Controlling the Photonic Properties of Cholesteric Cellulose Nanocrystal Films with Magnets

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ABSTRACT. The self-assembly of cellulose nanocrystals is a powerful method for the fabrication of bio-sourced photonic films with a chiral optical response. While various techniques have been exploited to tune the optical properties of such systems, the presence of external fields has yet to reported to significantly modify their optical properties. In this work, by using small commercial magnets (≈ 0.5-1.2 T) we were able to tune the orientation of the cholesteric domains in suspension as they assemble into films. A detailed analysis of these films shows an unprecedented control of their angular response. This simple and yet powerful technique unlocks new possibilities in designing the visual appearance of such iridescent films, ranging from metallic to pixelated or matt textures, paving the way to the development of truly sustainable photonic pigments in coatings, cosmetics and security labeling.

The increasing need of multifunctional materials with well-controlled properties can be met by adopting self-assembly strategies relying on bio-sourced nano-sized building blocks. Such approaches can offer a cost-effective and scalable solution to design materials with a desired optical response.[1] Cellulose nanocrystals (CNCs) are an excellent example of such a bio-
sourced nanomaterial, owing to a unique combination of chemical, mechanical, and optical properties,\cite{2,3} which explains the increase of interest in this system for applications as pigments,\cite{4} security coatings,\cite{5,6} sensing or responsive materials\cite{7-12} and mesoporous chiral nanotemplates.\cite{13-15}

Colloidal suspensions of CNCs exhibit a cholesteric liquid crystalline behavior above a threshold concentration\cite{16-20} that can be retained upon solvent evaporation to form dry films that display a strong photonic response. In particular, such films behave as standard cholesteric Bragg reflectors\cite{14} whose optical response is determined by their helix axis, $\mathbf{m}$, and pitch, $p$.\cite{21}

For these systems, the control of the pitch, and therefore the reflected wavelengths, can be successfully achieved by adjusting a variety of parameters.\cite{22-29,28,30,31} However, the orientation of the helix axis $\mathbf{m}$ in such films has been limited only by the specific geometrical conditions in which self-assembly occurs. Therefore the manipulation of the orientation of the helix $\mathbf{m}$ has so far not been addressed, or was at best limited to favor its vertical orientation uniformly across the sample.\cite{28,30,31} While the use of external fields, such as electric\cite{32-34} and magnetic,\cite{29,35-50} have been shown to provide a powerful control over the CNC orientation in suspensions, they have been so far considered impractical as a tool to tailor the photonic properties of the films. More specifically, it has been believed for over two decades that the magnetic orientation of the cholesteric phase in CNC suspensions required always very strong fields ($\geq 5$ T), which probably discouraged many from investigating this method, due to the seemingly limited applicability and thus relevance of this technique to produce useful aligned CNC-based materials. The alignment of CNCs under more accessible fields ($\leq 1$ T, e.g. with a pair of neodymium magnets) is indeed much more desirable for practical applications, but an attempt reported by Pan et al. using 0.2 T led to no significant control over the helix orientation.\cite{29} The orientation of cholesteric suspensions in magnetic fields is due to the intrinsic anisotropic diamagnetic susceptibility of the individual CNC,\cite{49} and their orientation
in low magnetic fields (0.56–1.2 T) is due to a cooperative effect in their cholesteric arrangement, as carefully quantified only recently in suspension by De France et al.,[50] and, to our knowledge, successfully illustrated only in rheological studies[51] and reinforced nanocomposite papers.[52]

In this work, we report the use of commercial neodymium (NdFeB) magnets as a powerful and versatile tool to control the orientation of the cholesteric domains and to produce colored CNC films with unique control over their final optical properties. To achieve this the suspension is evaporated in the immediate vicinity of NdFeB magnets, so that the local magnetic field perceived by the drying suspension induces a long-range order of the cholesteric phase, that is subsequently retained in the solid-state. By adjusting the spatial configuration of the magnet(s) with respect to the drying suspension, we are able to produce solid nanostructured films with improved uniformity in the orientation of the cholesteric axes, leading to large homogenous films, and especially to control its orientation. Figure 1 illustrates examples of the striking controllable optical effects obtained with this technique; here a selection of macroscopic images of chiral cellulose films cast using different magnets are shown. It should be noted that large magnets, as employed in Figure 1B, were preferred when casting films on extended surfaces, but we also demonstrated this effect using smaller magnets as well as patterned polymagnets® to locally template the optical properties of smaller portions of films with the same efficiency (cf. Figure 1B and Figure S6). While other templating methods have also been reported for CNC films, such as local temperature gradients,[53] local substrate variation[54] or multi-steps casting,[55] these magnetically-templated films present both enhanced optical contrast and unique angular response properties.
Figure 1. Films obtained from the slow evaporation of an aqueous suspension of CNCs in a dish placed over NdFeB magnets. (A–B) examples of films that were cast spanning two magnets, as indicated by the schematic in (C); (D) Exotically-patterned films can be obtained when casting on a patterned poly-domain magnet (polymagnet®) displaying opposite magnetization direction on the same face (the insert shows a schematic of the templating polymagnet®).

To better understand how the presence of a magnetic field affects the self-assembly of the CNCs, we cast the same starting suspension under the same conditions of temperature and humidity for three different magnetic environments ([CNC] = 8.5 wt.%, [NaCl] = 8.5 mM, Supporting Information, Section A, Figures S1-4): in the absence of a magnet (control sample), in a homogeneous vertical magnetic field, and at the junction between two magnets placed side-by-side, to obtain a highly tilted magnetic field near their junction (Figure 1C and Figure S5).

