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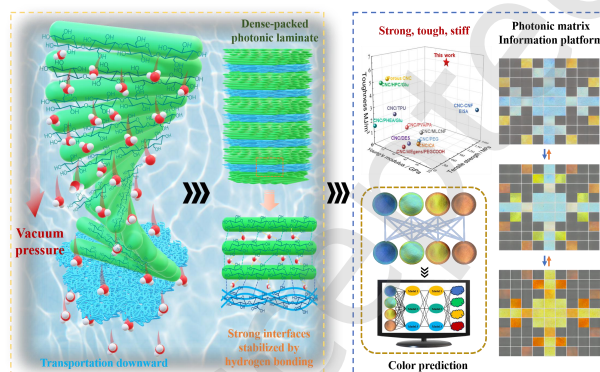
Strong, tough, and stiff nanocellulose photonic laminates with customized optical functions

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Vacuum-assisted layer-by-layer alternating assembly of cellulose nanocrystals and cellulose nanofibers yields robust, tough, rigid nanocellulose photonic laminates featuring densely packed stacking architectures. This strategy supports arbitrary color mixing and color prediction, and enables the construction of a photonic matrix platform toward information encoding and encryption.

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ABSTRACT: Construction of strong, tough, and stiff biophotonic materials with customized and extended optical performance is significant to expand sustainable optics while it remains challenging. Herein, we propose a vacuum-assisted layer-by-layer assembly of cellulose nanocrystal and cellulose nanofiber alternately to fabricate nanocellulose photonic laminates. This strategy leverages the VASA technique to regulate drying kinetics and the layer-by-layer method to harmlessly incorporate energy-dissipating phases, enabling the fabrication of homogeneous and densely-packed nanocellulose photonic laminates with finely-tailored optomechanical performances. Specifically, the resultant nanocellulose photonic laminates synergistically integrate load-bearing cellulose nanocrystal sublayers and energy-dissipating cellulose nanofiber sublayers, achieving a comprehensive combination of high strength, toughness, stiffness, and impact resistance. Moreover, the resulting nanocellulose photonic laminates demonstrate well controllability and flexible editability in stacking structure via layer-by-layer assembly variation, that enables versatile optical functionalities, including arbitrary color blending based on the RGB color model and machine-learning-assisted color prediction. Impressively, by integrating nanocellulose photonic laminates with diverse stacked architectures, we establish a photonic matrix platform featuring programmable color-switching responses for information encoding and encryption. This work takes a crucial step forward to sustainable photonic materials with excellent mechanical combinations and optical functionality for bio-enabled display technologies and security indicators.

KEYWORDS: Nanocellulose, photonic laminate, layer-by-layer assembly, all-in-one mechanical combination, optical customization.

1 Introduction

Cellulose nanocrystals (CNCs) are promising bio-based nanomaterials which can self-assemble into chiral nematic (cholesteric) organization via evaporation-induced self-assembly (EISA) strategy [1-3]. Specifically, CNC nanoparticles align along a common direction that rotates periodically along the helical axis, forming a helicoidal photonic structure. This periodic arrangement not only brings vivid iridescent structure color via Bragg reflection [4] but also imparts high modulus and great stiffness. The combined optical and mechanical attributes render CNC photonic structure compelling candidates for fabricating sustainable optical materials [5]. However, common EISA process of CNC nanoparticles typically generates defect-rich, mosaic-like domains and takes a long time. Those defects, arising from uncontrolled drying kinetics and capillary effects during solvent evaporation, compromise both mechanical properties and optical quality for the resulting iridescent photonic materials. In this context, conventional strategy for structure homogenization and performance optimization is incorporating compatible polymers [6-9] or small molecules [10-11] into CNC assemblies. However, the introduction of extra additives inevitably affects the ordering of CNC cholesteric assemblies, that puts a limitation

in the enhancement of optomechanical performance for CNC photonic materials. As an alternative strategy, the layer-by-layer stacking of chiral nematic CNC phases and random cellulose nanofiber (CNF) phases enables the achievement of high mechanical strength and toughness without compromising vivid optical iridescence [12]. However, this approach still suffers from several shortcomings, including high time consumption, low efficiency, and poor controllability.

Control over drying kinetics upon self-assembly process is essential for the high ordering of CNC cholesteric alignment, hence achieving great combination of optical and mechanical performances. As comparison to common EISA, vacuum-assisted self-assembly (VASA) process provides a compelling alternative strategy. VASA with directional vacuum pressure, remove solvent rapidly and meanwhile suppress capillary effect and residual stress upon CNC nanoparticles assembly [13]. That allows uniform chiral nematic alignment with minimizing structural defect in a fast and effective way. Consequently, VASA-enabled CNC photonic films demonstrate enhanced optical and mechanical performances, compared with those formed from EISA [14-15]. Despite the remarkable superiority of VASA strategy, the intrinsic rigidity of CNC nanocrystals with poor shear transfer

efficiency and the small CNC-CNC overlap lengths with weak interfacial interactions, still lead a typical mechanical brittleness for as-obtained photonic films [16]. Based on above, leveraging the VASA technique to regulate drying kinetics, together with the harmless incorporation of compliant, energy-dissipating binder phases or matrices into CNC cholesteric architectures, offers a promising strategy to strengthen and toughen CNC photonic materials without compromising their optical performance.

In this work, we develop nanocellulose photonic laminates which are stacked by CNC cholesteric layer and CNF bridging layer alternately, *via* vacuum-assisted layer-by-layer (VA-LbL) assembly strategy. By repeating the VASA procedure upon the stacking process, multi-layers of CNF are harmlessly and seamlessly intercalated into CNC cholesteric layers. Meanwhile, the vacuum-induced pressure exerted on the preformed layers promotes structural densification and enhances interfacial interactions. That generates nanocellulose photonic laminates with uniform structural color and a synergistic combination of mechanical strength, toughness, and stiffness. Moreover, as-adopted VA-LbL assembly strategy enables flexible and arbitrary adjustment in stacking layer combinations, that makes controllability and modulation in optical performances for the nanocellulose photonic laminates. As a result, the resulting photonic laminates demonstrate customized and programmable optical functions, including arbitrary color *via* RGB color model, machine-learning-assisted color prediction, and more impressively, programmable color-changing response for offering information encryption platforms.

2 Experimental Section

2.1 Preparation of CNC suspension

The CNC suspension was prepared from dried soft wood pulp according to the well-established sulfuric acid method [17]. Specifically, dried soft wood pulp was hydrolyzed in 64 wt.% sulfuric acid (16 mL sulfuric acid per gram of wood pulp) at 45°C with constant stirring for 45 min. The obtained suspension was diluted with ultrapure water to inhibit hydrolysis reaction followed by settlement overnight. Thereafter, the supernatant was removed, and the remaining white suspension was washed by centrifugation (7000 rpm for 8 min, two times) to remove extra sulfuric acid. Subsequently, the crushed-out cellulose was redispersed in water and subjected to dialysis (molecular weight cutoff: 14,000 Da) for a week. The water was changed every 6 h. After dialysis, the cellulose dispersion was subjected to centrifugation at 10,000 rpm for 20 min. The supernatant was collected to obtain CNC suspension with a concentration of ~0.75 wt.%. The obtained CNC suspension was concentrated to 1.7 wt.%, which is then subjected to ultrasound treatment with tip ultrasonication (Scientz, JY92-IIDN, 900 W) at 40% amplitude before use.

2.2 Preparation of nanocellulose photonic laminates

The nanocellulose photonic laminates were prepared *via* vacuum-assisted layer-by-layer assembly of CNC and cellulose nanofiber (CNF, purchased from ScienceK Nanocellulose Ltd.) alternately. Firstly, a very small amount of carbon nanotube (CNT) dispersion (1 wt.%, 30 μ L,

provided by XFANO materials Technology Co., Ltd.) as light absorber was added into CNC suspension (1.7 wt.%, 6 mL), and the composite was ultrasonicated for 20 s (5 s alternating frequency pulse mode, 40% amplitude). Thereafter, the composite suspension was subjected to vacuum filtration with a 0.22-micron polytetrafluoroethylene filter membrane under a stable vacuum of 0.08 MPa. That generated a vivid CNC layer. Then, another CNF layer was stacked on the CNC layer *via* the vacuum filtration of CNF dispersion (0.25 wt.%, 5 mL) with the same conditions. That formed a bi-layer CNC-CNF stacking laminate. Next, with repeating the vacuum filtration of CNC and CNF alternately, nanocellulose photonic laminates with multi-layer structure were obtained, which were denoted as CnFm, where n and m represent the total numbers of CNC and CNF layers, respectively. It should be pointed out that, for all nanocellulose photonic laminate stacking, CNT was added only in the first CNC layer, neither the other CNC cycling layers. As a contrast, evaporation-induced layer-by-layer assembly of CNC and CNF alternately was conducted to prepared CNC-CNF stacking structure.

2.3 Preparation of tri-layer photonic laminates with different colors

Based on above, tri-layer photonic laminates, *i.e.*, C2F1, were prepared *via* performing the vacuum filtration of CNC suspension, CNF dispersion, and CNC suspension in sequence, that forms a tri-layer stacking structure composed by CNC layer, CNF layer and CNC layer, from bottom to top. To prepare C2F1 laminates with different colors, CNC suspension was subjected to ultrasonication treatment for different time before vacuum filtration. Specifically, at a fix 40% amplitude, CNC suspensions were ultrasonicated for 20 s, 40 s, 50 s, 80 s, respectively. By using those CNC suspensions combined with CNF for VA-LbL assembly, correspondingly, tri-layer photonic laminates with color of blue, green, yellow, and red are obtained.

