

Flexible Photonic Films Based on Cellulose Nanocrystals with Temperature-responsive Structural Color

Wen-Huan Yao^{a,*}, Xin Ma^{a,†}, Yan-Xia Wang^{a,†}, An-Zhi Ma^a, Zheng-Rui Ma^a, Xiao-Xia Wang^a, Wei-Xia Kang^a, and Zebing Zeng^{b,*}

^a College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, China

^b State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, China

Electronic Supplementary Information

Abstract Stimuli-responsive photonic materials based on cellulose nanocrystals (CNCs) have attracted considerable interest for their applications in sensing, anti-counterfeiting, and smart windows. However, most existing thermo-responsive CNC composites rely on the lower critical solution temperature (LCST) behavior of polymers, such as poly(*N*-isopropylacrylamide), which often restricts the operating temperature range and results in discontinuous or hysteretic optical responses. Herein, we report a new strategy that avoids LCST-driven bulk volume transitions by introducing a cholesterol derivative (Chol-6) as a thermo-responsive steric regulator through its incorporation into a Chol-6-functionalized polyacrylamide (PAM) network within the CNC chiral nematic matrix. A water-soluble prepolymer (PAMC₄) bearing Chol-6 side chains was synthesized and co-assembled with glycerol and CNCs *via* evaporation-induced self-assembly (EISA) to produce flexible structurally colored films. Glycerol serves as a plasticizer to overcome the brittleness of pure CNC films and as a hygroscopic agent to facilitate solvent-mediated structural adjustment rather than directly enhancing reversibility. By systematically adjusting the Chol-6/glycerol ratio, the helical pitch and the corresponding structural color can be continuously tuned from blue to red. The optimized 8CNCs-2PAMC₄/G₁₀ film showed a 64 nm redshift of the reflection maximum upon heating from 25 °C to 80 °C, significantly exceeding that of the Chol-6-free control. Mechanistic studies revealed that the thermal response is primarily governed by the steric regulation of the Chol-6 side groups within the PAMC₄ network, which modulates hydrogen-bond-mediated interactions and promotes relaxation-driven helical pitch expansion, while the intrinsic chirality of Chol-6 contributes mainly to the formation and preservation of the chiral organization. This study reveals the unexplored role of chiral compounds in CNC-based photonic materials as thermo-responsive steric regulators beyond conventional chiral twist inducers, providing a new design strategy for tunable thermo-responsive photonic systems without relying primarily on polymer volume phase transitions.

Keywords Cellulose nanocrystals; Chiral nematic liquid crystal; Photonic film; Thermochromism; Steric hindrance

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INTRODUCTION

Smart materials, also called stimuli-responsive functional materials, are macromolecular systems that exhibit intelligent behavior characterized by sensitive responses and unique functionalities under external stimuli such as mechanical force, heat, humidity, pH, electric/magnetic fields, light, and chemicals.^[1,2] Among these, photonic stimuli-responsive functional materials have received significant attention because of their structurally colored responses to multiple stimuli that enable visual differentiation.^[3] Recently, cellulose nanocrystals (CNCs), notable for

their high strength, tunable structure, facile modification, biocompatibility, and biodegradability, have played an increasingly important role in this domain.^[4] Typically obtained *via* acid-catalyzed hydrolysis, CNCs can disperse well in water owing to their surface sulfate ester groups, which induce electrostatic repulsion.^[5,6] During water evaporation, CNCs self-assembled into a left-handed chiral nematic liquid crystalline phase.^[7,8] This helical structure persists in the yielding solid films after water evaporates, presenting iridescence when the helical pitch (*P*) corresponds to visible wavelengths.^[9,10]

Owing to their special helical hierarchical organization, CNCs films have a wide range of applications in sensing, anti-counterfeiting, and information storage.^[11–13] Among these, responsive sensors are particularly significant because *P* can be modulated to produce distinct optical signals. However, the inherent brittleness of pure CNCs films limits their practical applications. Integrating organic polymers with CNCs enhances flexibility while preserving birefringence. Yao *et al.*^[14]

* Corresponding authors, E-mail: wenhuanyao@163.com (W.H.Y.)
E-mail: zbzeng@hnu.edu.cn (Z.Z.)

† These authors contributed equally to this study.

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combined CNCs with poly(ethylene glycol) (PEG) to create photonic films with a 435 nm redshift due to humidity-induced pitch expansion. Poly(*N*-isopropylacrylamide) (PNIPAM) resins are especially attractive because of their dual thermal/humidity responsiveness. For example, Kelly *et al.*^[15] demonstrated a 40 nm blueshift in CNCs/PNIPAM films above the lower critical solution temperature (LCST) of PNIPAM, which resulted from volume shrinkage when the temperature was above the LCST. Wang *et al.*^[16] fabricated dual-thermal/humidity-responsive films by functionalizing CNCs with hydrazone-modified PNIPAM. Moisture absorption induces resin expansion, causing a redshift of up to 145 nm in the reflectance spectrum. Heating beyond PNIPAM's LCST of PNIPAM triggered resin shrinkage, resulting in a blueshift of up to 87 nm. Yu *et al.*^[17] developed a novel multiresponsive photonic film by co-assembling PNIPAM-grafted CNCs and WPU latex. Thermoresponsive PNIPAM was covalently bonded to CNCs via glutaraldehyde crosslinking, where aldehyde groups reacted with hydroxyl groups (—OH) on CNCs and amine groups (—NH) on PNIPAM.^[18] The resulting nanocomposite exhibited reversible humidity responsiveness (25%–98% RH) with excellent repeatability along with polarity-dependent solvent responses. Increasing the ambient temperature triggered PNIPAM shrinkage, consequently reducing film transmittance. These dual thermal and humidity responses demonstrate significant potential for anti-counterfeiting,^[19] sensing,^[20] and smart window applications.^[21]

Despite the numerous reported temperature-responsive CNC-based composite photonic films, their response mechanisms predominantly depend on the LCST of thermosensitive polymers (e.g., PNIPAM), which undergo a coil-to-globule transition upon heating.^[22] This LCST-governed mechanism inherently constrains the operational temperature window to a narrow range around the transition temperature and often leads to discontinuous or hysteretic optical changes. Moreover, the reflection bandwidth was limited by the volume collapse of the polymer network. Therefore, the development of alternative CNC-based composite photonic films that operate through distinct physical mechanisms and enable continuous, wide-range, and reversible thermal modulation remains highly desirable.

Chiral nematic (cholesteric) liquid crystals are typically derived from nematic phases, either by incorporating chiral dopants or from intrinsically chiral molecules.^[23] The helical twisting power (HTP) of a chiral compound is commonly used to describe its ability to induce helical twisting and to determine *P* according to the relationship $P = 1/(\text{HTP} \times c)$, where *c* represents the dopant concentration.^[24,25] In conventional thermally induced chiral nematic liquid crystal systems, temperature-dependent variations in HTP arising from conformational changes or intermolecular interactions of chiral dopants can effectively regulate the helical pitch, leading to thermally induced reflection shifts.^[26,27] However, in confined and hierarchically assembled systems, such as CNC-based photonic composites, the macroscopic optical response is not necessarily governed solely by HTP variations. The hierarchical assembly environment, steric interactions, and spatial constraints between the chiral components and host matrix may also play critical roles in determining the thermal evolution of the helical structure. In particular, when chiral units are

covalently integrated into polymer networks, their steric effects and conformational adaptability may provide additional pathways for regulating the CNC helical organization beyond conventional HTP modulation. Therefore, understanding and exploiting these alternative structural regulation mechanisms provide new opportunities for the design of thermally responsive CNC-based photonic materials.

