Supporting Information

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Photoresponsive and Polarization-Sensitive Structural Colors from Cellulose/Liquid Crystal Nanophotonic Structures

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Experimental Section

Materials: Microcrystalline cellulose (MCC) Avicel® PH-200 was received from DuPont. D- (+)-Glucose (GLU) (purity ≥ 99.5%), AmberLite® mixed bed ion exchange resin (MB20 hydrogen/hydroxide form), methanol, acetone, chloroform, potassium carbonate and iodomethane were obtained from Sigma Aldrich. Sulfuric acid (95-97%), silica gel 60 (40-63 µm) and flash sea sand were bought from Merck. 4-Cyano-4′-pentylbiphenyl (5CB) (> 98%) and 4-(4-Butylphenylazo)phenol were obtained from TCI Europe. All chemicals were used as received.

Preparation of CNCs: To obtain CNCs, a slightly modified preparation protocol was employed compared to literature.¹ MCC (20 g) was hydrolyzed at 45 °C for 75 min under magnetic stirring using sulfuric acid (247 g of 64 wt%). The reaction was stopped by diluting 10-fold with Milli-Q water and the suspension was left undisturbed overnight. Then, the supernatant was removed (~1 L) and the sediment was ultrasonicated for 2 min at 90% amplitude (1/2-inch tip, Vibra-Cell VCX 750, Sonics & Materials), followed by centrifugation at 15000 rpm (rcf = 18500 g (at rav), Beckman Coulter – Avanti® J-E centrifuge, JA-25.50 Rotor) for 5 min. The supernatant was discarded and the sediment was re-dispersed in the same amount of Milli-Q water as prior to centrifugation. The centrifugation step was repeated and after the third centrifugation, only the supernatant, which was more viscous now compared (because it contained CNCs) to the supernatant of the previous centrifugation step, was collected and dialyzed (cellulose membrane tube, 14 kDa molecular weight cut-off) until the pH of the water outside reached a steady state value (10 days). The obtained suspension was treated with 5 g of AmberLite® resin for 2 days. The resin was present in a cellulose membrane tube (molecular weight cut-off: 14 kDa), that was placed within the CNC suspension. The suspension was filtrated using the Whatman® Grade 541 filter paper. Finally, the CNC suspension was concentrated to 2.5 wt% and the measured pH was 2.3. The CNCs had a surface charge of 0.24 mmol g⁻¹ obtained as described previously.²
Fabrication of CNC/GLU films: A 1 wt% glucose solution in Milli-Q water was added to the 2.5 wt% CNC aqueous suspension and the suspension (present in a closed glass vial) was magnetically stirred for 16 h. CNC/GLU films with different weight % compositions were attained by varying the composition of the CNC/GLU suspension, while maintaining the total volume of the suspension at 10 mL. After 16 h, the suspension was solvent-cast in a polystyrene petri dish (6 cm diameter) and dried at ambient conditions for 2-3 days. To attain a pure CNC film, 10 mL of 2.5 wt% CNC suspension was solvent-casted.

Synthesis of 4-n-butyl-4′-methoxyazobenzene (BMAB): The mesogenic azobenzene dye 4-butyl-4′-methoxyazobenzene (BMAB) was prepared as reported previously.\textsuperscript{[3]} To a solution of 4-butyl-4′-hydroxyazobenzene (500 mg, 1.97 mmol) in acetone (40 ml), potassium carbonate (300 mg, 2.17 mmol) was added. The mixture was refluxed for 1 h and 0.5 M Iodomethane in acetone (10 ml, 5 mmol) was added dropwise. The solution was refluxed overnight in air and the disappearance of 4-butyl-4′-hydroxyazobenzene was checked by thin-layer chromatography (TLC). After cooling down to room temperature, the precipitated potassium iodide was filtered and the solution was then poured into water and extracted with CH\textsubscript{2}Cl\textsubscript{2}. The extract was concentrated and subjected to silica gel chromatography (1% MeOH in CH\textsubscript{2}Cl\textsubscript{2}) to give 4-butyl-4′-methoxyazobenzene (BMAB) as a yellow liquid crystal (383 mg, 1.43 mmol, 73%): \textsuperscript{1}H-NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta\) 1.07 (t, \(J = 8\) Hz, 3H), 1.50 (q, \(J = 8\) Hz, 2H), 1.74 (q, \(J = 8\) Hz, 2H), 2.77 (t, \(J = 8\) Hz, 2H), 3.87 (s, 3H), 7.08 (d, \(J = 12\) Hz, 2H), 7.41 (d, \(J = 8\) Hz, 2H), 7.99 (d, \(J = 8\) Hz, 2H), 8.06 (d, \(J = 8\) Hz, 2H).