2.4 Characterization

The particle size and zeta potential of the CNC suspension were characterized by dynamic light scattering (DLS, Malvern Zetasizer Nano ZS90). Morphology of CNC and CNF was observed *via* transmission electron microscopy (TEM, JEOL JEM-F200 and JEM-2100P). Microstructures of as-stacked laminates were analyzed by a field-emission scanning electron microscope (SEM, JEOL JSM-7800) using 5 kV accelerating voltage. Samples were gold sputtered for 60 s prior to SEM observation. The FT-IR spectra were acquired by Bruker INVENIO-S FT-IR spectrometer. The types and distribution of water molecules within stacking laminate were characterized using a low-field NMR spectrometer (NIUMAG MicroMR12-025V). POM images were obtained with a Leica DM2700P polarization microscope in reflection mode with crossed polarizers. The UV-vis spectra were recorded on Ultraviolet-visible-near infrared spectrometer (Shimadzu SolidSpec-3700). The tensile test was conducted using a universal tensile tester (Instron 68TM-10) equipped with a load cell of 10 kN. Samples were cut into strips 30 mm in length and 5 mm in width. At least five specimens from each sample were tested with a speed of 5 mm/min to

obtain reliable data. Impact resistance for the laminates was evaluated by drop ball impact tests. A standardized steel ball (diameter: 10 mm, mass: 4.08 g) is dropped vertically from a specific height to strike the laminates. A high-frame-rate camera was used to capture the entire impact process to determine both the impact velocity and rebound velocity. Impacted surface of the laminate observed under a laser scanning microscope (KEYENCE VK-X150).

3 Results and discussion

3.1 VA-LbL assembly of nanocellulose photonic laminates

Given the high efficiency of the VASA technique in fabricating CNC photonic materials [13] and the capability of layer-by-layer (LbL) assembly to enable the harmless and seamless intercalation of CNFs within CNC cholesteric layers [12], herein we propose a VA-LbL assembly strategy to alternating deposition of CNC and CNF, that yields robust, tough, and stiff nanocellulose photonic laminates with well-defined stacked architectures and diversified optical functionalities (Figure 1a). For this, CNCs were firstly extracted from softwood pulp using a well-established sulfuric-acid hydrolysis method [17]. The obtained nanoparticles exhibit a typical needle-like morphology with an average length of ca. 185 nm and an average diameter of ca. 14 nm (Figure S1a). These nanoparticles show excellent colloidal stability in distilled water without noticeable precipitation (Figure S1b), as evidenced by the highly negative zeta potential of approximately -49 mV (Figure S1c). As-obtained CNC suspension is then subjected to the VASA process, that produces iridescent CNC layer with vivid

structure color (Figure S2a). SEM observation reveals a uniform left-handed chiral nematic phase formed within CNC layer (Figure S2b). Subsequently, VASA of CNF dispersion was conducted to deposit another CNF layer onto preformed CNC layer. The resulting CNC-CNF bi-layer stacking shows optical appearance identical to the bottom CNC layer (Figure S3a), due to that great optical transparency of CNF layer (Figure S3b) permits the light reflected from the bottom CNC layer to propagate through the layer structure. Another, the top CNF layer presents a “squashed” structure seamlessly interconnected with the bottom CNC layer, without any damage on the cholesteric alignment of CNCs (Figure S3c). With repeating VASA of CNC and CNF alternately, CNC-CNF stacking structure can be extended in a uniform and controllable manner. In this way, series of nanocellulose photonic laminates with different stacking configurations were successfully fabricated and denoted as CnFm (Figure S4a), where n and m represent the total numbers of CNC and CNF layers, respectively. For example, C2F1 represents a tri-layer sandwich structure consisting of two CNC layers and one CNF layer arranged in a CNC-CNF-CNC configuration. Notably, the adopted VA-LbL technique enables the fabrication of high-quality nanocellulose photonic laminates more efficiently than the evaporation-induced layer-by-layer assembly (EI-LbL) method, which is rather time-consuming (Figure S5a). Moreover, the photonic laminates fabricated via VA-LbL exhibit superior structural color uniformity relative to those prepared using the EISA-based LbL method (Figure S5b).

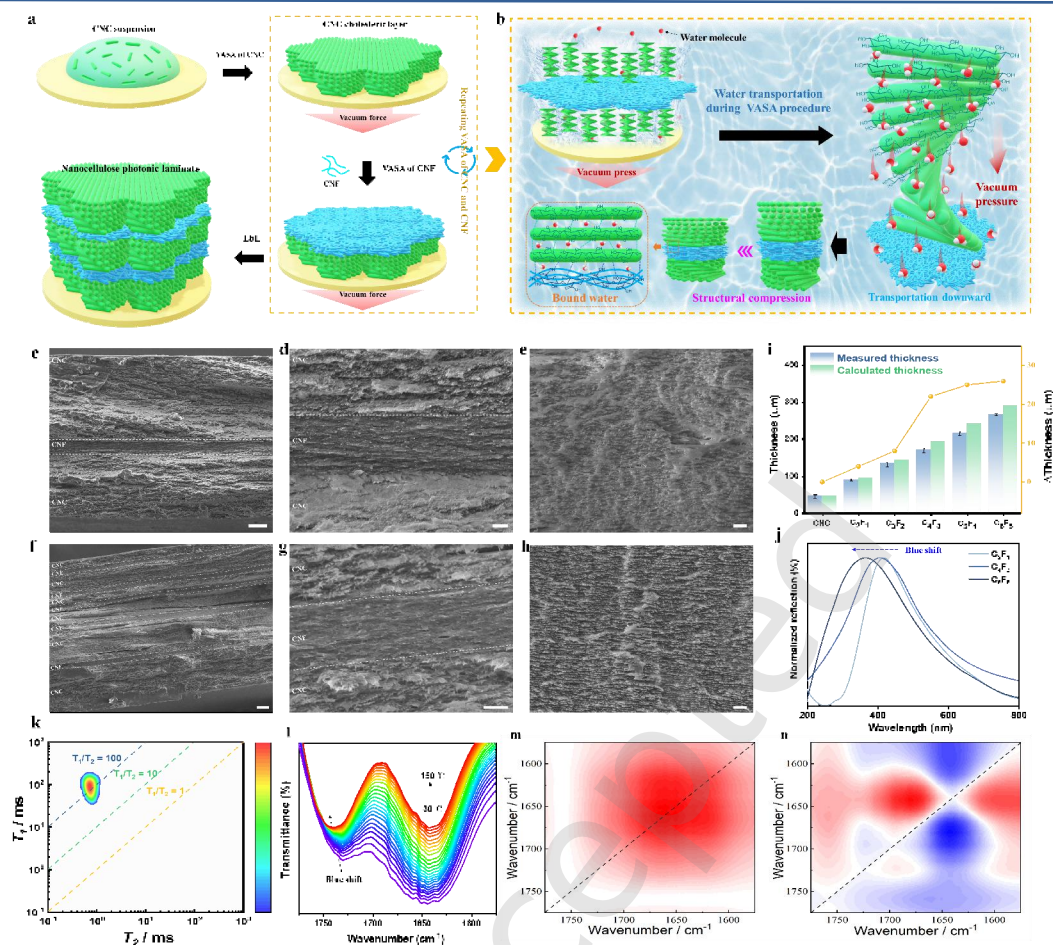


Figure 1 (a) Illustration of fabricating nanocellulose photonic laminate *via* VA-LbL technique. (b) Illustration of structural compression and rich bound water within the stacking structure during repeating VASA procedure. SEM images of (c) cross section, (d) CNC-CNF layer interface, and (e) CNC cholesteric organization for C2F1 laminate. SEM images of (f) cross section, (g) CNC-CNF layer interface, and (h) CNC cholesteric organization for C6F5 laminate. (i) The measured and calculated thickness values and the thickness difference (Δ thickness) between measured and calculated thickness for all nanocellulose photonic laminates. (j) UV-vis reflection spectra of C2F1, C4F3, and C6F5 laminates. (k) Low-field ^1H T_1 - T_2 2D map showing water distribution and state within C2F1 laminate. (l) Temperature-variable FT-IR spectra of C2F1 laminate upon heating from 30 to 150°C. (m) 2D-COS synchronous and (n) asynchronous spectra generated from panel (l). Scale bar: (c, f) 10 μm , (d, e, g, h) 1 μm .

The microstructures of different nanocellulose photonic laminates were analyzed *via* SEM observation. Typically, for C2F1, it reveals a CNC-CNF-CNC sandwich stacking with a dense tri-layer structure consisting of distinct CNC and CNF phases (Figure 1c). At higher magnification, well-defined and coherent interfaces are clearly detected between adjacent CNC and CNF layers (Figure 1d), implying strong interfacial interaction and structural integration between neighboring phases. Moreover, zooming in CNC layer, a pseudo-layered helical architecture with chiral nematic ordering is evident (Figure 1e), without any disturbance from CNF interlayer. With stacking number gradually extended, the corresponding nanocellulose laminates show the tight packing between CNC and CNF layers with strong interfacial integration (Figure S4b). Even the number of stacking layer up to eleven, the resulting C6F5 comprised by six CNC layers and five CNF layers clearly reveals a multi-layer architecture where CNC and CNF sublayers are seamlessly connected with strong interfaces (Figure 1f, g). Within CNC sublayers that the chiral nematic ordering is

always well-maintained (Figure 1h). It indicates excellent stability and reproducibility of as-adopted VA-LbL assembly strategy for the stacking of photonic laminates. That is in sharp contrast to EI-LbL assembly of CNC and CNF, which generates defects-rich, loosely-packed, and interface-blurry structure (Figure S6).

Next, the thickness values of as-stacked nanocellulose photonic laminates were measured and compared to their theoretical thickness values calculated from the sum thicknesses of the individual CNC and CNF layers. Notably, for all laminates, as-measured thickness values are consistently lower than the theoretical ones (Figure 1i). The deviation between the measured and theoretical values is progressively enlarged with the stacking number increased (Figure 1i). Moreover, C6F5 laminate prepared *via* 11 repetitions of VASA process shows a maximum reflection peak (λ_{max}) at 365 nm, showing blue shift of 40 nm and 49 nm compared with the λ_{max} of C4F3 and C2F1 laminates, which are prepared *via* 7 and 3 repetitions of VASA process, respectively (Figure 1j). Those results

strongly suggest the structural densification occurred during repeating VA-LbL assembly procedure. This phenomenon might be attributed to that the vacuum-driven water transport downward during every VASA process, compresses the preformed CNC and CNF layers, thus densifying the entire stacked structure (Figure 1b).

