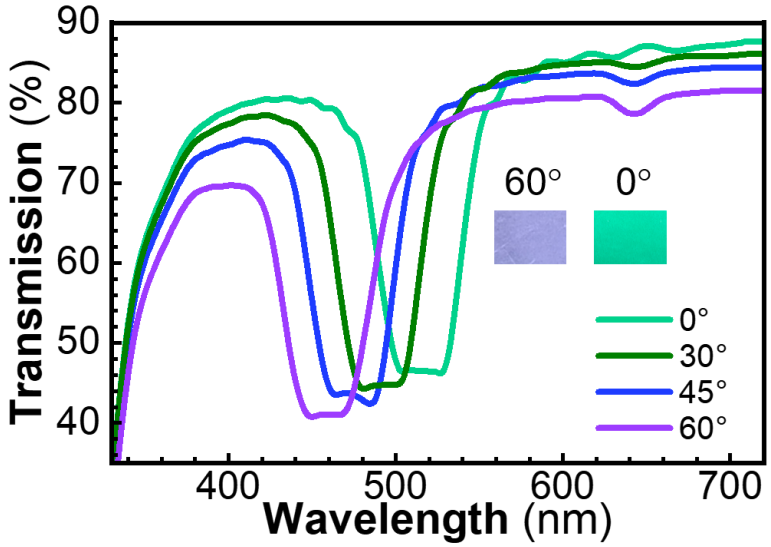

Fig. S7 Angle-dependent UV−*vis* spectra of the CLCN-UCNPs-coated PET film. Inset: photographs of the film with viewing angles of 0° and 60°.

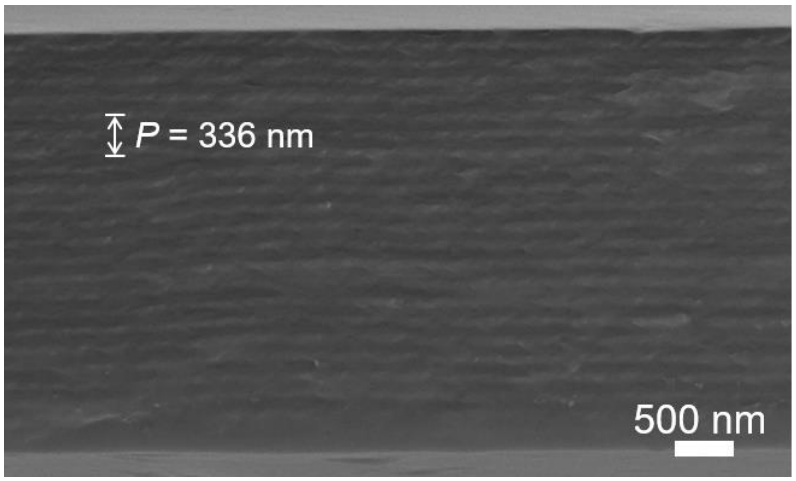

Fig. S8 Cross-sectional FE-SEM image of the CLCN-UCNPs-coated PET film.

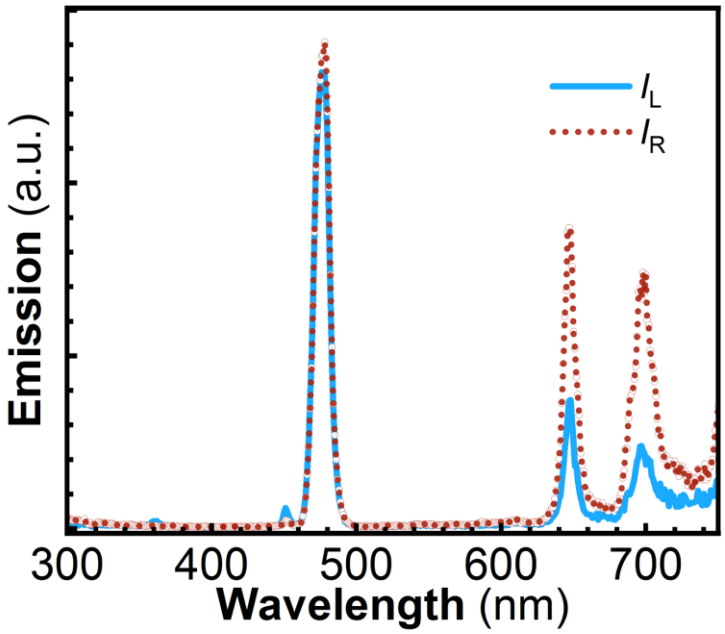

Fig. S9 Emission spectra of the PMMA-UCNPs film through RH- and LH-CP excited by a 980 nm laser.

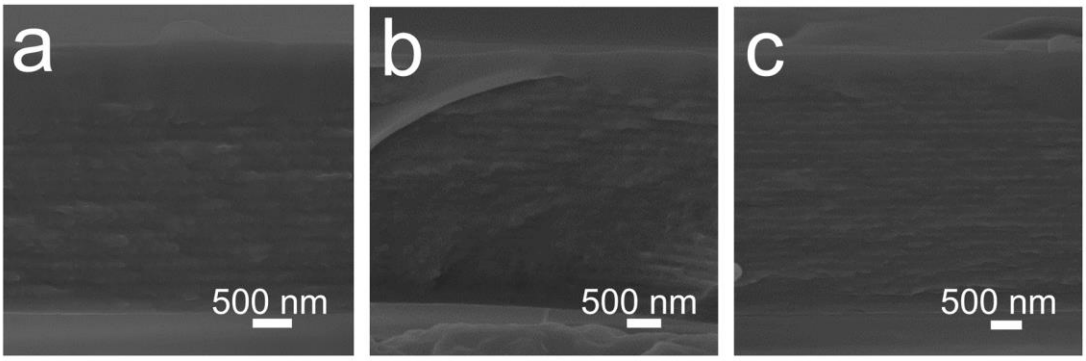

Fig. S10 Cross-sectional FE-SEM image of the CLCN-coated PET film with different concentration of CA-*iso*: (a) 3.6 wt%, (b) 4.0 wt%, and (c) 4.2 wt%.

