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Chiral nematic mesoporous silica films enabling multi-colour and On-Off switchable circularly polarized luminescence

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Experimental Section

Materials

All Chemicals were used as received without further purification. Tetramethoxysilane (TMOS) was purchased from Aladdin Industry Corporation. Cellulose cotton pulp board was purchased from Hebei Paper Group of China. Sulphuric acid (H_2SO_4, AR) was purchased from Beijing Chemical Works. Rhodamine B (CR) was purchased from Beijing Chemical Works. poly[9,9-bis((6-N,N,N-trimethylammonium)hexyl)fluorine-alt-co-(1,4-benzo-{2,1',3}-thiadiazole)] (PFBD) and carbon dots (CDs) were prepared according to reported procedures.[1, 2] Milli-Q water was used for all experiments. The left and right-handed circularly polarizers covering the visible spectra were purchased from Wenzhou Guoyang Glasses Co Ltd.

The extraction process of CNC

For the preparation of CNC, 50 g of bleached commercial cotton pulp was milled using a commercial pulper containing 1000 mL of deionized water, followed by oven-drying. Next, 20 g of milled pulp was hydrolyzed in 200 mL of 64 wt% H_2SO_4 (1 g pulp / 10 ml H_2SO_4) aqueous solution under vigorous stirring at 50 °C for 90 min. The pulp slurry was diluted with a large amount of cold deionized water to stop the hydrolysis, and allowed to precipitate overnight. The supernate was poured out and the remaining suspension was centrifuged three times to remove all soluble cellulose materials. Finally, the white thick suspension was placed into a Millipore ultrafiltration cell (model 8400) to wash with deionized water, dialyzed against slow running water for several days until the pH of solution was stable at about 2.4. The thick pulp slurry from the Millipore cell can be diluted to a desired concentration.[3]

The preparation of CNMS film

150 μL TMOS was added to 5 mL of 3 wt% CNC suspension and stirred at room temperature for 1 h to hydrolyze. Then the mixture was poured into the petri dish with diameter of 5.5 cm to evaporate. After slow evaporation at room temperature, free-standing films of the CNC/silica composite materials were obtained. For pyrolysis of the cellulose, the composite film was heated at a rate of 2 $^oC\ min^{-1}$ to 100 ^oC, kept at that temperature for 2 h, then heated to 540 ^oC at 2 $^oC\ min^{-1}$, kept at that temperature for 6 h. Then free-standing chiral nematic silica films were obtained after cooling to room temperature.[4]

The preparation of $CNMS_n$-RhB film

To obtain composite films with different PBG, CNC aqueous suspension was sonicated using a Sonics Vibra-Cell (VCX-750, Sonics & Materials. Inc) equipped with a 13 mm probe. In a typical procedure, 250 mL of 3 wt% CNC suspension was placed into five 100 mL glass beakers, respectively. Every glass beaker contained 50 mL CNC suspension. Then the suspension in five glass beakers was sonicated at 50% of the maximum power for 0 min, 0.5 min, 1 min, 1.5 min, 2 min. 150 μL TMOS was added to 5 mL of 3 wt% CNC suspension and stirred at room temperature for 1 h to hydrolyze. Then the mixture was poured into the petri dish to evaporate. After slow evaporation at room temperature, free-standing films of the CNC/silica composite materials were obtained. For pyrolysis of the cellulose, the composite film was heated at a rate of 2 $^oC\ min^{-1}$ to 100 ^oC, kept at that temperature for 2 h, then heated to 540 ^oC at 2 $^oC\ min^{-1}$, kept at that temperature for 6 h. After immersed into Rhodamine B solution, free-standing $CNMS_{555}$-RhB, $CNMS_{590}$-RhB, $CNMS_{630}$-RhB, $CNMS_{670}$-RhB and $CNMS_{700}$-RhB were obtained.