In addition, with VA-LbL assembly proceeded, as-preformed multilayer structure lengthens the transport route for the downward migration of water, that facilitates the retention of water molecules (namely bound water) within the final stacked laminate structure. Taking CNC-CNF-CNC tri-layer stacking structure as a representative, two-dimensional (2D) low-field ^1H -NMR analysis shows that the corresponding C2F1 laminate exhibits a distinct relaxation peak characterized by a longitudinal relaxation time of $T_1 \approx 90.7$ ms and a transverse relaxation time of $T_2 \approx 0.74$ ms (Figure 1k), which is close to the characteristic T_2 value of ~ 1 ms associated with ice-like bound water confined within nanoscale voids on crystalline cellulose surfaces [18]. Notably, the T_1/T_2 ratio is over 100, which is significantly higher than the commonly accepted threshold value ($T_1/T_2 = 10$) used to distinguish liquid-like water from solid-like bound water [18]. Those results indicate strong spatial confinement of water molecules, implying the presence of rich “ice-like” bound water confined within CNC-CNF-CNC tri-layer stacking structure. Variable-temperature FTIR spectroscopy confirms strong water-involved hydrogen-bonding interactions within CNC-CNF-CNC tri-layer stacking architecture. Obviously, with heating, the peak signal at ~ 1650 cm^{-1} associated with bound water [19] gradually becomes weakened due to the thermal dissociation of water-cellulose hydrogen bonding (Figure 1l). Additionally, the characteristic peak located ~ 1730 – 1740 cm^{-1} assigned to the carbonyl ($\text{C}=\text{O}$) stretching of CNF, exhibits a progressive blue shift stem from the disruption of water-mediated interactions (Figure 1l). Synchronous 2D-COS spectra display pronounced auto-peaks for both vibrations, revealing that bound water and carbonyl groups are highly sensitive to thermal perturbation and positively correlated (Figure 1m). In the asynchronous 2D-COS spectra (Figure 1n), water-involved hydrogen bonds evolve earlier than carbonyl-involved hydrogen bonds. It indicates that, with heating treatment, the bound water molecules preferentially remove that makes free hydroxyl groups exposed, which then re-interact with carboxyl groups on CNFs, hence leading the reconstruction and strengthening of the interface.

3.2 Mechanical performances of nanocellulose photonic laminates

Benefiting from the densely stacked architecture with robust hydrogel-bond-stabilized interfaces, together with the toughening effect contributed by bound water, as-prepared nanocellulose photonic laminates exhibit substantially improved mechanical performances. Specifically, single CNC layer (C1F0) exhibits common brittle fracture with an ultimate tensile strength (σ) of 52 ± 6 MPa and an elongation at break (ϵ) of only $0.95 \pm 0.07\%$, with a low toughness of 0.29 ± 0.14 MJ m^{-3} (Figure S7). By introducing a CNF interlayer (with thicknesses of 3, 5, and 7 μm , respectively) between two CNC layers, the resulting C2F1 laminates display enhancements in both σ and ϵ relative to the C1F0 (Figure S7, Figure S8). Furthermore, for these tri-layer C2F1 laminates, ϵ increases whereas σ decreases as the thickness of the CNF interlayer rises (Figure S8). Accordingly, the 5 μm -thick CNF interlayer was chosen for the subsequent stacking procedure. Thereby, as further increase in stacking layer number, progressive and continuous improvement in both σ and ϵ is evident (Figure 2a), meanwhile come with gradient increase in toughness yet without obvious decline in Young's modulus (Figure 2b). That implies simultaneous strengthening and toughening effects without sacrificing the stiffness. It might be attributed to as-adopted VA-LbL assembly strategy ensuring the high uniformity in the stacking structure, even with repetitions of VASA procedure for many times. Consequently, C6F5 laminate with a total stacking number reaching 11, achieves the highest σ of 160 ± 5 MPa, the largest ϵ of $6.23 \pm 0.29\%$, together with a high Young's modulus of 3.63 ± 0.31 GPa and a dramatic toughness of 5.98 ± 0.57 MJ m^{-3} over 20-fold higher than 0.29 MJ m^{-3} for single CNC layer. Such exceptional mechanical combinations for C6F5 laminate outperform most of CNC-based photonic materials (Figure 2c) [9-10, 12, 20-27]. We claim the synergistic effects including: (i) the interlayer slippage between adjacent CNC and CNF sublayers, (ii) the strong interface for stress transferring, (iii) the plasticization effect of bound water, and (iv) the reorientation of CNCs and CNFs, together contribute efficient energy dissipation hence substantially enhancing the overall mechanical performance for the nanocellulose photonic laminate. However, when the total stacking number reaches 13, the corresponding C7F6 laminate shows simultaneous reductions in σ and ϵ (Figure S9) relative to the C6F5, which might be ascribed to amplified structural defects with increased stacking layers.

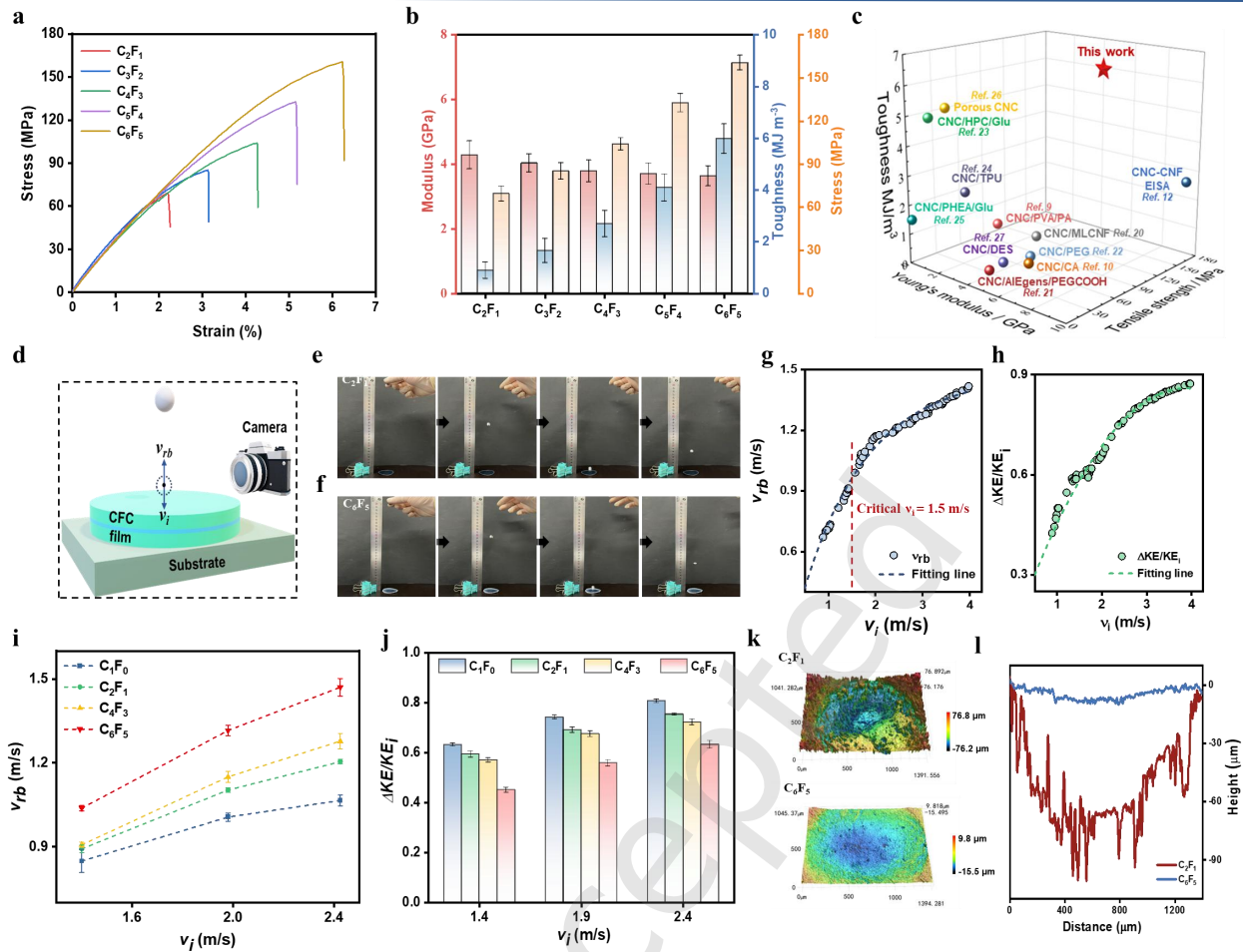


Figure 2 (a) Stress-strain curves of nanocellulose photonic laminates from C₂F₁ to C₆F₅. (b) Bar graphs comparing the stress, Young's modulus, and toughness for all nanocellulose photonic laminates. (c) Comparing strength, stiffness, and toughness between C₆F₅ laminate and previously reported CNC-based chiral nematic films. (d) Setup for ball drop impact test. Capturing the ball drop impact test processes for (e) C₂F₁ and (f) C₆F₅ laminates. (g) Coefficient of restitution (i.e., v_{rb}/v_i) and (h) normalized kinetic energy loss ($\Delta KE/\Delta KE_i$) as function of v_i , when C₂F₁ is subjected to ball drop impact test. Comparing (i) the v_{rb} and (j) the corresponding normalized kinetic energy loss, when C₁F₀, C₂F₁, C₄F₃, C₆F₅ are subjected to ball drop impact test with different v_i . (k) 3D LSM images and (l) the corresponding cross-sectional profiles, of the surfaces of C₂F₁ and C₆F₅ laminates after ball drop impact test.