In this study, we selected the cholesterol derivative Chol-6 as a chiral functional component to regulate the helical assembly of CNC photonic films. The steroid framework of Chol-6 provides intrinsic chirality, whereas its flexible molecular structure enables temperature-dependent conformational adjustment and steric interactions within the CNC matrix through its incorporation into the PAM network. Rather than relying solely on the variation in HTP, we propose that the temperature response originates primarily from the thermally regulated steric effects of Chol-6 pendants within the PAM-*C_n*-modified CNC matrix, which modulates the packing arrangement and helical pitch of CNC assemblies. Glycerol was co-introduced to serve two complementary roles, as a plasticizer to mitigate the inherent brittleness of pure CNC films, and as a hygroscopic agent to enable water-assisted swelling, thereby facilitating solvent-mediated structural adjustment during thermal modulation. *N,N'*-methylenebisacrylamide (MBA) was also co-introduced as a light crosslinker to improve mechanical integrity. Although cholesterol derivatives and glycerol have been individually explored in CNC-based photonic systems, their synergistic integration and use of chiral molecular steric regulation to achieve thermally tunable photonic structures remain largely unexplored. Unlike conventional approaches based on polymer phase transitions (e.g., PNIPAM), which often suffer from narrow temperature windows and limited optical tunability, this strategy provides an alternative pathway for achieving thermal structural regulation through molecular-level steric modulation rather than relying primarily on bulk polymer phase transitions. Through the incorporation of Chol-6, the temperature-induced steric modulation of chiral components was directly translated into reversible changes in the CNC helical organization and the corresponding structural colors. Based on this concept, we fabricated flexible thermoresponsive films with structural color through free-radical copolymerization combined with evaporation-induced self-assembly (EISA).^[28] The effects of the Chol-6/glycerol ratio on the optical properties, helical pitch evolution, and microstructural characteristics were systematically investigated. Furthermore, comprehensive evaluations of the mechanical properties,^[29] humidity-induced responsiveness,^[30] and thermal response behavior^[31] were conducted to elucidate the structure–property relationships and reveal the underlying mechanism responsible for the reversible thermochromic behavior of CNC-based composite photonic films.

EXPERIMENTAL

Materials and Chemicals

Microcrystalline cellulose (MCC) was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Sulfuric acid (H₂SO₄, 98 wt%) and dichloromethane (DCM, AR) were obtained from Tianjin Zhiyuan Chemical Reagent Co., Ltd. (Tianjin, China). Cholesterol (Chol, 98%), acrylamide (AM, 99%), and 2,2'-

azobis (2-methylpropionitrile) (AIBN, 98%) were purchased from Macklin Biochemical Co., Ltd. (Shanghai, China) and InnoChem (Shanghai, China), respectively. 4-((6-(Acryloyloxy)hexyl)oxy)-benzoic acid (AHBA, 97%), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC), (98%), 4-dimethylamino-pyridine (DMAP, 98%), 2-hydroxy-1-(4-(2-hydroxyethoxy)phenyl)-2-methylpropan (Irgacure 2959, 98%), propane-1,2,3-triol (G, 98%), and *N,N'*-methylenebisacrylamide (MBA, 98%) were supplied by Bide Pharmatech Co., Ltd. (Shanghai, China). All chemicals were used without further purification, except for AIBN, which was recrystallized from methanol. Deionized water was obtained using a Yupu Series ultrapure water purifier (UPD-1-10t, Sichuan, China).

Synthesis and Preparation

Synthesis of Chol-6: AHBA (7.56 g, 25.86 mmol), EDC (2.48 g, 12.93 mmol), DMAP (0.78 g, 6.39 mmol), and DCM (50 mL) were premixed. Then, after a DCM solution (30 mL) of Chol (5.00 g, 12.93 mmol) was added dropwise under ice-bath conditions, the mixture was proceeded at 25 °C for 24 h. Subsequently, the reaction was quenched with saturated NaHCO₃ solution and extracted three times alternatively with saturated NaHCO₃ (50 mL) and DCM (200 mL). The collected organic phase was dried over anhydrous MgSO₄ overnight and then further purified by flash chromatography (silica gel, DCM/PE, 1/1 V/V) to afford the target compound as a white solid in 46.80% yield. ¹H-NMR (400 MHz, CDCl₃, TMS, δ, ppm): 7.96 (s, 2H), 6.89 (d, *J*=8.8 Hz, 2H), 6.40 (dd, *J*=17.3, 1.5 Hz, 1H), 6.16–6.07 (m, 1H), 5.82 (dd, *J*=10.4, 1.6 Hz, 1H), 5.41 (d, *J*=3.6 Hz, 1H), 4.81 (s, 1H), 4.17 (t, *J*=6.6 Hz, 2H), 4.00 (t, *J*=6.4 Hz, 2H), 2.43 (s, 2H), 2.04–0.86 (m, 38H), 0.69 (s, 3H). ¹³C-NMR (600 MHz, CDCl₃, TMS, δ, ppm): 166.32, 165.81, 162.73, 131.53, 130.55, 128.58, 123.11, 122.67, 113.96, 74.21, 67.95, 64.48, 56.71, 56.15, 53.43, 42.34, 39.76, 39.53, 38.31, 37.07, 36.67, 36.20, 35.81, 31.95, 31.90, 29.02, 28.55, 28.25, 28.03, 27.96, 25.74, 24.31, 23.84, 22.83, 22.57, 21.07, 19.40, 18.73, 11.87 (Fig. S1 in ESI).

Synthesis of prepolymers: a series of prepolymers containing AM and Chol-6 at varying mass ratios were synthesized and designated as PAMC_{*n*} ("*n*" means the mass percentage of Chol-6 to AM in a specific prepolymer, Fig. 1a). As a control, a prepolymer PAM containing only the AM monomer was synthesized. Taking the preparation of prepolymer PAMC₄ as an illustrative example. Under an inert atmosphere, a mixture of AM (5000.00 mg, 70.40 mmol), Chol-6 (200.00 mg, 0.30 mmol), AIBN (156.00 mg, 0.95 mmol) and 15 mL of anhydrous THF was heated at 65 °C for 2 h. Water was then added to terminate the reaction. No further purification was required. The solid obtained After removing the solvent was dried at 40 °C under vacuum for 48 h, resulting in a white powder-like PAMC₄.