Preparation of CNC/GLU film with BMAB/5CB: The 4.4 mol% BMAB in 5CB was prepared by mixing BMAB (50.1 mg) with 5CB (1.01 g) under heating (40 °C) and magnetic stirring for 1h. The LC mixture was cooled back to room temperature prior to further use. An amount of 15 µL of the LC mixture was dissolved in 0.985 mL of chloroform. Pieces (ca. 5 x 5 mm) of CNC/GLU films were cut out and placed on top on microscope slides. An amount of 5 µL (on film CNC/GLU = 55/45) or 15 µL (on film CNC/GLU = 39/61) of the LC in chloroform was drop-casted on top of CNC/GLU
films. After ca. 2 min the chloroform had evaporated and the top part was covered with a cover glass (borosilicate glass, 22x22 mm, thickness No. 1.5, VWR 631-0125) and partially sealed with tape around the edges to hold the cover glass in place. The samples were stored at ambient conditions at least one month prior to measurements and some samples (the CNC/GLU = 39/61 films with LC droplets) were heat-treated for two days (40 °C for one day followed by 50 °C for another day). This was performed in case that LC molecules were able to permeate into the CNC/GLU film, but, as noted in the main manuscript, no swelling of the samples was observed and hence the LC molecules remained on the outer surface of the CNC/GLU films.

**Characterization**

*Polarized optical reflection and optical images* were obtained at normal incidence using a custom-made polarization dependent micro-spectroscopic setup. Samples were illuminated using a 50 W halogen lamp attached to a microscope (Nikon Eclipse L200N, Japan) equipped with a linear polarizer, an appropriate achromatic quarter-wave plate (Thorlabs, Inc., AQWPO5M-580), a long pass filter (Thorlabs FEL0550) and the reflected light was collected from the camera port with an optical fiber (Thorlabs; 150-µm) core connected to a spectrometer (Ocean OpticsHR 4000, USA). This setup allowed us to collect reflected light from an area of a few micrometers. When collecting light reflection from LC droplets (on top of CNC/GLU films), measurements were acquired close to the center of the droplets to avoid possible artifacts from the droplet edges. An objective lens with 20x magnification, corresponding NA = 0.30 was used to record spectra. Polarized optical images (images in Figure S12a) were obtained by placing the specimen between two linear polarizers that were arranged in crossed configuration in transmission mode in the polarizing microscope analyzed at 20x magnification with the specimen being rotated from 0 to 135°.

In the case of UV-light exposure experiments, the sample was removed from the microscope, subjected to UV-light (λ = 366 nm, Mineralight Lamp Model UVGL-58) and reinserted into the
microscope followed by polarized optical reflection measurements using either incident RCP or LCP light. A Thorlabs FEL0550 filter was used during these measurements to only illuminate the sample with light at wavelength above 550 nm. All measurements were performed at room temperature (around 21 °C).

Polarized optical microscopy between crossed linear polarizers in reflectance mode (images in Figure 1c-1e and Figure S1 and S2 in SI) was performed using a Leica DMRM light microscope (Leica, Germany) equipped with a Kappa DX40 camera and 20x air objective.

Polarized optical microscopy between crossed linear polarizers in transmission mode (images in Figure S3, S11 and S12b) was performed using an Axio Vert.A1 inverted Light Microscope (Carl Zeiss, Germany) equipped with a Zeiss AxioCam 305 color camera (Zeiss Zen 2.6 software (blue edition)), 7.2W LED lamp (Cree XHP35A HI, 800 nm > λ > 400 nm) and 63x or 40x air objective.

Contact angle measurements were performed using a DataPhysics OCA40 micro system (DataPhysics GmbH). 1 µL droplets of 5CB or 4.4 mol% BMAB in 5CB were gently deposited on the fabricated films and the contact angle was analyzed when the spreading ceased after about 15 seconds. The contact angles were analyzed with the OCA20 software using tangential fitting and the results are reported as the average and standard deviation from at least three individual measurements.