Beyond in-plane tension, out-of-plane impact resistance of as-stacked nanocellulose photonic laminates is investigated *via* a ball drop test, as illustrated in Figure 2d. Specifically, a steel ball is released from various heights (h_i) to impact the sample with different impact velocity (v_i), and the rebound height (h_r) and corresponding rebound velocity (v_{rb}) are recorded. The coefficient of restitution (e) related to the elastic recovery capability and the normalized kinetic energy loss ($\Delta KE/\Delta KE_i$) defined as the fraction of incident kinetic energy dissipated during impact, are calculated from v_i and v_{rb} using the following equations [28]:

$$e = \frac{v_{rb}}{v_i} \quad (1)$$

$$\frac{\Delta KE}{KE_i} = 1 - \frac{v_{rb}^2}{v_i^2} = 1 - e^2 \quad (2)$$

Firstly, C₂F₁ laminate was subjected to ball impact experiment to evaluate the impact resistance of CNC-CNF-CNC sandwich structure (Figure 2e). As we can see, v_{rb} and v_i almost follows a positive linear relationship when v_i is below 1.5 m/s (Figure 2g). It suggests the v_{rb}/v_i value (i.e., e value) changes very slightly, reflecting C₂F₁ laminate

having good elastic recovery behavior with very little energy loss under $v_i < 1.5$ m/s. When v_i is over 1.5 m/s, the increment in v_{rb} slows down with v_i increased, along with the e value gradually decreased from approximately 0.75 to 0.42. It indicates the poor elastic recovery coupled with large energy loss for C₂F₁ laminate under high-velocity impact. Additionally, the value of $\Delta KE/\Delta KE_i$ gradually increases from 0.4 to 0.9 with v_i increased (Figure 2h), further confirming high fraction of energy dissipated under intense impact. Moreover, the value of $\Delta KE/\Delta KE_i$ approaches a plateau at high $v_i > 3.7$ m/s, it suggests that C₂F₁ is approaching its maximum energy dissipation capacity or the verge of macroscopic failure. The impact resistance of nanocellulose photonic laminates with multi-layer stacking structure layers is also studied *via* the ball drop test (Figure 2f). Remarkably, for nanocellulose photonic laminates with different stacking structures, with a fixed v_i , the more stacking layers, the higher v_{rb} (Figure 2i). On the contrary, $\Delta KE/\Delta KE_i$ values decrease as stacking layer extended at a fixed v_i (Figure 2j). It is evident that the expansion in stacking structure great improves the impact

resistance for nanocellulose photonic laminates. Indeed, visually, 3D laser scanning microscope (3D LSM) images (Figure 2k) and the corresponding cross-sectional profiles (Figure 2l) show that, under the ball impact test with the same v_i , C2F1 presents an indentation deeper than that of C6F5, inferring a poorer impact resistance.

According to the results, we explain the impact resistance behavior for nanocellulose photonic laminate as below. For CNC-CNF alternating stacking structure, upon impact, the cholesteric organization of CNC layer atop is firstly engaged, which act as “photonic spring” for storing elastic energy *via* the compression of helical structure. Once the compression reaching a certain critical threshold, the helical structure is densely packed and transitions into a stiff, load-bearing plate, which efficiently transfers the remaining energy downward. At this moment, the underlayer CNF phase functioning as “mechanical ligament”, ensures efficient loading transfer and inhibiting crack propagation to prevent cracks originating within the top CNC layer from catastrophically propagating across the whole laminate. In this principle, for multi-layer laminates, the repeated alternating stacking of CNC “photonic springs” and CNF “mechanical ligaments” makes a high proportion of impact energy to be stored and released progressively, that leads long energy-transfer path and prolonged energy-transferring duration, thus contributing efficient energy dissipation and achieving excellent impact resistance.

3.3 Color expansion and prediction for nanocellulose photonic laminates

Due to great controllability and high uniformity in the stacking structure enabled by VA-LbL assembly strategy, we allow precise modulation and management in the optical properties of as-stacked nanocellulose photonic laminates. Specifically, *via* single VASA with CNC, the resulting CNC film (marked as CNC1) shows a blue color with a $\lambda_{\max}$ at 382 nm with an intensity of 8.9% (Figure 3a, Figure S10). Doubling CNC suspension dose and then subjected to single VASA, the resulting CNC film (Marked as CNC2) shows an enhanced hue of 13.2 at $\lambda_{\max}$ of 413 nm (Figure 3a, Figure S10). Such improvement in reflection is derived from the thick CNC cholesteric layers enabling strong multi-layer interference. However, stacking two layers of CNC1 *via* performing two VASA processes, that produces a blue bi-layer photonic laminate (marked as C2F0) exhibiting a 21.8% reflection higher than 13.2% reflection for CNC2 (Figure 3a, Figure S10), even both

having the same CNC composition while different stacking structure. Once intercalating a CNF interlayer (with a thickness of 5 μm) between two CNC layers, the resulting tri-layer C2F1 laminate reveals a 28.4% reflection at $\lambda_{\max}$ of 417 nm (Figure 3a, Figure S10). It is attributive to that the presence of CNF interlayer not only increases the number of reflecting interfaces within stacking structure to contribute additional coherent reflection, but also acts as a dielectric slab to induce constructive interference between light reflected from adjacent upper and lower CNC layers (Figure 3b). Note that the CNF layer thickness affects the optical reflection of the C2F1 photonic laminate (Figure S11). Remarkably, a CNF layer with an appropriate thickness, which can induce strong constructive interference meanwhile generating limited light scattering, contributes to the improved optical performance of photonic laminate. Beyond blue tri-layer photonic laminates, series of tri-layer photonic laminates with different colors including green, yellow, and red, which are prepared with the same VA-LbL assembly procedure while tuning the sonication dose applied to CNC suspension, also demonstrate enhanced hue compared with the corresponding single-layer CNC laminates (Figure S12). Remarkably, CNC-CNF-CNC sandwich architecture brings benefits for enhancing the optical property of the photonic laminate. Based on this, we extend CNC-CNF-CNC sandwich architecture in the photonic laminate to further improve the optical property. As expected, C4F3 with 3 cycles of CNC-CNF-CNC sandwich architecture exhibits 30.7% reflection at $\lambda_{\max}$ of 407 nm, and C6F5 laminate with 5 cycles of CNC-CNF-CNC sandwich architecture reveals a dramatic reflectance intensity of 40.6% at $\lambda_{\max}$ of 366 nm (Figure 3a), approaching the reflection limitation of 50% for common CNC photonic materials. Such improvement in reflectance is ascribing to the synergistic effects of the increased optical period and the suppressed optical scattering arising from dewatering-induced structural densification [29, 30]. Additionally, polarized optical microscopy (POM) images show that, with the repetition of CNC-CNF-CNC sandwich architecture increased, the resulting photonic laminates show brighter, more uniform, and emerged large-size domains (Figure 3c), well matching the increase in reflection intensity as CNC-CNF-CNC sandwich architecture extended in photonic laminates. That confirms the optical property improvement for photonic laminate enabled by the extension in the stacking structure with VA-LbL assembly strategy.

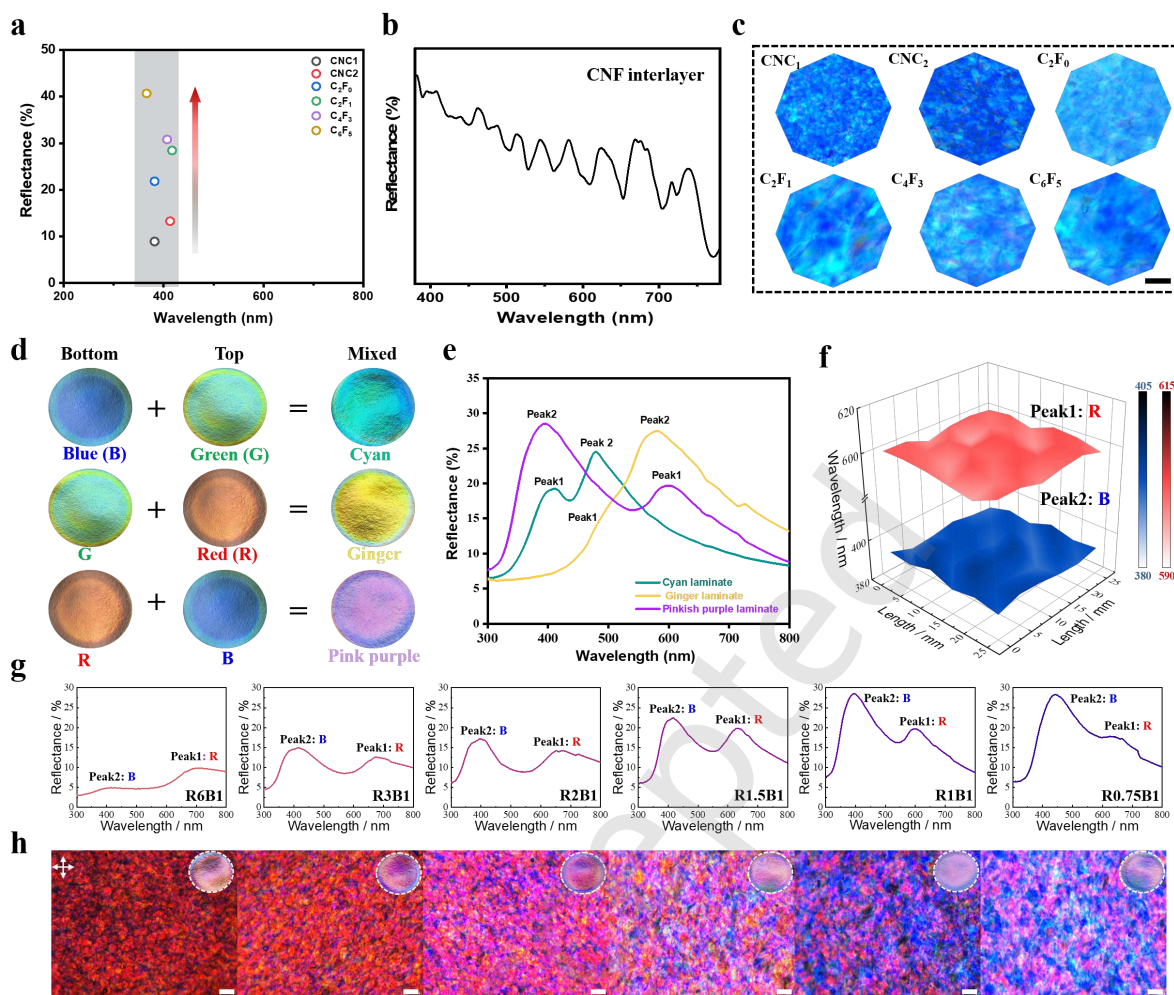


Figure 3 (a) Comparison in the reflectance intensity of CNC1, CNC2, C₂F₀, C₂F₁, C₄F₃, and C₆F₅. (b) Reflectance spectrum of CNF interlayer showing strong film interference effect. (c) POM images of CNC1, CNC2, C₂F₀, C₂F₁, C₄F₃, and C₆F₅. Scale bar: 50 μ m. (d) Photos of as-mixed cyan, ginger, and pink purple tri-layer laminates, and (e) the UV-vis reflection spectra. Peak1 and Peak2 corresponding to the CNC fundamental layer at bottom and top, respectively. (f) UV-vis reflection mapping of the whole surface of pink purple tri-layer laminate. (g) UV-vis reflection spectra of different tri-layer laminates with stacking combination of red CNC layer-CNF interlayer-blue CNC layer, from bottom to top, while with difference thickness in the bottom and top CNC layers. RxBy: red CNC layer at the bottom and blue CNC layer at the top, with thickness ratio of x:y between the bottom and top layer. (h) The corresponding POM images and photos (insets) of those as-mixed tri-layer laminates. Scale bar: 100 μ m.