Preparation of CNCs suspensions: CNCs were prepared *via* sulfuric acid hydrolysis.^[14] The general procedure was as follows: a mixture of MCC (10 g) and 64 wt% sulfuric acid (87.5 mL) was stirred at 50 °C for 80 min. The reaction was quenched with cold deionized water (10-fold that of the sulfuric acid solution). After overnight centrifugation, the supernatant was discarded. The turbid layer was centrifuged (8000 r/min, 10 min) and repeatedly washed with deionized water until homogeneous. The resulting suspension was dialyzed (MWCO: 8–14 kDa) against deionized water for five days until

a neutral pH was achieved. The dialyzed CNCs were dispersed *via* ultrasonic treatment and concentrated to 3 wt%. The final suspensions were stored in a refrigerator to prevent deterioration.

Preparation of photonic films: all composite photonic films were prepared by evaporation-induced self-assembly (EISA) (Figs. 1b and 1c).^[32] The preparation of CNCs-*g*-PAMC₄ composite film with different glycerol contents is a typical procedure. Specifically, a PAMC₄ aqueous solution (3 wt%) was blended with CNCs suspensions (3 wt%) in an 8:2 mass ratio (CNCs:PAMC₄). Irgacure 2959 and MBA were subsequently added to achieve the final mass ratio for mixture/irgacure 2959/MBA=100:5:3. G was then introduced at 10 wt%, 20 wt%, and 30 wt% relative to the total CNCs-PAMC₄ mass. The mixture was stirred for 5 h, followed by ultrasonication for 10 min in the dark. 8 mL of aforementioned mixture solution was poured into polystyrene petri dishes (Ø=6 cm) and subjected to EISA at 25 °C/80% RH in darkness. After the self-assembly was completed,^[33,34] the obtained films were UV-cured (10 mW/cm², 15 min) to initiate polymerization. The final composite films were designated as 8CNCs-2PAMC₄/G₁₀, 8CNCs-2PAMC₄/G₂₀, 8CNCs-2PAMC₄/G₃₀. The reference samples included pure CNCs films, composite films formed by Chol-6-free PAM and CNC at different mass ratios, named 9CNCs-1PAM to 6CNCs-4PAM; 8CNCs-2PAM composite films with different glycerol contents, designated as 8CNCs-2PAM/G₁₀, 8CNCs-2PAM/G₂₀, and 8CNCs-2PAM/G₃₀, respectively; and 8CNCs-2PAMC₄ composite films without Irgacure 2959, MBA, or G. Detailed information is provided in Table S2 (in the electronic supplementary information, ESI).

Characterization

¹H-NMR and ¹³C-NMR spectra were recorded on a Varian Mercury-400plus spectrometer (400 MHz, USA) and Agilent DD2 spectrometer (600 MHz, USA), respectively, using CDCl₃ or D₂O with TMS as the internal standard. XPS was performed using a Thermo Fisher ESCALAB QX1 instrument with monochromatic Al K_α radiation (1486.6 eV). High-resolution spectra were acquired at a pass energy of 30 eV (step size 0.1 eV) and calibrated to C 1s at 284.8 eV. Data were processed using Avantage software with Shirley background subtraction and Gaussian-Lorentzian peak fitting. Gel permeation chromatography (GPC) was performed on an Agilent 1260 Infinity II equipped with 4.6 μm x 250 mm chromatographic columns and a refractive index detector, using H₂O as the eluent at 1.0 mL/min and 35 °C. Calibration was performed using PEG standards. CNC was diluted to 0.01 wt% for morphology analysis *via* transmission electron microscopy (TEM, Hitachi HT7820, Japan). Particle size and zeta potential were determined using dynamic light scattering (DLS 500, Litesizer, Austria). The transmittance spectra of the films were characterized using a UV-Vis spectrophotometer (UV-2355, China) with samples perpendicular to the beam path and air as the reference. The crystalline structures were characterized by X-ray diffraction (XRD, D8-Advance, Germany) with Cu K_α radiation (λ=1.54 Å), scanning 10°–40° (2θ) at 0.1 (°)/min under 40 kV/40 mA. Polarized optical microscopy (POM, WY-630 MS, China) was used to examine the chiral nematic organization using crossed polarizers. The cross-sectional morphologies of the samples were observed by scanning electron microscopy (SEM, Zeiss UL-TRA Plus, Germany) at 5.0 kV after gold sputter coating. Thermal