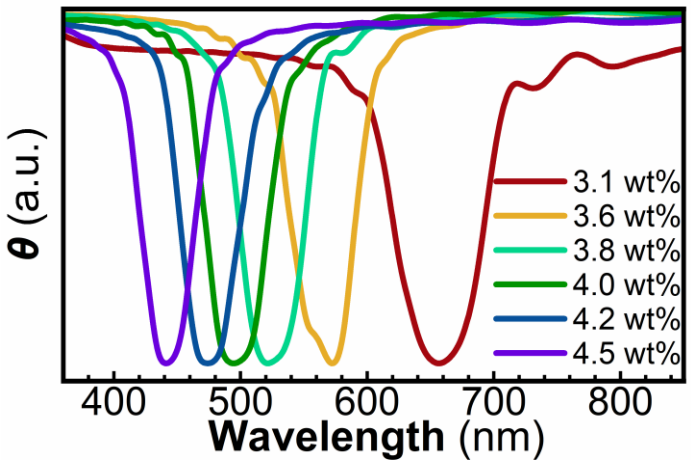

Fig. S11 CD spectra of CLCN-coated PET films with different concentrations of CA-*iso*.

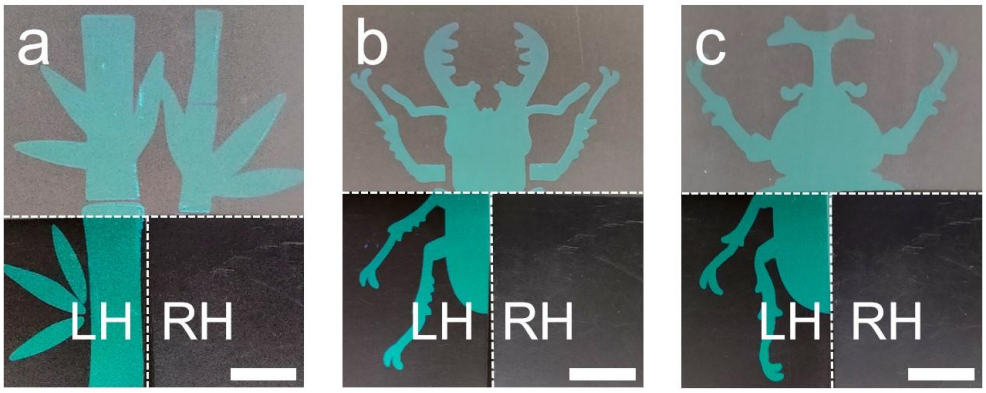

Fig. S12 Images of CLCN-UCNPs-coated PET films with (a) a bamboo pattern, (b) and (c) beetle patterns viewed directly (top), through LH- and RH-CP, respectively (bottom). Scale bar: 1.0 cm.

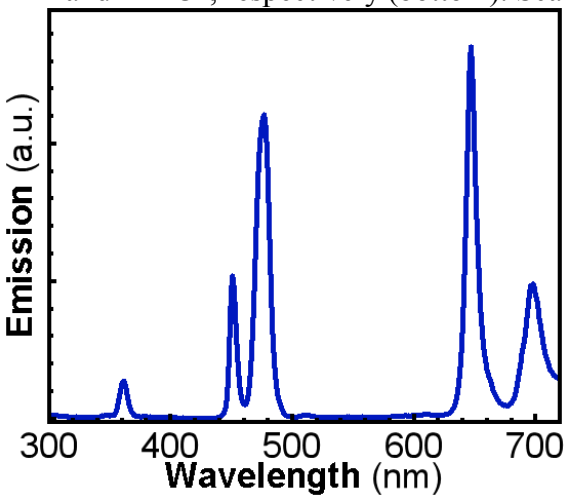

Fig. S13 Emission spectrum of the CLCN-UCNPs-coated PET film with the bamboo pattern excited by a 980-nm laser.

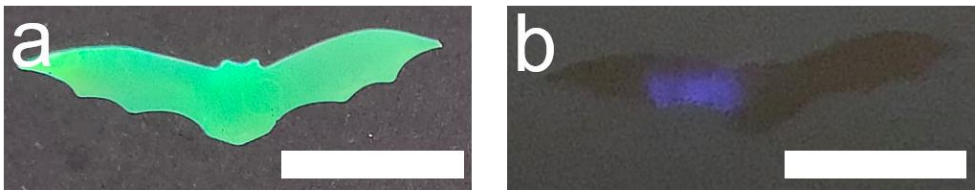

Fig. S14 Images of the free-standing CLCN-UCNPs film with a bat pattern exposed to (a) daylight and (b) a 980-nm laser using a beam expander. Scale bar: 1.0 cm.