As-proposed VA-LbL assembly strategy also allows flexible combination of different-colored CNC layers into one laminate, that capable to gain diverse nanocellulose photonic laminates with arbitrary coloration *via* color mixing based on RGB model. As shown in Figure 3d, taking CNC-CNF-CNC tri-layer laminate as prototype, the combination of blue CNC layer—CNF interlayer—green CNC layer from bottom to top, produces a cyan tri-layer laminate. In this way, ginger and pinkish purple tri-layer laminates are obtained *via* the combinations of green CNC layer—CNF interlayer—red CNC layer and red CNC layer—CNF interlayer—blue CNC layer, from bottom to top, respectively (Figure 3d). UV-vis spectra of those tri-layers laminates reveal two reflection peaks coinciding with the corresponding foundation CNC layers at bottom and top (Figure 3e). It indicates that the two different CNC fundamental layers are independent with each other, and the constructive interference between light reflected from the top and bottom fundamental CNC layers contributes to

the final coloration for as-mixed tri-layer laminates. Moreover, the mixed tri-layer laminate shows high uniformity in color. Taking pinkish purple tri-layer laminate as an example, the UV-vis reflection mapping reveals only ca. 15 nm differences in the $\lambda_{\max}$ at fundamental peak1 and peak2 across the whole laminate area (Figure 3f). Additionally, the color of as-mixed tri-layer laminates can be adjusted *via* tuning the thickness of two CNC fundamental layers. As we can see, with tuning the thickness ratio between the bottom and top CNC fundamental layers from 6:1 to 0.75:1 (Figure 3g), which is associated with the reflection intensity regulation in the two fundamental CNC layers, the resulting mixed tri-layer laminates reveal a gradient shift in color from red-dominated to purple-dominated. That is in consistence with optical photos of those tri-layer laminates (Insets in Figure 3h), the corresponding POM images variation (Figure 3h), and CIE analysis (Figure S13), all of which reveal gamut variations from red to purple.

Next, we further extend the color base of tri-layer nanocellulose photonic laminates by randomly combining blue (B), green (G), yellow (Y), and red (R) CNC fundamental layers in pairs and then tuning the thickness ratio between the two CNC fundamental layers (Figure 4a). That produces varieties of tri-layer nanocellulose photonic laminates with extremely-extended colors, which are marked as MxNy, where M and N represent the bottom and top CNC fundamental layer, respectively, x/y represents the thickness ratio of the bottom and top CNC fundamental layers (Figure 4b and Figure S14). For example, B2G1 represents a tri-layer laminate comprised by a blue CNC layer at the bottom, a CNF interlayer, and a green CNC layer at the top, with the thickness ratio of 2:1 between the bottom and the top CNC layers. CIE analysis reveals those tri-layer laminates having a wide and random gamut distribution (Figure 4c). By using those colors as a database for machine learning, we realize the color prediction of tri-layer nanocellulose photonic laminate with specific color. For this, a multi-model fusion color parameter conversion system is utilized to link the

chromaticity points (X, Y) in CIE diagram to the stacking combination for the target tri-layer laminates (Figure 4d, Color prediction model in SI). The chromaticity points in the region of both X and Y axes from 0.2 to 0.5, covering all the colors of as-mixed tri-layer laminates, are subjected to training by machine learning. It turns out that as-trained color prediction model achieves an accuracy exceeding 95% (Figure 4e), almost approaching the chromaticity limit attainable by those tri-layer laminates under the current variable conditions. To prove the accuracy, we select six chromaticity points (P1-P6) randomly, and those points are read and translated to the corresponding stacking combination formulations for the target tri-layer laminates. Those combination formulations then guide us to prepare the corresponding tri-layer photonic laminates (Figure 4f). As expected, those tri-layer photonic laminates prepared based on as-predicted combination formulations reveal color hue highly in consistence with those as-preselected chromaticity (Figure 4f), demonstrating precise color prediction for nanocellulose photonic laminates.

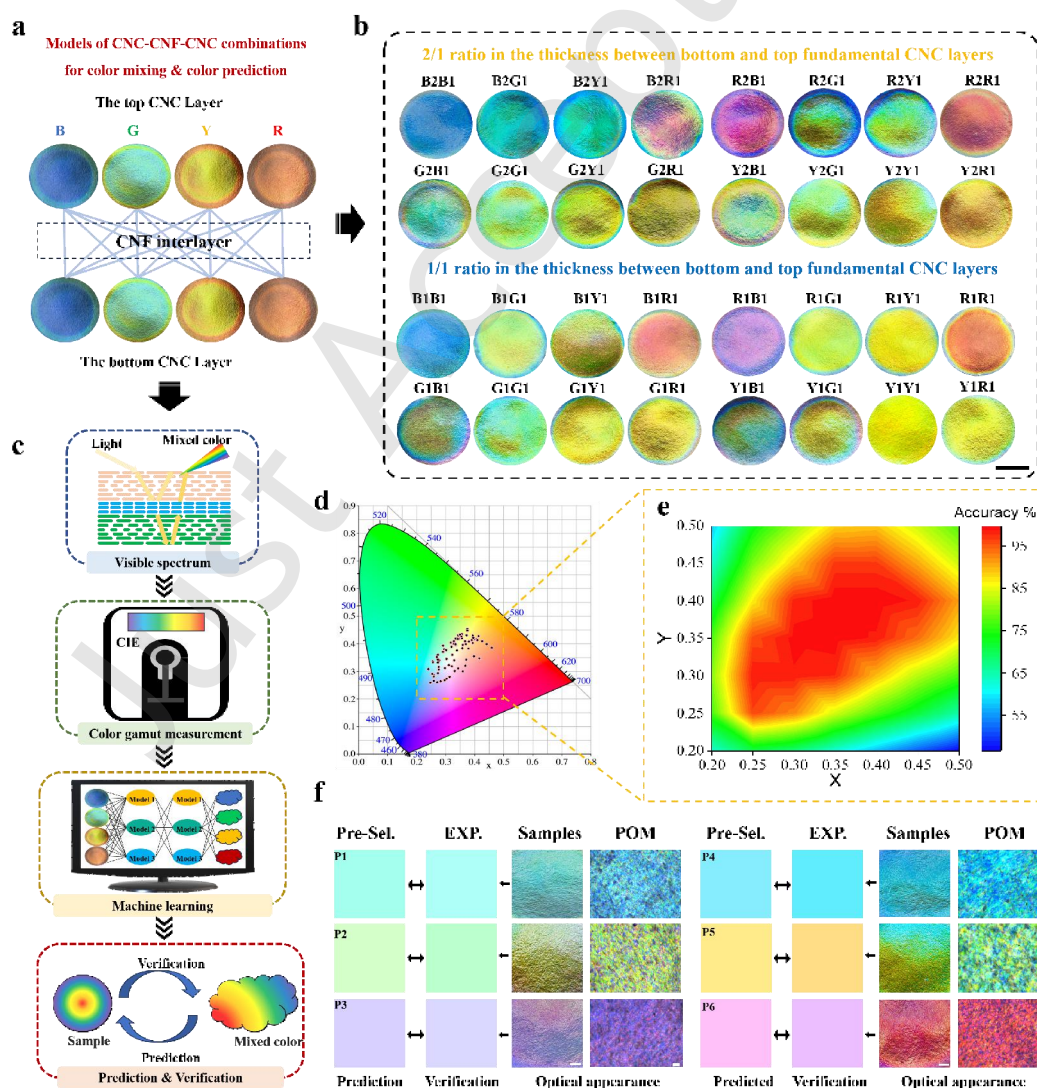


Figure 4 (a) Schematic diagram of color mixing based on blue (B), green (G), yellow (Y), and red (R) CNC fundamental layers by using CNC-CNF-CNC tri-layer stacking layer as structure prototype. (b) Optical photos of as-mixed tri-layer photonic laminates with extremely-extended colors. Scale bar: 2 cm. (c) Schematic illustration of color prediction using machine

learning. (d) The corresponding CIE diagram for as-mixed colors of tri-layer photonic laminates, and (e) the accuracy of as-developed model for color prediction using chromaticity points in CIE diagram as the database. (f) Verifying the accuracy of the model for color prediction in practice. Scale bar: 0.5 cm in Samples and 100 μm in POM images. Abbreviation: Pre-Sel. and EXP. referring pre-selected and experimental, respectively.

3.4 Photonic matrix with programmable optical response for information encryption

Since water infiltrating into CNC cholesteric organization that induces fast red shift in color, CNC photonic materials with differential water infiltration capability would present distinct optical response. In this principle, nanocellulose photonic laminates possess distinct layer structures, which differentiate their color-changing

responses to water stimuli. As we can see, for blue nanocellulose laminates with different stacking layers, the redshift rate in their colors gradually slows down with the stacking layer increased from C1F0 to C6F5 (Figure 5a). Such differential color-changing response allows us to develop an information matrix platform with programmed dynamic optical function for encryption and anti-counterfeiting.