The three obtained dry films display striking differences visible by naked eye, as shown in Figure S6. The reported photographs of the three samples were taken under the same illumination conditions, and highlight how the scattering response of the samples changes for
the different magnetic field configurations. Similar observations are reported for different suspensions, with varying ratios of NaCl:CNC (Figure S7).

To capture the unusual angular dependence of the optical response, the films were systematically analyzed by angular resolved optical spectroscopy.\[^{56,57}\] With this technique, a collimated white light beam illuminates the sample at a defined angle and the scattering response from the sample is collected across a wide range of angles. The comparison of the three samples (no field, vertical, and tilted magnetic fields) is summarized in Figure 2. Scattering plots in Figure 2A-C and 2D-F report the intensity of the reflected light in $\log_{10}$-scaled black-blue-yellow colors for different angles of collection and for an angle of incident of 0 and -30 degrees, respectively.

The optical response of these films relies on the fact that the CNC rods are locally aligned with their long axis along a director $\mathbf{n}$ that rotates at the submicron-scale and describes a left-handed helix, characterized by its helix axis $\mathbf{m}$ and its pitch $p$, the latter being defined as the distance separating rods of the same orientation after a 360° rotation.\[^{21}\] The structural color of the film arises from the diffraction of the incident light, which locally obeys the Bragg law inside the film, $\lambda = n p \cos \theta'$, where $\lambda$ is the wavelength of the reflected light, $n$ the average optical index and $\theta'$ the angle defined locally between the incident light and the helix axis $\mathbf{m}$. As a result, the non-uniform orientation of the helix $\mathbf{m}$ in polydomains films contributes to their pixelated and rainbow-like appearance.\[^{58}\]

As shown in Figures 2A and 2D, the films prepared without any magnet display a broadened angular wavelength response, indicating a broad distribution of orientations of cholesteric structures inside the film. In this case, the homeotropic anchoring of $\mathbf{m}$ on the top and bottom interfaces is favorable to the vertical alignment of the cholesteric structure, but in practice such effect has a limited efficiency throughout the film thickness.\[^{28}\]

In contrast, films assembled in the presence of the magnetic field can enhance the intensity of the reflected light only for a selected range of angles. Specifically, for a vertical magnetic
field, the film shows a strong specular reflection (i.e. $\langle \theta_{\text{out}} \rangle = |\theta_{\text{in}}|$, Figure 2B,E), in the
direction perpendicular to the sample surface, indicating that the cholesteric structure is well
aligned throughout the film with m oriented normally to the film surface. Even more
interestingly, the sample dried in a tilted magnetic field displays a strong reflection at an angle
of $\langle \theta_{\text{out}} \rangle = 5^\circ$ with respect the normal of the sample surface ($\langle \theta_{\text{out}} \rangle \neq |\theta_{\text{in}}|$, Figure 2C,F).
These observed optical responses suggest an underlying cholesteric structure for each sample
that is summarized in the schematics of the Figure 2G-I.
Figure 2. Angular resolved optical spectroscopy of CNC films assembled under three different conditions: no field ($H = 0$), vertical ($H \uparrow \neq 0$), and tilted magnetic field ($H \swarrow \neq 0$, measured in position $x = +2.5$ mm, cf. axes definition in Figure S6C, S13B). The intensity of the light diffracted by the sample is reported in $\log_{10}$-scale with its spectral composition (i.e. wavelength $\lambda$) for each angle of detection ($\theta_{\text{out}}$) when the probing incident light is either normal ($\theta_{\text{in}} = 0^\circ$, A-C) or tilted ($\theta_{\text{in}} = -30^\circ$, D-F). A model fitting the data is proposed in Figure
S15. (G-I) Schematics of the orientation of the cholesteric nanostructures responsible for the observed optical response (white arrows symbolize white incident light and specular reflection). (J) Schematic of the goniometer and definition of the angles $\theta_{\text{in}}$ and $\theta_{\text{out}}$. (K) Photograph of the off-specular response of a film with a tilted cholesteric structure. For the sake of clarity, the incident and diffracted light beams are grazing a screen placed in the background of the diffraction plane.

The effect of the magnetic field applied upon drying is further analyzed using polarized optical microscopy, as reported in Figure 3. Polarization resolved reflection images of the three previous samples were collected in bright field and dark field configuration in order to distinguish the polarization features of their local optical response. A Bertrand lens was then used to further image the full scattering response in $k$-space.

The sample prepared in the absence of a magnetic field displays signal in both left- and right-handed circular polarization and in both bright and dark field configurations due to the presence of highly tilted cholesteric domains (Figures 3A and 3E). This broad and polychromatic angular response is confirmed by the observations in $k$-space (Figure 3I) and is in good agreement with films containing highly tilted domains.

In contrast, samples prepared under magnetic fields reflect predominantly left-handed polarized light in bright field with little scattered light observed. For vertically-aligned fields mostly blue light is reflected at normal incidence in bright field with a net contrast between left- and right-handed circular polarization, as expected only for vertically-aligned domains (Figure 3B, 3F, 3J). For a tilted magnetic field, the contrast between left and right decreases (Figure 3C-D) and the diffracted light is reflected off-line with a clear red-shift (Figure 3K-L), that becomes more apparent in dark field (Figure 3G-H).
Figure 3. Polarized optical micrographs of films prepared in zero field (H = 0, far left), in vertical field (H\(\uparrow\)), and for two increasingly tilted magnetic fields (H\(\uparrow\)) and (H\(\mathcal{Q}\)). The films were analyzed in (A–D) bright field and (E–H) dark field respectively, using either a left- (↺) or right-circularly polarized filter (↻), and (I–L) in k-space, as imaged with a Bertrand lens.

