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Electronic Supplementary Information:

Chiral fluorescent films of gold nanocluster and photonic cellulose with modulated fluorescence emission

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Materials and Characterization

All chemicals were used as received without further purification. Bovine serum albumin (98%) (BSA) and hydrogen tetrachloroaurate (Ⅲ) hydrate (99.8%) ($HAuCl_4$) were purchased from J & K Scientific Ltd. 2, 4, 6-trinitrophenol (TNP) was purchased from Aladdin Industrial Corporation. Cotton pulp board was purchased from Hebei Paper Group of China.

Surface morphologies were characterized with JEOL-6700 F filed emission scanning electron microscope (SEM) at an accelerating voltage of 3KV. Transmission electron microscopy (TEM) and energy dispersion X-ray (EDX) elemental mapping analysis were conducted on a FEI Tecnai G2S-Twin F20 with a field emission gun operating at 200 kV. X-ray photoelectron spectroscopy (XPS) was conducted on Thermo Fisher Scientific ESCALAB250 spectroscopy. Ultraviolet-visible (UV-vis) spectroscopy was conducted on a Shimadzu UV-1800 UV-vis spectrophotometer. Absorption spectra were collected by mounting free-standing films so that the surfaces of the films were perpendicular to the beam path. Circular dichroism (CD) experiments were carried out on a BioLogic MOS-450 spectropolarimeter and the films were mounted normal to the beam path. Polarized optical microscopy (POM) was performed on Leica DM4000M Versatile Upright Microscope. Laser scanning confocal microscopy (LSCM) was performed on Olympus FV1000. Zeta potential and was performed on Malvern Zetasizer Nano ZS90. Photoluminescence spectra were recorded on a FluoroMax-4 fluorescence spectrophotometer (Horiba Scientific). The luminescence decay curves were recorded on a FLS920 fluorescence spectrometer (Edinburgh Instrument).

Preparation of AuNC

AuNC was synthesized according to the method of Yin's work with some modification. In a typical experiment, aqueous $HAuCl_4$ solution (5 mL, 10 mM) was added to BSA solution (5 ml, 50 mg/mL) and the mixture was stirred for 1 min when the $HAuCl_4$ solution was added completely. NaOH solution (0.5 mL, 1 M) was introduced 10 min later, and the reaction was allowed to proceed at 37 ℃ for 12 h. The obtained AuNC was placed in a dialysis membrane tube and dialysed with de-ionized water changed three times a day for 2 days. The solution from the membrane tubes was diluted to 2.5 mM, then stored at 4 ℃.

Preparation of CNC

Fully bleached, commercial cotton pulp was first milled in a commercial pulp machine to get small pieces of pulp, then allowed to dry in the oven at 30 ℃. The milled pulp was hydrolysed in 64% sulfuric acid (1 g pulp/10 mL H_2SO_4) with vigorous stirring at 45 ℃ for 90 min. The cellulose suspension was diluted with de-ionized water (about ten times the volume of the acid solution used) to stop the reaction, and allowed to placed overnight. The clear top layer was decanted and the remaining cloudy layer was centrifuged (8000 rmp, 6 min). The supernatant was decanted and the resulting thick white slurry was washed two times with deionized water. The thick white suspension was injected in a Millipore stirred ultrafiltration cells (model 8400) to wash the suspension with deionized water until the pH of the suspension became constant in a period of time. The suspension from the Millipore cell was then diluted to desired concentration.

The CNC suspension was prepared by titration the acidic CNC using 0.1 M NaOH aqueous solution until pH = 7. The titration was performed with a pH meter (PB-10, Sartorius).

Sonication was used to increase the pitch in suspension and shift the reflection band of CNC film toward longer wavelength. Neutral CNC suspension was sonicated using a Sonics Vibra-Cell (VCX-750, Sonics & Materials. Inc) equipped with a 13 mm probe. In a typical procedure, 40 mL of 3% CNC suspension was placed in a 100 mL glass beaker and sonicated at 20% of the maximum power for different times.

