When pursuing sustainable approaches to fabricate photonic structures, nature can be used as a source of inspiration for both the nanoarchitecture and the constituent materials. Although several biomaterials have been promised as suitable candidates for photonic materials and pigments, their fabrication processes have been limited to the small to medium-scale production of films. Here, by employing a substrate-free process, structurally coloured microparticles are produced via the confined self-assembly of a cholesteric cellulose nanocrystal (CNC) suspension within emulsified microdroplets. Upon drying, the droplets undergo multiple buckling events, which allow for greater contraction of the nanostructure than predicted for a spherical geometry. This buckling, combined with a solvent or thermal post-treatment, enables the production of dispersions of vibrant red, green, and blue cellulose photonic pigments. The hierarchical structure of these pigments enables the deposition of coatings with angular independent colour, offering a consistent visual appearance across a wide range of viewing angles.
Colour is an essential form of communication in our society, with the production and use of dyes and pigments dating back to prehistoric times. In the last few decades, the available colour palette has been enlarged and diversified enormously by the development of so-called interference or effect pigments. While such photonic pigments are increasingly found in a wide variety of consumer products, spanning from automotive paints and security inks to textiles, cosmetics and food, they often rely on the use of energy-intensive methods, synthetic polymers or inorganic materials (whose extraction raises ethical concerns). When considering sustainable approaches to photonic pigments, nature can be used as a source of inspiration in terms of both the nanoarchitecture and the constituent materials. Inspired by the hierarchical arrangement of cellulose found in structurally coloured plants, here we report a substrate-free, emulsion-based methodology to produce cellulosic photonic pigments with vibrant colour spanning across the entire visible spectrum.

It is well known that colloidal suspensions of cellulosic nanocrystals (CNCs) spontaneously self-organise above a certain volume fraction into a cholesteric (i.e., chiral nematic) colloidal liquid crystal, whereby the individual nanoparticles align locally along a helicoidal structure. Moreover, evaporating a cholesteric CNC suspension can lead to photonic films that display vibrant, iridescent colour. However, the self-assembly of CNCs confined within a spherical geometry, such as that of an emulsified droplet, has failed to produce microparticles with structural colour in the visible range, despite the attempts of several research groups. The colour of CNC-based photonic materials is defined by the periodicity of the underlying helicoidal nanoarchitecture, referred to as the ‘pitch’, \( p \). In general, the value of the pitch is affected by suspension-related parameters (e.g., pH or ionic strength) and, once the suspension is kinetically arrested, by the geometry in which self-assembly takes place. We previously reported that for a hierarchical spherical geometry undergoing isotropic contraction, the relationship that regulates the pitch with the CNC volume fraction scales as \( p \propto \phi^{-1/3} \), instead of \( p \propto \phi^{-1} \), as expected for vertically aligned domains in a drying film. This reduced compression leads to microparticles with pitch values in the micron-range, correlating to reflectance in the infrared regime rather than at visible wavelengths. In this study, the inherent limitation of CNC self-assembly under spherical confinement is overcome by exploiting the interfacial buckling of kinetically arrested microdroplets of an aqueous CNC suspension. This emulsion-based methodology combines a careful optimisation of the aqueous CNC suspension with the controlled removal of water from the buckled CNC microparticles, resulting in vibrant red, green, and blue dispersions of cellulosic photonic pigments. Furthermore, we show that the hierarchical structure of these pigments enables the production of coatings with angular independent structural colour.