To reveal the influence of the magnetic field on the internal cholesteric arrangement of the CNC films, their cross-section is investigated using scanning electron microscopy (SEM),\textsuperscript{[60]} as reported in Figure 4. The film prepared without magnetic field shows clearly a polydomain structure: the orientation of the cholesteric domains is less controlled (Figure 4A). In contrast, the film prepared under a vertical magnetic field seems perfectly monodomain and highly uniform in both orientation and pitch (Figure 4B), although some disclinations remain visible. Similarly, the film prepared in presence of a tilted magnetic field (Figure 4C) displays locally a homogeneous cholesteric monodomain but with a clear tilt with respect to the film-air interface, explaining the unusual optical angular response. We found no previous example of such control of the cholesteric tilt in the literature. Different magnifications are presented in
**Figure S10** and a further film with extremely tilted regions ($\beta_f \sim 17^\circ$) is presented in **Figure S11**.

Surprisingly, the film structure in the area dried directly above the junction between the two magnets displays a clear zig-zag pattern (Figure 4D, more examples on **Figures S11-13**). We interpret this pattern as the result of mechanical buckling of the cholesteric structure upon unidirectional vertical compression perpendicularly to its helix axis $m$. The vertical compression is expected to play an important role in this drying geometry (*i.e.* the solvent evaporates from the top while the surface area is kept constant) from the moment the drying suspension reaches a threshold concentration where the kinetic arrest occurs and the mutual orientation of the rods cannot relax anymore.\(^{[61-64]}\)

These undulations are fundamentally different from the *Helfrich-Hurault* or related instabilities\(^{[65-68]}\) observed in confined cholesterics under the influence of external fields coupling parallel to the local director $n$. So far we observed similar buckling waves only in a spherical microdroplet geometry,\(^{[62]}\) and is consistent with a lower compressibility of the cholesteric structure normal to $m$, which is expected in this system.\(^{[63]}\)
Figure 4. Scanning electron microscopy (SEM) of the cross-sections of CNC films prepared: (A) in absence of magnetic field ($H = 0$); (B) in a vertical magnetic field ($H↑$); (C) in a tilted magnetic field ($H↗$) and (D) in a nearly horizontal field ($H→$). While the absence of a magnetic field leads to a cholesteric polydomain structure with various tilts and pitches, the application of such magnetic field upon drying leads to a homogeneous pitch and orientation in either vertical or tilted direction (see Figure S10 for different magnifications), while a perfectly horizontal field leads to more complex zig-zag patterns indicating buckling phenomena (see Figures S11-13 for further examples).
While we clearly demonstrate that casting CNC suspensions on NdFeB magnets does successfully induce an alignment of the cholesteric structure in the final film, it would be misleading to conclude that the final alignment in the dry film corresponds to the local direction of the magnetic field applied during casting. Indeed, the vertical compression upon drying is expected to affect the final tilt of the cholesteric nanostructures. To clarify this point, we compared the observed tilt of the cholesteric structures in the films with the local tilt of the magnetic field at the same position during the casting. For this purpose, the magnetic field was mapped experimentally and further computed to expand its local tilt across the whole sample cross-section (SI, Section D, Figures S11-12). We found that the tilt of the cholesteric structures is always much smaller than the corresponding tilt of the magnetic field. For instance, we measured a final tilt, $\beta_f$ of $\sim 4\text{-}6^\circ$ (defined from the vertical axis) in a position ($x = 2.5 \text{ mm}$) where we measured the field to be $65\text{-}70^\circ$, i.e. rather horizontal than vertical.

To account for the distortion of the cholesteric structure upon vertical compression, we use a simple compression model adapted from Ericksen-Leslie theory\textsuperscript{[57,69]} (details in SI, Section E). Our simplified model allows capturing the linear deformation expected from an assembly of cholesteric domains of identical pitch and purely randomized orientations. Neglecting any mechanical anisotropy that could explain the observed buckling, this purely geometrical model predicts the final tilt $\beta_f$ and pitch $p_f$ of the structure for an initial tilt $\beta_i$ and pitch $p_i$, and a macroscopic compression ratio $\alpha$ ($0 < \alpha < 1$), corresponding roughly to the volume fraction of the suspension at the kinetic arrest. Interestingly, this model also captures the increase of the pitch as the tilt increases (Figure 4B-D), which in turns, using Bragg’s and Snell laws,\textsuperscript{[57,70,71]} explains the observed red-shift of the scattering at higher angles (Figure 2A,D, Figure 3i-L, and Figure S16-17). Indeed, a small blue-shift would be otherwise expected from a film with a constant pitch distributed along various directions,\textsuperscript{[57]} which validates our model.
Exploiting this approach, we find that the calculated initial tilt $\beta_i$ of the domains is still significantly lower ($\beta_i \sim 20–30^\circ$) than the corresponding tilt of the magnetic field ($\beta_H \sim 65–70^\circ$) where they were observed. The mismatch between these two tilt values indicates that other phenomena also play an important role in defining the initial alignment $\beta_i$ of the cholesteric domains under magnetic field. Indeed, mechanisms such as tactoid coalescence and relaxation of the cholesteric orientation have been reported recently.$^{[30,36,72]}$ Moreover, the alignment of cholesteric fields under both external fields and conflicting anchoring conditions usually involves a Fréedericksz transition.$^{[73,74]}$ Such transition is characterized by a magnetic field threshold required to tilt the liquid crystalline alignment, while the resulting alignment profile is usually given by a compromise between both conditions and the minimization of the director distortion. We believe that the anchoring will get stronger upon further drying as the vertical confinement increases,$^{[62,75]}$ contingent that it occurs before the sample becomes kinetically arrested. This can cause a complex self-assembly behavior upon drying that could impact the tilt of the final cholesteric structure.

