

Bio-organic chiral nematic materials with adaptive light emission and on-demand handedness

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Real-time active control of the handedness of circularly polarized light emission requires sophisticated manufacturing and structural reconfigurations of inorganic optical components that can rarely be achieved in traditional passive optical structures. Here, we report robust and flexible emissive optically-doped biophotonic materials that facilitates the dynamic optical activity. These optically active bio-enabled materials with a chiral nematic-like organization of cellulose nanocrystals with intercalated organic dye and strong circularly polarized photoluminescence with a high asymmetric factor. Reversible phase-shifting of the photochromic molecules intercalated into chiral nematic organization enables alternating circularly polarized light emission with on-demand handedness. Real-time alternating handedness can be triggered by either remote light illumination or changes in the acidic environment. This unique dynamic chiro-optical behavior presents an efficient way to design emissive bio-derived materials for dynamic programmable active photonic materials for optical communication, optical coding, visual protection, and visual adaptation.

1. Introduction

Skins of various creatures such as beetles, birds, fish, and fruits show distinctive structural colors caused by the complex hierarchical organization of the primarily organic constituents.^[1,2,3,4] Such colors originate from the complex interplay of scattering, interference, and diffraction of light. A subset of these biological entities possess chiral mesostructures, resulting in interesting circular dichroism (CD) caused by the selective light reflection of circularly polarized light (CPL).^[5] Such chiral photonic organization at multi-length scales has been used to help living creatures survive in dynamic environments through adaptive appearance, camouflage, and inter-insect communication.^[6] One remarkable example in nature is fireflies, which have left and right bioluminescent organs (lanterns) composed of different chiral photonic nanostructures and chiral dielectric mediums which use selective light reflection for delivering strong optical signals for sexual communication.^[7,8] These organs emit polarized light of both left- and right-handedness by passing through the cuticle layers of its left and right lanterns with different morphologies (**Figure 1a**).^[8]

Among birefringent synthetic materials with a helical arrangement, cholesteric or chiral nematic liquid crystals (LCs), sandwiched between electrodes can be controlled by an external e-field.^[9] To date, artificially structured metal-inorganic materials have been explored to design unusual optical functionalities for 3D optical display, polarization encoding, meta-surface, meta-lens, holograms, stereo displays, complex vortex beams, and optical cloaking.^[10,11,12,13,14] Well-defined freestanding plasmonic gold helices, which predominately interact with light of the same handedness, were fabricated by two-photon direct laser writing.^[15] However, these complex constructs on glass, polymer, and metal substrates are difficult to build into flexible elements and require sophisticated and costly multi-step fabrication processes. Moreover, these structures exhibit significant absorption losses, and are static-by-design and thus lacking the ability to adapt quickly to changing environments.^[16]

Bio-mimicking the unique features of macroscopic chiral mesostructures of living organisms provides a powerful approach to manipulate the optical activity particularly the enhancement of the optical rotation orders of magnitude larger than the intrinsic chirality of naturally occurring materials.^[17,18] Using optical metamaterials integrated with optically-active chiral bio-templates through a simple single-step bottom-up self-assembly process could offer an efficient way to investigate a chiroptical response.^[19,20] A chiral nematic lyotropic LC dispersion of high-aspect-ratio nanocrystals can be processed into a solid films with iridescent structural colors and a left-handed helical sense.^[21] These chiral nematic structures can be integrated with optically active components such as quantum dots (QDs),^[22,23] dyes,^[24,25] and

up-conversion nanoparticles^[26] to generate CPL emission via host-guest co-assembly. Chiral emissive CNC composites with achiral luminophores enable to generate strong passive right-handed CPL emission with high asymmetry due to higher-order organization of macroscopic helical structure of CNCs rather than molecular chirality.^[24] Despite recent progress in the fabrication of chiral emissive materials, CPL emission relies on a passive light source through selective light reflection of chiral nematic structure, limiting static optical activities in CPL emission of solid-state. Although few studies have been focused on enabling both CPL emissions with both handedness by controlling selective reflection with manipulation of helical pitch, the polarization quality of left-handed CPL emission resulting from chiral induced emissive dopants was not comparable with right-handed CPL emission and the mechanism for left-handed CPL emission remained unclear.^[25,27] Furthermore, there have been no attempts to realize real-time switching ability of handedness in CPL emission. Clearly, the direct generation of CPL with dynamic switchable handedness will facilitate application as advanced optical devices such as electro-tunable optical diodes.^[28,29,30] To generate direct emission from achiral optical components embedded into chiral structure, the careful materials design for interaction between the host and guest components in co-assembly process is critically important for realizing tailored chiral induction. Integrating dynamic phase changing elements with chiral geometry for controlling reflection or transmission of light at an interface might provide a platform for dynamic optical functionality.

Hence, we suggested doped chiral nematic materials to control selective reflection or transmission of light propagation for the dynamic optical functionality of flexible and emissive biophotonic composites. We demonstrate robust, flexible, freestanding, emissive bio-enabled materials by integrating phase-shifting organic dye molecules as molecular dopants into chiral photonic biomaterials. These films exhibit dynamic circular polarized emission with on-demand handedness controlled by remote chemical and light stimuli. For this molecular doping, we use spiropyran (SP) organic molecules as the optically active component as they possess excellent photostability, high quantum yields, and multifunctional responsivities. The SP photochromic dopant incorporated into the chiral nematic photonic template of the cellulose nanocrystals triggers the real-time dynamic CPL emission with switchable handedness, which is unachievable in traditional inorganic photonic materials.

2. Results and Discussion

2.1. Hierarchical self-assembly of chiral organization with hybrid CNC-SPs

As known, upon exposure to external stimuli, the ring-closed form SP can reversibly isomerize to the ring-opened form merocyanine (MC) with induced photoluminescence.^[31] In addition, the protonation of MC leads to MCH^+ under acidic conditions with the appearance of a characteristic band at $\sim 420\text{ nm}$.^[31] For the fabrication of optically-active hybrid biophotonic structures, we mixed these photochromic molecules in a LC CNC dispersion (Figures 1b and 1c; Figures S1-S3, Supporting Information). Mixed CNC-SP dispersions exhibited a purple color due to the stable MC dopant in the polar medium and gradually changed back to a colorless appearance due to the reverse dye isomerization when exposed to visible/UV light (Figure 1c).

Subsequently, we confirmed that CNC-SP dispersions gradually changed to protonated merocyanine (MCH^+) form with yellow color under low pH conditions of the CNC dispersion with a sulfonic acid group (Figure 1c). Negatively charged CNC surfaces stabilize MCH^+ entities by Columbic attractions, hydrogen bonding, and Van der Waals interactions between the surface hydroxyl groups and SP molecules.^[32] The effective average diameter of the CNC-SP nanostructure, $4.6 \pm 1.0\text{ nm}$, is close to that of pristine CNCs, $4.4 \pm 0.8\text{ nm}$, indicating an absence of SP aggregation on CNC surfaces when a small amount of SP ($< 0.5\text{ wt.}\%$) is used (Figure 1d; Figure S1, Supporting Information). Evaporation-induced assembly of negatively charged CNC-SP LC dispersions results in the formation of uniform thin films (**Figure 1b**; Figures S2 and S3, Supporting Information).

In this study, we used two types of SP molecules, one with and one without OH^- end groups, to investigate the role of hydrogen-bonding on film properties (Figure S4, Supporting Information). CNC films doped with SP without OH^- groups showed random aggregation of organic molecules (Figure S4, Supporting Information).^[31,33] Doping with OH^- -terminated SP molecules resulted in a uniform film confirmed by atomic force microscopy (AFM) with vivid structural colors and characteristic fingerprint-like textures with random orientation of the microscopic LC tactoids (Figures 1e-g; Figure S5, Supporting Information). Brilliant photoluminescence with a fingerprint pattern is characteristic of these CNC-SP films in contrast to the conventional CNC films which exhibit no photoluminescence (Figure 1h).^[22]

The OH^- end group in the SP molecule facilitates intermixing due to better solubility in water and the hydrogen-bonding network formation as confirmed by FTIR (Figure S6, Supporting Information). The spectra of pure CNC films show characteristic peaks at 3338 and 3290 cm^{-1} , corresponding to an intermolecular hydrogen bonding network.^[34,35] The C-H stretching at 2904 cm^{-1} is observed for all CNC-SP materials, and the stretching vibration of the hydroxyl

groups in hybrid CNC-SP nanostructure can be found in the 3000-3600 cm^{-1} range, confirming that the presence of SP did not disturb the network of hydrogen bonds of the CNC.