**Results**

Fabrication of structurally coloured CNC microparticles. In order to produce CNC microparticles with visible colour, an aqueous CNC formulation was first identified that yielded the smallest obtainable pitch when independent of any geometric constraints. It was found that films cast from the anisotropic phase of a commercial CNC suspension (Univ. Maine, 7.0 wt%), in the presence of additional salt ([NaCl]/[CNC] = 100 \( \mu \text{mol g}^{-1} \)) have an average pitch of 141 ± 9 nm, which results in reflection in the ultraviolet region (Supplementary Fig. 1). As summarised in Fig. 1a, the same aqueous CNC suspension was then emulsified in hexadecane via a flow-focusing microfluidic device to produce monodisperse water-in-oil microdroplets (\( \phi \approx 160 \mu \text{m} \)). Upon controlled, slow drying beneath a hexadecane layer, the randomly oriented cholesteric CNC domains inside each microdroplet merged and reorganised to form a radially aligned Frank–Prýce monodomain structure (Supplementary Video 1 and Supplementary Fig. 12). Further water loss triggered the onset of kinetic arrest, with the periphery of the droplet arresting first due to a radial concentration gradient within the droplet that arose from the evaporative flux at the interface. The earlier arrest at the droplet interface contributed to the formation of a shell that then buckled due to the interplay between compressive capillary forces (that shrink both the droplet radius and surface area as the droplet dries) and the mechanical resistance of the solidifying cholesteric CNC shell to a reduction in its total surface area. Significant buckling of the radially aligned cholesteric shell enhanced the pitch compression within the arrested droplet, allowing the inherent limit of the spherical geometry to be overcome and resulting in microparticles that display visible colour.

The initial buckling resulted in red-coloured microparticles (\( \phi \approx 100 \mu \text{m} \)), however additional compression of the pitch was required to produce the dispersions of green and blue CNC microparticles shown in Fig. 1b. This was controllably achieved by applying a thermal or solvent post-treatment to further collapse and buckle the microparticles, as summarised in Supplementary Fig. 2 and discussed in detail later. The irregular and buckled surface of the microparticles can be visualised by dark-field microscopy (Fig. 1c). Unlike concentrically ordered photonic microspheres, the majority of the reflected light is at oblique angles, providing a less directional optical response as evidenced by the microparticles appearing less vibrant in bright-field microscopy (Supplementary Fig. 3). Microspectroscopy of individual CNC microparticles confirmed that the colour arises from a single reflection peak that is predominantly left-circularly polarised (Fig. 1d), validating the underlying helicoidal architecture is the same as observed for photonic CNC films.

**Accessing additional pitch compression via desiccation.** The change in the visual appearance of the CNC microparticles arising from the additional compression upon treatment with a polar solvent is exemplified in Fig. 2. The dried microparticles were first washed with \( n \)-hexane to remove residual non-volatile hexadecane and surfactant. In this non-polar solvent, the microparticles do not swell and a predominately red colour was reflected (Fig. 2a). When the \( n \)-hexane was subsequently evaporated, the microparticles appeared white due to strong surface scattering at the air–particle interface, but without a noticeable volume change (Fig. 2b). The CNC microparticles were then immersed in methanol, leading to a small degree of swelling and the reappearance of the red colour due to a reduced refractive index contrast at the particle–solvent interface (Fig. 2c). However, upon evaporation of methanol, the microparticles experienced a significant volume reduction and consequently a pitch compression (Fig. 2d), such that subsequent re-immersion in \( n \)-hexane revealed blue colouration (Fig. 2e). Less polar solvents can be used to induce smaller volume contractions that result in intermediate colours, with the green CNC microparticles shown in Fig. 1b obtained with isopropanol. Notably, while repeated washing with isopropanol does not induce any further colour change, exposing the isopropanol-washed microparticles to a more polar solvent (e.g., methanol) results in a further irreversible blueshift (Supplementary Fig. 4).