To conclude, we have shown that the magnetic fields generated by common NdFeB magnets can be used to achieve unprecedented control over the self-assembly of cellulose nanocrystals into colorful films. We demonstrate an improved homogeneity of the cholesteric pitch and orientation and, more importantly, the possibility to specifically orient the cholesteric structure either vertically or away from the usual planar orientation into specific directions. In this latter case, the resulting tilted structures reflect selected wavelengths off-specularly from the air-film interface, enabling a complete separation of their chiroptical response from the unspecific light reflected at the air-film interface.

Controlling the orientation of the cholesteric helix is fundamental to the design of the angular optical response of cellulose-based films. The helix orientation directly impacts the visual appearance of the films and therefore their use in coatings and cosmetics. Furthermore, gaining control over the directionality of the photonic response uniquely enables the design of
complex optical properties that could encode in the same film different scattering and polarization features e.g. for security labeling applications. Finally, the simplicity of this method to improve the homogeneity of CNC-based nanostructured films suggests that it could be of benefit to all applications where high quality optical or mechanical properties are desired, such as sensors or nano-templating agents.

Experimental Section

Cellulose nanocrystals suspension: Cellulose nanocrystals were obtained from acid hydrolysis\textsuperscript{[76]} of Whatman No. 1 cellulose filter paper (30 g) with sulfuric acid (64 wt.%, 420 mL) at 66 °C for 30 minutes, before quenching with deionized ice and water and purification by centrifugation and dialysis against deionized water (described in more detail in SI, Section A). The suspension was then tip-sonicated, vacuum-filtered, and finally concentrated to 14.5 wt.% with an osmotic bath of poly(ethylene glycol) (PEG 35 kDa). This constituted the starting batch. Unless otherwise specified, the films presented in this work were obtained by dilution with milli-Q water and sodium chloride (0.1 M) with a fixed [NaCl]/[CNC] ratio of 100 mmol·kg\textsuperscript{-1}. The imaging of the rods by atomic force microscopy (AFM), their conductometric titration\textsuperscript{[77]} and their phase diagram are presented in the supporting information (Section A and Figures S1-3).

NdFeB magnets: Two types of Nickel-plated neodymium magnets (NdFeB) were used. Except where otherwise specified, large rectangular magnets (ref. F390-N42, N42 grade, (x,y,z) dim. L40×W40×H30 mm\textsuperscript{3}, First4magnets) with magnetization along z-axis were used (Figure S10). The magnetic field close to their upper surface was experimentally measured (Figure S14) and further calculated (Figure S15) throughout the sample cross-section. An additional small disk-shaped magnet (ref. 1000573, Polymagnet\textsuperscript{®}) with a patterned concentric magnetization was used to further demonstrate the local control over the cholesteric alignment (Figure 1 and Figure S8).
**Film fabrication:** Starting aqueous CNC suspension ([CNC] = 14.5 wt.%) was diluted with milli-Q water and NaCl 0.1 M to reach [CNC] = 8.5 wt.% at a fixed [NaCl]/[CNC] ratio and was homogenized with a vortex stirrer. The suspension was then placed in a petri dish (35 mm non-treated PS, ref. 430588, Corning, VWR) and left drying while covered with an open plastic lid in ambient conditions (T ~ 22 ± 2 °C, RH ~ 30 ± 5%, with a drying time on the order of a week, cf. Figure S4). Magnetic fields were applied to drying suspension by placing the dishes in immediate vicinity of the magnet(s), as described in Figure S5 and S14-15.

**Characterization:** The samples optical and structural properties were investigated using different settings, including direct observation, angular resolved optical spectroscopy, polarized optical microscopy and scanning electron microscopy, as described in more details in the Supporting Information.

**Supporting Information**
Supporting Information is available from the Wiley Online Library or from the author. Additional data related to this publication is available at the University of Cambridge data repository ([https://doi.org/10.17863/CAM.9517](https://doi.org/10.17863/CAM.9517)).