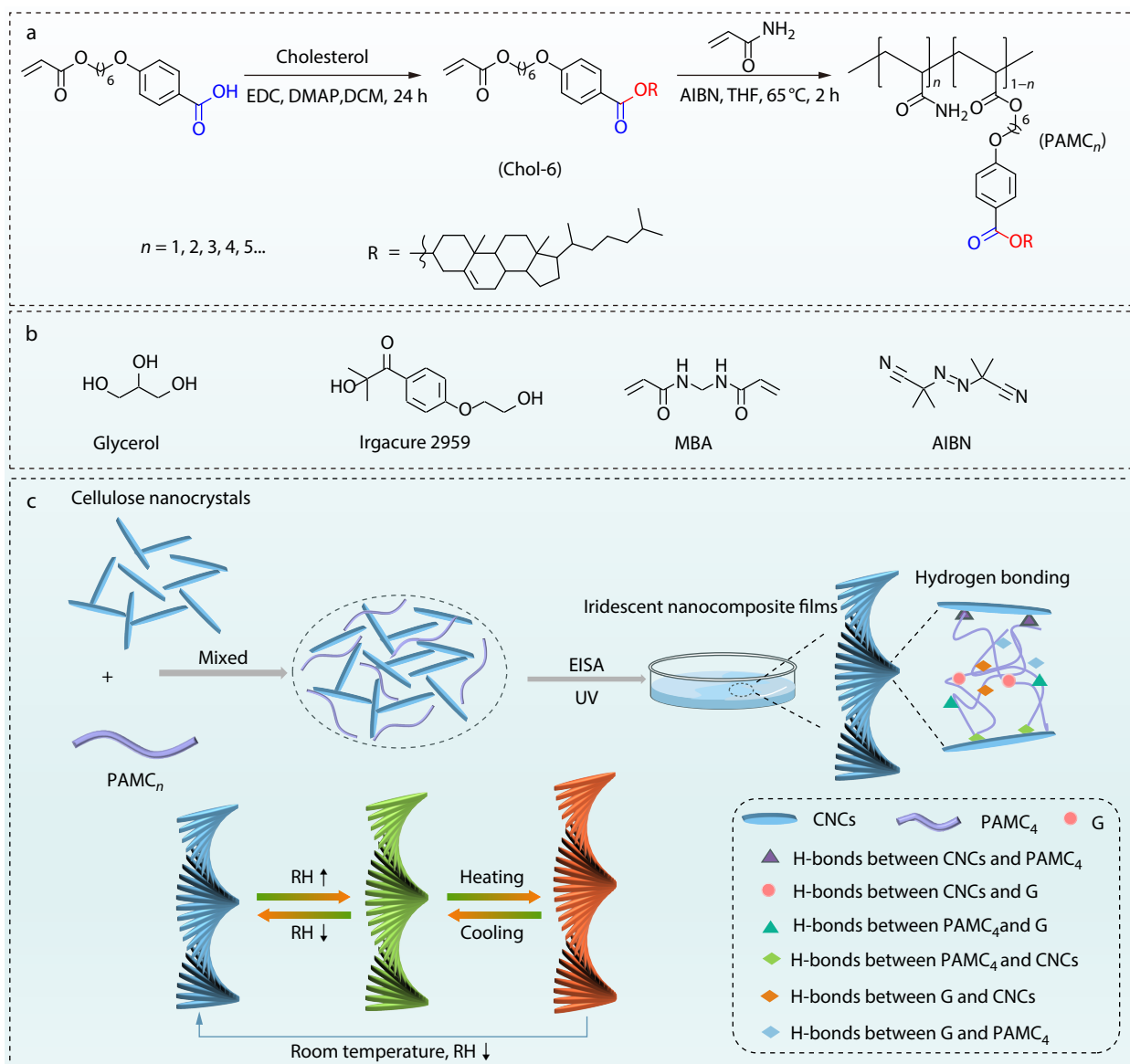


Fig. 1 (a) The synthetic route of Chol-6 and PAMC_n, (b) the molecular structures of the used chemical reagents, and (c) the schematic illustration of the fabrication and stimuli-responsive mechanism of the nanocomposite film.

stability was evaluated *via* thermogravimetric analysis (TGA, TA Q50) at 25–800 °C and 20 °C/min under nitrogen atmosphere. The mechanical properties were measured at room temperature using a universal testing machine (EZ-Test, Japan) at a crosshead speed of 1 mm/min with rectangular specimens (30 mm × 10 mm; $n=3$ replicates). A climate chamber (LTH-100, China) was used to establish a controlled relative humidity environment for the humidity-dependent responsiveness study. The samples were equilibrated at each target humidity for 1 h before testing. For thermal-dependent responsiveness, samples were pre-equilibrated in H₂O/EtOH (2/3, V/V) at ambient temperature to mitigate solvent swelling. Following equilibration, transmittance spectra were recorded using a UV-Vis spectrophotometer in a circulating bath (Great Wall, DHJF-4005, China) after 20 min of thermal stabilization at each target temperature. Three replicate measurements were performed at each humidity point and at each temperature point to eliminate fortu-

itous experimental errors and improve repeatability.

RESULTS AND DISCUSSION

Characterization of CNCs

TEM analysis showed that the CNCs exhibited a rod-like morphology (Fig. 2a) with average dimensions of approximately 150 nm in length and 10 nm in width. These values were in close agreement with the average particle size determined by DLS ($D_h=141.66$ nm). Moreover, the measured zeta potential of -16.36 mV confirms sufficient electrostatic stabilization to enable CNC self-assembly (Fig. 2b).

Selection of Prepolymer

As a common liquid crystal building block, cholesterol and its derivatives with inherent left-handed chirality can provide various liquid crystal phases and are typically used as chiral additives in thermotropic liquid crystals, and the HTP value increas-

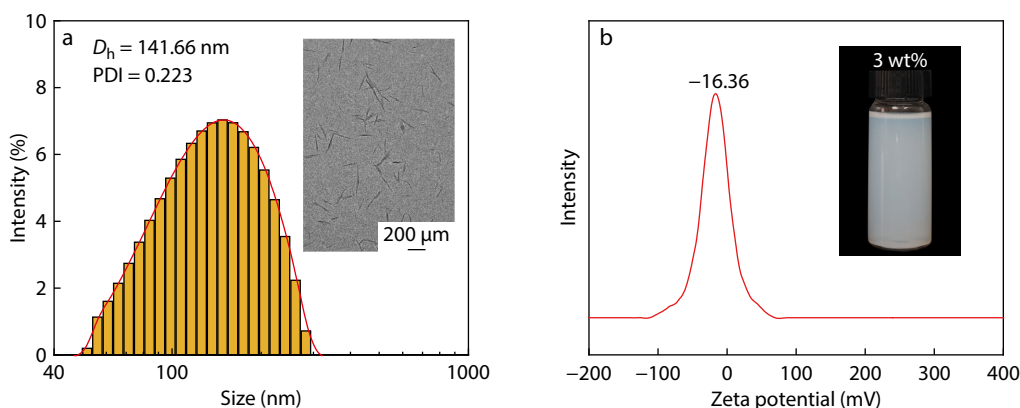


Fig. 2 (a) Hydrodynamic size distribution of the CNCs from DLS, with a representative TEM image in the inset; (b) Zeta potential measurement, with a macroscopic photograph of the suspension in the inset.

es with heating.^[35] However, their inherent hydrophobicity restricts their direct co-assembly with CNCs during the fabrication of water-evaporation-induced photonic films.^[36,37] To enhance aqueous compatibility, we synthesized the prepolymers PAMC_n through free radical copolymerization of the cholesterol derivative Chol-6 with water-soluble acrylamide precursors. Because of the low content of Chol-6 in the prepolymer series and the associated solubility limitations, no characteristic signals of Chol-6 were observed in the ¹H-NMR and FTIR spectra (Figs. S2 and S3 in ESI). Nevertheless, GPC measurements revealed a marked increase in both molecular weight and dispersity, and XPS detected carbon and oxygen binding energy peaks assignable to the O—C=O and C—O moieties in Chol-6. These results collectively confirm the successful synthesis of the prepolymer series and the effective incorporation of the Chol-6 units into the PAM chains (Figs. S4, S5 and Table S1 in ESI). As expected, this modification significantly enhanced the water solubility and colloidal stability of the Chol-6. Notably, the turbidity of the prepolymer suspension increased progressively (*i.e.*, transparency decreased) with increasing Chol-6 mass ratio, indicating the successful conjugation of Chol-6-bearing polymer chains and their subsequent assembly into micelles or aggregates (Fig. S6 in ESI). Subsequently, to evaluate the cooperative self-assembly capabilities of these prepolymers with CNCs and their impact on the structure and performance of the resulting composite films, composite films were prepared using the EISA method.

Consistent with previous literature, the macroscopic visible color of all films (including control samples from 9CNCs-1PAM to 6CNCs-4PAM) shifted from blue to red or showed increased whiteness as the mass ratio of the prepolymer increased (Fig. S7 in ESI). Transmission spectroscopy revealed that with increasing prepolymer content, the central position of the reflection peak gradually red-shifted, which was consistent with the structural color changes observed by the naked eye (Fig. S8 in ESI). Moreover, the decrease in reflection intensity observed in the transmission spectra implies a reduction in the orderliness of the helical hierarchical structure. These observations indicate that, at appropriate doping concentrations, the prepolymers can penetrate the periodic layered arrangement of the chiral nematic structure formed by the self-assembly of CNCs, thereby increasing *P* and causing a red shift in the structural color. Notably, at a fixed total prepoly-

mer loading, a higher proportion of Chol-6 induced a more pronounced redshift and greater attenuation of the reflection peak. This effect is attributed to the steric hindrance of Chol-6; it occupies a larger volume within the periodic layered architecture, leading to more significant pitch expansion, a clearer chromatic shift, and more severe disruption of the ordered helical hierarchical structure (Fig. S8h in ESI). Subsequent SEM results of the fracture surfaces on selected samples confirmed both the above findings and our hypothesis, demonstrating that increased prepolymer content and the presence of Chol-6 indeed expanded *P* and led to a reduction in the regularity of the layered structure (Fig. S9 in ESI).