UV-vis transmission spectra of pristine CNC film or CNC/GLU films were obtained using a UV-vis spectrophotometer (Shimadzu UV 2550) in the wavelength range 300-800 nm. Measurements were performed at 40% RH and 21°C.

Scanning electron microscopy was performed using a Hitachi SEM S-4800 at an acceleration voltage of 1 or 3 kV. Cross-sections of films were prepared by freezing in liquid nitrogen, followed by fracturing and mounting on Al-stubs. In the case of surface analysis of films, the films were dipped quickly in chloroform, followed by mounting on Al-stubs. If needed, the samples were sputter-coated with Pt/Pd (60/40) using a Cressington 208HR sputter coater equipment for a time period of 10 s, resulting in a coating thickness of ca. 1 nm.
Transmission Electron Microscopy was performed using a Hitachi HT7700 at an acceleration voltage of 100 kV. A droplet (10 µL) of CNC suspension in Milli-Q water was deposited on Formvar/carbon-coated 400 or 200 mesh copper grids (TED PELLA or Micro to Nano) and left to dry. For length estimation (histogram in Figure S6) a well dispersed 0.0126 wt% CNC suspension in Milli-Q water was used that had been ultrasonicated for 1 min (at 40% amplitude 1/2-inch tip, Vibra-Cell VCX 750). Otherwise a 0.0025 wt% CNC suspension in Milli-Q water was used that had been magnetically stirred for 24 h. No staining was applied to the grids. All the micrographs were obtained with a charge-coupled device camera.

Figure S1. POM taken between crossed polarizers in reflectance mode of a neat CNC film (left), a violet (CNC/GLU=66/34) (middle) and green (CNC/GLU=52/48) nanocomposite film (right). Scale bars: 200 µm.

Figure S2. POM images (crossed polarizers, reflectance mode) of the nanocomposite film with CNC/GLU =55/45 observed at two different areas, one of which (right) contained several more green microdomains. Scale bar: 200 µm.
Fingerprint patterns in two CNC/GLU films are shown in Figure S3. Such patterns arise in a dry film when the chiral nematic axis is not parallel to the height of the film. In other words, it confirms the presence of tilts of the helical axis within the films.\textsuperscript{[4]} Fingerprint textures were observed for all films investigated in this study.

Figure S3. POM taken between crossed polarizers in transmission mode showing fingerprint textures. CNC/GLU =55/45 and 46/54. Scale bars: 50 µm
**Figure S4.** SEM image of a cross-section of a nanocomposite film (CNC/GLU=55/45). Scale bar: 2 µm.

**Figure S5.** SEM image of the film surface of a nanocomposite film with CNC/GLU = 52/48. The high level of directional alignment of CNCs is apparent. Scale bar: 1 µm.
Figure S6. Representative TEM micrographs of CNCs. Histogram showing the distribution in CNC lengths (n=500) from TEM micrographs.
Figure S7. SEM images of film surfaces of a neat CNC and a nanocomposite film (CNC/GLU=66/34). CNCs are aligned on the film surface. Scale bars: 2 µm.
Figure S8. SEM images obtained at two different positions of a CNC/GLU film (66/34) while keeping the same sample orientation. We observe clear variation in the local directional CNC alignment between the two positions (shown with white arrows). Scale bars: 1 µm.
**Figure S9.** Average contact angles (std) for liquid crystal droplets on top of three different films ($4 \geq n \geq 3$).

| CNC/GLU | CA(std) 5CB | CA(std) BMAB/5CB |
|---------|-------------|------------------|
| 100/0   | 29°(±2)     | 20°(±4)          |
| 55/45   | 36°(±1)     | 30°(±1)          |
| 39/61   | 31°(±2)     | 33°(±1)          |

**Figure S10.** Reflection of incoming RCP and LCP light for a liquid crystal (LC) droplet on top of a nanocomposite film and the nanocomposite film itself (CNC/GLU = 39/61). The black arrow in (a) points to the LC droplet and the white arrow points to the nanocomposite film with no LC. Measurements performed on the (b) LC droplet (center region of droplet) and (c) the nanocomposite film next to the droplet. In (d) the superposition of the reflectance spectra (LCP, RCP) in (b). Scale bars: 250 µm (a).
The liquid crystal mixture (4.4 mol% BMAB in 5CB) will adopt a non-homeotropic orientation at the cover glass interface, see Figure S11.