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**References**
Commercial magnets can be used to control the optical properties of cholesteric cellulose nanocrystals films, resulting in photonic structures with an unprecedented photonic response. This striking effect unlocks new possibilities in the already broad range of photonic applications of such systems; from colorants, to sensors and security devices.

cellulose nanocrystals, colloid liquid crystals, magnetic fields, cholesteric, photonic crystals

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Controlling the Photonic Properties of Cholesteric Cellulose Nanocrystal Films with Magnets
Supporting Information

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A Suspension characterization

A.1 Suspension preparation

Cellulose nanocrystals were obtained from the hydrolysis of Whatman No. 1 cellulose filter paper (30 g) with sulfuric acid (64 wt.%, 420 mL) at 66 °C under high mechanical stirring. The reaction was quenched by two-fold dilution with deionized ice and water after 30 min. Soluble cellulose residues and acid were removed by centrifugation (three steps at 20,000 g of 20 min each) and dialysis against deionized water (MWCO 12–14 kDa membrane), and a stable suspension of [CNC] = 2.54 wt.% was obtained. At this stage, conductivity titration against sodium hydroxide (0.01 M) indicated \([H^+]_{(1)} = [\text{[–OSO}_3\text{]–}] = 221 \text{ mmol·kg}^{-1}\) of CNC. The suspension was then tip-sonicated in an ice bath (Fisherbrand Ultrasonic disintegrator 500 W, amplitude 30% max, tip Ø 12.7 mm, 5000 J·g\(^{-1}\) of CNC applied by steps of 200 mL) and vacuum-filtered (8.0 μm then 0.8 μm nitrocellulose, Sigma-Aldrich). The suspension was then concentrated up to 14.5 wt.% by placing it in a dialysis membrane (MWCO 12–14 kDa) immersed in an osmotic bath of poly(ethylene glycol) (PEG 35 kDa, Sigma-Aldrich, used as received). This constituted the starting batch.

At this stage, the CNCs appear as elongated and polydisperse nanorods, as illustrated in Figure S1 using Atomic Force Microscopy (AFM). Moreover, a second conductivity titration against sodium hydroxide indicated \([H^+]_{(2)} = 190 \text{ mmol·kg}^{-1}\) of CNC and \([\text{–COOH}] = 19 \text{ mmol·kg}^{-1}\) (cf. Figure S2), the difference between the two \([H^+]\) being attributed to both possible desulfonation and \([\text{Na}^+]\) contamination from PEG, as evidenced by elemental analysis (data not shown).
A.2 Atomic Force Microscopy (AFM) imaging

Figure S1. AFM image of the CNCs used in this work (cf. details in Section F.1)

A.3 Conductometric titration

Figure S2. Conductometric titration of CNC suspension (0.600 wt.%, 19.54 mL) against NaOH 9.96 mM (in presence of [KCl] = 1 mM). (A) Full scale (values corrected from dilution
effect), and (b) enlargement at the equivalence points (first indicating –OSO\textsuperscript{−} groups and the second –COOH groups (which are not charged at the low pH employed in this work).

### A.4 Phase diagram of the CNC suspension

Suspensions of CNCs were prepared at three different [NaCl]/[CNC] ratios and further diluted with milli-Q water were transferred to flat capillaries (ref. 3536-050, 0.30 × 6.00 × 50 mm\textsuperscript{3}, CM Scientific) and sealed with nail polish. The samples were observed after 14 days between crossed polarizers to visualize the anisotropic phase. A diagram of the isotropic/cholesteric phase transition was built by reporting the volume ratio of the isotropic and anisotropic phase. (Figure S3).

**Figure S3.** Phase diagram of CNC suspensions for various ratio of [NaCl]/[CNC] used in this work: (A) observation of suspensions of increasing [CNC] concentration at a fixed ratio of [NaCl]/[CNC] = 100 mmol·kg\textsuperscript{−1} (between polarizers a few degrees away from the cross-polarization configuration, to better show the two phases on a grey background); (B) proportion of anisotropic (cholesteric) phase reported from the observation of such capillaries after 14 days. At low concentration the cholesteric is mostly planar (helix axis \textbf{m} parallel to the viewing direction) and appears darker (due to the enhanced rotation power of the micron-sides pitch) while defects with Grandjean textures (\textbf{h} normal to viewing direction) appear as bright “oily streaks”.\textsuperscript{[1]}
cast in a Petri dish and covered with a 3D-printed lid to slow down the evaporation of the solvent. Unless specified, the resulting films had a thickness of 85-95 μm (cf. SEM images of the cross-sections).

**Figure S4.** Suspension height in function of the evaporation time, illustrating the evaporation rate of the solvent leading to the film formation.

The two main magnetic configurations that were used to control the magnetic field orientation were:

1. A vertical magnetic field (Figure S4A-B)
2. A continuously tilted magnetic field (Figure S4C-D)
Figure S5. Photographs of the magnets used for the main films investigated in this work. (A-B) two vertically stacked parallel magnets with a 14 mm ABS 3D-printed spacer to keep the magnets apart. (C) two magnets placed side-by-side on top of an iron plate (the sample was covered with a 3D-printed lid – not shown – to slow down the solvent evaporation). (D) Experimental visualization of the magnetic lines with iron filings immersed in silicon oil.
Figure S6. Photographs of cellulose nanocrystal films obtained from identical suspensions ([CNC] = 8.5 wt.%, [NaCl] = 8.5 mM) and cast under three different magnetic environments: (A) no magnetic field, (B) vertical magnetic field, (C) tilted magnetic field. The photographs were taken from the same observation angle (θ_{out} ~ 20°) using a diffuse white light from either the same angle (θ_{in} ~ 20°, i.e. specular) or different angle (θ_{in} ~ 55°) in order to visualize the cholesteric domains of different orientation. The schematics of the corresponding magnetic fields for these three samples are respectively shown in (D, E, F).
Figure S7. Macroscopic photographs of cellulose nanocrystals films observed in either specular ($\theta_{in} \sim \theta_{out} \sim 20^\circ$) or off-specular ($\theta_{in} \sim 55^\circ$, $\theta_{out} \sim 20^\circ$) conditions, after being prepared under no magnetic field (left) or under a vertical magnetic field (right) from a suspension of [CNC] = 8.5 wt.% and different ratios $R = [\text{NaCl}]/[\text{CNC}]$: (A–B) 100 mmol·kg$^{-1}$ (as in Figure S6), (C–D) 50 mmol·kg$^{-1}$ and (E–F) 25 mmol·kg$^{-1}$. In all cases, the vertical magnetic field applied during casting reduced effectively the diffraction in off-specular conditions.
Figure S8. Magnet with patterned magnetization (ref. 1000573, N50 grade, Ø 19.05 mm, thick. 3.175 mm, Polymagnet®, Correlated Magnetics Research). (A) Photograph of the magnet taken as used (left) and covered with iron filings in order to visualize the lines of reversing magnetizations (i.e. lines of strongest field). (B) Schematic of the Polymagnet® magnetization pattern as provided from the manufacturer (with red and blue indicating opposite magnetization along the cylindrical axis).