The preparation of $(CNMS\text{-}RhB)_y$

To obtain CNMS-RhB films with different thickness, 2 mL TMOS was added into 65 mL 3 wt% CNC suspension and stirred for 1 h to hydrolyze. Then 3 mL, 5 mL, 7 mL ,9 mL, 11 mL, 13 mL, 15 mL mixture were poured into petri dish with a diameter of 5.5 cm, respectively. After slow evaporation at room temperature, different thickness CNC/silica composite films were obtained. For pyrolysis of the cellulose, the composite film was heated at a rate of 2 $^oC\ min^{-1}$ to 100 ^oC, kept at that temperature for 2 h, then heated to 540 ^oC at 2 $^oC\ min^{-1}$, kept at that temperature for 6 h. Then different thickness of free-standing CNMS films were obtained after cooling to room temperature. After immersed into Rhodamine B solution, $(CNMS\text{-}RhB)_{32}$, $(CNMS\text{-}RhB)_{56}$, $(CNMS\text{-}RhB)_{78}$, $(CNMS\text{-}RhB)_{102}$, $(CNMS\text{-}RhB)_{125}$, $(CNMS\text{-}RhB)_{162}$ and $(CNMS\text{-}RhB)_{188}$ were obtained.

The preparation of $CNMS\text{-}RhB_z$

To obtain composite film with different loading amount, different concentration of Rhodamine B solution were prepared. CNMS films were immersed in Rhodamine B solution with 5 ppm, 10 ppm, 25 ppm, 50 ppm, 100 ppm, 200 ppm for 15 min, 30 min, 45 min, 60 min, 75 min, 90 min. After washed with water and dried, weighing the mass fraction of films before and after Rhodamine B infiltration, $CNMS\text{-}RhB_{0.5\%}$, $CNMS\text{-}RhB_{0.9\%}$, $CNMS\text{-}RhB_{1.3\%}$, $CNMS\text{-}RhB_{1.8\%}$, $CNMS\text{-}RhB_{2.4\%}$ and $CNMS\text{-}RhB_{3.8\%}$ composite films were obtained.

The preparation of CNMS-CDs-PFBD-RhB

A certain amount of CDs, PFBD and RhB solution were mixed together. Then CNMS films were immersed into the mixture for some time. After washed with water and dried, CNMS-CDs-PFBD-RhB composite films were obtained.

Characterization

Scanning electron microscopy (SEM) images were characterized on a JEOL-6700F field emission scanning electron microscope at an accelerating voltage of 3 kV. Transmission electron microscopy (TEM) images were conducted on a FEI Tecnai G2S-Twin with a field emission gun

operating at 200 kV. Ultraviolet-visible (UV-vis) spectra were recorded by mounting free-standing films perpendicular to the beam path on a Shimadzu UV-1800 UV-visible spectrophotometer. Circularly polarized luminescence (CPL) measurements were performed with a JASCO CPL-200 spectrometer. Circular dichroism (CD) spectra were recorded on a BioLogic MOS-450 spectropolarimeter with the transmittance mode. The samples were mounted normal to the beam. The helical pitch was tuned by ultrasonic treatment using Sonics VCX750. Polarized optical microscopy (POM) images were conducted on Leica DM400M microscope with images taken by polarizers in a perpendicular arrangement.

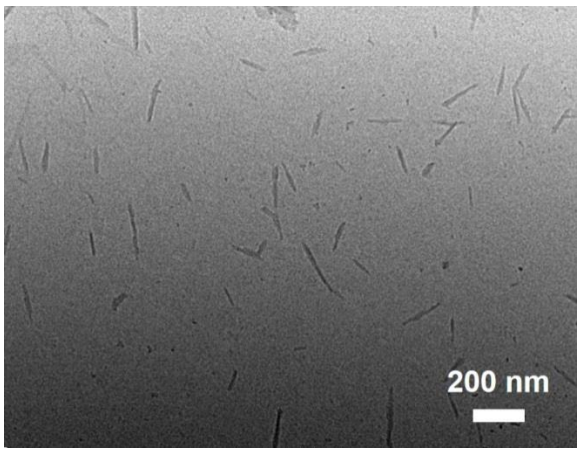


Fig. S1 TEM image of CNC.