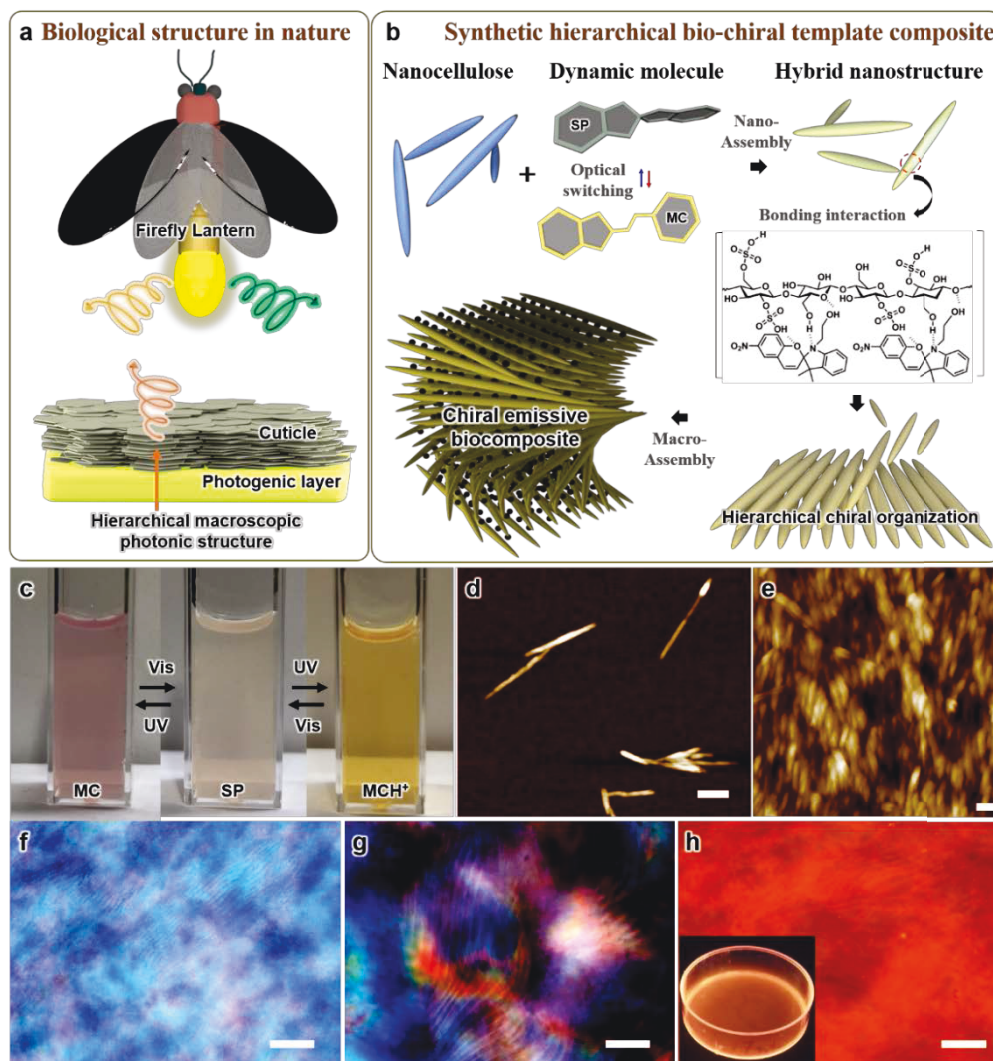


Figure 1. Hybrid chiral CNC-SP nanostructure. Schematic illustration for a) hierarchical macroscopic biological structures from lanterns of fireflies generating bioluminescence with both CPL handedness and b) hierarchical assembly process to fabricate bio-inspired, macroscopic, chiral emissive CNC-SP nanostructure. c) Photographs of CNC-SP dispersion treated by UV light (left), visible light (middle), and under acidic environments (right). AFM image of surface morphology of d) individual CNC-SP hybrid nanostructure and e) solid CNC-SP films e. The scale bar is 100 nm. Optical microscope image of assembled hybrid chiral CNC composite film with SP functionalized with hydroxyl group under f) bright-field mode and g) dark-field mode without cross-polarizer. The scale bar is 10 μm . h) Fluorescent microscope image of chiral emissive hybrid CNC-SP films showing bright photoluminescence with fingerprint features. Scale bar is 10 μm . Inset image indicates as-fabricated hybrid CNC-SP films on petri dish (60 mm $\times$ 15mm) under 365nm UV light.

With the addition of a small amount of SP, the C-H bond undergoes a small shift from 2904 cm^{-1} to 2914 cm^{-1} .^[36,37] A new peak at 2850 cm^{-1} belongs to the symmetric stretching modes

of the $-\text{CH}_2$ in SP.^[38] The CH_2 symmetric stretching $\nu_{\text{sym}}(\text{CH}_2)$ peak can be utilized to analyze the packing of SP molecules on CNCs.^[39] It is known that for ordered crystalline structure the $\nu_{\text{sym}}(\text{CH}_2)$ peaks shift below 2852 cm^{-1} , whereas less ordered structures possess blue shift. The $\nu_{\text{sym}}(\text{CH}_2)$ peak shift from 2867 cm^{-1} to 2849 cm^{-1} in CNC-SP materials indicates the ordered assembly of SP molecules on the CNC surface (Figures 1b; Figure S6, Supporting Information). The CNC-SP form free-standing films with excellent mechanical strength compared to traditionally brittle CNC films with an ultimate strain of $2.6 \pm 0.4\%$ and a strength of $34.5 \pm 5\text{ MPa}$ (**Figures 2a-c**).^[40]

In contrast, CNC-SP films show vastly improved mechanical performance with an ultimate strain of $5.8 \pm 0.8\%$, a mechanical strength of $58.7 \pm 8\text{ MPa}$, and a three-fold higher toughness, $0.34 \pm 0.04\text{ MJ m}^{-3}$ vs $0.09 \pm 0.03\text{ MJ m}^{-3}$ (Figure 2c; Figure S7, Supporting Information). This enhancement can be attributed to additional energy dissipation during deformation caused by small molecule physical crosslinking via hydrogen-bonded network due the presence of hydroxyl end groups.^[41,42]

All CNC-SP films with different SP concentration (0.3 - 2.0 wt.%) possess vivid structural colors due to Bragg reflection from the periodic helical organization (Figure S8, Supporting Information). The CNC-SP films show a predominantly blue color and random tactoid orientation similar to the pristine CNC films (Figure S8, Supporting Information).^[43]

SEM images of film cross-sections confirm chiral nematic organization with a Bouligand layered morphology, well-defined sub-micrometer pitch length, and the absence of microscopic phase separation of the SP dopant (Figure 2d). A further increase of SP concentration (up to 10%) interrupts the helical organization and results in optical losses and the disappearance of the iridescence (Figure S9, Supporting Information).

Finally, as-fabricated CNC-SP films showed clear difference under left- and right-circular polarizers due to the selective light reflection of left-handed CPL caused by the helical organization (Figure 2e). The optical behavior of the CNC-SP films changes after UV-illumination at 365 nm (Figures 2f and 2g). Transmission UV-vis spectra for pure CNC films show a traditional peak at 325 nm wavelength caused by a photonic bandgap related to the pitch length of a chiral nematic structure (Figure 2f).^[44]

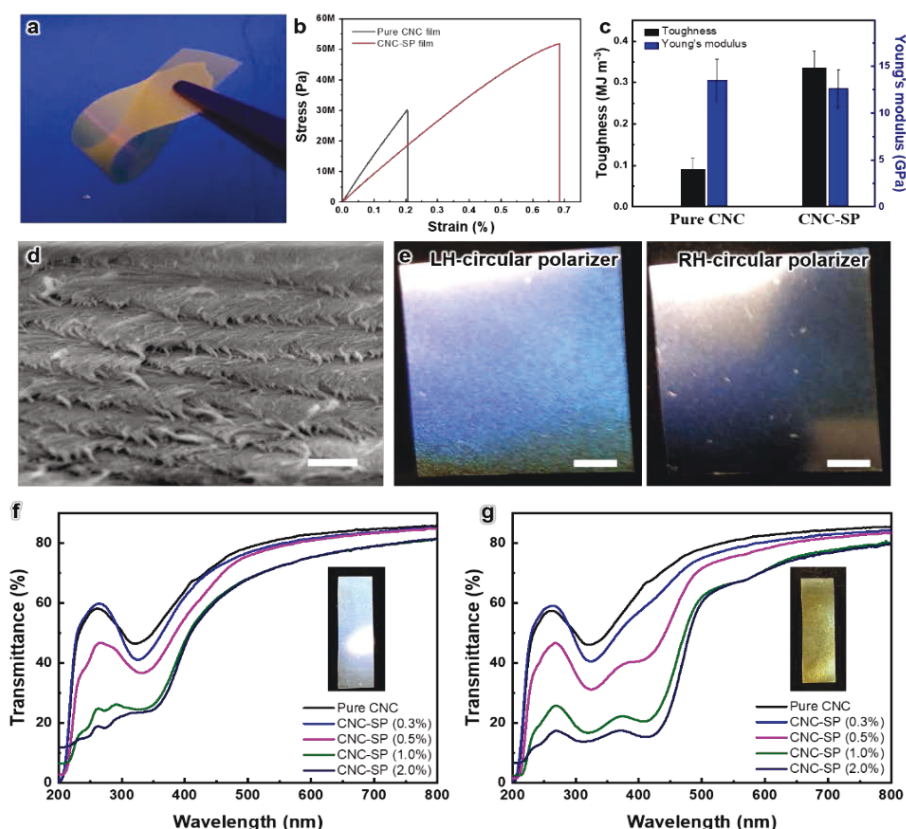


Figure 2. Properties of free-standing CNC-SP films. a) Photograph of free-standing bended chiral emissive CNC-SP film under 365 nm UV light. b) Representative stress-strain curves of pure CNC films and CNC-SP films with 1 wt.% of SP loading. All films were cut into 2 mm x 40 mm samples. Five samples for CNC and CNC-SP films were collected for each mechanical test. c) Comparison of mechanical performance in toughness and Young's modulus for pure CNC films and hybrid CNC-SP films. d) SEM image of a cross-section of the interior layer of the CNC-SP films with periodic chiral organization. The scale bar indicates 500 nm. e) Photographs of hybrid CNC-SP films under left-handed circular polarizer (left) and right-handed circular polarizer (right). Scale bars indicate 4 mm. Transmittance spectra of f) as-prepared CNC-SP films and g) UV-treated CNC-SP films with increasing SP concentration. Inset images show corresponding CNC-SP films before/after UV light irradiation.

In general, the photonic band gap of CNC composite films increases with increasing the concentration of dopant to 30-50%, leading to an increase of helical pitch distance.^[35] However, with increasing SP concentration to 2 wt.%, overall transmittance decreases due to SP absorption, and no significant shift of photonic bandgap is observed because a small amount of SP molecules doped to nanocrystals does not affect the helical pitch (Figure 2f; Figure S10, Supporting Information). In contrast, under 365nm light, CNC-SP films exhibit two peaks at ~325 and ~420 nm caused by a phase transition to MCH⁺ phase that are overlapped with the photonic peaks (Figure 2g). Coupling of chiral photonic properties of CNC host matrix and

switchable photochromic absorption of SPs results in the rich optical appearance of CNC-SP films with complex coloration (Figures. 2f and 2g).

2.2. Induced chirality of emitted light

The addition of SP molecules into the baseline chiral photonic organization causes active left-handed CPL emission with large asymmetry (**Figure 3a**). The key features for obtaining active CPL emission with high asymmetry are the formation of a twisted stacking of SP molecules due to a high helical twisting power of chiral CNC templates, affecting light polarization.^[41, 42, 45, 46] To elucidate and confirm the optical activity of SP embedded into helical organization through host–guest interaction and the hierarchical self-assembly, we investigate the chiroptical properties of CNC-SP films as a photochromically reversible system. To assess the chiroptical properties of these CNC-SP films, CD measurements were compared to those of pure CNC and SP films (Figure 3b).

Both the CNC-SP and pure CNC films show positive CD peaks, indicating left-handed chirality, while pure SP films do not show any CD signal confirming their achiral character (Figure 3b). Interestingly, the positive CD peaks for CNC-SP films are red-shifted compared to that of pure CNC films, while the photonic bandgap of CNC-SP films is not changed (Figures S10 and S11, Supporting Information).^[47] The gradual reduction of CD peak intensity is caused by the absolute reduction of light intensity due to light extinction by the SPs molecules (Figure S11, Supporting Information). The positive CD peak is related to the composite handedness of chiral nematic CNC-SP films with the peak position determined by the position of maximum absorption of the individual components in the case when the photonic bandgap wavelength of the films overlaps with the absorption band of doping molecules.^[47] Under 365 nm UV irradiation, CD spectra for CNC-SP films showed local reduction of the CD signal caused by optical absorption of MCH⁺ whose wavelength is matched to the spectral position of small dips at the wavelength of 425 nm, resulting in the appearance of an induced CD peak (Figure 3c; Figures S11 and S12, Supporting Information). Notably, we observed that there is no apparent induced CD peak caused by optical coupling of CNC-SP when photonic bandgap wavelength of the films is far away from optical absorption wavelength of SP (Fig. S12).