The effectiveness of the methanol treatment on different sized microparticles was tested. It was found that although microparticles of three sizes (\( \phi \approx 26, 80, 124 \mu \text{m} \)) all demonstrated a
similar blue appearance after methanol treatment, the circular polarisation of the optical response differed (Supplementary Fig. 5). While the smallest microparticles reflect predominantly left-circularly polarised light, similar to conventional drop-cast CNC films,30 the largest microparticles showed comparable intensity in both circular polarisations (Fig. 2f–j). This trend in polarisation response can be attributed to the distortion of the helicoidal architecture within the buckled microparticles. First, the local shear of the cholesteric domains causes a distortion of the CNC helicoidal arrangement, which results in the reflected light having an elliptical polarisation that is still predominantly left-handed, i.e. that can be decomposed in a main left-circularly polarised (LCP) component as well as a small right-circularly polarised (RCP) component.12,31 Second, at a larger scale the buckling of the interface results in highly tilted cholesteric regions, effectively acting as birefringent retardation plates. This enables the conversion of incident RCP light into LCP light, which can be reflected by deeper cholesteric regions within the microparticles, and then converted back into RCP light.32,33 These effects are expected to be more prevalent in larger microparticles since they are both thicker and more buckled (Supplementary Fig. 6).

Given that methanol and isopropanol are able to form hydrogen bonds with water and thus act as dehydrants (e.g. methanol is routinely used to fix proteins34,35), the volume contraction and corresponding pitch reduction induced by washing the ‘dry’ CNC microparticles with a polar solvent was attributed to the removal of residual water. This was verified by studying the effect of thermal treatment on the hexane-washed microparticles. Specifically, the microparticles were exposed to a constant temperature chosen between 40 and 200 °C for sixty minutes in a dry nitrogen atmosphere (Supplementary Fig. 7), followed by optical microscopy in refractive index-matching oil \((n = 1.55)\) at ambient temperature (Fig. 3a). Despite an apparent linear decrease in diameter with temperature, the CNC microparticles heated below 100 °C present only minor colour change suggesting this initial volume contraction had little impact on the buckled surface (Supplementary Fig. 8a). However, samples exposed to temperatures above 100 °C displayed a more significant blueshift, with microparticles heated at 200 °C

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**Fig. 1 Photonic pigments via the confined self-assembly of cellulose nanocrystals.** a Schematic summarising the preparation of photonic microparticles: (i) the aqueous CNC suspension was emulsified in hexadecane via a microfluidic flow-focusing device, upon which the cholesteric domains self-organise and merge into a radially aligned monodomain (Frank–Pryce structure); (ii) at a later stage of drying, the microdroplet becomes kinetically arrested and buckles; (iii) once drying is complete, CNC microparticles are formed with a complex surface morphology and visible red colouration; (iv) controlled removal of residual water within the microparticle induces additional buckling resulting in a further blueshift, enabling a full spectrum of photonic microparticles to be produced. b Photographs showing red, green, and blue cellulosic photonic pigments suspended at ca. 3.5 mg mL\(^{-1}\) in ethyl cinnamate \((n = 1.56)\). The vial is 22 mm in diameter. c Dark-field microscopy images of individual CNC microparticles in refractive index oil \((n = 1.55)\) and (d) associated micro-spectra of individual microparticles, collected through left-handed circularly polarisation (LCP, solid line) and right-handed circularly polarisation (RCP, dashed line) filters. The spectra are normalised against a white Lambertian diffuser coated with the same refractive index oil.
exhibiting a blue appearance comparable to their methanol-washed analogues (Supplementary Fig. 8b and Fig. 1d). Importantly, while the solvent-treated CNC microparticles disintegrate upon immersion in water, the microparticles heated at 200 °C maintain their integrity and ability to reflect visible light (with a moderate redshift), possibly as a result of the additional thermal desulfation of the CNCs (Supplementary Fig. 9)\(^\text{36-39}\).