Figure S9. Examples of films cast from an initially lower CNC concentration ([CNC] = 2%wt., [NaCl] = 1 mM, V = 2 mL) in the vicinity of a NdFeB magnet (L45×W45×H25 mm³, grade N42, First4magnets), and under ambient conditions (T = 23 °C; RH ~ 30%, uncovered, evaporation time ~ 2 days), proving the efficiency of the technique in controlling the helix axis in even faster self-assembly conditions. (A) Casting conditions; (B–C) corresponding films after evaporation (film thickness ~ 25 µm); (D) magnetic field mapping of the magnet used (produced from K&J Magnetics, Inc., https://www.kjmagnetics.com/calculator.asp?).
C  Sample cross-sections using SEM

Figure S10. Scanning electron microscopy (SEM) of cross-sections of CNC films, prepared (A-D) in absence of magnetic field ($H = 0$); (E-H) in a vertical magnetic field ($H \uparrow$); (I-L) and in a tilted magnetic field ($H \swarrow$). The air-film interface is included to orientate the cholesteric axis with respect to the interface, as well as the homogeneity of the pitch throughout the sample thickness.
Figure S11. Scanning electron microscopy (SEM) of cross-sections of CNC films prepared from a similar suspension (i.e. same hydrolysis batch, dialysis, no tip sonication, no filtration, concentrated with PEG 35 kDa, [CNC] = 5.8 wt.%, [NaCl] = 0 mM) and observed in the region of highly tilted magnetic field ($\beta_H \geq 65^\circ$). The cholesteric structure appears much more tilted and shows signs of buckling in the center of the film. The cross-section appears partially out-of-focus due to the break being slightly out-of-plane.

Figure S12. Scanning electron microscopy (SEM) of cross-sections of CNC film at the region of almost horizontal magnetic field ($\mathbf{H} \rightarrow$) on a film cast from a different suspension (i.e. same hydrolysis batch, dialysis, no tip sonication, no filtration, concentrated with PEG 35 kDa, [CNC] = 5.8 wt.%, [NaCl] = 0 mM). An increasing tilt of the cholesteric structure is noticeable further from the magnet surface (i.e. from the former liquid-substrate interface), in agreement with an increasing tilt of the magnetic field, and finally a buckling of the cholesteric structure due to the vertical compression occurring upon drying.
Figure S13. Scanning electron microscopy (SEM) of cross-sections of CNC film at the region of horizontal magnetic field $\mathbf{H}$). The cholesteric structure present a clear zig-zag pattern (highlighted with dashed lines) with a periodicity varying locally from 2 to 10 µm, indicating buckling phenomena under vertical compression of the cholesteric structures that were initially oriented with a horizontal helix axis $\mathbf{m}$ before the vertical compression.
D Magnetic field mapping above the magnets

**Figure S14.** Experimental mapping of the magnetic field $\mathbf{H}$ (i.e. expressed as the magnetic induction $\mathbf{B} = \mu_0 \mathbf{H}$) produced in the vicinity of the two magnets assembled side-by-side with vertical anti-parallel magnetization. (A) Magnetic field measured experimentally (Lakeshore 450 Gaussmeter with MMTB-6J04-VG transverse Hall probe) along a line of coordinate $(z = +3.5 \text{ mm}, \ y = 0 \text{ mm})$, passing at the (upper) liquid-air interface of the suspension when cast; (B) Scaled side-view of the magnets used and the corresponding vectorial field from the data in (A). The insert in (B) displays the 3D view of the arranged magnets and defines the $(x,y,z)$ axes.
Figure S15. Magnetic field profile calculated above the junction of the two magnets. The resulting field was calculated as a linear superposition of two magnetic fields generated independently by single N42 grade magnets – of dimension 40×40×60 mm$^3$ in order to account for the effect of the iron substrate (resources: https://www.dextermag.com/resource-center/magnetic-field-calculators/field-calculations-for-rectangle). (A) Magnetic induction $\mathbf{B} = \mu_0 \mathbf{H}$ calculated at the top interface (air-liquid) at $z = 3.5$ mm from the top surface of the magnets, in extremely agreement with experimental measurements (open symbols) and at the bottom interface (liquid-substrate) at $z = 1.7$ mm from the top surface of the magnets (filled symbols). (B) Visualization of the vectorial field in the $(x,z)$ cross-section of the film. The thickness of the liquid is scaled to its initial level at the starting concentration (i.e. $V = 2$ mL).
E  Modeling of the optical response of the films