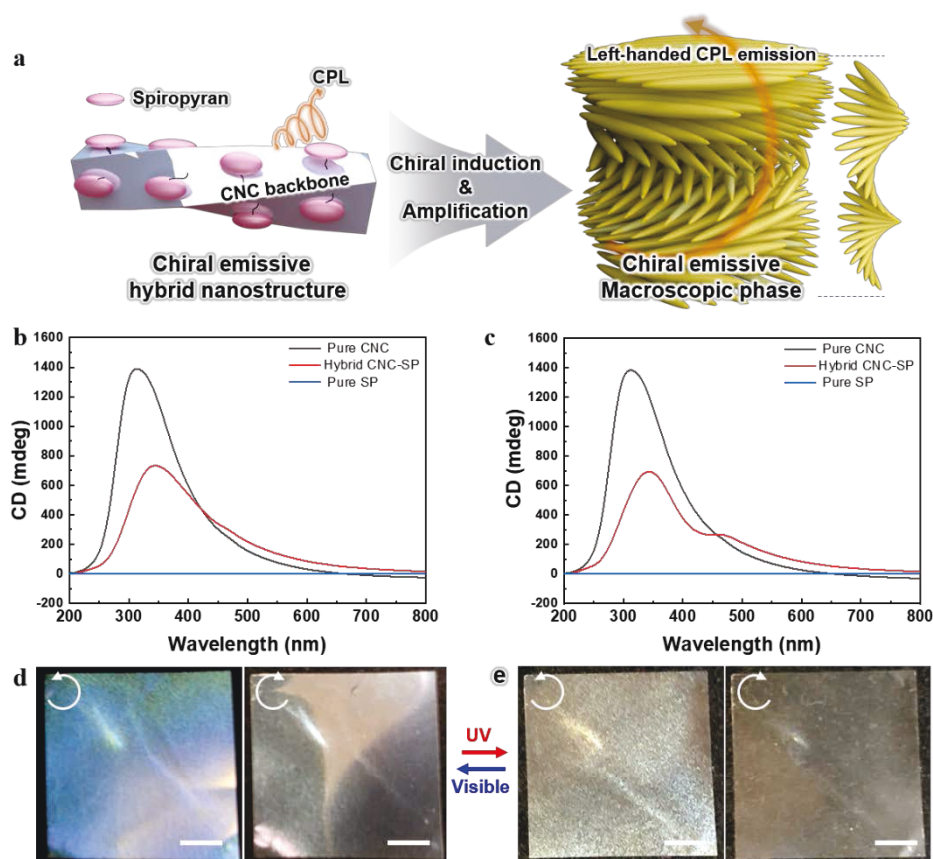


Figure 3. Dynamic chiro-optical behavior of CNC-SP films. a) Schematic illustration of chiral induction and amplification of SP via hierarchical self-assembly of macroscopic chiral nematic hybrid CNC-SP films enabling dynamic color changes due to tunable optical behaviors combined with Bragg's reflection and photo-switchable absorption of SP. b, c) CD spectra of as-fabricated pure CNC, CNC-SP, and SP films under b) visible light and c) 365 nm UV light, respectively. d, e) Photographs of hybrid CNC-SP films under left-handed circular polarizer (left) and right-handed circular polarizer (right) after d) the irradiation of visible or e) UV light, respectively.

Unique chiroptical behavior of CNC-SP films can be attributed to both the light reflection due to the chiral nematic structure and the light absorption in a chiral environment when the dimensions of the achiral guest are much smaller than the host's nanocrystal dimensions (Figure 3a).^[47] Remarkably, photonic structure-induced blue coloring of CNC-SP films combined with photochromic absorption of MCH^+ (yellow) showed a clear difference in optical density under left- and right-handed circular polarization (Figures 3d and 3e).^[45] Thus, this behavior indirectly supports the idea that SP molecules are incorporated into the chiral structure and are organized along the nanocrystals, leading to chiral induction with large optical activity that facilitates active left-handed CPL emission with high asymmetry.

2.3. Switching handedness of CPL emission

In order to characterize the photoluminescence of CNC-SPs, the fluorescence spectra of pure SP solutions and CNC-SP dispersions with different SP content were directly compared (Figure S14, Supporting Information). At all SP concentrations, CNC-SP dispersions showed higher photoluminescence compared with that of the pure SP solution that can be attributed to the reduced aggregation of intercalated SP dopants (Figure S14, Supporting Information).^[48]

The highest photoluminescence intensity was observed at 0.5% of SP, and above this concentration, gradual quenching of the photoluminescence occurs due to MC aggregation (Figure S14, Supporting Information). Although the spiropran molecule is modified with hydroxylic group to induced hydrogen bonding with CNCs, spirpyrans are easily aggregated in the water at high concentration because of aggregation, resulting in fluorescence quenching.³¹ Such aggregates might affect the formation of chiral nematic phase of CNC-SP, diminishing local twisting abilities of CNC-SP and reducing CPL emission. To evaluate CPL emission in CNC-SP suspension, photoluminescence was measured using left- and right-handed circular polarizers (Fig. S15). No chiral emission was observed for the SP solution, while CNC-SP suspension shows favorable right-handed CPL emission for a 0.5% - 2 % SP content due to chiral induction of spiropyran decorated in the surface of individual CNCs.^[49,50]

We further investigated the CPL behavior of CNC-SP films produced with different SP doping concentration via evaporation-induced self-assembly process. As a result, CNC-SP films exhibit bright emission with a high asymmetric factor. In fact, strong left-handed CPL emission at 640 nm was observed for the 0.5% CNC-SP film (Figure S16). The intensity of the left-handed CPL channel is much higher than that of the right-handed CPL channel due to direct light propagation without any disturbance of the photonic bandgap at 325 nm (Figure S16). It can be suggested that spiropyran molecules are attached to the surface of individual nanocrystals with hydrogen bonding inducing chirality amplification and enabling direct left-handed CPL emission with high asymmetry when the photonic bandgap does not interfere with the emission wavelength.

The CD asymmetric factor of the CPL emission, $|g_{lum}|$, is determined using the following equation:

$$|g_{lum}| = \frac{2 \times (I_L - I_R)}{(I_L + I_R)} \quad (1)$$

where I_L and I_R are the photoluminescence intensity observed in left- and right-handed polarization, respectively.^[51] Minimal doping of SP into the chiral nematic structure results in a high asymmetry of 0.39 (**Figure. 4a**; Figure S16, Supporting Information). The CPL emission of CNC-SP films with different photonic band gaps was monitored (Figures S17 and S18, Supporting Information). The photonic bandgap of the films can be manipulated by controlling

the CNC interactions using sonication prior to film casting, leading to an increase of helical pitch distance, due to increased ionic strength of CNCs (Figures S17).⁵² Calculated $|g_{\text{lum}}|$ values reach 0.2 below 550 nm and decrease to -0.2 to -0.4 for higher wavelengths of photonic bandgap (Figure 4b). Thus, left-handed CPL emission of CNC-SP films switched to right-handed CPL emission for a photonic bandgap above 550 nm (Figure 4b; Figure S18, Supporting Information). Strong right-handed CPL emission was obtained when the photonic bandgap and emission wavelength were matched, leading to the preferential reflection of left-handed CPL (Figure S18, Supporting Information). Once the photonic bandgap is close to the photoluminescence emission peak position, the selective light reflection induced by chiral nematic structure of CNC with left-handed helical sense and acting as CPL filter enables control of the passive right-handed CPL emission. In the contrary, direct light propagation generated by chiral-induced spiropyran in helical organization enables left-handed CPL emission when photonic bandgap does not overlap with emission band (Figure 4b).^[24] Overall, chiral photoluminescence can be selectively generated with a high contrast of left- and right-handed CPL emission by controlling the photonic bandgap, leading to forbidden propagation with the same handedness and direct light propagation without disturbance of the photonic bandgap.

To further assess the control ability of spontaneous chiral photoluminescence, we fabricated CNC-SP films with a 645 nm photonic bandgap, enabling strong right-handed CPL emission due to selective reflection contribution of left-handed CPL (Figure 4c). Initially, CNC-SP films showed extremely low photoluminescence under 365nm UV light illumination due to the closed-form SP molecules (Figure 4c, left). After SP molecules isomerize to MCH^+ form, the film shows strong chiral photoluminescence at a 640 nm wavelength (Figure 4c, middle). Such reversible isomerization of the SP to MCH^+ form facilitates the on/off chiral photoluminescence of CNC-SP films (Figure 4c). This unique behavior can be controlled reversibly and remotely by changing the light source between UV and visible light.

UV-treated CNC-SP films can also be converted to the MCH^+ phase by remotely exposing them to acidic environmental conditions. This chemical conversion generated intense green chiral photoluminescence (after drying at 60°C) due to reversible proton dissociation where the phase transition from MCH^+ to protonated ring-closed SP (SPH^+) occurs upon isomerization (Figure 4c, right).^[31,53] Structural photonic colors are not significantly affected by the reversible isomerization process (Figure S19, Supporting Information). However, fast dynamic changes were observed for CPL emission upon exposure to chemical stimuli with a real-time response within few seconds (Video S1 in Supporting Information).