To quantify the amount of residual water in the CNC microparticles, samples with and without methanol treatment were characterised by thermogravimetric analysis (TGA), as reported in Fig. 3b. As expected, both curves exhibit a large mass loss starting at 250 °C, corresponding to the thermal degradation of cellulose\(^\text{40}\). However, prior to reaching this temperature, a significant mass loss (ca. 35%) was recorded in the sample without methanol treatment, while a much smaller mass loss (ca. 10%) was observed for the methanol-treated sample. After correcting for desulfation (see Supplementary Discussion 1), the mass fraction of removable water was calculated to be approximately 30% for the untreated sample. Scanning electron microscopy (SEM) measurement of the highly buckled CNC microparticles showed a decrease in the average diameter from 88.5 ± 0.8 \(\mu\)m to 77.9 ± 0.5 \(\mu\)m upon methanol treatment (Fig. 4a, b and Supplementary Table 1). This corresponds to a 12.1 ± 1.1% diameter decrease, which, given it underestimates the impact of buckling, is in good agreement with the value of 13.9% estimated from the TGA analysis and calculated in Supplementary Discussion 1. Another important indication of the dehydrant effect of methanol is the reduced mass loss upon pyrolysis above 250 °C, which suggests that reaction with water to form CO and CO\(_2\) no longer occurs (Supplementary Fig. 10)\(^\text{41}\). This further supports our hypothesis that both solvent and thermal treatment cause a blueshift in the reflected colour by the removal of residual water.
As expected from the optical analysis, SEM cross-sections of the microparticles revealed that the cholesteric domain remains locally well-aligned to the highly buckled surface (Fig. 4c, d). The pitch measured in regions away from the hinge of a fold \( p_{\text{limb}} \), which are primarily responsible for the visual appearance) are consistent across multiple regions and microparticles, with the average pitch \( p_{\text{limb}} \) reduced from 396 ± 31 nm to 269 ± 16 nm after the methanol treatment, in agreement with the observed optical response (Fig. 4e, f). In contrast, the pitch measured in the hinge of a fold \( p_{\text{hinge}} \) (contributing to a negligible volume fraction) was much more variable and depended on the fold tightness, with \( p_{\text{hinge}} \approx p_{\text{limb}} / \cos \theta \), where the fold angle \( \theta \) is defined in Fig. 4. Interestingly, the percentage of pitch compression in the limbs is ca. 32%, which matches well with the volume contraction of the microparticle (32.1 ± 1.5%) rather than the reduction in diameter (12.1 ± 1.1%) as estimated from SEM (cf. Fig. 4a, b). This indicates that buckling of the spherical microparticle allows the pitch to be locally compressed more significantly than expected for this geometry²⁰. This greater compression, approaching that of a drop-cast film, is what enables reflection at visible wavelengths to be achieved. A multi-step buckling process, as suggested by the SEM images, can explain the mechanism of pitch compression and the route to volume shrinkage. Upon each buckling event during the microparticle drying process, \( p_{\text{hinge}} \) would stop contracting and thus would "record" a transient pitch, while \( p_{\text{limb}} \) would continue to shrink uniformly (with a corresponding \( \theta \) increase), giving rise to coherent colour across the microparticle. This process would repeat, resulting in additional buckling events, leading to several generations of hinges where the oldest folds have the largest \( p_{\text{hinge}} \) and \( \theta \). While buckling events facilitate the removal of water from the microparticles (as described below), they also increase the ability for the resulting distorted structure to withstand greater mechanical stress. In contrast to a drop-cast CNC film, where complete collapse of the cholesteric phase is achieved upon evaporation, this behaviour makes it increasingly difficult for residual water to escape upon drying under ambient conditions. As such the removal of this trapped water requires additional mechanical deformation, achievable either by displacement with a polar solvent or by thermal treatment, to allow capillary forces to further contract the microparticle.