The cholesterics order at the kinetic arrest is initially defined by a pitch $p_i$ and a tilt angle $\beta_i$ (where the index $i$ stands for initial). Upon further drying, the cholesteric structure experiences in the first approximation a unilateral compression along the $z$ direction characterized by a factor $\alpha$ ($0 < \alpha < 1$), while the dimensions remained unaffected in the $(x,y)$ plane. Following this, and adapting from the formula derived in the Supporting Information of a previous publication,$^2$ the new cholesteric structure is defined by a new pitch $p_f$ and a tilt angle $\beta_f$ (where the index $f$ stands for final) related to the initial as:

$$\beta_f = \tan^{-1}[\alpha \tan \beta_i] \quad (S1)$$

$$p_f(\beta_f) = p_i(\beta_i)/\sqrt{\sin^2 \beta_i + \alpha^2 \cos^2 \beta_i} = p_i(\beta_i)/\sqrt{\sin^2 \beta_f + \alpha^{-2} \cos^2 \beta_f} \quad (S2)$$

The model of the optical response of the film, as probed with the goniometer for a given set of algebraic angles ($\theta_{in}$, $\theta_{out}$), is derived from the previous formula by applying the Fergason’s formula$^3$ (which arises from the Bragg law for cholesterics corrected by Snell law):

$$\beta_f = \frac{1}{2} \sin^{-1}\left(\frac{1}{n} \sin \theta_{out}\right) + \frac{1}{2} \sin^{-1}\left(\frac{1}{n} \sin \theta_{in}\right) \quad (S3)$$

$$\lambda = n p \cos\left[\frac{1}{2} \sin^{-1}\left(\frac{1}{n} \sin \theta_{out}\right) - \frac{1}{2} \sin^{-1}\left(\frac{1}{n} \sin \theta_{in}\right)\right] \quad (S4)$$

where $n$ is the average optical index of the film, taken here as $n \sim 1.56$. Importantly, the algebraic value $\theta_{in}$ of the incident angle is either zero or negative in this work, according to the angle convention of the Figure 2i.

The fits shown in Figure S16 are obtained with $\alpha = 0.175$ and $p_i = 1.7 \ \mu m$ taken constant for any $\beta_i$ between -89° and +89°, and correspond to a kinetic arrest undergone at a concentration of $[\text{CNC}]_{KA} \sim \alpha = 17.5 \ \%v/v \sim 25 \ \text{wt.\%}$, while the initial tilt of the cholesteric structure in the sample exposed to a tilted magnetic field is within $\beta_i \sim 20–25^\circ$, significantly smaller than the tilt of the magnetic field itself ($\beta_H \sim 65–70^\circ$).
Figure S16. Experimental fit of the optical response of cholesteric CNC films. The angular resolved optical spectroscopy of CNC films prepared (A) in $\mathbf{H} = 0$ (same as Figure 2D) and (B) in $\mathbf{H} \neq 0$ (same as Figure 2F) are represented using a $\log_{10}$-scale of the light intensity. On top of those experimental data were added: (i) in dashed yellow lines, the different $\beta_f$ angles corresponding to the final tilt of cholesteric domains in the dry films and contributing to the observed diffraction; (ii) in dashed while lines, the different $\beta_i$ angles corresponding to the initial orientation of a cholesteric domain as it gets compressed further down from the kinetic arrest towards the dry film; (iii) in solid red line, the fit of the optical response assuming a randomized starting orientation of their $\mathbf{m}$ axis, which fits well the case of $\mathbf{H} = 0$ while for $\mathbf{H} \neq 0$ it indicates that a final tilt of $\beta_f = +3–5^\circ$ in the film corresponds to an initial tilt of $\beta_i = +15–30^\circ$ in the suspension.

Figure S17. Photograph illustrating the optical response of a film cast at the edge between two magnets and illuminated using a large incident light spot ($\Omega \sim 20$ mm) covering an area where the local cholesteric tilt explores various extreme tilts in the horizontal plane. As a
result, the film displays a strong optical response with a net red-shift as the angle $\theta_{\text{out}}$ increases. Note that the scattering is significantly reduced outside the horizontal plane (i.e. containing the different $\mathbf{m}$ axes and the incident light wavevector $\mathbf{k}_i$), due to the alignment of the cholesteric domains mostly within this plane.

F Instrumentation

F.1 Atomic Force Microscopy

Atomic force microscopy (AFM) images were acquired with an Agilent 5500, collected in tapping mode (OTESPA-R3 tip) and at room temperature over a $5 \times 5 \, \mu\text{m}^2$ area. AFM samples were prepared by drop-casting 10 $\mu$L of a diluted CNC suspension (~0.002 wt.%) onto freshly peeled mica that was functionalized prior to deposition by applying poly(L-lysine) aqueous solution (~0.1%, MW 150kDa) for 1 min and subsequent washing with milli-Q water and dried under a nitrogen flow. After deposition of the CNC suspension for 1 min, the samples were rinsed and dried in the same conditions.

F.2 Photography

Macroscopic pictures were taken with a color camera (Nikon D3200 18-55vr II KIT with Hoya Filter close up +2) and diffuse incident white light.