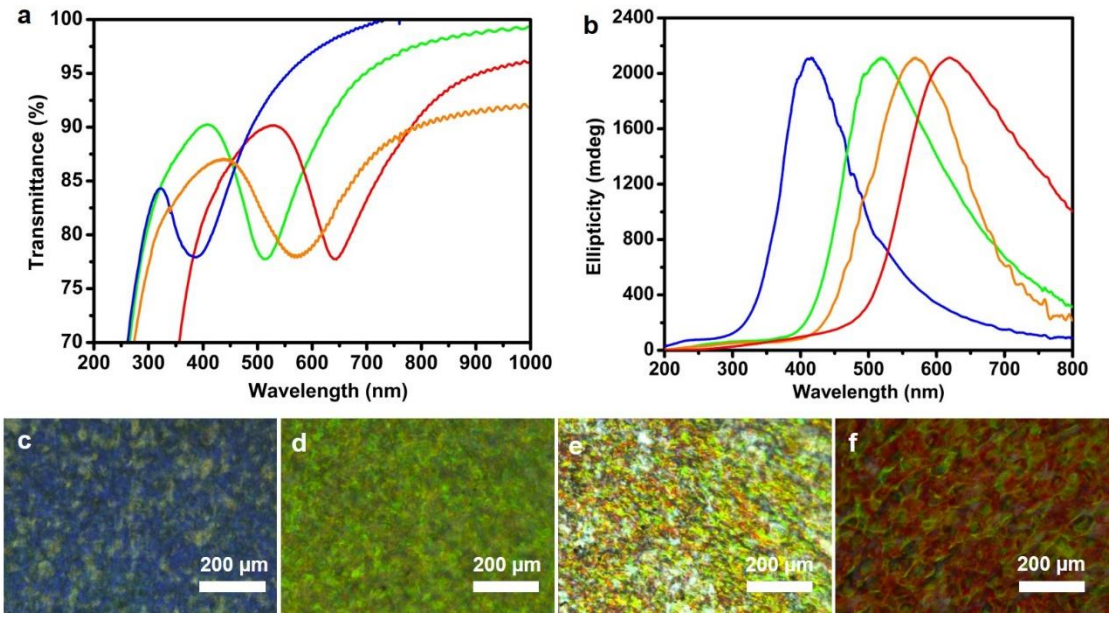


Fig. S2 Characterization of different colors of CNMS films ranging from near UV to near IR. (a) UV-Vis transmission spectra. (b) CD spectra. (c-f) POM images.