**Figure S11.** POM image (crossed polarizers, transmission mode) of the liquid crystal mixture (4.4 mol% BMAB in 5CB) between two cover glasses (22x22mm). An amount of 5 µL of LC was present between the two cover glasses. The pattern shows that the LC mixture is unaligned. Scale bar: 100 µm.
The birefringent properties of the LC droplets on top of two different CNC/GLU films is illustrated in Figure S12a and b. When rotating the samples between crossed polarizers (linearly polarized light), a clear alternating change in the intensity within the droplet could be observed, e.g. a bright area in...
the droplet becomes dark and then bright again with rotation. In Figure S12b (best seen after 45° rotation) a pattern can also be observed inside the droplet that resembles that of the CNC/GLU film surrounding the droplet. The sample in Figure S12a is the same sample as presented in Figure 3 in the main manuscript (the arrow in Figure S12a points to the droplet measured in reflection in Figure 3).

Supplementary Note 1 – Modulation of LCP light fraction

We define a plane wave \( \hat{E}_0 \) traveling along \( z \) as:

\[
\hat{E}_0 = \hat{E}_x + \hat{E}_y = E_{0x}\hat{x}e^{i(kz-\sigma t)} + E_{0y}\hat{y}e^{i(kz-\sigma t+\delta)} = (E_{0x}\hat{x} + E_{0y}\hat{y}e^{i\delta})e^{i(kz-\sigma t)} = \begin{bmatrix} E_{0x} \\ E_{0y}e^{i\delta} \end{bmatrix} \begin{bmatrix} \hat{x} \\ \hat{y} \end{bmatrix} e^{i(kz-\sigma t)}
\]

where \( \delta \) is the phase difference between the field components in \( x \) and \( y \). \( k \) is the wave number and \( \sigma \) is the frequency. \( E_{0x} \) and \( E_{0y} \) are the amplitudes in \( x \) and \( y \) while \( E_x \) and \( E_y \) also contain the phase information. For the case of \( E_{0x}=E_{0y}=\frac{1}{\sqrt{2}}E_{tot} \), we get:

\[
\hat{E}_0 = \frac{1}{\sqrt{2}}E_{tot}\begin{bmatrix} 1 \\ e^{i\delta} \end{bmatrix} [\hat{x},\hat{y}]e^{i(kz-\sigma t)}
\]

For arbitrary phase shift \( \delta \) we then have:

\[
\begin{bmatrix} E_x \\ E_y \end{bmatrix} = \frac{1}{\sqrt{2}}E_{tot}\begin{bmatrix} 1 \\ e^{i\delta} \end{bmatrix}
\]

Linear and circular polarized light can be represented as:

- Linear polarization at 45°: \( \begin{bmatrix} E_x \\ E_y \end{bmatrix} = \frac{1}{\sqrt{2}}E_{tot}\begin{bmatrix} 1 \\ 1 \end{bmatrix} \)
- Linear polarization at -45°: \( \begin{bmatrix} E_x \\ E_y \end{bmatrix} = \frac{1}{\sqrt{2}}E_{tot}\begin{bmatrix} 1 \\ -1 \end{bmatrix} \)
- Left-handed circular polarization: \( \begin{bmatrix} E_x \\ E_y \end{bmatrix} = \frac{1}{\sqrt{2}}E_{tot}\begin{bmatrix} 1 \\ i \end{bmatrix} \)
- Right-handed circular polarization: \( \begin{bmatrix} E_x \\ E_y \end{bmatrix} = \frac{1}{\sqrt{2}}E_{tot}\begin{bmatrix} 1 \\ -i \end{bmatrix} \)

where we have used \( e^{i0} = 1, e^{i\pi} = -1, e^{i\pi/2} = i \) and \( e^{-i\pi/2} = -i \).
As alternative to the linear basis, the wave can also be described using orthogonal LCP and RCP polarization states $\hat{L}$ and $\hat{R}$, using the following transformation:

$$\hat{x} = \frac{1}{\sqrt{2}} (\hat{R} + \hat{L})$$

$$\hat{y} = \frac{i}{\sqrt{2}} (\hat{R} - \hat{L})$$

This gives:

$$\begin{bmatrix} E_x \\ E_y \end{bmatrix} [\hat{x}, \hat{y}] = \frac{1}{\sqrt{2}} E_{tot} \begin{bmatrix} \frac{1}{\sqrt{2}} (\hat{R} + \hat{L}) \frac{i}{\sqrt{2}} (\hat{R} - \hat{L}) \end{bmatrix} = \frac{1}{2} E_{tot} \begin{bmatrix} 1 - ie^{i\delta} \end{bmatrix} [\hat{L}, \hat{R}]$$