Figure 5 (a) Photos of the color-changing response with water stimulated for different laminate blocks. (b) Three models of information encryption and decryption based on photonic matrix. (c, d) Photonic matrix comprised by C3F2 and C5F4 blocks for model I-type information encryption and decryption. (e) Photonic matrix comprised by C2F1 and C6F5 blocks for model II-type information encryption and decryption. (f) Photonic matrix comprised by C1F0, C2F1, C3F2, C4F3, and C5F4 blocks for model III-type information encryption and decryption.

To develop matrix platform, nanocellulose photonic laminates with different stacking structures were cut into small square blocks with size of $500 \times 500 \mu\text{m}$, which are then used as photonic pixels. By choosing square blocks with different color-changing response to water stimulus followed by assembling them into a matrix with special patterns, that forms different information platforms (i.e., Type I, II, III, as illustrated in Figure 5b) with dynamic optical transition between non-informational state and information visualization display, thereby enabling encoding and decoding. Based on this, firstly, C3F2 and C5F4 blocks, both having similar initial blue color, are used

as photonic pixels to assemble a 5×18 matrix (Type I), in which an invisible “2169” pattern is assembled using C3F2 blocks and the other pixels are C5F4 blocks. Under this configuration, initially, the matrix is in an encryption status without any information (Figure 5c). Upon water stimulus for 120 s, the hidden “2169” numbers become readable for information decryption. With removing the stimulus (i.e., dehydration) that the information disappears and the matrix goes back to encrypted state (Figure 5c). In the same way, a more complicated 25×25 matrix is assembled with C3F2 and C5F4 blocks, which allows to display a scannable QR code under water

stimulus (Figure 5d). Another information matrix (Type II) comprised by C2F1 and C6F5 blocks with different initial color is constructed, where C2F1 blocks are used to assemble a special “WTU” pattern and C6F5 blocks as the background. As shown in Figure 5e, initially, “WTU” pattern is readable due to the color difference between the two blocks. With water stimulus for 10 s, color change occurs for both C2F1 and C6F5 blocks and they present very similar colors. It might be attributed to that the color-changing response difference at this moment precisely matches the initial color difference between C2F1 and C6F5 blocks. Therefore, “WTU” pattern is invisible and the matrix turns into encryption status. As the water continues to stimulate (for 120 s), the color-changing response difference between C2F1 and C6F5 blocks makes a color difference between them again, hence leading “WTU” pattern to be read for decryption (Figure 5e). Finally, we develop a more complicated matrix (Type III) with a special floral pattern by using five kinds of photonic pixels, i.e., C1F0, C2F1, C3F2, C4F3, and C5F4, and C6F5 blocks, *via* special configuration design. Due to the time lag in the color-changing response of those blocks, consequently, the floral pattern within the matrix shows continuous color variations with water stimulus proceeded (Figure 5f). Moreover, besides customized dynamic optical functions, the information matrix platform for encryption and anti-counterfeiting enabled by nanocellulose photonic laminates delivers outstanding stability. Evidently, the preprogrammed photonic matrix retains fast and reversible color-switching responsiveness even after 20 hydration-dehydration cycles (Figure S15), exhibiting promising practical potential for multimodal decryption based on color gradience.

4 Conclusions

In summary, we develop nanocellulose photonic laminates with a multi-layer architecture comprised by CNC and CNF layers alternately stacked *via* vacuum-assisted layer-by-layer assembly strategy. This strategy combines the VASA technique to regulate drying kinetics and the layer-by-layer method to harmlessly incorporate energy-dissipating phases, that makes uniformity, densification, and precise controllability for strong, tough, and still nanocellulose photonic laminates. Ascribing to the great integration of stiff CNC cholesteric layer and tough CNF layer, with strong interfaces stabilized by hydrogen bonding interaction, the resulting photonic laminates impart exceptional mechanical synergy including strength of 160 MPa, toughness of 5.9 MJ m⁻³, and stiffness of 3.6 GPa, as well as demonstrate impressive out-of-plane impact resistance. Moreover, the high uniformity and flexible modulation of CNC cholesteric sublayers within the CNC/CNF alternating stacking, allows the resulting photonic laminates with extended and customized optical functions like arbitrary color blending *via* RGB color model, machine-learning-assisted color prediction, and programmable water-induced color-changing response, far beyond the monotonous modulation in the color of common photonic materials. The unique combination of high mechanical performance and enriched photonic functions in nanocellulose photonic materials, positions

them as sustainable, high-security, high-performance leading candidates for bio-enabled display technologies and security indicators.

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Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.”

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.”

Author contribution statement

Y. H. T.: Methodology, Data curation, validation, software, writing - original draft. B. Q. S.: Formal analysis, investigation, software. W. L. X.: Supervision. X. F. Z.: Conceptualization, supervision, writing - review and editing, project administration. All the authors have approved the final manuscript.

Use of AI statement

None.

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Electronic Supplementary Material

Strong, tough, and stiff nanocellulose photonic laminates with customized optical functions

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Color prediction model

CIE was collected on a colorimeter (X-Rite USA, Colori7) to analyze the colors of as-mixed tri-layer photonic laminates. As-obtained hue points (X, Y) of those laminates in the CIE chromaticity diagram were associated with their stacking layers combination accordingly, via a multi-model fusion color matching parameter conversion system. The mapping relationship between the hue points (X, Y) and the stacking layers combination is complex and nonlinear. The hue points of all samples were used as datasets for model fitting training. Machine learning sub-models with distinct mathematical characteristics and applicable ranges were selected and integrated using an adaptive weighted fusion strategy. The machine learning sub-models are list as below:

K-Nearest neighbor model 1 (M1): For data-dense regions, interpolation is performed based on the assumption of local similarity [1]. Given an input point (P), the model searches for the k samples in the all-training datasets (D) with the smallest Euclidean distances (d_i). The reciprocal of the d_i is used as a weight (w_i), with a constant ($\epsilon = 0.001$) added to prevent the denominator from becoming zero. The predicted chromaticity coordinates (X_{pred} , Y_{pred}) can then be obtained. A and B represent the ultrasonic treatment times for the pre-dissolved solutions of the lower and upper photonic laminates, respectively. a and b represent the volumes of the pre-dissolved solutions for the lower and upper photonic laminates, respectively.

$$P=(A,B,a,b) \quad (1)$$

$$D=\{(A_i,B_i,a_i,b_i,X_i,Y_i)\}_{i=1}^N \quad (2)$$

$$d_i=\sqrt{(A-A_i)^2+(B-B_i)^2+(a-a_i)^2+(b-b_i)^2} \quad (3)$$

$$w_i=\frac{1}{d_i+\epsilon} \quad (4)$$

$$X_{pred}=\frac{\sum_{i=1}^k w_i X_i}{\sum_{i=1}^k w_i} \quad (5)$$

$$Y_{pred}=\frac{\sum_{i=1}^k w_i Y_i}{\sum_{i=1}^k w_i} \quad (6)$$

Radial basis function neural model 2 (M2): For moderately sparse data regions, a Gaussian kernel function was employed as the basis function (fd_i) [2]. The kernel width parameter ($s = 15$) was introduced to control the smoothness of the interpolation. Similarly, for input point P, calculate its d_i with D to obtain w_i . Note that the predicted chromaticity coordinate (X_{pred} , Y_{pred}) here was consistent with the functional expression of M1 and is not shown again.

$$w_i=\phi(d_i)=e^{-\left(\frac{d_i^2}{\sigma^2}\right)} \quad (7)$$

Multivariable linear regression model 3 (M3): For data dilution or marginal regions, extrapolation is performed based on the local linearity assumption [3-4]. Select nearest neighbor samples ($k = 5$) for P to construct a multiple linear regression model. Assume a linear relationship exists between coordinate X and the four parameters of the prepared sample (the same applies to Y). Let M denote the design matrix and X the observation vector. Derive the normal equations and estimate the coefficients b using the least squares method. The coordinates (X_{pred} , Y_{pred}) were obtained (where g corresponds to b).

$$X=\beta_0+\beta_1A+\beta_2B+\beta_3a+\beta_4b+\epsilon \quad (8)$$

$$\beta=[\beta_0,\beta_1,\beta_2,\beta_3,\beta_4]^T \quad (9)$$

$$M \in \mathbb{R}^{k \times 5} \quad (10)$$

$$X=[X_1,X_2,\dots,X_k]^T \quad (11)$$

$$(M^T M)\beta=M^T X \quad (12)$$

$$X_{pred}=\beta_0+\beta_1A+\beta_2B+\beta_3a+\beta_4b \quad (13)$$

$$Y_{\text{pred}} = \gamma_0 + \gamma_1 A + \gamma_2 B + \gamma_3 a + \gamma_4 b \quad (14)$$

Adaptive weighting fusion model 4 (M4): Dynamic weights were assigned to the three models based on the minimum distance ($d_{\min}$) between P and D, yielding the coordinates ($X_{\text{pred}}, Y_{\text{pred}}$) of the fused prediction value derived from the integrated models.

$$d_{\min} = \min_{i=1, \dots, N} d_i \begin{cases} < 10, M_1 * 0.6 + M_2 * 0.3 + M_3 * 0.1 \\ 10 \sim 25, M_1 * 0.2 + M_2 * 0.6 + M_3 * 0.2 \\ > 25, M_1 * 0.1 + M_2 * 0.3 + M_3 * 0.6 \end{cases} \quad (15)$$

$$(X_{\text{pred}}, Y_{\text{pred}}) = \sum_{j=1}^3 w_j (X_j, Y_j) \quad (16)$$

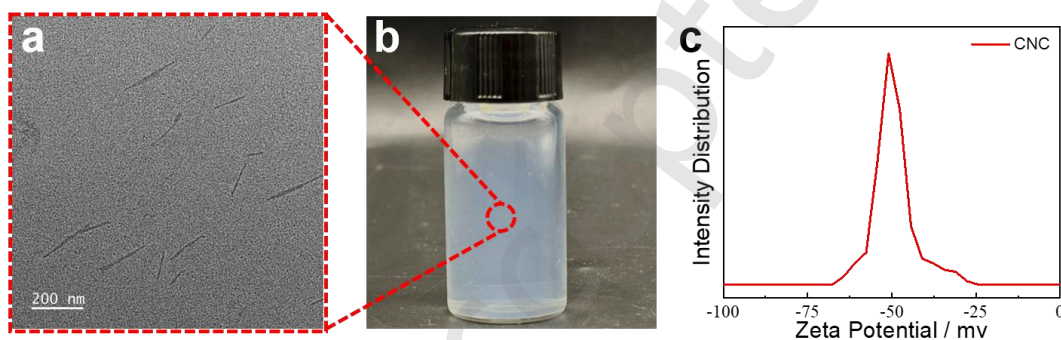


Figure S1 (a) TEM image of CNCs. (b) Photo of CNC suspension. (c) Zeta potential of CNC suspension.