**Fig. 4 The role of interfacial buckling on the pitch of the radially aligned CNC microparticles.** Scanning electron microscopy (SEM) images of a representative microparticle (a) prior to and (b) after treatment with methanol, showing the volume contraction and increase in buckling. Corresponding cross-sectional images in (c) and (d) show the related decrease in the pitch of the helicoidal structure. e, f Limb and hinge pitches of (e) hexane-washed and (f) methanol-treated microparticles plotted as a function of the fold angle \( \theta \), as defined in the inset schematic. For both samples, the limb pitch is independent of \( \theta \), while the hinge pitch generally follows the stated trigonometric relationship.
source, the CNC suspension employed in this study becomes kinetically arrested at a sufficiently low volume fraction (6.4% v/v). Combining this with the small initial pitch in suspension (facilitated by a steep $\phi^{-1.9}$ power law prior to kinetic arrest) and the use of only the fully anisotropic phase (expanding an early radial self-organisation upon emulsification), it allows for visibly coloured CNC microparticles to be achieved\textsuperscript{20}. For completeness, a dish-cast film with vertically aligned domains was also prepared from the same CNC suspension (Supplementary Fig. 1), and the pitch was found to agree with the $\phi^{-1}$ scaling law expected for the film geometry when assuming the same kinetic arrest transition as for the drying microdroplets\textsuperscript{12,20}.

Two different mechanisms can be independently responsible for the anisotropic compression that results in buckling of the kinetically arrested Frank–Pryce structure. First, an arrested cholesteric suspension may preferentially compress along the helical axis upon water loss. Indeed, strong alignment of rigid fibres can lead to anisotropic swelling or contraction that is favoured in the perpendicular direction\textsuperscript{43,44}, and to anisotropic Young moduli in the dry state\textsuperscript{45}. For the radial helical arrangement of the Frank–Pryce structure, this results in an imbalance of radial to orthonodal compression upon volume contraction\textsuperscript{46,47}, leading to an excess of surface area to maintain a spherical shape. Second, the concentration front propagating inwards in the arrested droplet can lead to a more rigid shell that resists orthonodal compression upon further volume contraction\textsuperscript{48}. Indeed, buckling of a spherical shell was reported for drying droplets of isotropic colloidal particle suspensions\textsuperscript{24}, while it was prevented when high solvent permeability was maintained\textsuperscript{49}, suggesting that buckling can be solely driven by the kinetics of water loss. In the latter case, an insufficient orthonodal contraction is compensated by an enhanced radial compression. Regardless of the precise mechanism, the high resistance of the drying microparticle to orthonodal compression prevents volume contraction if the spherical shape is maintained, so buckling is a necessary condition for further water removal. Interestingly, buckling also comes with high deformation costs and makes further volume contraction more difficult. As it contracts, the concentric cholesteric structure undergoes several buckling events resulting in several generations of wrinkles, which are increasingly able to resist further orthonodal compression despite the low water vapour pressure. This explains why capillary forces were not able to completely compress the ‘dry’ microparticles in hexane, while further desiccation with either polar solvent or by heat treatment allowed for further compression and buckling with higher order wrinkles.

An important consequence of anisotropic compression and buckling is a steeper pitch decrease than that predicted by the power law for an isotropic contraction ($p \propto \phi^{-1/3}$). To understand how the formulation of the initial CNC suspension influences the formation of a Frank–Pryce structure and its evolution into a buckled, coloured microparticle, three variations were prepared and compared against the standard (anisotropic) formulation (Fig. 6), with the self-assembly also monitored over time (Supplementary Figs. 12–15). A 50% dilution of the standard CNC suspension resulted in a more pronounced core-shell morphology within the drying droplets, resulting in irregular, collapsed microparticles with larger-period wrinkles. This morphology led to more inter- and intra-particle variations in colour, however it is notable that all microparticles were blue-green after subsequent methanol treatment. In a second variation, the isotropic fraction of the original CNC suspension was emulsified instead of the anisotropic fraction. The inability of this suspension to assemble into a Frank–Pryce structure within the microdroplet resulted in the formation of more spherical microparticles with only fine surface buckling. Faint structural colour arises from this thin shell, while the disordered, polydomain core leads to significant broadband scattering (i.e., whiteness). In a third variation, electrolytes (i.e., NaCl) were not added to the CNC suspension, resulting in a fully anisotropic and viscous suspension at 7.0 wt.%. Although the resulting microparticles were buckled, weak cyan colour was only apparent after