Preparation of AuNC$_x$-CNC composite films

In a typical producer, different volume of prepared AuNC (0, 0.5, 1, 2, 3, 4 mL) solution was added to 5 mL neutral CNC (3 wt %) suspension respectively and the mixture was stirred at room temperature for 60 min to obtain a homogeneous mixture. Then the suspension was dried on polystyrene Petri dishes (60 mm) for 2 days at ambient temperature to give rise to free-standing iridescent chiral nematic AuNC-CNC films. The obtained films were defined as AuNC$_x$-CNC (x = 0, 0.5, 1, 2, 3, 4).

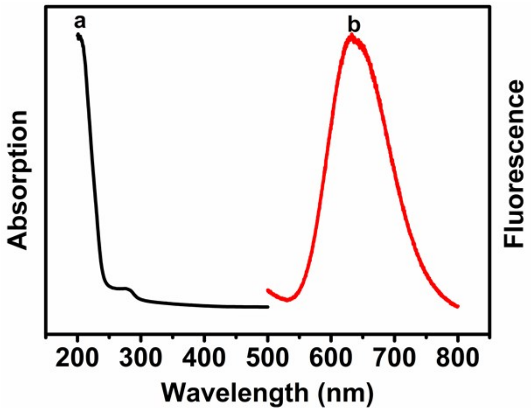

Fig. S1 Characterizing the 2.5 mM AuNC solution: **(a)** Absorption spectrum. (b) Fluorescence emission spectrum.

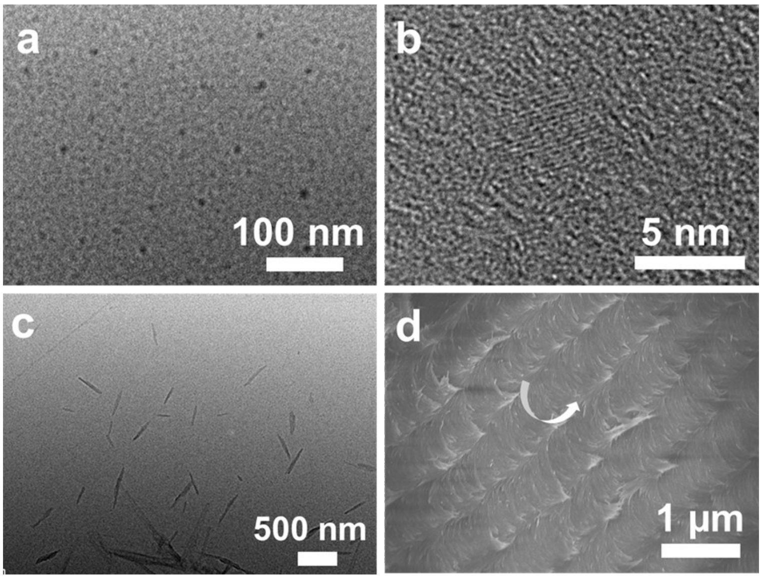

Fig. S2 (a, b) Low magnification and high magnification TEM image of AuNC. (c) TEM image of CNC nanorods. (d) High magnification SEM image of CNC showing left-handed periodical arrangement.

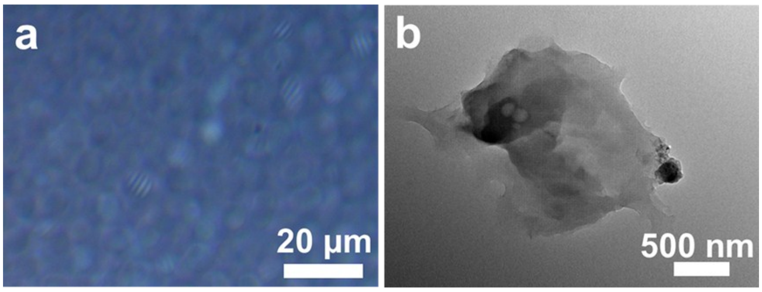

Fig. S3 (a) POM image of an $AuNC_4$:CNC suspension containing 4.0 mL of the AuNC solution observed during room temperature evaporation, showing a fingerprint texture characteristic of chiral nematic ordering. (b) TEM of the $AuNC_4$-CNC film.