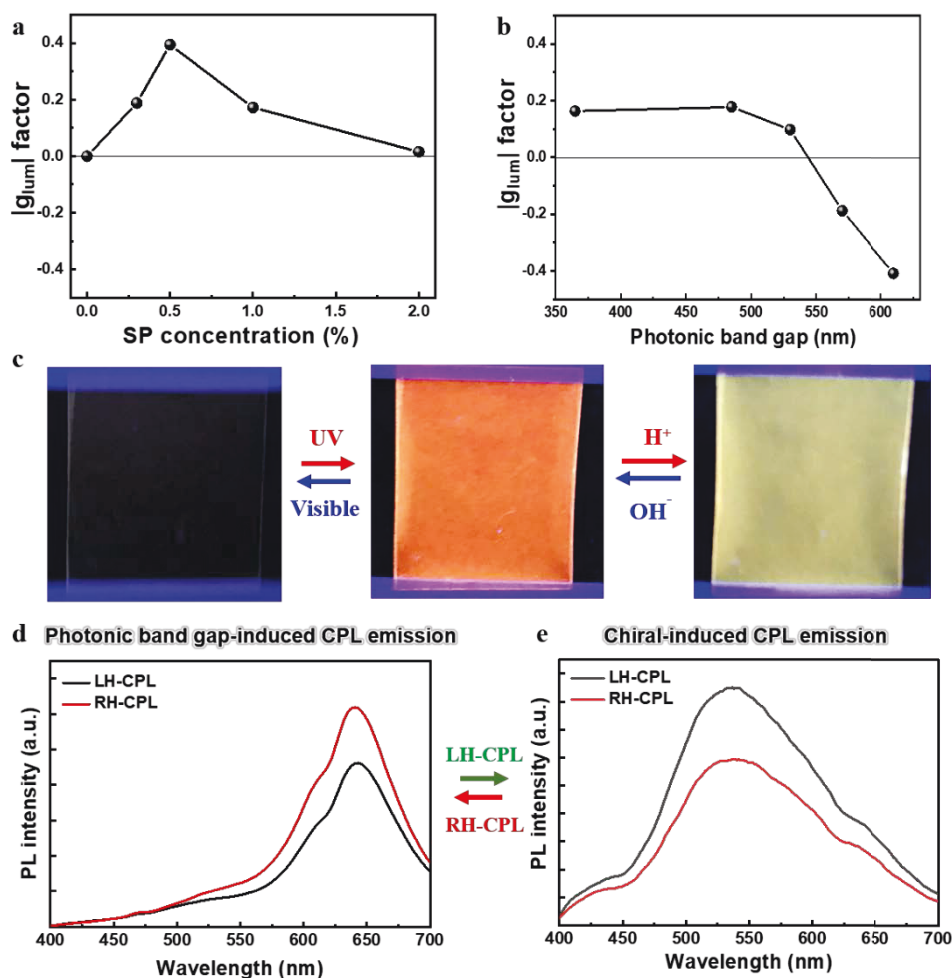


Figure 4. Switching CPL emission with different handedness. a) $|g_{lum}|$ value of CPL emission for hybrid CNC-SP films fabricated by different doping concentration of spiropyrans with 325 nm photonic band gap. b) $|g_{lum}|$ value of CPL emission for hybrid CNC-SP films with different photonic band gap wavelengths, calculated from photoluminescence intensities measured under left- and right-handed circular polarization. Spiropyrans were used with 0.5 wt.% of doping concentration for all CNC-SP films. c) Photographs of hybrid chiral CNC-SP films without further treatment (left), with remote treatment by water vapor (middle) and citric acid vapor (right), showing dynamic chiral emission at a different wavelength under 365nm UV light. Photoluminescence spectra of chiral emission at different wavelengths for hybrid CNC-SP films treated by d) water vapor and e) citric acid vapor.

For chiral emission at 640 nm, we confirmed that CNC-SP films generate right-handed chiral emission due to selective left-handed CPL reflection from the left-handed helical organization of CNC (Figure 4d). In contrast, strong left-handed CPL emission of CNC-SP films at 535 nm was triggered when the films were exposed to an acidic environment (Figure 4e). The asymmetric factor, $|g_{lum}|$ of 0.61 achieved here is much higher than those reported for chiral-induced CPL emission with CNC materials.^[25,27,50] The origin of active CPL emission in our

work is distinguished with passive right-handed CPL emission with negative g_{lum} value induced by overlapping between photonic bandgap and emission band (Figure S20).^[22,24,25,26]

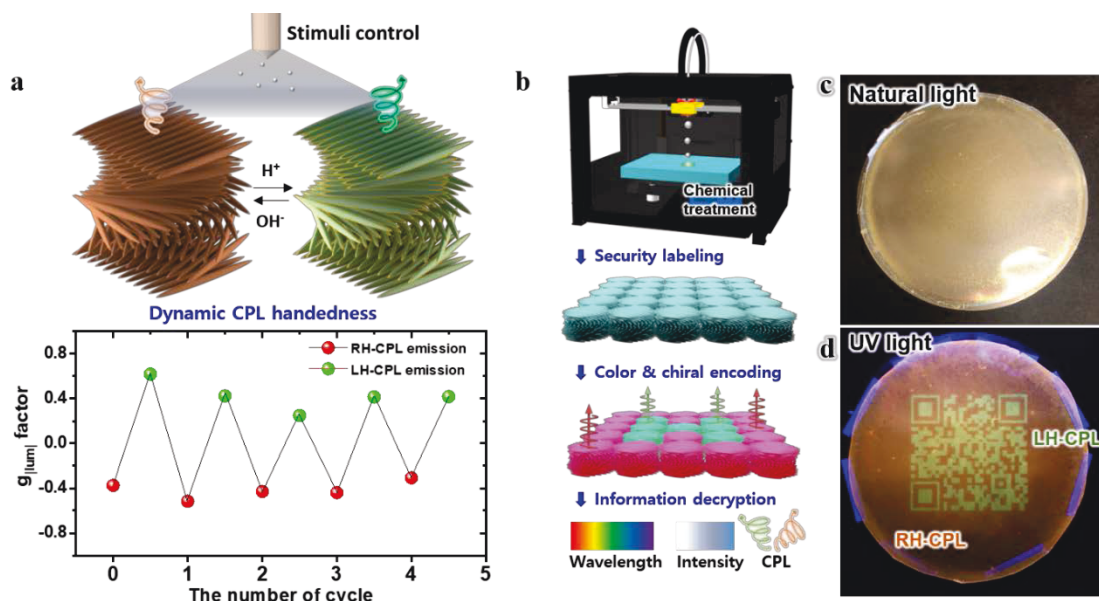


Figure 5. Dynamics CPL in chiral emissive CNC-SP films. a) Schematic illustration with dynamic CPL emission of CNC-SP films under external stimuli (top) and the variation in $|g_{lum}|$ values for dynamic CPL emission of hybrid CNC-SP films (bottom), showing switching ability in CPL handedness during cycling tests with acid and water vapor. b) Chiral patterning with chemical treatment, allowing for the control of chiral emission wavelength and CPL handedness for potential high-level security optical labeling. QR code printed on chiral emissive CNC-SP film using photochemical printing, showing c) uniform appearance under natural light, but d) different green and red CPL emission with opposite handedness under 365 nm UV light.

To further investigate dynamic control of the light emission, we triggered the reversible isomerization of SP molecules by changing the surrounding pH environment through exposure to acid and water vapor treatments in an alternating manner (**Figure 5a**, top). It was confirmed that CNC-SP films enabled dynamic switching of CPL emission handedness without significant degradation of the $|g_{lum}|$ value during multiple repeating cycles (Figure 5a, bottom). During repeated switching, CNC-SP films maintained their initial CD peak position at ~ 640 nm without significant shift, indicating stable photonic organization (Figure S21, Supporting Information).

We further suggest the exploration of dynamic CPL for anti-counterfeiting concept by demonstrating CNC-SP films with different CPL handedness at different emission wavelengths (see Experimental; Figure 5b).^[54] Direct writing of QR code by ink-jet printing with droplets containing an acidic solution, placed on top of chiral emissive CNC-SP films (Figure 5b). In this approach, different patterns can be encoded and triggered by the pH-initiated phase

transition of CNC-SP films. The CPL pattern was invisible under natural light, while the printed QD code became visible under UV light by generating different CPL emissions, green CPL emission vs. red CPL emission, from untreated surrounding areas, which could be decrypted by a QR code scanner, directly connect to the web link of our research group (Figures 5c and 5d).

3. Conclusion

In conclusion, mechanically robust, flexible, and emissive biophotonic materials combined with phase transition of organic dopants exhibiting unique reversible, real-time circular polarization control by light and chemical stimuli. The co-assembly of optically active organic components into the ordered chiral templates enabled the strong chiral-induced left-handed CPL emission with a large asymmetry factor. In these films, dynamic phase-shifting dopants act as built-in triggers to manipulate the overall CPL emission with unique on-demand handedness alternation. The remote control of dynamic light propagation in chiral nematic solid films offers a new design platform for mechanically robust biophotonic materials with dynamic optical properties, which are also lightweight, biocompatible, and biodegradable. This study also highlights the synergistic solid-state active chiroptical flexible materials via facile and ambient-friendly wet-fabrication process.

We demonstrated that concepts of active light emissive bio-organic materials can be further extended to various types of stimuli-responsive optically dynamic applications for seamlessly printed-into CPL-controlled security features and biophotonic sensor elements. The dynamic switching of CPL emission handedness, reconfigured and triggered by phase-shifted photochromic dopant molecules, might lead to the emergence of next-generation optically active chiral ambient-friendly biophotonic materials for encoding security systems and optical memory materials and structures, which are critically important for anticounterfeiting, light waveguiding, sensing, hidden communication, environmental adaptivity, and wearable artificial skin.

4. Experimental Section

Materials: All CNCs used in this study were obtained from soft wood pulp as described earlier.^[55] Spiropyran (1,3,3-Trimethylindolino-6'-nitrobenzopyrylospiran) and OH-functionalized spiropyran (1-(2-hydroxyethyl)-3,3-dimethylindolino-6'-nitrobenzopyrylospiran) were purchased from TCI chemicals. Spiropyranes were dissolved in N-Methyl-2-Pyrrolidone (NMP) before use. All other reagents and solvents used were

purchased through Sigma-Aldrich and used as received. Zeta-potential was obtained with a Malvern Zetasizer Nano ZS.

Materials Preparation of CNC suspension: The CNC suspension was prepared by the well-established sulfuric acid method. The dried soft wood pulp (17.00 g) was hydrolyzed in sulfuric acid (16 mL of a sulfuric acid per gram pulp) with a concentration of 64 wt.% at 45°C with constant stirring for 60 min. The resulting as-synthesized yellow suspension was diluted to 10 times volume with D.I water to quench the hydrolysis. The solution was left untouched for 12 h, during which the hydrolyzed wood pulp separated from the DI water. The upper solution was discarded and the remained suspension was purified twice by centrifuging at 6000 rpm for 5 min to remove extra sulfuric acid. Afterward, the dialysis process was conducted on the re-dispersed suspension with dialysis membrane tubes with a 14 kDa for a week (the water was changed every 6 h) until the pH value of the water was constant. After dialysis, the cellulose dispersion was centrifuged at 10,000 rpm for 20 min, and the aqueous suspension was kept, while the remaining semisolid aggregate at the bottom was discarded. Ultrasonication was carried out on the obtained CNC dispersion with a tip sonicator for 20 min (Qsonica Q125, 700 W) at 50 % amplitude. The CNC solution was concentrated by controlled water solution evaporation. The needle-like CNCs with an average diameter of ~5 nm and length of ~200 nm (Figure S1, Supporting Information) showed long-term stability due to the high surface potential of -48 mV caused by negatively charged sulfate groups (Figure S2, Supporting Information).