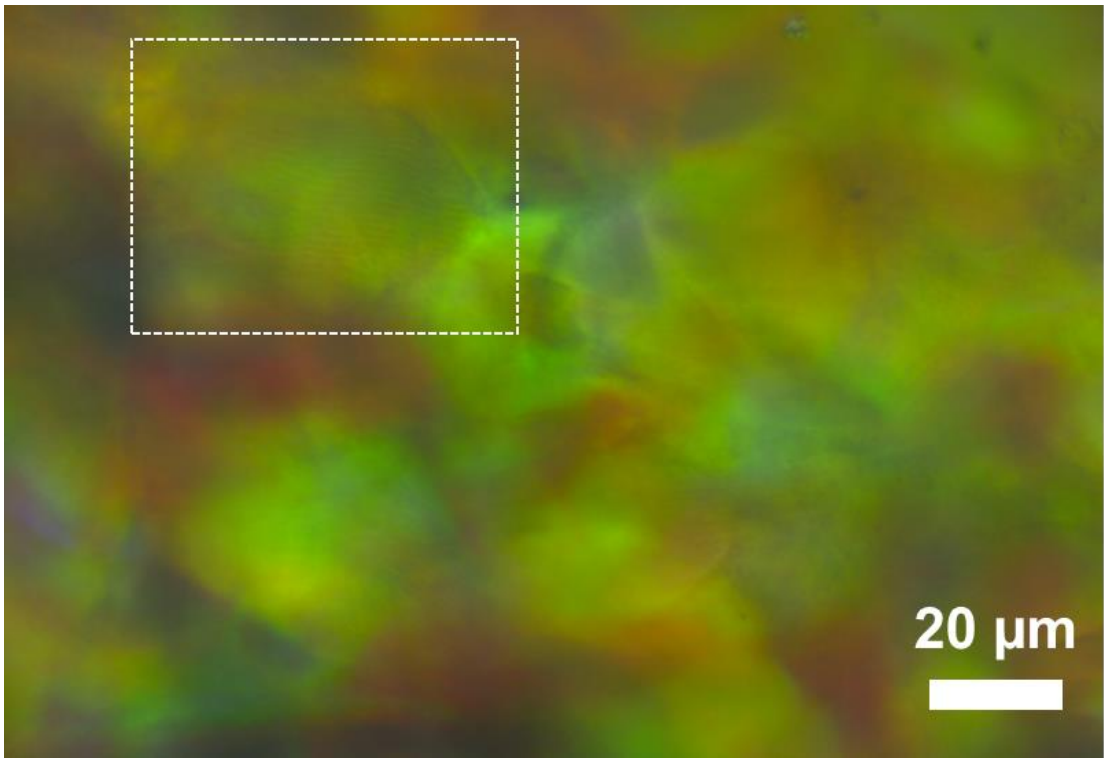


Fig. S3 High magnification POM image with fingerprint texture.

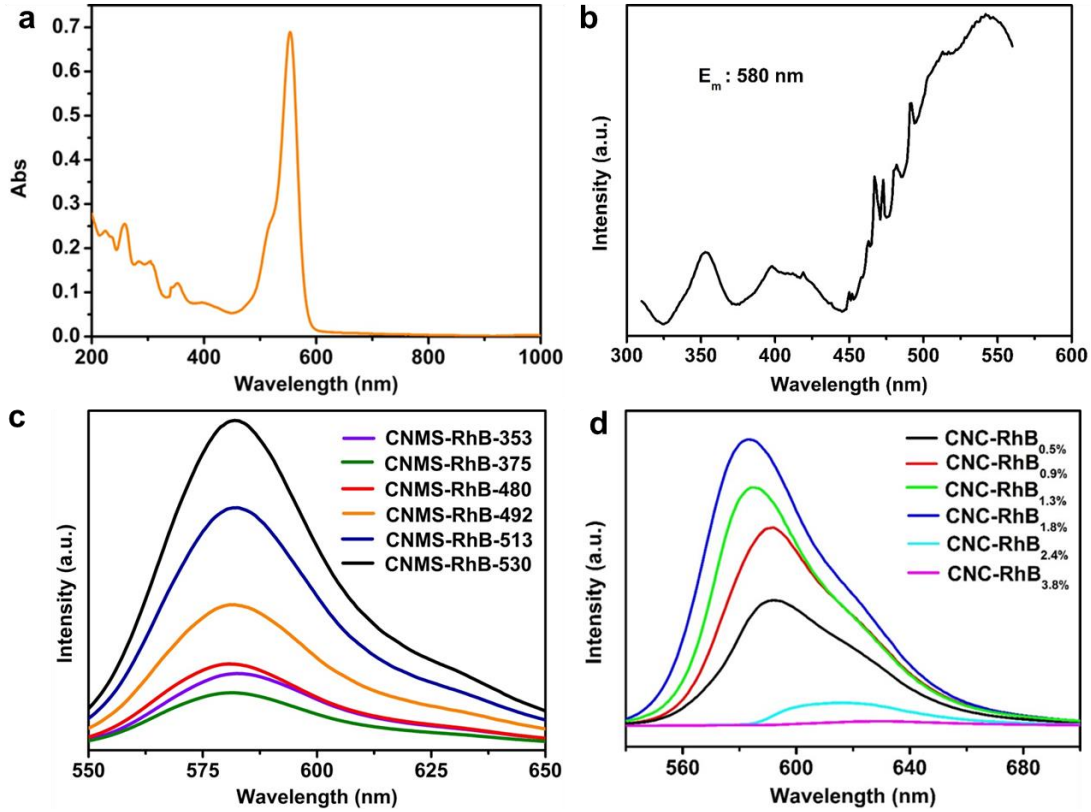


Fig. S4 (a) UV-vis absorption spectrum of Rhodamine B. (b) PLE spectrum of Rhodamine B. (c) PL spectra of CNMS-RhB-x with different excitation wavelength. X = 353, 375, 480, 492, 513, 530. (d) PL spectra of CNMS-RhB_z with different loading amount. Z = 0.5%, 0.9%, 1.3%, 1.8%, 2.4%, 3.8%.