Table S1 Volume of 2.5 mM AuNC solution added to 5 mL of 3.0 wt% CNC suspension, and ζ-potential of the suspension mix.

Volume of AuNC added to the CNC suspension (mL)	**C_{AuNC} in AuNC-CNC mixed suspensions (mM)**	**ζ-potential (mV)**
0	0	-51.7
0.5	0.23	-37.3
1.0	0.42	-35.0
2.0	0.71	-34.3
3.0	0.94	-32.8
4.0	1.11	-33.3

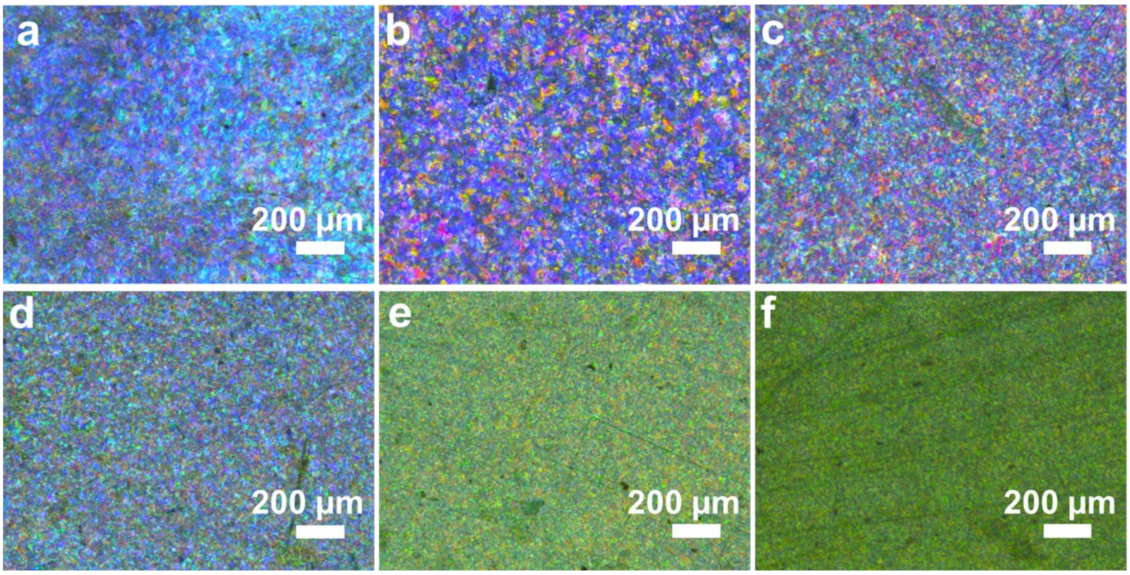

Fig. S4 POM images of the $AuNC_x$-CNC films from suspension mixes containing varying amount of the AuNC solution (a to f: x = 0, 0.5, 1, 2, 3 and 4).