Fabrication process for self-assembled chiral luminescent hybrid CNC-SP films: 20 mg of SP was added in 400 µl of NMP solvent to make a uniform SP solution. As-prepared SP solution was added into 10 mL of concentrated CNC dispersion (relative weight ratio of CNC : SP = 99.7 : 0.3, 99.5 : 0.5, 99: 1, 98 : 2 wt.%) and mixed with stirring for 12 hours under visible light to completely form the hybrid CNC-SP individual nanostructures. The mixture was then drop-cast into polystyrene Petri dishes (60 mm in diameter) to allow solvent evaporation-induced self-assembly in air (55% RH, 20 °C) without external environment influences except for ambient air flow throughout the room. After two days of drying, homogeneous, iridescent, and luminescent films were present in the petri dish.

CPL patterning: A piezoelectric ink-jet printing apparatus (JetLabII Inkjet Printer) was utilized with the 40 µm diameter nozzle under an ambient environment condition to generate the chiroptical patterning. Programmed QR code was printed on free-standing CNC-SP films using 10 wt.% citric acid with a volume of ~80 pL at a velocity of ~2 m/s.

Characterization: AFM was conducted to investigate individual CNC-SPs using a Bruker Dimension Icon in soft tapping mode at 0.7 Hz.^[56] The AFM images were acquired using a silicon tip with an 80 kHz resonant frequency and 2.7 N m^{-1} force constant in air. Scans were collected for various surface areas: $5 \times 5 \text{ }\mu\text{m}$, $1.7 \times 1.7 \text{ }\mu\text{m}$, and $500 \times 500 \text{ nm}$, with 512×512 pixel resolution. Samples were spin cast at 3000 rpm using diluted CNC-SP solution onto piranha treated silicon wafers. Nanocrystals dimensions (height) were calculated in the NanoScope software by performing section analysis. All images were flattened prior to measurements and the sections made normal to the nanocrystals. Quantitative nanomechanical mapping (QNM) was conducted to investigate surface morphology and to map the nanomechanical properties of CNC and CNC-SP films using a Bruker Dimension Icon. The CNC and CNC-SP films were scanned in the QNM mode at a scan rate of 0.5 Hz using the resolution of 512×512 pixels. For QNM, AFM probes (MikroMasch, HQ:XSC11/AL BS) were used with spring constants in the range of 1.5–2.2 N/m and a tip radius of $\sim 8 \text{ nm}$. All images were analyzed using Bruker Nanoscope Analysis 2.0 software.

SEM was performed on a Hitachi SU-8230 instrument, using 5 kV accelerating voltage. The SEM cross-sections were obtained by cutting the film with a razor blade and adhering the film pieces with carbon tape on the SEM mount side normal to the surface. Samples were sputter coated with gold for 60 s, for a layer thickness of $\approx 2 \text{ nm}$, prior to SEM analysis.

For measuring mechanical properties of CNC-SP films, a universal tensile tester (Shimadzu EZ-SX 500 N) was used to measure the tensile stress–strain curves of CNC-SP films with a speed of 0.1 mm/min under ambient condition (25 % of humidity). All films were cut into $2 \text{ mm} \times 40 \text{ mm}$ samples. Five samples for CNC and CNC-SP films were collected for each mechanical test, respectively. The cross-sectional area of the film samples, force applied, and displacement were individually recorded. From corresponding stress versus strain curves, the toughness, ultimate tensile strength, elongation to break, and Young's modulus were calculated. Thicknesses of CNC and CNC-SP films were measured by using vernier caliper with $48 \pm 8 \text{ }\mu\text{m}$ and $69 \pm 4 \text{ }\mu\text{m}$, respectively.

Optical microscope images were obtained with an Olympus BX51 microscope in the reflection mode and under bright field with crossed polarizers to characterize the photonic surface of CNC-SP films. The CD spectrum was collected using an Applied Photophysics Chirascan plus. Optical properties were analyzed using UV–vis-NIR (Shimadzu 3600plus). Circularly polarized photoluminescence was characterized using a Shimadzu UV 2450 under a broadband left- and right-handed circular polarizers, respectively.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

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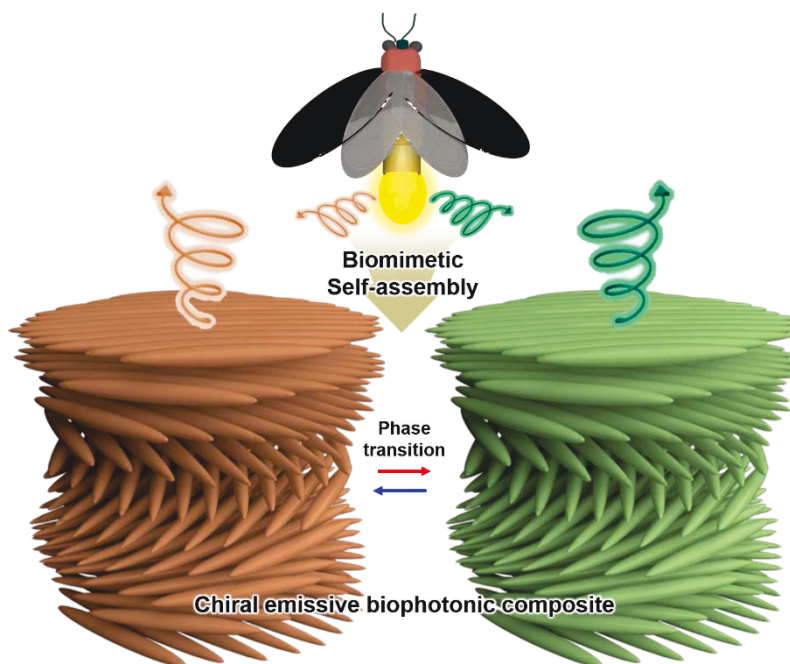
Conflict of Interest

The authors declare no conflict of interest.

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ToC figure (55 mm broad $\times$ 50 mm high)

Robust and flexible chiral emissive bio-nanocomposite with chiral nematic-like organization that mimic biological photonic mesostructure observed in nature are demonstrated. Small molecules built-in chiral mesostructure are assembled along helical arrangement, allowing to generate strong active circularly polarized light emission. Real-time phase transition of the molecules integrated into biophotonic structure enables highly asymmetric circularly polarized light emission with on-demand handedness.

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Supporting Information

Bio-organic chiral nematic materials with adaptive light emission and on-demand handedness

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Keywords: Optically-active bio-nanocomposites, chiral emission, dynamic chirality, chiral nematic materials, reversible handednesses.

Video S1: Dynamic CPL emission

Real-time video streaming of dynamic CPL emission under 365 nm UV light irradiation by remotely spraying water vapor. Green chiral emission with left handed-CPL generated from hybrid CNC-SP films with size of 18 mm x 18 mm, switched to red chiral emission with RH-CPL after a few minutes of drying.

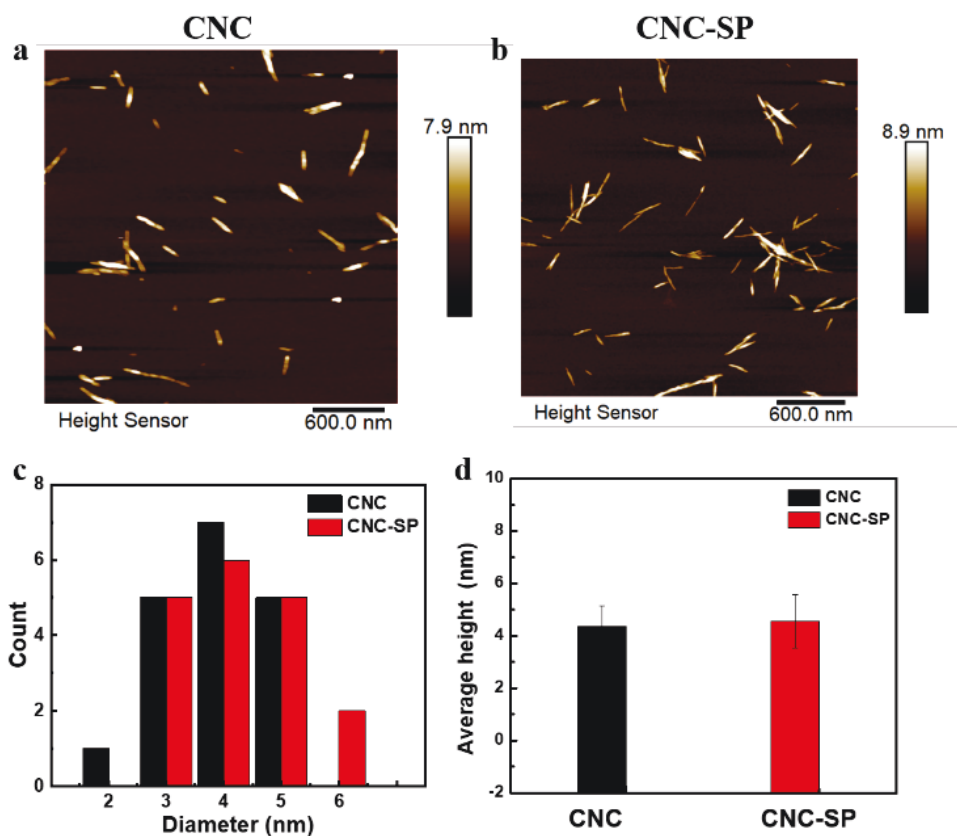


Figure S1. (a, b) AFM images of individual CNC and CNC-SP nanostructures. (c) Diameter distribution of individual CNCs and CNC-SP nanocrystals. (d) Analysis of average height for individual CNC and CNC-SP nanocrystals.

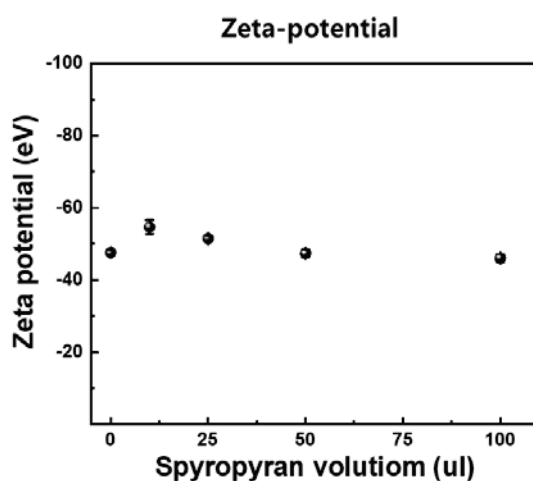


Figure S2. Zeta-potential of CNC and CNC-SP solution with increasing SP concentration.