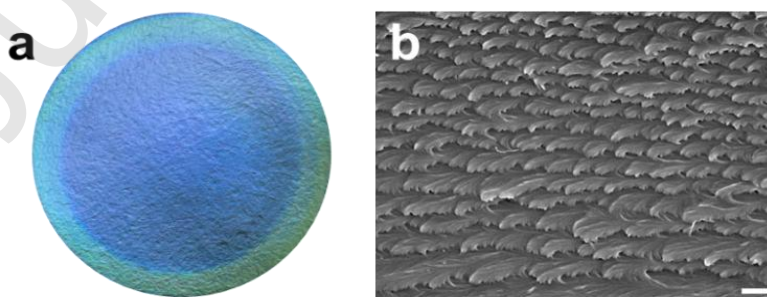


Figure S2 (a) Photo of single-layer CNC laminate. (b) SEM images of single-layer CNC laminate. Scale bar: 1 μm .

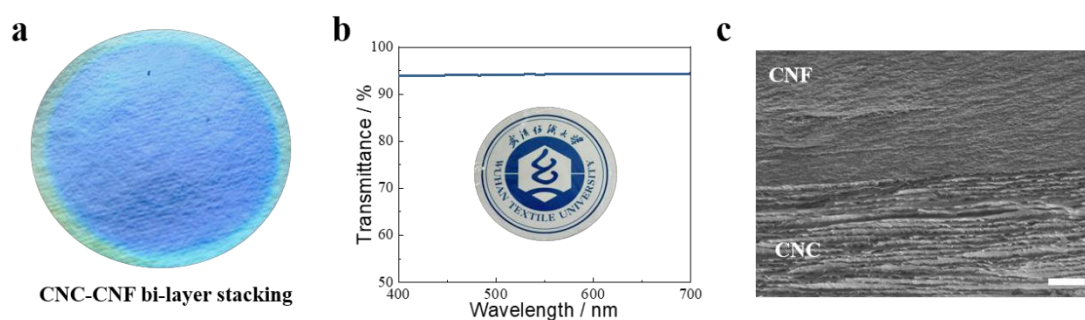


Figure S3. (a) photo of CNC-CNF bi-layer stacking. (b) UV-vis transmittance spectrum of CNF layer. Inset is the photo of CNF layer. (c) Cross-sectional SEM image of CNC-CNF bi-layer stacking. Scale bar: 1 μm.

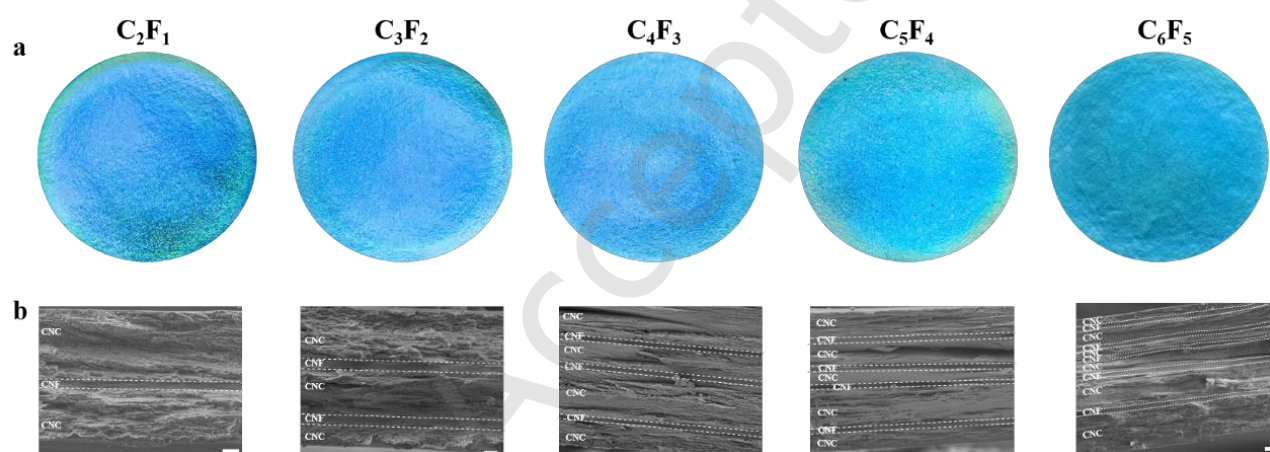


Figure S4 (a) Photo of different nanocellulose photonic laminates and (b) the corresponding cross-sectional SEM images. Scale bar: (b) 10 μm.

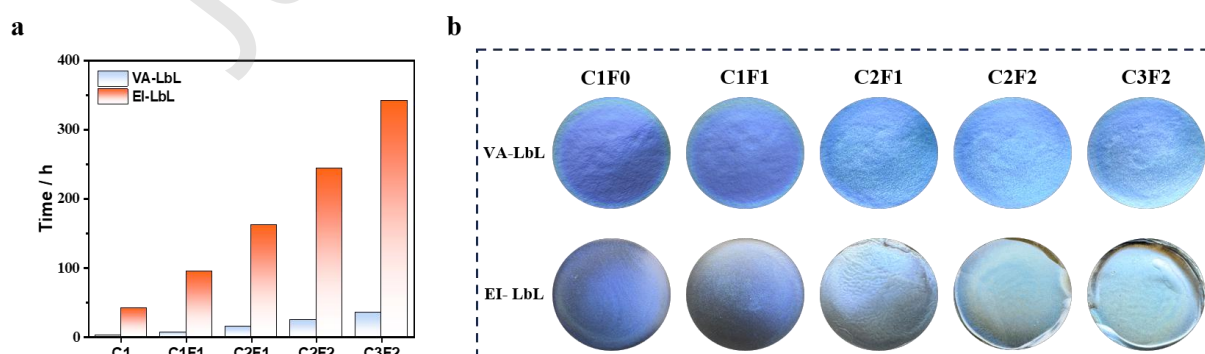


Figure S5 (a) Comparison of the time consumption for VA-LbL and EISA-based LbL in fabricating photonic laminates, and (b) photos of the corresponding photonic laminates.

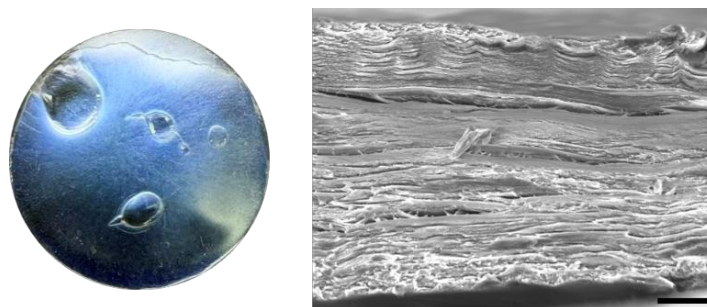


Figure S6 Photo of tri-layer CNC-CNF-CNC film prepared via EI-LbL strategy. (b) The corresponding cross-sectional SEM image. Scale bar: 10 μm .

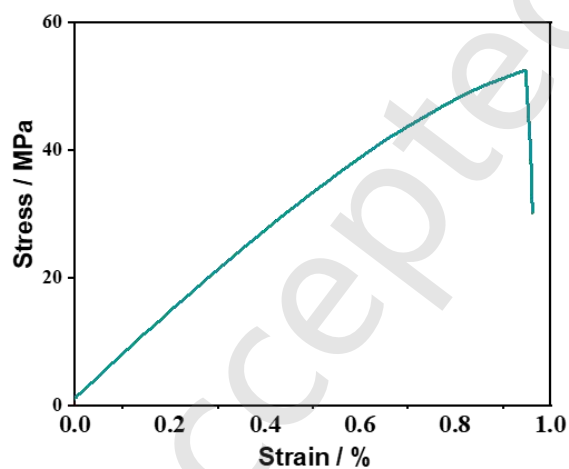


Figure S7 Stress-strain curve of single-layer CNC film.

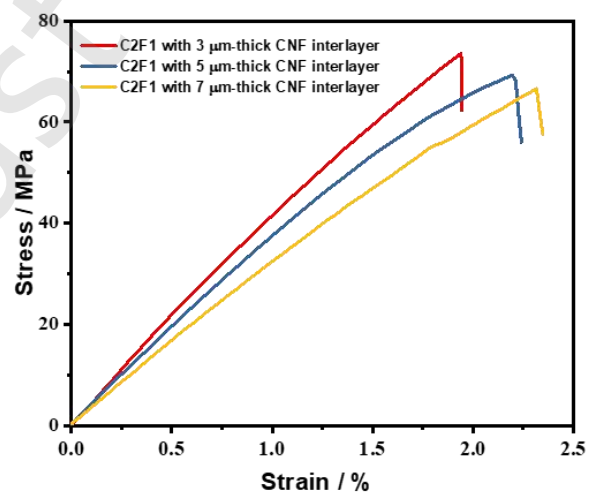


Figure S8 Stress-strain curves of C2F1 laminates with CNF interlayer having different thickness.

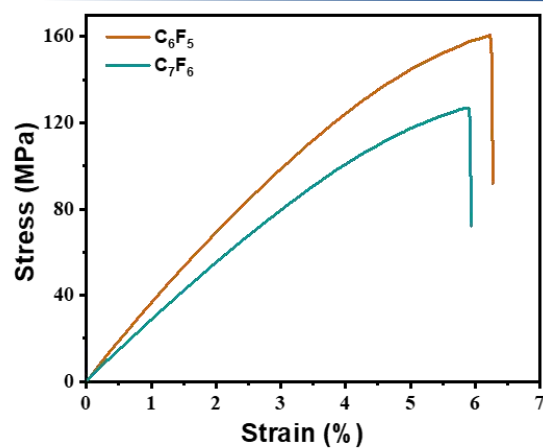


Figure S9 Stress-strain curve of C7F6 and C6F5 laminates.