![Fig. 5 The reduction in the cholesteric pitch upon drying a microdroplet of CNC suspension to form a photonic microparticle.](https://example.com/fig5.png)

The cholesteric pitch measured in the droplets by polarised optical microscopy (triangles) initially decreases following $p \propto \phi^{-1.9}$, until a transition at $\phi = 6.4\% \text{ v/v}$, upon which it initially appears to follow $p \propto \phi^{-1/3}$ (see inset). An extrapolation of $p \propto \phi^{-1}$ from this transition is in reasonable agreement with SEM cross-sectional analysis of the corresponding film (square), validating this is the onset of kinetic arrest ($\phi_{ka}$). Extrapolation of the $p \propto \phi^{-1/3}$, does not match with the pitch measured from the red and blue microparticles (respectively red and blue diamonds), with the additional pitch compression attributed to progressive buckling post kinetic arrest. By considering the isoperimetric quotient $Q$ of the microparticle cross-sections, the pitch they would have if buckling could be prevented can be estimated (circles), which is in good agreement with the $p \propto \phi^{-1/3}$ power law, confirming the key role of buckling in causing additional radial pitch contraction upon further compression. Error bars represent the average deviation of $\rho_{emb}$ from SEM cross-sections.
Angular-independent colour from photonic pigments. To demonstrate the potential use of the CNC microparticles as photonic pigments within a paint or coating, green microparticles were embedded in a polydimethylsiloxane (PDMS) film and optically characterised under two representative observation conditions. In the first configuration, the embedded film was observed at a fixed illumination angle (\(\alpha_i\)) with respect to the viewing direction and the sample itself was rotated at different angles (\(\alpha_s\)) defined with respect to the viewing direction (Fig. 7a, b). Direct observations showed green reflection with no detectable colour change for the explored angles (\(\alpha_s\)). Angular-resolved optical spectroscopy confirmed the optical response remained centred at the same wavelength (approximately 490 nm, Fig. 7c). In the second observation configuration, the sample was illuminated at normal incidence and the viewing direction was scanned, which corresponds to maintaining equal illumination (\(\alpha_i\)) and sample (\(\alpha_s\)) angles, such that \(\alpha_i = \alpha_s \in [0^\circ, 90^\circ]\), Fig. 7d). In this case, only a limited blueshift in the peak wavelength (i.e., \(\Delta\lambda \approx 25\) nm, \(\Delta\lambda/\lambda < 5\%\)) was detected (Fig. 7e). These two complementary configurations, performed in off-specular conditions as defined with respect to the film interface (i.e., \(\alpha_s \neq 2\alpha_i\)), demonstrate the non-iridescent character of the microparticles when embedded in the PDMS matrix, which sharply contrasts with the strong iridescence observed for dish-cast CNC films\(^{12}\).

The origin of the angular independence can be explained by a simple model based on ray-tracing analysis. As the macroscopic angular optical response of the buckled CNC microparticles matches surprisingly well with that of a radially aligned cholesteric sphere (Supplementary Fig. 17)\(^{28,50}\), each embedded CNC microparticle was approximated by a microsphere with a concentric multi-layer architecture (Supplementary Fig. 18). Due to Snell’s law, the light reflected from the microparticle has a
The critical maximum angle that allows for transmission through the PDMS-air interface (Supplementary Fig. 19). This limits the range of Bragg angles that contribute to the observed macroscopic optical response. From this model, the maximum expected spectral shift is limited to $\Delta \lambda = 0.5\%$ in the first configuration and $\Delta \lambda = 6.5\%$ in the second configuration (Fig. 4b, d), validating the use of these microparticles as non-iridescent photonic pigments.