Figure S3. Photograph of LC phase CNC-SP dispersion under cross-polarizer.

Different chemical structure of spiropyran

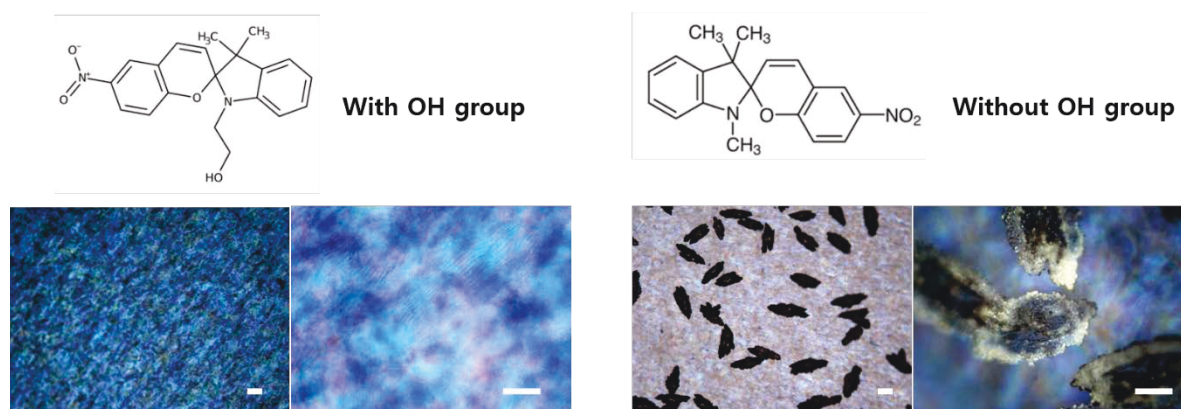


Figure S4. Chemical structure of SP functionalized with/without OH-group (upper). Optical microscope image of assembled hybrid chiral CNC composite film with SP functionalized with hydroxyl group (left) and without hydroxyl group (right) under bright-field mode without polarizer. All scale bars indicate 10 μm .

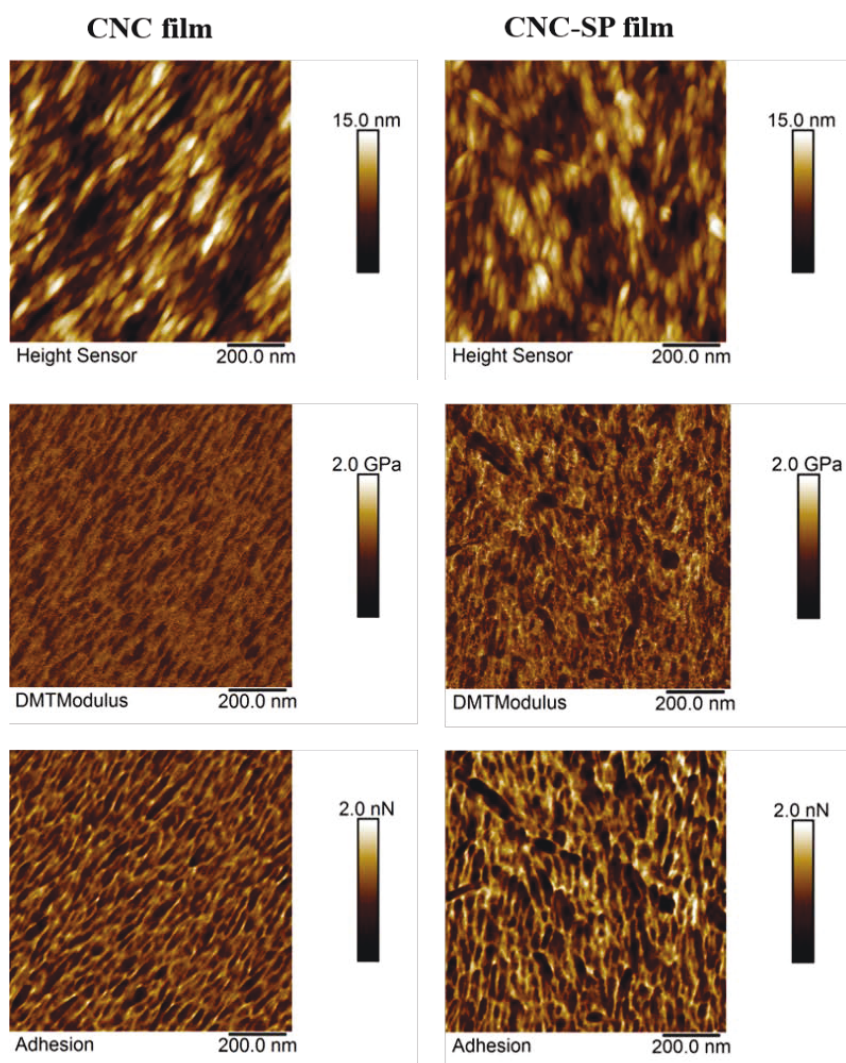


Figure S5. High-resolution AFM-QNM images of CNC films (left) and CNC-SP films (right). The elastic modulus (center) and adhesion (bottom) images. Both films showed uniform distribution in modulus and adhesion without any phase separation.

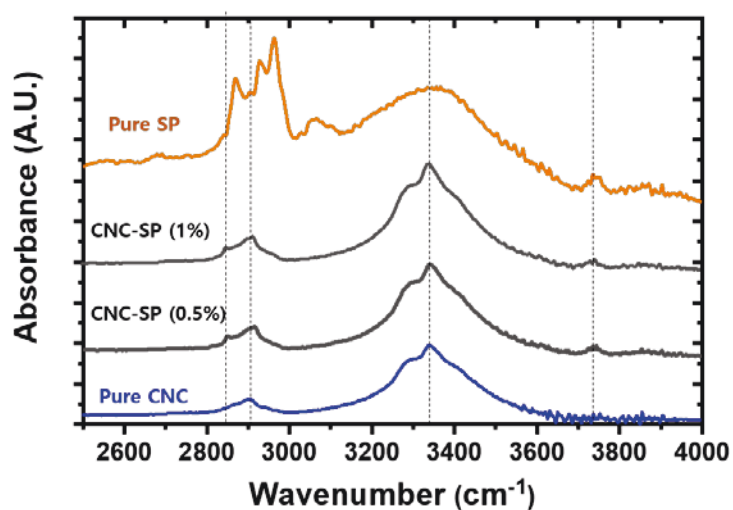


Figure S6. FTIR analysis of pure CNC, CNC-SP, pure SP films.

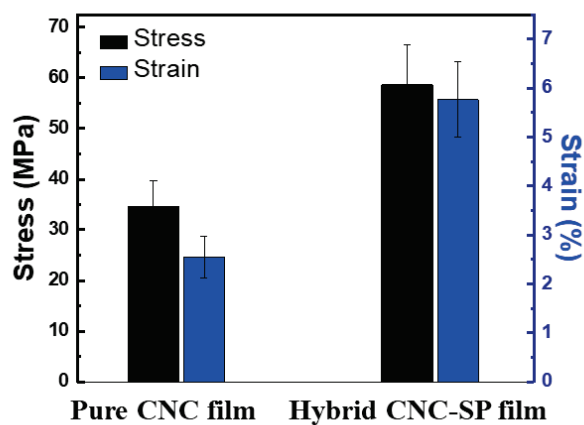


Figure S7. Comparison of mechanical performance in tensile strength and elongation at break for pure CNC and hybrid CNC-SP films.

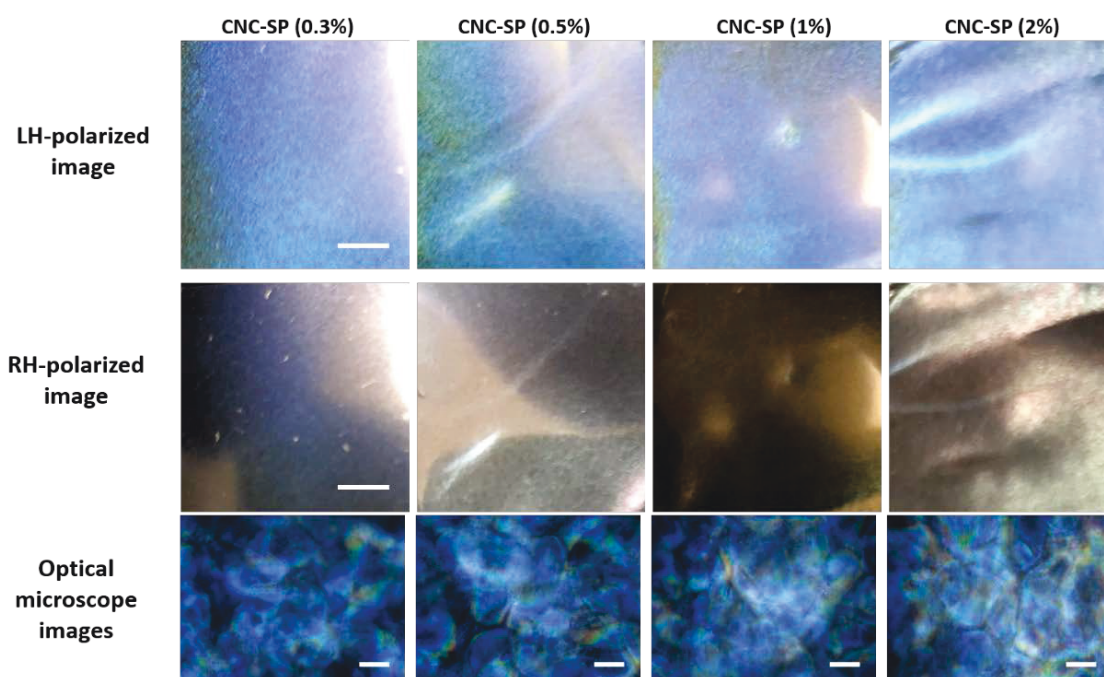


Figure S8. Optical images of hybrid CNC-SP films as a function of SP doping concentration (0.3% - 2%). All hybrid CNC-SP films show clearly different appearance under left- and right-circular polarizer (top and middle, scale bars indicate 5mm). Optical microscope images of corresponding hybrid CNC-SP films under bright-field mode without polarizer. The scale bars indicate 10 μm (bottom).