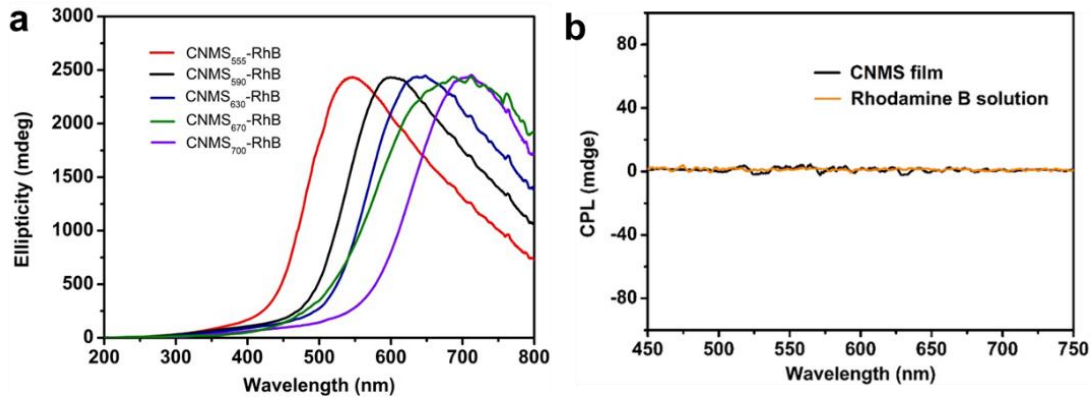
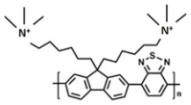
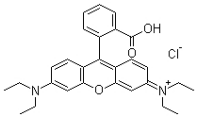


Fig. S5 (a) CD spectra of $CNMS_n$-RhB with different PBG. (b) CPL spectra of neat CNMS film and Rhodamine B solution.

Table S1 Information of luminophores.

Category	**Abbreviation**	**Formula**	**Size (nm)**	**Zeta Potential (mV)**	**λ_{ex} (nm)**	**λ_{em} (nm)**
Carbon Dot	CD		5-12	35.2	365	440
Light-emitting polymer	PFBD		6-30	38.7	420	535
Dye	RhB			34.6	540	590

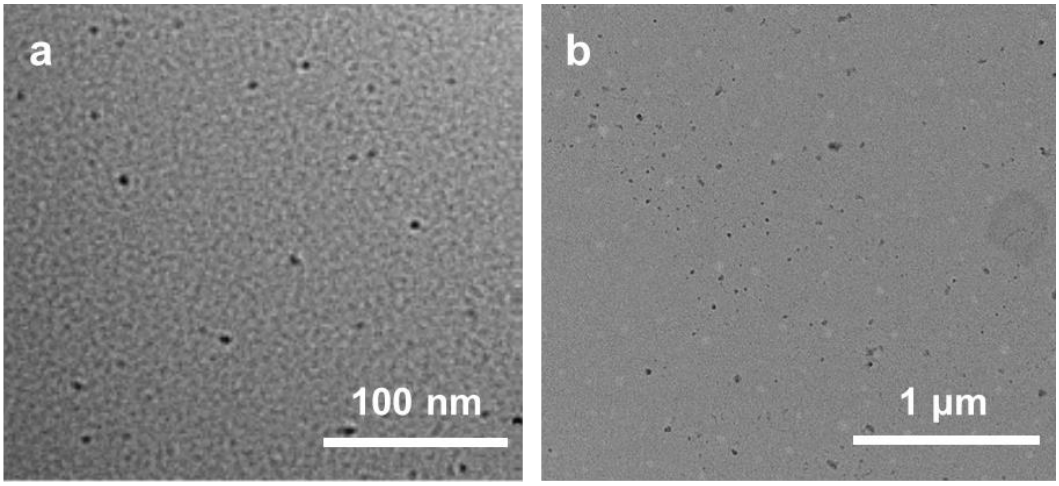


Fig. S6 TEM images. (a) CDs. (b) PFBD.