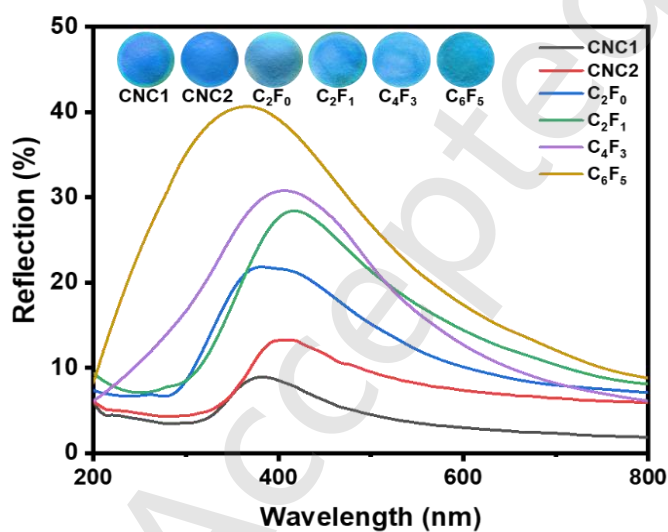


Figure S10 UV-vis Reflectance spectra of CNC1, CNC2, C2F0, C2F1, C4F3, and C6F5.

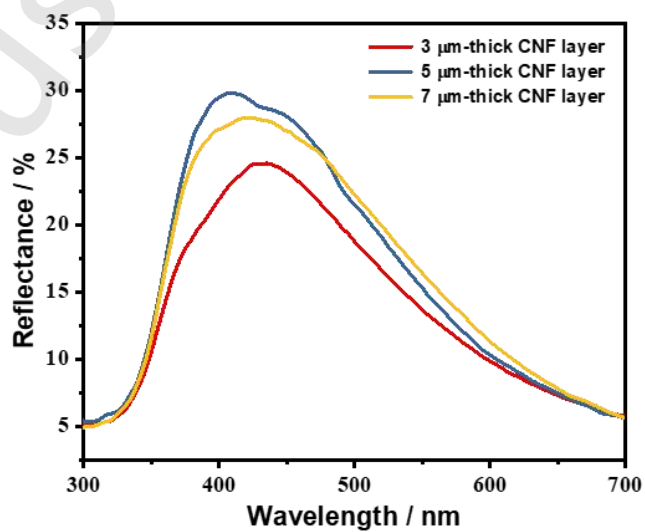


Figure S11 UV-vis Reflectance spectra of C2F1 laminates with CNF interlayer having different thickness.

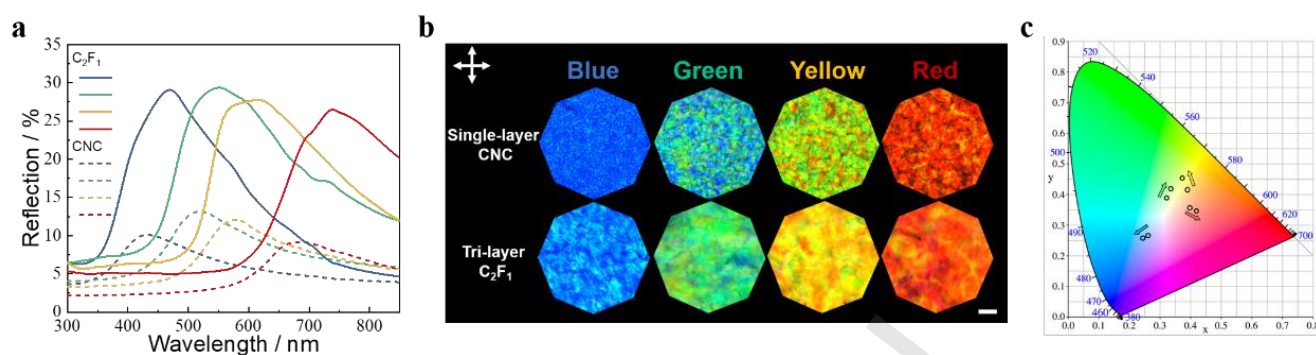


Figure S12 (a) UV-vis spectra, (b) POM images, and (c) the corresponding CIE diagram of C₂F₁ tri-layers with different structural colors and the corresponding CNC single layers. Scale bar: (b) 50 μm.

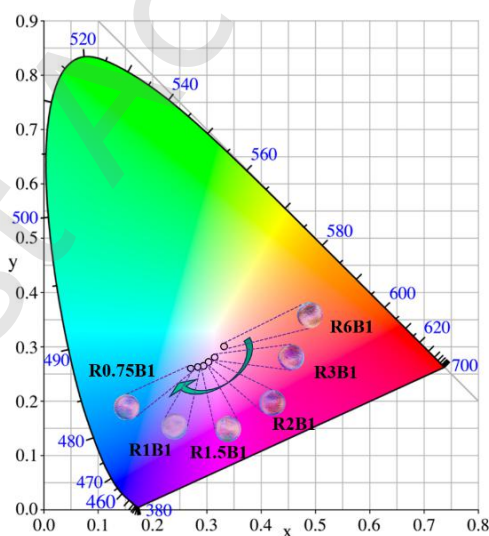


Figure S13 CIE diagram of the as-mixed C₂F₁ tri-layer laminates comprising by red CNC layer-CNF interlayer-blue CNC layer, from bottom to top, respectively, while with different thickness ratio between the bottom and top CNC fundamental layer.

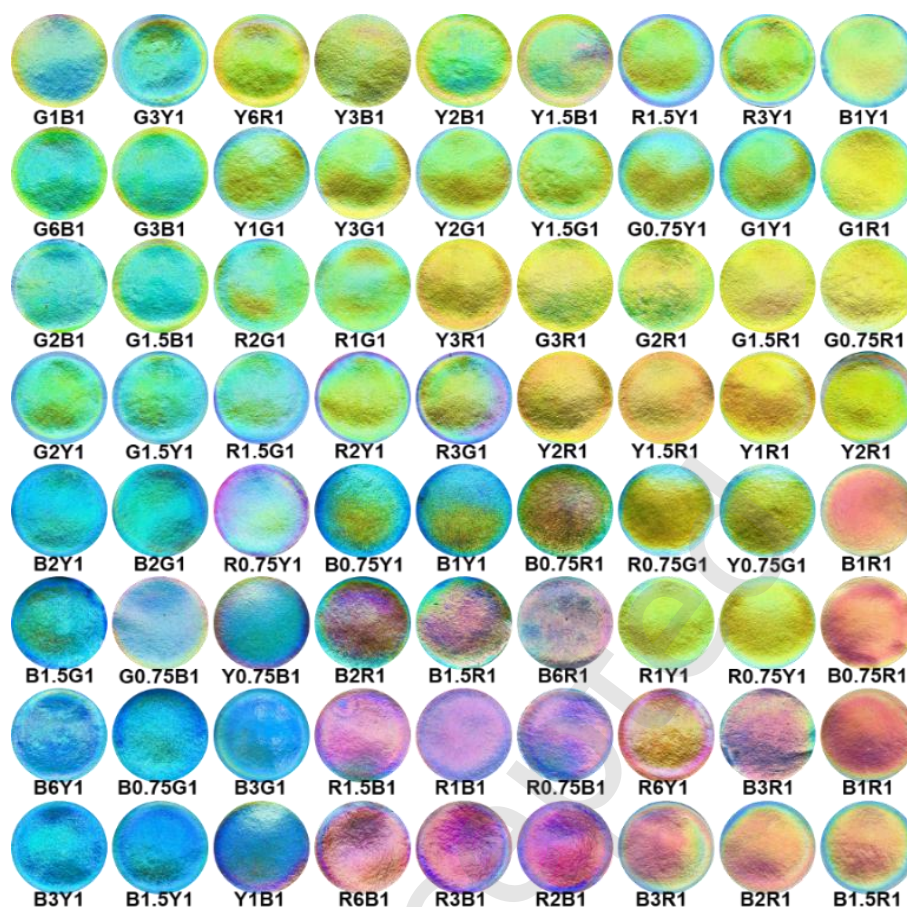


Figure S14 Photos of as-mixed tri-layer laminates with extremely-extended colors via color blending according to RGB model, which are marked as $MxNy$, where M and N represent the bottom and top CNC fundamental layer, respectively, x/y represents the thickness ratio of the bottom and top CNC fundamental layers.

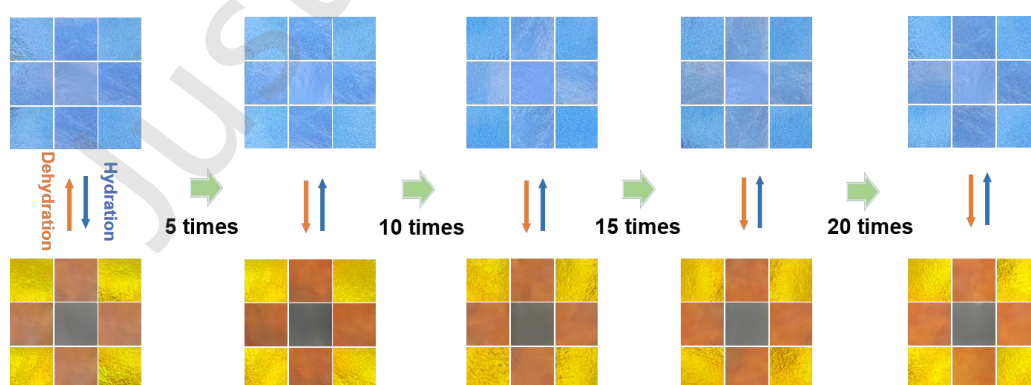


Figure S15 Stability of photonic matrix comprised by C1F0, C2F1, and C3F2 blocks for information encryption upon hydration-dehydration cycles.

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