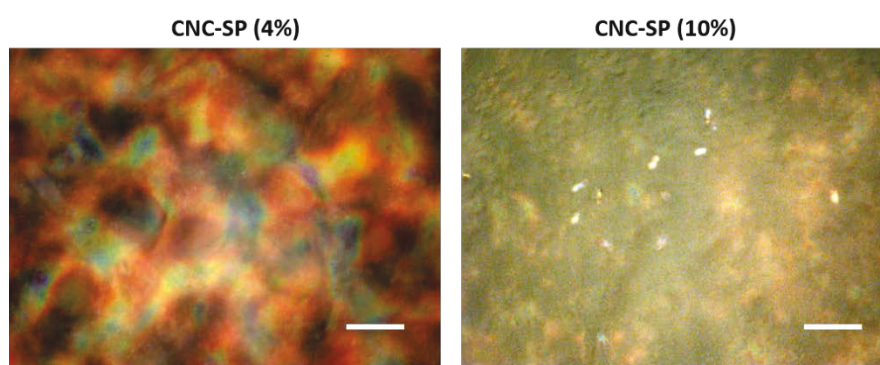


Figure S9. Optical microscope images of hybrid CNC-SP films with 4 wt.% and 10 wt.% doping concentration of SPs under bright-field mode without polarizer. The scale bars indicate 10 μm .

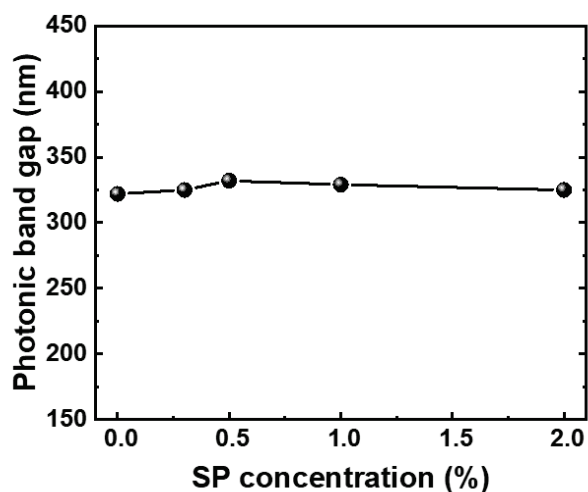


Figure S10. Photonic band gap of hybrid CNC-SP films as a function of SP concentrations, obtained from transmission data.

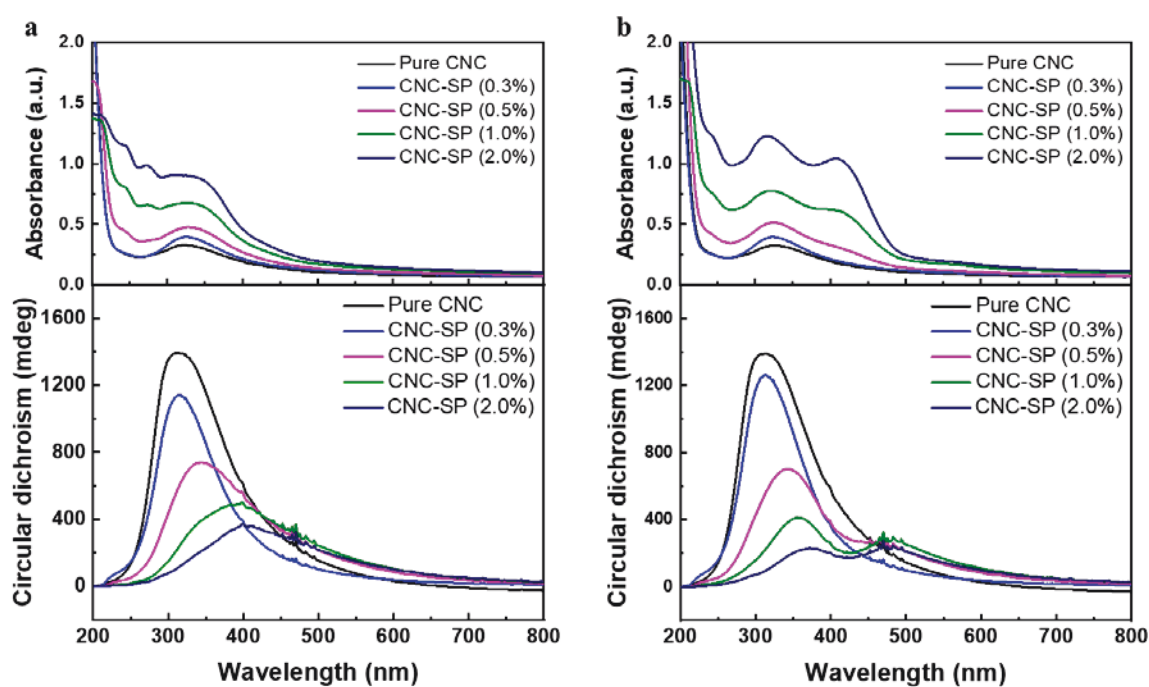


Figure S11. Dynamic chiroptical properties of hybrid CNC-SP films. (a, b) The extinction spectra (top) and CD spectra (bottom) of (a) as-fabricated CNC-SP films and (b) UV-treated CNC-SP films as a function of different SP concentration.

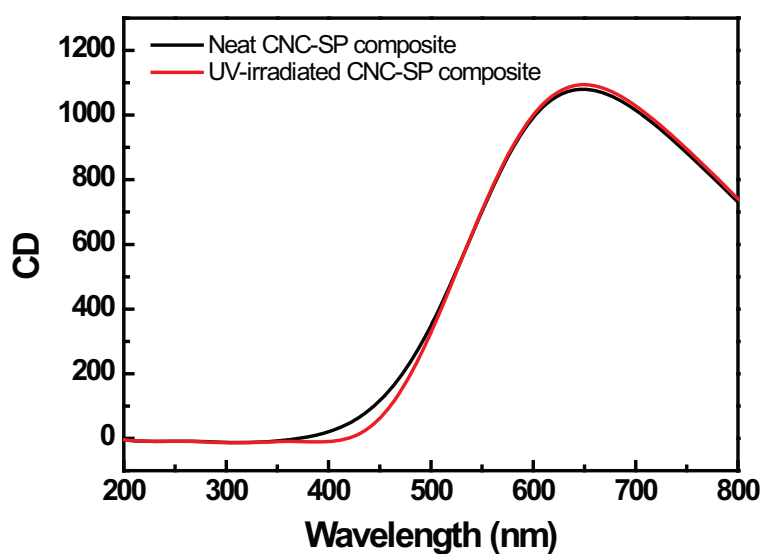


Figure S12. CD spectra of hybrid CNC-SP films with 650 nm photonic bandgap under UV/Visible light irradiation.

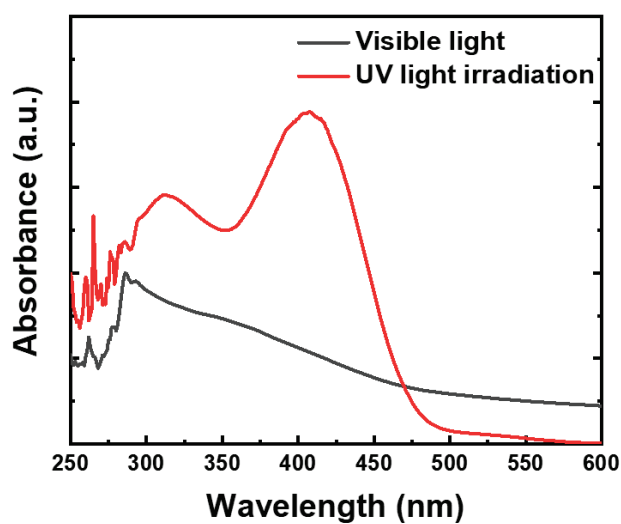


Figure S13. Optical absorbance of CNC-SP dispersion. Optical absorption behavior of CNC-SP solution mainly depends on SP absorption. CNC-SP dispersion under UV light irradiation changes to MCH+ phase.

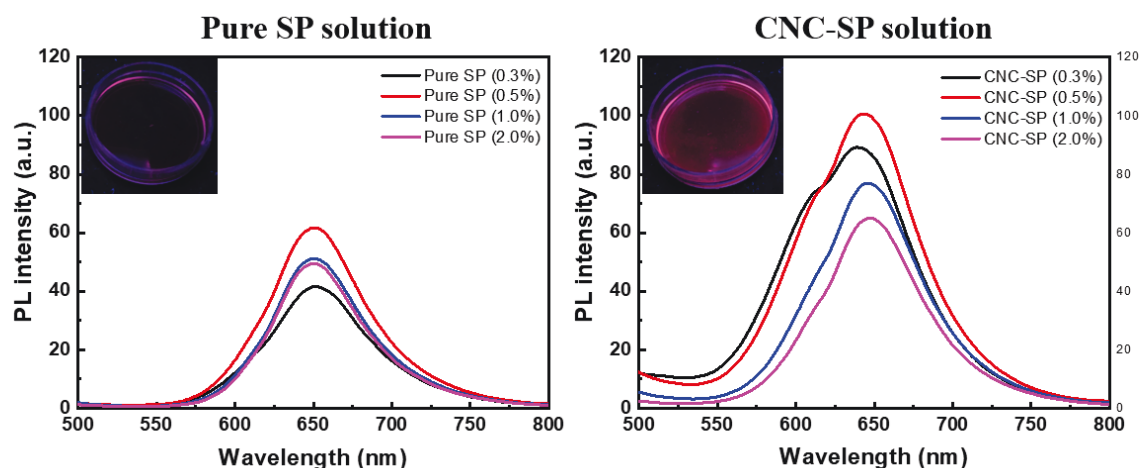


Figure S14. Photoluminescence intensity of pure SP and CNC-SP solution with different SP concentrations. Relative weight ratio (CNC : SP = 99.7 : 0.3, 99.5 : 0.5, 99 : 1, 98 : 2 %) was used to determine the amount of added SP components. The same amount of SP components were dispersed in water with the same acidic condition as the CNC dispersion for the pure SP solution. Inset images show corresponding photographs of emissive pure SP and CNC-SP solution (0.5%) in petri dish.