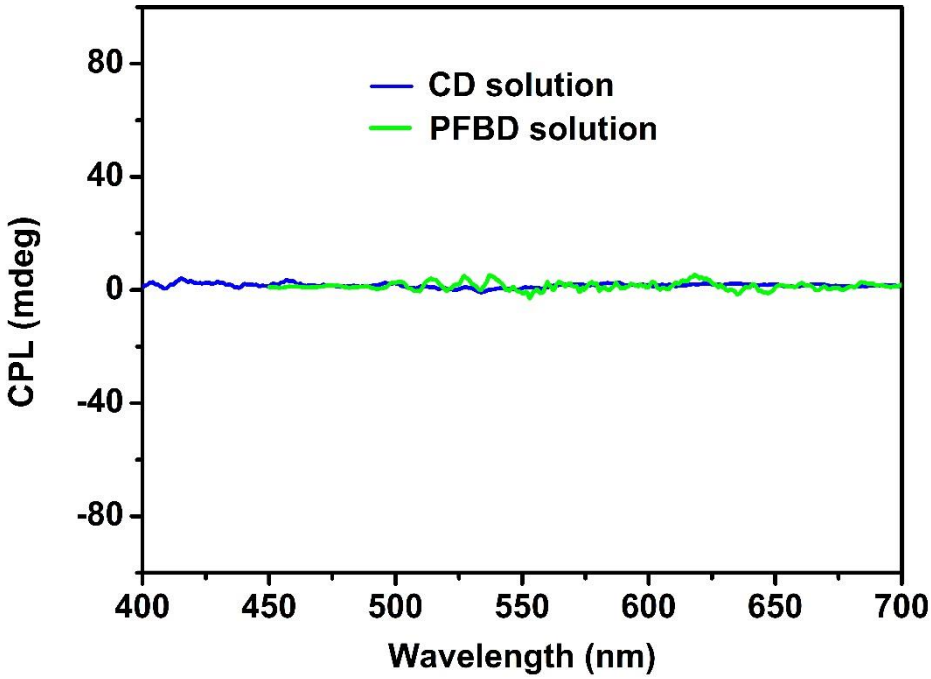


Fig. S7 CPL spectra of CDs and PFBD solution.

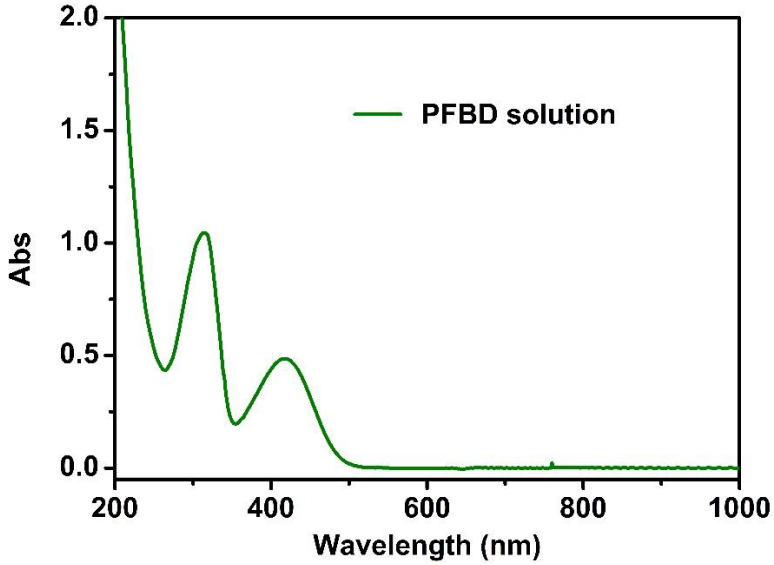


Fig. S8 UV-Vis absorption spectra of PFBD.

References

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