To maximize the doping concentration of Chol-6 in the composite film and facilitate further research in the visible light region, we selected a system with a prepolymer PAMC₄ CNCs of 8:2 for subsequent studies (denoted as 8CNCs-2PAMC₄).

Photonic Properties of CNCs-*g*-PAMC₄ Composite Films

Circular dichroism (CD) characterizes chiral organization through the differential absorption of circularly polarized light (CPL), defined as $CD = A_L - A_R$, where A_L and A_R represent the absorbance of left- and right-handed CPL, respectively.^[38,39] Positive CD signals confirm that both pure CNC films and composites preserve left-handed chirality, indicating that the PAM, glycerol, and PAMC₄ additives maintain the native chiral architecture derived from CNC self-assembly (Fig. 3a).

The corresponding transmittance spectra and photographs revealed significant optical shifts. The 8CNCs-2PAMC₄ film exhibits a substantial redshift from $\lambda_{max}=433$ nm (pure CNCs) to 604 nm. The progressive incorporation of glycerol further redshifted λ_{max} to 628 nm (8CNCs-2PAMC₄/G₁₀), 718 nm (8CNCs-2PAMC₄/G₂₀), and 774 nm (8CNCs-2PAMC₄/G₃₀) (Fig. 3b). This total shift of 341 nm correlates with the visual color transition from blue to yellow, orange, and deep red (Fig. 3d). The uniform iridescence observed across the composites originated from their internal photonic structures, and chromatic changes were directly linked to structural modifications. Complementary POM (Fig. 3e) images show characteristic birefringent fingerprint textures, indicative of planar-aligned chiral nematic phases. SEM analysis of the fracture surfaces (Fig. 3f) reveals conserved helical nanolayered structures with chiral nematic ordering, where

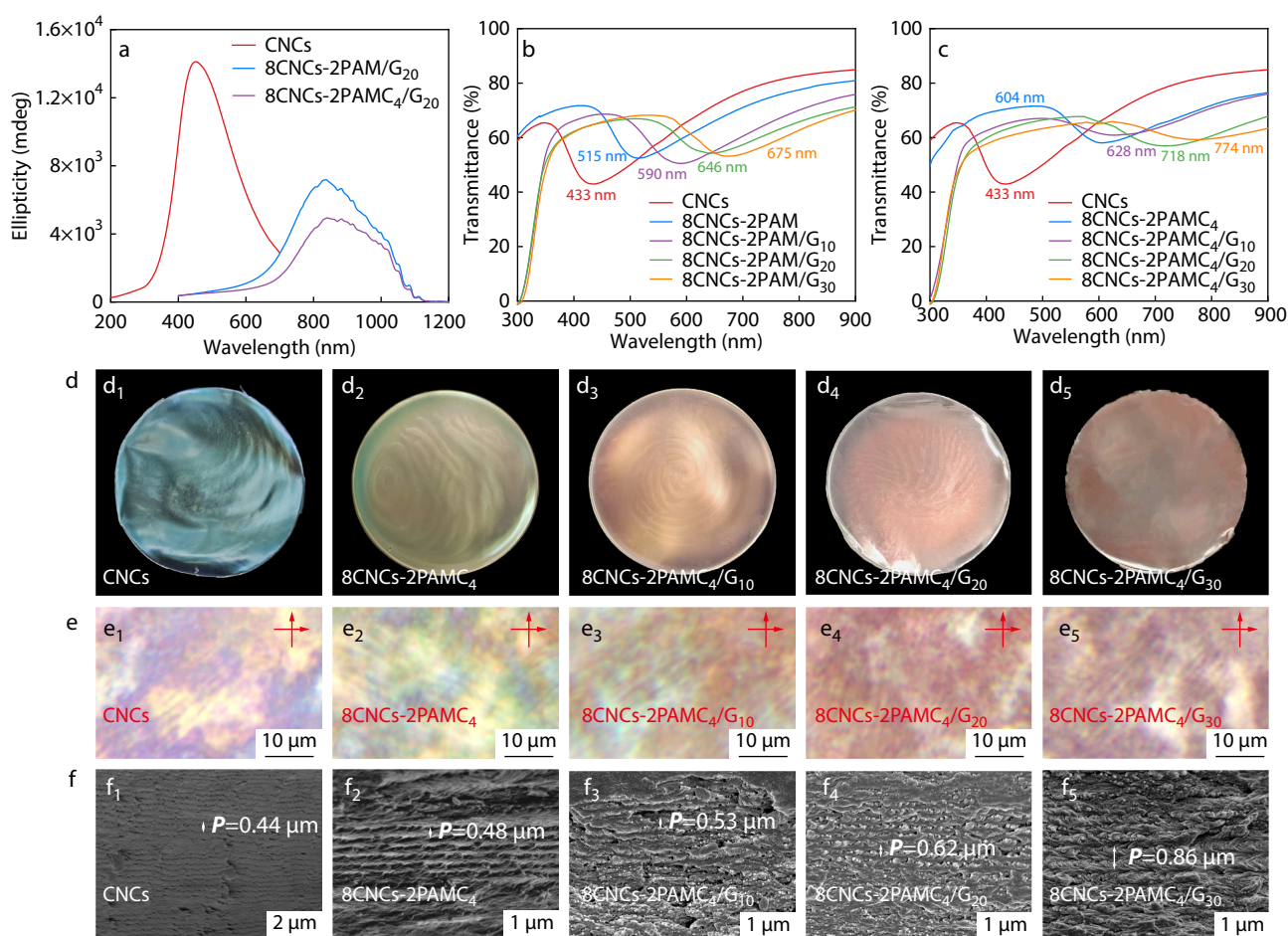


Fig. 3 (a) CD spectra, (b, c) transmission spectra, (d) optical photographs, (e) POM micrographs, and (f) SEM images of the composite films.

the interlayer distance (corresponding to $P/2$) increases proportionally with the additive content. Collectively, these results demonstrate that the incorporation of PAMC₄ and glycerol expands the chiral architecture without disrupting fundamental CNC-directed self-assembly. The control composite films (including 8CNCs-2PAM, 8CNCs-2PAM/G₁₀, 8CNCs-2PAM/G₂₀, and 8CNCs-2PAM/G₃₀) exhibited similar evolutionary trends (Fig. 3c). Optical images, POM micrographs, and SEM images are shown in Fig. S10 (in ESI).

Characterization of CNCs-g-PAMC₄ Composite Films

Figs. 4(a) and 4(b) reveal that both pure CNCs and all composite films retain the characteristic crystalline structure of cellulose I, exhibiting distinct diffraction peaks at the (101), (101), and (200) crystallographic planes. This confirms that the introduction of PAM, PAMC₄, and glycerol preserved the cellulose crystalline framework. Although all the films maintained the characteristic cellulose I crystalline structure, the XRD patterns revealed a progressive decrease in the intensity and sharpness of the diffraction peaks upon the addition of PAM, PAMC₄, and glycerol, accompanied by a more prominent amorphous background. These observations indicate that the additives penetrate the inter-rod regions and disrupt the lateral packing of the CNCs, resulting in a slight reduction in crystallinity without altering the native cellulose crystal form. We propose that PAMC₄ and glycerol molecules permeate the amorphous regions and inter-rod

mesopores of the CNC scaffold while forming hydrogen bonds with the surface hydroxyl groups. This molecular intercalation expands the layered structure *via* hydrogen bonding, thereby increasing P and ultimately inducing a redshift in the structural color.