**Discussion**

Starting from a commercially available CNC suspension, we successfully prepared cellulose photonic pigments that can reflect colour across the full visible spectrum, overcoming the large pitch inherent to spheroidal CNC microparticles. The key to additional pitch compression was interfacial buckling, which was achieved by an appropriate initial CNC source and formulation, as well as the controlled removal of residual water by either thermal or polar solvent post-treatment. The interfacial buckling distorted the helicoidal architecture of the microparticles, giving rise to reflection of both LCP and RCP light, which is rarely observed for CNC films. Importantly, cellulose photonic pigments embedded in a matrix display angular independent structural colour, in contrast to the iridescence of drop-cast photonic films. Finally, while recent progress has been made to upscale photonic CNC film production\(^6\), using an emulsion-based route allows for pigments to be directly produced in a single step without the need for a substrate. Furthermore, due to the good colour tolerance with respect to the microparticle size, this approach should be transposable from microfluidics to larger scale emulsion methods, such as membrane emulsification, which would enable them to be produced via a continuous fabrication process. As such, these cellulose photonic pigments offer a sustainable, biocompatible and scalable solution to the colourant industry, where there is a demand to transition away from synthetic polymers and unrenewable minerals to those derived from natural materials.

**Methods**

**Cellulose nanocrystal suspension.** The cellulose nanocrystal suspension was purchased from the Process Development Center of the University of Maine (batch no. 2015-FPL-077). The as-received suspension was provided pH-neutralised (i.e., negatively charged CNCs due to $-\text{OSO}_3^-$ groups, with Na$^+$ counter-ions), and was used as received, i.e., no tip sonication or thermal treatment was applied. The measured concentration of the suspension was 10.7 wt.% (A&D, MX-50 moisture analyser). Consistent with previous benchmarking studies\(^5\), the zeta potential and Z-average size were respectively recorded to be $-43.5 \pm 1$ mV and $121 \pm 2$ nm (Malvern Zetasizer Nano ZS; $[\text{CNC}] = 0.25$ wt.%, $[\text{NaCl}] = 5$ mM, passed through a $0.8$ μm cellulose acetate syringe filter). A 6.0 wt.% dilution of this commercial suspension had a conductivity of $477 \pm 6$ μS cm$^{-1}$ (Mettler Toledo InLab 752-6MM) and a pH of 4.8 (Mettler Toledo InLab Micro Pro-ISM; measured in the presence of an excess of K$^+$ ions). Conductometric titration of an acidified CNC suspension (0.5 wt.%, 20 mL) against sodium hydroxide (0.01M) revealed $[-\text{OSO}_3^-] = 398$ μmol g$^{-1}$ and $[-\text{COO}^-] = 9$ μmol g$^{-1}$. The acidified
The reflected light could also be filtered with a quarter wave plate and a linear polariser mounted at different orientations to distinguish between left- or right-hand circularly polarised light. To perform a round-trip transmission measurement, the microscope was coupled to a spectrometer (Avantes, AvaSpec-HS2048) using an optical fibre (Avantes, FC-UV200-2-SR, 200 μm core size) in confocal configuration. The reflectance spectra were normalised in dark-field in left-circular polarisation against a white diffuser (LabSphere SRS-99-010) coated with the same refractive index oil (Supplementary Fig. 21). The time-lapse series were recorded on an Olympus IX-71 inverted microscope, using Olympus UPlanFLN (×10, NA 0.30) and LUCPlanFLN (×40, NA 0.60) objectives with an additional 1.6x magnifying lens, and imaged with a CMOS camera (Pixelink PL-D725CU-T). Where noted, transmission images were collected through crossed polarisers with an additional full-wave retardation (i.e., tint) plate (Olympus, U-TP530) to both enhance the overall brightness and contrast of the image, and to indicate the orientation of the cholesteric domains. Photos of vials containing microparticles dispersed in ethyl cineaminate (Sigma-Aldrich, \( \text{C}_8\text{H}_{16}\text{N}_2\text{O}_2\), 1.585) were recorded under diffuse illumination (i.e., fluorescent ceiling light) with a Samsung Galaxy S9+ smartphone.