As example for LCP light ($\delta = \pi/2, 5\pi/2, \ldots$), this correctly gives:

$$\frac{1}{2} E_{tot} \begin{bmatrix} 1 - ie^{i\pi/2} \end{bmatrix} [\hat{L}, \hat{R}] = \frac{1}{2} E_{tot} \begin{bmatrix} 1 - i^2 \end{bmatrix} [\hat{L}, \hat{R}] = E_{tot} \begin{bmatrix} 1 \end{bmatrix} [\hat{L}, \hat{R}]$$

The fractions of LCP and RCP light intensity ($f_{LCP}$ and $f_{RCP}$) becomes:

$$f_{LCP} = \frac{1}{4} |1 - ie^{i\delta}|^2$$

$$f_{RCP} = \frac{1}{4} |1 + ie^{i\delta}|^2$$

For our system, we have $\delta = \Delta\phi + \pi/2$ and $\delta = \Delta\phi - \pi/2$ for LCP and RCP incident light, respectively, finally resulting in:

$$f_{LCP} = \frac{1}{4} |1 - ie^{i\Delta\phi \pm \pi/2}|^2$$

We now use the equation above to calculate the estimated optical response of the hybrid cellulose/LC nanophotonic system presented in Figure 2g (also presented in Figure S10) of the main manuscript. We approximate the broad LCP reflection of the pure CNC/GLU film (i.e. outside the LC droplet area, the reflection spectrum in Figure S10c) as a Gaussian plus a flat reflection background. This is presented as the dashed blue line in Figure S13 together with the experimental data as a solid blue line. To obtain the response from the hybrid structure (i.e. on the LC droplet) we modulate the same Gaussian using the function for $f_{LCP}$ above (Eq. 3 in main manuscript) and again add a flat reflection offset. We used Eq. 1 in the main manuscript to calculate the spectral variation of $\Delta\phi$, using $d = 25 \mu m$ and birefringence $n_e - n_0 = 0.23$. The red and black curves in Figure S13 present the final results for incident LCP and RCP light, respectively, with calculated results as dashed lines and experimental results as solid lines.
Figure S13. Experimental (solid lines) and calculated (dashed lines) reflection spectra for pure CNC/GLU film illuminated by LCP light (blue, LCP cellulose) and hybrid cellulose/LC nanophotonic structure illuminated by LCP light (red, LCP hybrid) and RCP light (black, RCP hybrid). The LCP cellulose was approximated as $R_{\text{LCP cellulose}} = R_{\text{Gaussian}} + R_{B,\text{cellulose}}$, with $R_{\text{Gaussian}} = Be^{-(\lambda-\lambda_{\text{peak}})^2/2c^2}$. The optical responses for the hybrid structure was then calculated as $R_{\text{LCP/RCP hybrid}} = R_{\text{Gaussian}} \cdot f_{\text{LCP/RCP}} + R_{B,\text{hybrid}}$. Parameters: $B = 10\%$, $c = 50$ nm, $R_{B,\text{cellulose}} = 18\%$, $R_{B,\text{hybrid}} = 9\%$, $\lambda_{\text{peak}} = 615$ nm.
Absorption spectra for 5CB, BMAB and 4.4 mol% BMAB in 5CB. The spectra are shown before and after exposure to UV light (λ ~ 365 nm). Prior to UV-light exposure, the trans-BMAB is present, whereas after UV-light exposure cis-BMAB is present. These spectra match those previously reported in literature. After UV-light exposure, cis-BMAB absorbs light below ca. 550 nm, indicating that light below this wavelength is needed to recover the trans-isomer of BMAB.

Figure S14. Absorption spectra of 5CB, BMAB and 4.4 mol% BMAB in 5CB. Absorption spectra before and after UV exposure (λ ~ 365 nm). LCs were present in chloroform.
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