The incorporation of PAMC₄ with glycerol significantly improved the mechanical performance of the CNC composite films.^[23] As shown in Fig. 4(c), the composite films exhibited enhanced tensile strength and elongation at break compared to the pristine CNC films. The maximum tensile strength was 11.35 MPa, while the elongation at break was 19.73%. These improvements originated from the synergistic effects of glycerol-induced plasticization and PAMC₄-mediated network reinforcement. The PAM backbone enhances stress transfer through interactions with CNC nanocrystals, whereas the Chol-6 pendants in PAMC₄ regulate intermolecular organization and contribute to network integrity. Glycerol increases molecular mobility and alleviates the inherent brittleness of the CNC matrix. With increasing glycerol content, the tensile strength gradually decreased owing to excessive plasticization and weakened intermolecular interactions, although the flexibility of all composite films remained substantially improved.

Notably, the 8CNCs-2PAM/G₁₀ composite film without Chol-6 exhibited a tensile strength of 16.82 MPa and elonga-

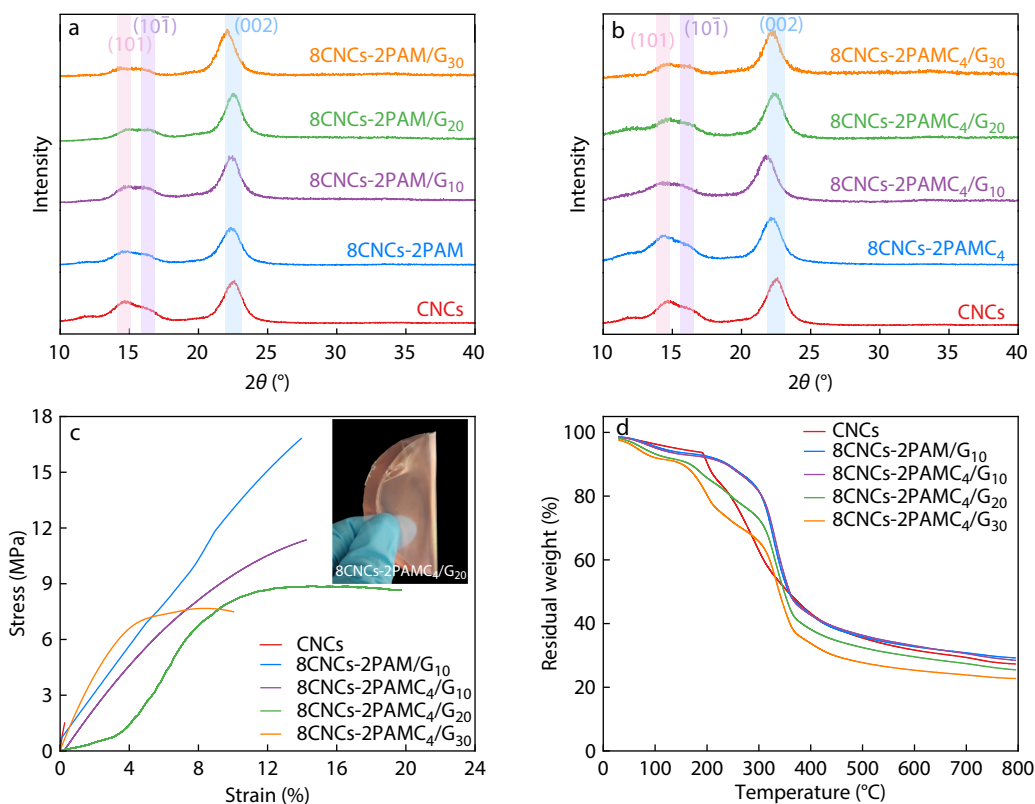


Fig. 4 (a, b) XRD patterns, (c) stress-strain curves, and (d) TGA curves of the composite films.

tion at break of 13.95%, demonstrating the reinforcing effect of the PAM network. After replacing PAM with Chol-6-functionalized PAMC₄, the tensile strength decreases to 11.35 MPa while maintaining comparable elongation at break (14.23%). This reduction may be attributed to the steric effects of the bulky cholesterol pendants, which partially disrupted the compact intermolecular packing within the composite network. Nevertheless, the introduction of Chol-6 provided additional functional regulation while preserving the flexibility of the CNC composite films. These results demonstrate that the mechanical performance of the final composites is governed by the combined effects of the PAMC₄-mediated reinforcement, glycerol-induced plasticization, and Chol-6-dependent structural regulation.

Thermal stability comparison (Fig. 4d) reveals that pure CNCs exhibit two weight loss stages at approximately 100 and 190 °C, corresponding to the removal of adsorbed water and thermal decomposition of cellulose, respectively. In contrast, the incorporation of PAM and PAMC₄ shifted the onset of degradation to higher temperatures from 191 °C for pure CNC to 215 °C for CNCs-PAM/G₁₀ and 230 °C for CNCs-PAMC₄/G₁₀. This enhancement originates from two aspects: the PAMC₄ surface coating acts as a thermal barrier that impedes heat transfer and the amide groups suppress proton-catalyzed hydrolysis through proton scavenging. Owing to the hygroscopic nature of glycerol, increasing its content gradually lowered the initial degradation temperature because residual moisture remained after drying.^[40] This residual moisture leads to additional mass loss *via* evaporation between 100 and 200 °C as well as accelerated decomposition

via moisture-mediated reactions at elevated temperatures. Thus, glycerol concentration determines the thermal stability of the system. Moreover, at high temperatures (>400 °C), samples with higher glycerol content exhibited lower char residue. This is because, on one hand, glycerol is completely volatilized during thermal decomposition without forming solid residuals; on the other hand, a higher glycerol content dilutes the relative proportion of carbon-forming components in the system, such as organic polymer chains and CNCs, thereby further reducing the char yield. Water contact angle measurements confirmed that the anti-wetting performance increased with a higher Chol-6 content or lower glycerol loading (Fig. S11 in ESI).

Humidity Response

The CNC-*g*-PAMC₄ composite films exhibited pronounced humidity responsiveness. As the RH increased from 30% to 90%, the embedding of water molecules induced a progressive red-shift in its $\lambda_{\max}$ position (Fig. 5a and Fig. S13 in ESI). This phenomenon originates from humidity-driven structural alterations within the chiral nematic layered structure.