AngULAR-RESOULED OPTICAL SPECTROSCOPY. A laboratory-built goniometer was used to analyse the angular response of the CNC microparticles. A white light source (Schott KL1500 set to 3300 K) was used to illuminate as a collimated incident beam with a spot size of approximately 6 mm and at a fixed angle of 0°. The detector was mounted on an arm attached to a motorised rotation stage and coupled the light into an optical fibre (1000 μm core) connected to a spectrometer (Avantes AvaSpec-HS2048, 1024 × 256). The sample was mounted on a rotation stage at the centre of the goniometer. The recorded light intensity was normalised with respect to the white Lambertian diffuser in air, while the exposure time was adjusted using an automated high dynamic range (HDR) method53. For the microparticle-embedded films, the angular measurement was performed following powder. To image the interior of the microparticles, they were cryo-fractured using the following protocol: (i) the microparticles in suspension were mounted on aluminium stubs using conductive carbon tape and interfaced with a spectrometer (Avantes AvaSpec-HS2048XL). The sample was mounted on a rotation stage at the centre of the goniometer. The reflected light could also be filtered with a quarter wave plate and a linear polariser mounted at different orientations to distinguish between left- or right-hand circularly polarised light. To perform a round-trip transmission measurement, the microscope was coupled to a spectrometer (Avantes, AvaSpec-HS2048) using an optical fibre (Avantes, FC-UV200-2-SR, 200 μm core size) in confocal configuration. The reflectance spectra were normalised in dark-field in left-circular polarisation against a white diffuser (LabSphere SRS-99-010) coated with the same refractive index oil (Supplementary Fig. 21). The time-lapse series were recorded on an Olympus IX-71 inverted microscope, using Olympus UPlanFLN (×10, NA 0.30) and LUCPlanFLN (×40, NA 0.60) objectives with an additional 1.6x magnifying lens, and imaged with a CMOS camera (Pixelink PL-D725CU-T). Where noted, transmission images were collected through crossed polarisers with an additional full-wave retardation (i.e., tint) plate (Olympus, U-TP530) to both enhance the overall brightness and contrast of the image, and to indicate the orientation of the cholesteric domains. Photos of vials containing microparticles dispersed in ethyl cineaminate (Sigma-Aldrich, \( \text{C}_8\text{H}_{16}\text{N}_2\text{O}_2\), 1.585) were recorded under diffuse illumination (i.e., fluorescent ceiling light) with a Samsung Galaxy S9+ smartphone.

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Transmission electron microscopy (TEM). Micrographs were captured using a Talos F200X G2 microscope (Thermo Scientific, FEI) TEM operating at 200 kV and a CCD camera. Samples were prepared as follows: (i) The CNC suspension was diluted in ultrapure water in two successive steps, first to 0.1 wt.% then to 0.005 wt.%. (ii) A TEM grid (Agar Scientific S160-3 Carbon film 300 mesh Cu) was plasma treated, followed by deposition of a drop of the 0.005 wt.% CNC suspension. This was left to sit on the grid for 90 s before gently removing all residual liquid with filter paper (Whatman). (iii) The CNCs were stained with uranyl acetate solution for 60 s, with excess liquid again removed by blotting.

Data availability

All raw data relating to this publication is freely accessible from the University of Cambridge data repository (https://doi.org/10.17863/CAM.27840).
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Author contributions

Experiments were designed by R.P. and T.Z.; photonic microspheres were fabricated and characterised by R.P. and T.Z.; SEM was performed by T.Z. and analysed by B.F.-P. and T.Z.; photonic pigments based on iridescent cellulose nanocrystal films. Carbohydr. Polym. 122, 367–375 (2015).

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Competing interests
The authors declare no competing interests.

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Correspondence and requests for materials should be addressed to Silvia Vignolini.

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