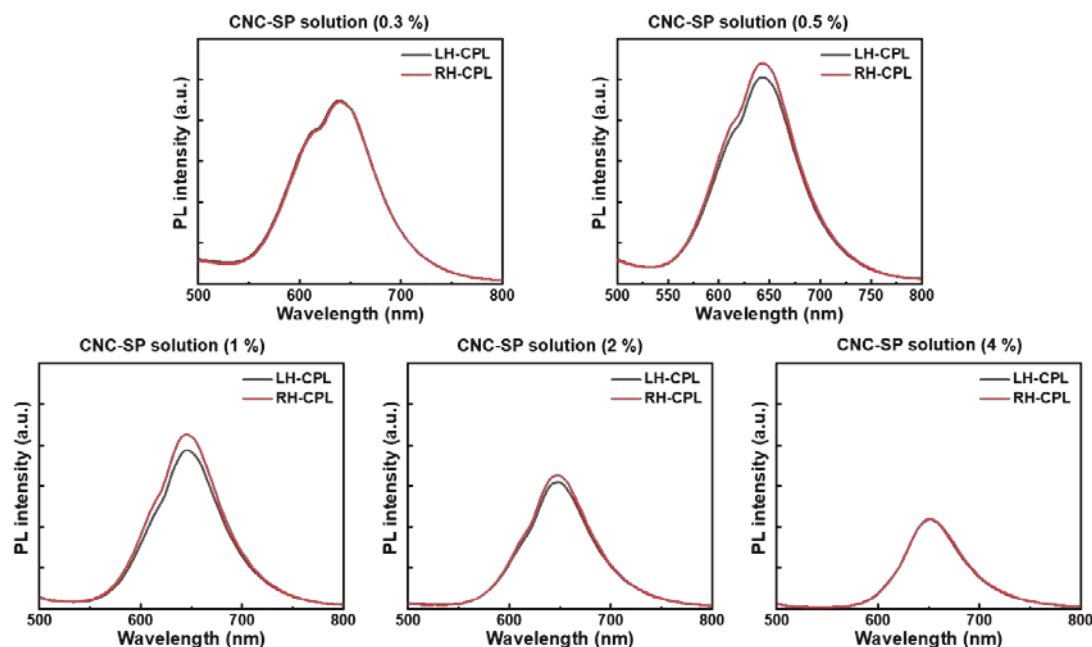


Figure S15. Photoluminescence of pure SP and CNC-SP solution with different SP concentrations, measured under left- and right-handed circular polarizers.

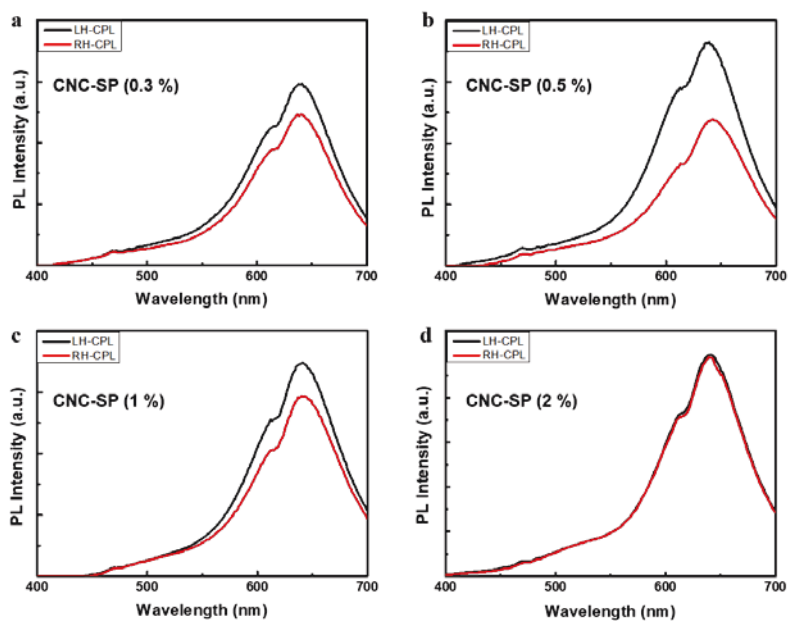


Figure S16. (a-d) Photoluminescence spectra for CPL emission of hybrid CNC-SP films with 325 nm photonic band gap as a function of different SP doping concentrations using left- and right-handed circular polarizers.

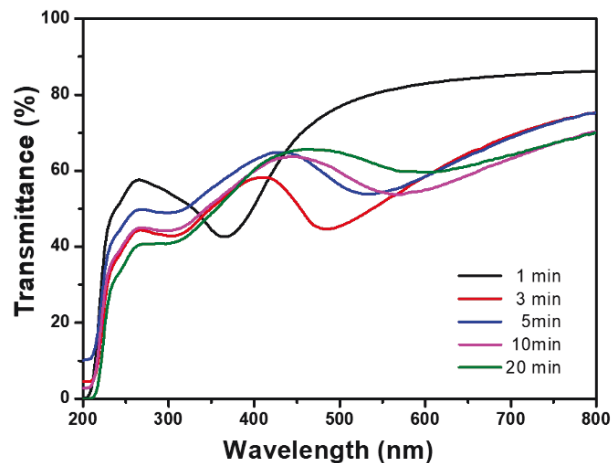


Figure S17. Transmission spectra of hybrid CNC-SP films with different photonic band gaps produced via different sonication times of CNC dispersion.

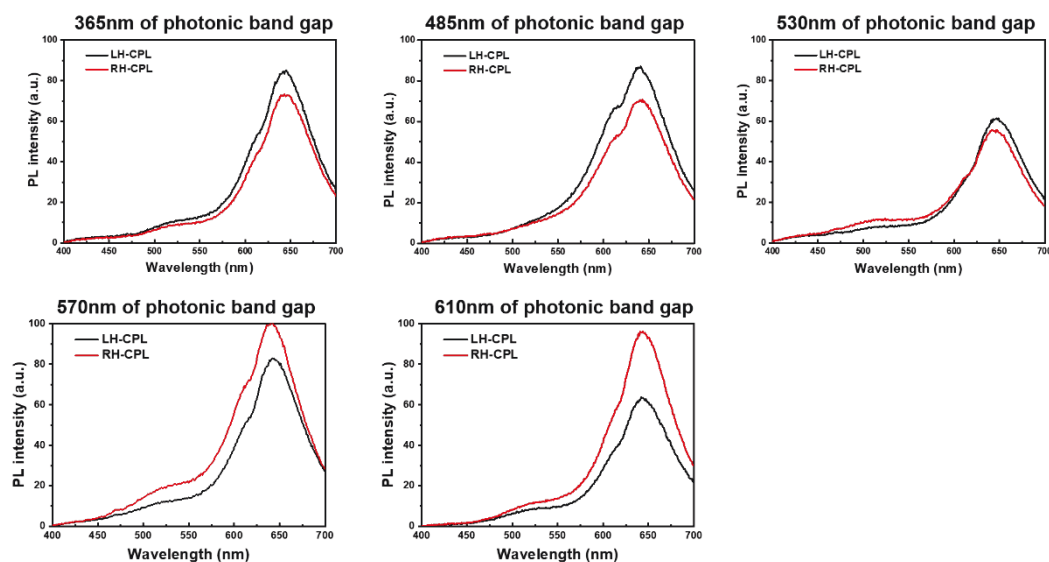


Figure S18. Photoluminescence spectra for CPL emission of hybrid CNC-SP films as a function of photonic band gap wavelength, measured under left- and right-handed circular polarizer, respectively.

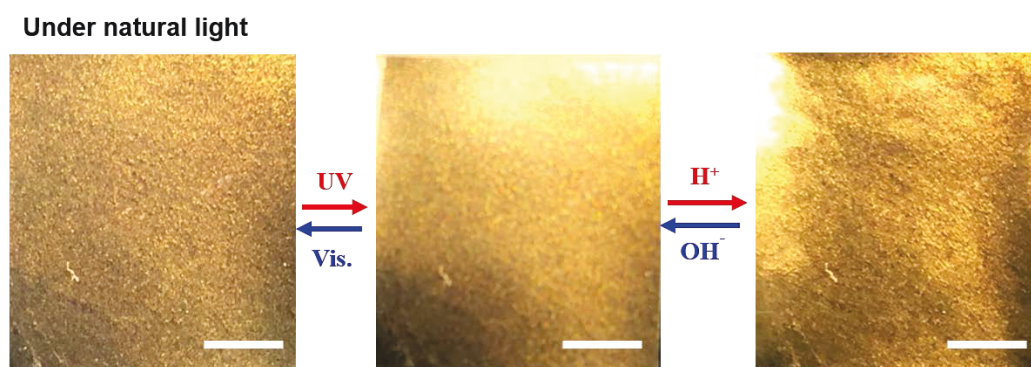


Figure S19. Photographs of hybrid chiral CNC-SP films without further treatment (left), with remote treatment by water vapor (middle) and citric acid vapor (right) under natural light. The photonic band gap of the films is a 645 nm.

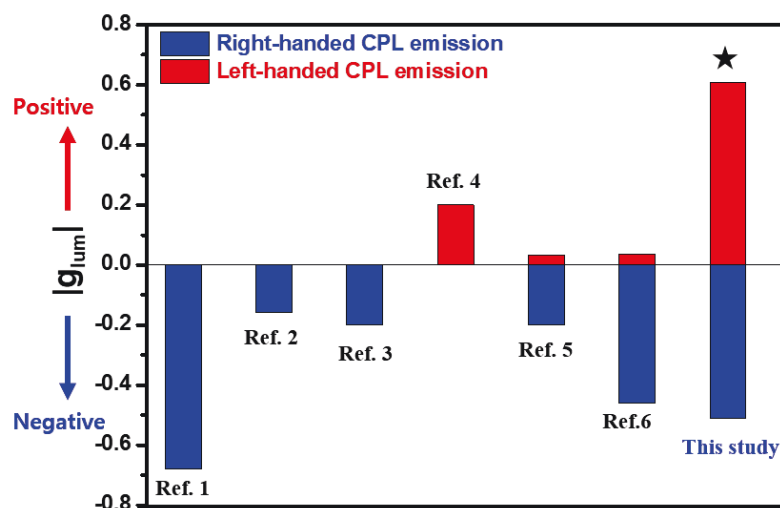


Figure S20. The comparison of $|g_{lum}|$ in CPL emission for CNC-based composite materials.^[1-6]

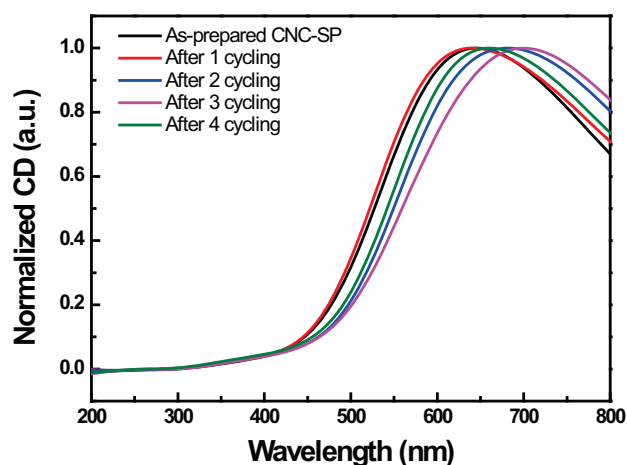


Figure S21. CD spectrum of hybrid CNC-SP films during cycling treatment with acidic water – neutral water vapor.

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