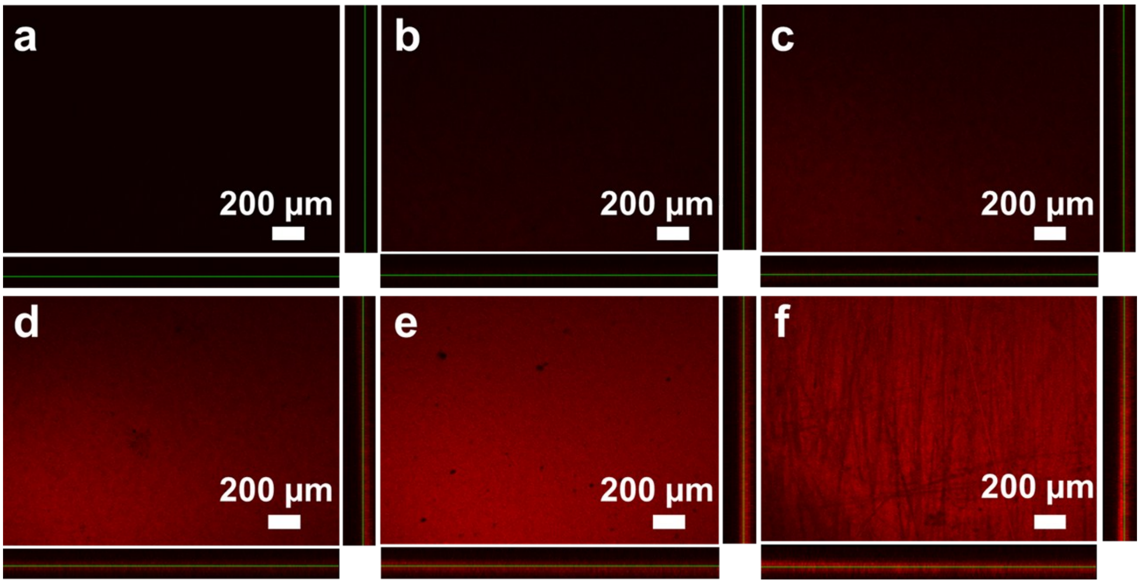

Fig. S5 LSCM images of the surface (large area) and the cross section (right and bottom bar) of the $AuNC_x$-CNC films (a to f: x = 0, 0.5, 1, 2, 3 and 4).