F.3 Angular-resolved optical spectroscopy

Angular-resolved optical spectroscopy was carried out using a bespoke goniometer: a xenon lamp (HPX-2000, Ocean Optics) was used as a light source and a spectrometer (AvaSpec-HS2048, Avantes) was used to extract the scattered optical signal. The sample was mounted on a rotating stage in the center of the goniometer and was illuminated with a collimated incident beam (light spot size $\Theta \sim 6 \, \text{mm}$). A detector was mounted on an arm attached to a motorized rotation stage, and coupled the scattered light into an optic fiber connected to the spectrometer. The recorded light intensity was normalized with respect to a white Lambertian diffuser, while the exposure time was adjusted using an automatized high-dynamic-range (HDR) method. Measurements were carried out at fixed incident light angles (either $0^\circ$
or -30°, defined algebraically from the normal of the sample interface, see Figure 2J and section E) and by scanning the scattered spectral intensity collected with the rotating detector.

F.4 Polarized optical microscopy

Polarized optical microscopy was performed in reflection mode on a customized Zeiss Axio microscope using a halogen lamp (Zeiss HAL100) as a light source using Koehler illumination. Bright field (BF) and dark field (DF) images of the films were both recorded with 20× Epiplan Apochromat objective (NA 0.6, WD. 1.7 mm) and a CCD camera (UI-3580LE-C-HQ, IDS) after filtering the reflected light with a quarter-wave plate and a linear polarizing filter with adjustable mutual orientation, in order to distinguish left- (LCP) and right-circularly polarized (RCP) light.

The optical response was also observed in k-space using a different setting: the microscope was equipped with a 50× Epiplan Apochromat objective (NA 0.95, WD. 0.28 mm) mounted above a Bertrand lens (ref. 453671-0000-000, Carl Zeiss), a beam-splitter coupled to a linearly polarized white light source from an optical fiber (core diameter 50 µm, light spot size on the sample Ø ~ 1 µm), and above the beam-splitter, an analyzer crossed with respect to the polarizer, and finally a CCD camera. A grating of periodicity 1200 grooves·mm⁻¹ (ref. GR13-1205, Thorlabs) was used to calibrate the k-space. The incident light was therefore \( \theta_{in} = 0^\circ \) and the collected light \( \theta_{out} = \sin^{-1}(\text{NA}) \).

F.5 Scanning electron microscopy

Scanning electron microscopy (SEM) images of film cross-sections were acquired using a Zeiss Leo Gemini 1530VP system, working at 90° with respect to the electron beam. SEM samples were mounted on aluminum stubs using conductive carbon tape and, to minimize surface charging, sputtered with a 5–10 nm layer of Au/Pd (Emitech K550; I = 55 mA for 10–14 s). The acceleration voltage used was 5.0 kV, and the working distance was kept within 3–4 mm.
G Supplementary discussion regarding pitch variation under vertical magnetic field

Pan et al. previously investigated the effect of a weak vertical magnetic field (0.2 T) during the preparation of cholesteric CNC films.\textsuperscript{[4]} In contrast to this work, the authors used different sets of low initial concentrations (0.1% – 2%) and evaporation time (0.5 h – 8 h). As a result, they did not report enhancement of the homogeneity in their films (which show clear polydomain structure) or angular controlled optical response, and their conclusions suggested that increasing the evaporation time led to higher pitches (also confirmed independently\textsuperscript{[5]}) and the additional application of the vertical magnetic field increased this effect.

More recently, De France et al.\textsuperscript{[6]} conducted an in-depth analysis by SAXS of CNC orientation in suspension under low magnetic fields and observed a similar effect, which can be summarized as following: As the order of the cholesteric phase increases, the volume fraction of domain boundaries and dislocations significantly decreases, and since these regions do not allow the same packing of CNCs as within the domains themselves, the local density of CNC rods in these domains is locally higher, for mass conservation reasons. While the reported effect is fairly limited, the strong dependence of the chiral twist with the local concentration of CNCs explains qualitatively such a trend.

From this explanation, the increase of the pitch under magnetic field does not appear to be due to the magnetic field itself, but to the increased order it promotes at larger scales. Furthermore, this reported pitch-increasing effect of the magnetic field could be relabeled as a pitch-decreasing effect of disorder in the cholesteric phase.

In the present work, the already high concentration used in the initial cast suspension (8.5% wt.) combined with the extended evaporation time (over a week) leads to small amounts of domain boundaries, even for clearly polydomain samples cast without any magnetic field. For this reason, the optical properties do not allow for discerning any pitch increase in magnetically aligned with respect to non-aligned samples. However, our modeling (cf.
Section E) successfully illustrates how initially tilted domains produce, after vertical unidirectional compression, tilted cholesteric domains of larger pitches, while the smallest pitches are found in the domains initially vertically oriented. For this reason, the film cross-section of non-aligned films will statistically expose many tilted cholesteric domains of larger dimensions than those observed in a film cast under a vertical magnetic. This tendency can explain the observations reported in Figure S18, where the reflectivity spectra of the films prepared in the absence and in the presence of a magnetic field are compared. These spectra are collected over a large macroscopic surface (spot size $\varnothing = 4.4$ mm, area of illumination $\sim 15$ mm$^2$) in order to average out the high variability of the local optical response of films prepared without any magnetic field (experimental settings: double-ended fiber (R200-7-SR, 00S-003413-01, Oceanoptics), incident light NA = 0.216, fiber-to-sample distance $10 \pm 0.5$ mm, white diffuser (USRS-99-010 AS-01158-060) used as a reference).

**Figure S18.** Reflectivity spectra comparing the same samples as in Figure 2A-B, using a double-ended fiber, and normalized to their maximum intensity (illumination area $\sim 15$ mm$^2$).
References