Under low RH conditions, the structure maintained a tightly packed, ordered configuration.^[41] Progressive water incorporation upon humidity elevation expanded the interlayer spacing, triggering a structural transition from a densely packed to an expanded configuration. Consequently, this transition enlarges *P*, ultimately leading to a red shift in $\lambda_{\max}$. Compared with the reference sample (without Chol-6), possessing identical glycerol content (Fig. S12 in ESI), the humidity responsiveness of the composite films is reduced. This reduction is primarily attributed to the introduction of the hy-

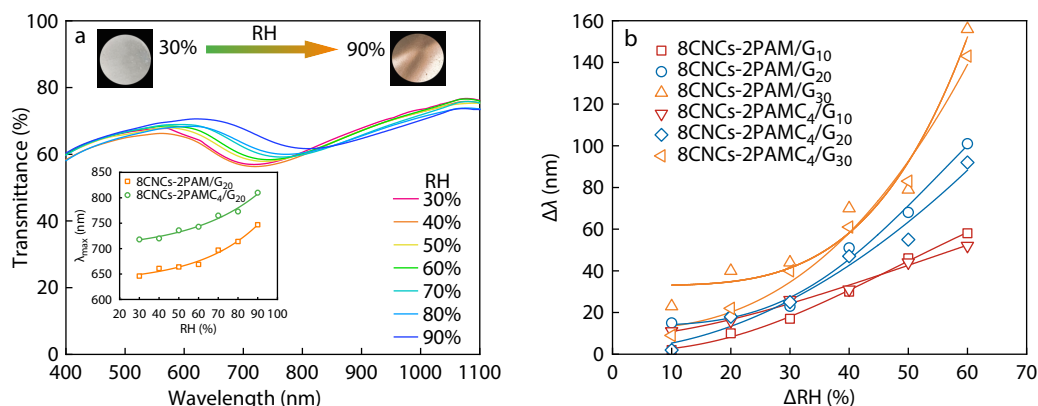


Fig. 5 (a) Humidity-dependent transmittance spectra of the 8CNCs-2PAMC₄/G₂₀ composite films, illustrating the relationship between RH and $\lambda_{\max}$ in the inset; (b) Dependence of $\Delta\lambda$ on ΔRH .

drophobic Chol-6, which diminishes the surface hydrophilicity of the material and compromises its water-absorbing capacity under high-humidity conditions, thereby weakening the humidity-induced optical response. Furthermore, the intensity of the humidity response for all the composite films showed a positive correlation with the glycerol content (Fig. 5b). This correlation arises because the glycerol molecules are rich in hydroxyl groups. As glycerol content increased, the concentration of these hydrophilic groups substantially enhanced the hygroscopicity of the material.^[42,43] Consequently, an elevated RH facilitates greater water molecule incorporation into the helical layered structure, resulting in a more pronounced pitch expansion and red-shift. These findings were consistent with the wetting properties of the composite films.

Thermal Response

The thermal response behavior of the composite films at swelling equilibrium was characterized using variable-temperature transmission spectroscopy (Fig. 6 and Figs. S14–S16 in ESI). The results demonstrate that increasing the Chol-6 content or decreasing the glycerol content significantly enhances the temperature-induced $\lambda_{\max}$ red-shift in the composite films.

This enhancement significantly surpassed that of the Chol-6-free reference, reaching a maximum reflection wavelength shift of 28 nm (about 77% increase; Table 1). Notably, this progressive redshift differs from the typical thermal responses of cholesteric derivatives in conventional liquid crystal systems.^[44] This behavior is unlikely to be governed solely by conventional HTP-mediated regulation. Instead, it was primarily attributed to the steric regulation of Chol-6 within the confined CNC chiral nematic matrix. Although Chol-6 possesses intrinsic chirality, the relatively low effective HTP contribution under the ultralow doping levels used in this system (0.57 wt%–0.67 wt%) and its covalent incorporation into the PAM network make a direct HTP-dominated mechanism unlikely. In contrast, bulky cholesterol moieties introduce steric interactions that modulate the hydrogen bond-mediated network within the composite matrix. This modification of the hydrogen-bonding environment was supported by the enhanced hydrophobicity of the films (Fig. S11 in ESI), and the decreased intensity and full width at half maximum of the hydroxyl-associated absorption band (Fig. S17 in ESI), suggest-

ing the presence of altered intermolecular interactions within the composite network. Upon heating, the reduced intermolecular constraints and enhanced molecular mobility facilitated relaxation of the CNC assembly. Meanwhile, changes in the hydration state^[45] electrostatic interactions associated with sulfate ester groups^[46] and reduced intermolecular cohesion^[47] collectively promote expansion of the helical pitch, resulting in a progressive $\lambda_{\max}$ redshift.

Direct microstructural evidence for thermally induced pitch expansion was obtained from cross-sectional SEM imaging of the 8CNCs-2PAMC₄/G₁₀ film at different temperatures (Figs. 6c–6e). At 25 °C, the average interlayer distance (corresponding to approximately $P/2$) was measured as 530 nm, which increased to 560 nm at 45 °C and further to 580 nm at 75 °C. This about 9.4% increase in the observed interlayer spacing provides direct evidence that the helical pitch expands upon heating, in excellent agreement with the observed 64 nm redshift (Table 1) (calculated according to the Bragg reflection relationship $\lambda = nP\sin\theta$ with $\theta=90^\circ$ and $n=1.55$). These SEM observations provide clear microstructural evidence supporting the proposed thermally induced network relaxation involving Chol-6-mediated steric regulation and weakened hydrogen bond-mediated interactions.

Overall, the observed thermal response is primarily attributed to the bulky nature of the Chol-6 moieties, which, despite their rigid steroid core, retain sufficient conformational flexibility in their side-chain linkage to the polymer backbone through the alkyl spacer connecting the cholesterol units to the PAM backbone. Upon heating, the dynamic weakening of hydrogen-bond-mediated interactions, combined with the temperature-dependent rearrangement of cholesterol-containing polymer segments, facilitates the relaxation of the CNC chiral nematic structure and expansion of the helical pitch. Unlike conventional chiral dopants that exhibit a thermal response mainly governed by dynamic changes in HTP, the Chol-6 units in our system contribute to thermochromism through a synergistic mechanism that involves both temperature-dependent conformational adaptation and matrix-mediated steric regulation.