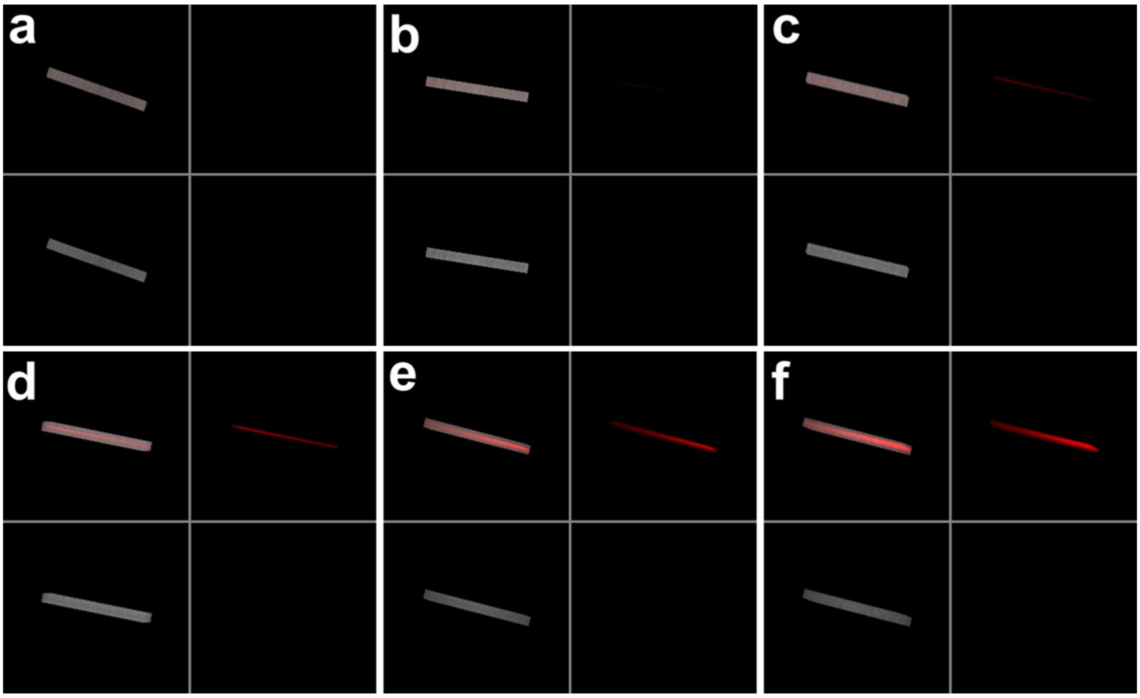

Fig. S6 Three-dimensional images of AuNC$_x$-CNC films (a to f: x = 0, 0.5, 1, 2, 3 and 4) showing uniform distribution of AuNC (1260 μm×1260 μm×120 μm).

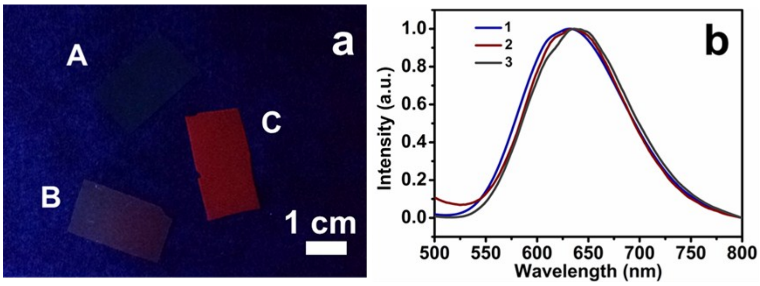

Fig. S7 (a) Photograph of red fluorescent AuNC$_x$-CNC films viewed under 365 nm light (x = 0, 1 and 4 for A, B and C, respectively). (b) Fluorescence emission spectrum: (1) AuNC$_4$-CNC composite film, (2) AuNC$_4$:CNC suspension mix and (3) the AuNC solution, showing redshifted peak position.

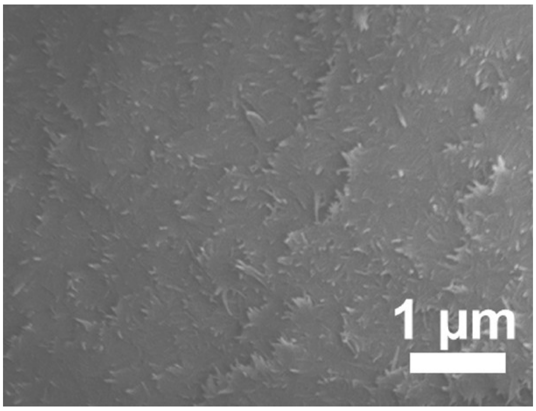

Fig. S8 SEM of a solid film obtained from a AuNC:CNC suspension mix containing 5.0 mL of the AuNC solution, showing no chiral nematic ordering.

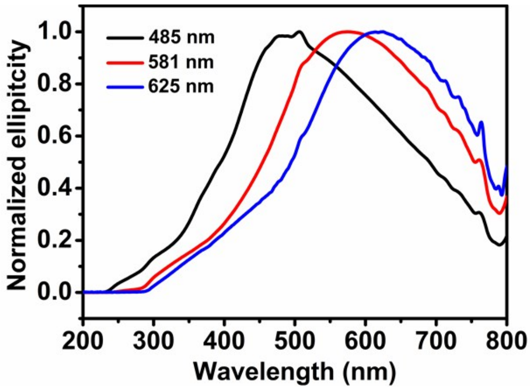

Fig. S9 CD spectra of AuNC$_1$-CNC films with different stopband positions.

Table S2 The photoluminescence decay time constant of AuNC$_1$-CNC ($\lambda_{stopband}$) of varying stopband position.

Code	Decay time constant (μs)	
	τ_1	τ_2
AuNC$_1$-CNC film (485 nm)	0.008	1.183
AuNC$_1$-CNC film (581 nm)	0.011	1.228
AuNC$_1$-CNC film (625 nm)	0.012	1.251