It should be noted that the 8CNCs-2PAM film without Chol-6 also exhibits a weak thermal response, which may originate from thermally induced changes in the CNC chiral nematic arrangement and polymer network dynamics. Temperature

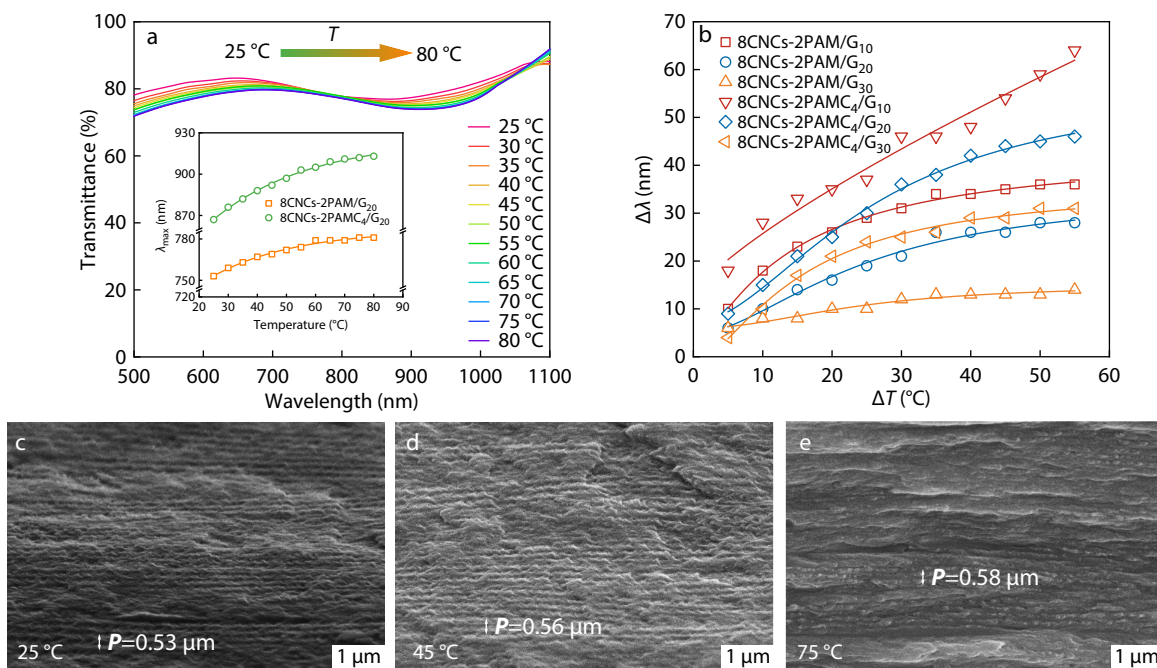


Fig. 6 (a) Temperature-dependent transmittance spectra of the composite films, illustrating the relationship between temperature and $\lambda_{\max}$ in the inset; (b) Dependence of ΔT on $\Delta\lambda$; (c–e) SEM images of the composite films at different temperatures.

Table 1 $\Delta\lambda$ values of the composite membranes as a function of Chol-6 and G content.

Sample name	Content of Chol-6 (wt%)	Total redshift of $\lambda_{\max}$ (nm)	$\Delta\lambda$ (nm)
8CNCs-2PAM/G ₁₀	0	36	0
8CNCs-2PAM/G ₂₀	0	28	0
8CNCs-2PAM/G ₃₀	0	14	0
8CNCs-2PAMC ₄ /G ₁₀	0.67	64	28
8CNCs-2PAMC ₄ /G ₂₀	0.62	46	18
8CNCs-2PAMC ₄ /G ₃₀	0.57	31	17

Marginal notes: $\Delta\lambda$ = total redshift of the experimental group $\lambda_{\max}$ – the total redshift of the control $\lambda_{\max}$.

variation can influence the molecular mobility, intermolecular interactions, and hydrated state of the composite matrix, leading to a slight modulation of the helical pitch. However, the structural regulatory capability of the Chol-6-free system remains limited. The incorporation of Chol-6 moieties into the PAM network provides an additional steric regulation pathway, allowing more pronounced and reversible thermal modulation of the CNC helical structure and corresponding structural color.

To further evaluate the reversibility of the thermal response, heating–cooling cycle experiments were performed under hydrated conditions ($\text{H}_2\text{O}/\text{EtOH} = 2/3$, V/V; Fig. S18 in ESI). The films exhibited repeatable thermal modulation, with the reflection wavelength shifting between approximately 865 nm and 893 nm during cycling. Nevertheless, an incomplete recovery of the initial reflection position was observed, indicating thermal hysteresis. This behavior may arise from the slow relaxation and reconstruction of the Chol-6-modulated CNC/PAMC₄ network, together with solvent-induced changes in network swelling and redistribution of mobile glycerol molecules during immersion. After removal from the solvent environment, the reflection peak remained blue-shifted by about 28 nm relative to that in the hydrated state, suggesting partial contraction and rearrangement of the com-

posite helical structure.

CONCLUSIONS

In summary, a water-soluble prepolymer, PAMC₄, was synthesized via free-radical copolymerization of chiral monomer Chol-6 with acrylamide. A novel CNC-based photonic film was subsequently fabricated by co-assembling PAMC₄, glycerol, and CNCs through EISA, followed by post-polymerization. The resulting composite integrates humidity/thermal responsiveness with improved toughness, where PAMC₄ provides structural reinforcement and glycerol enhances the flexibility. Precise modulation of the PAMC₄ and glycerol content enabled continuous structural color tuning across the visible range. Notably, the 8CNCs-2PAMC₄/G₁₀ film exhibited a 64 nm redshift in $\lambda_{\max}$ upon heating from 25 °C to 80 °C. This thermochromic behavior is primarily attributed to the thermally activated steric regulation of Chol-6 within the CNC chiral nematic matrix, which weakens intermolecular interactions and expands the helical pitch. Although the intrinsic helical twisting ability of Chol-6 contributes to the formation of the chiral structure, its direct contribution to thermal modulation is limited under current conditions. Instead, bulky and conformationally adaptive Chol-6 moieties act as thermo-responsive steric regulators, providing an alternative

strategy for tuning CNC-based photonic materials beyond conventional LCST-type polymer systems. Future studies will focus on further optimizing the molecular structure of chiral regulators, improving their compatibility and stability within CNC composite matrices, and enhancing the reversibility and cycling durability of thermo-responsive photonic films.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-026-3829-9>.

Data Availability Statement

The data supporting the findings of this study are available from the corresponding authors upon reasonable request.

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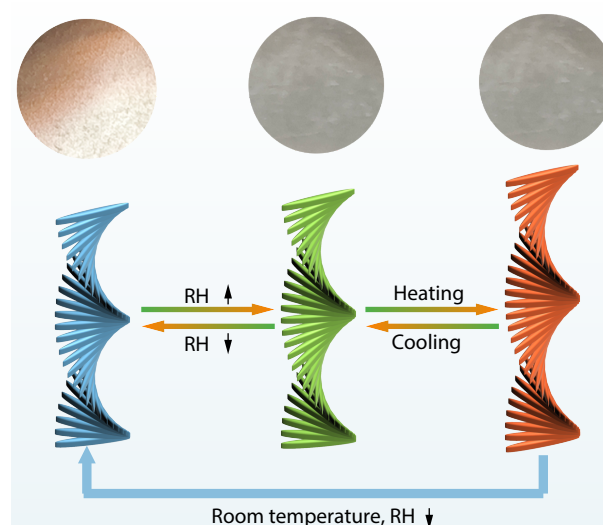
Graphical Abstract

Flexible Photonic Films Based on Cellulose Nanocrystals with Temperature-responsive Structural Color

Wen-Huan Yao, Xin Ma, Yan-Xia Wang, An-Zhi Ma, Zheng-Rui Ma, Xiao-Xia Wang, Wei-Xia Kang, and Ze-Bing Zeng

Northwest Normal University; Hunan University

Thermal activation of Chol-6 steric regulation drives cellulose nanocrystal (CNC) helical pitch expansion, enabling a 64 nm redshift through temperature-induced network re-organization.



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