Electronic Supplementary Material (ESI) for Materials Horizons.

Supporting Information

When Nanocellulose Meets Diffraction Grating: Freestanding Photonic Paper with Programmable Optical Coupling

Guang Chu[1, 2], *Dan Qu*[1], *Andrea Camposeo*[3]*, *Dario Pisignano*[3, 4]* *and Eyal Zussman*[1]*

[1] NanoEngineering Group, Faculty of Mechanical Engineering, Technion-Israel Institute of Technology, Haifa 3200003, Israel

[2] Bio-based Colloids and Materials, Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, P.O. Box 16300, FI-00076 Aalto, Espoo, Finland

[3] NEST, Istituto Nanoscienze-CNR, Piazza S. Silvestro 12, I-56127 Pisa, Italy

[4] Dipartimento di Fisica, Università di Pisa, Largo B. Pontecorvo 3, I-56127 Pisa, Italy

Corresponding Author:

meeyal@technion.ac.il

dario.pisignano@unipi.it

andrea.camposeo@nano.cnr.it

1. Materials and Apparatus

All chemicals were used as received without further purification. Poly (vinyl alcohol) (PVA, MW = 31000) and sulfuric acid (H_2SO_4, 98 wt%) were purchased from Sigma-Aldrich. Poly (dimethyl siloxane) (PDMS, Sylgard 184 Silicone Elastomer Kit) was obtained from Dow Corning. Cotton pulp board was purchased from Hebei Paper Group of China.

Polarized optical microscopy (POM) was carried out by using an Olympus BX51-P microscope with images taken by polarizers in a perpendicular arrangement to verify the anisotropy of the composite samples. Evaluation of the POM images were based on the ImageJ processing package. Surface morphologies of the samples were characterized using a Zeiss Ultra Plus high-resolution scanning electron microscope (HR-SEM) at an accelerating voltage of 3 kV. AFM measurements were performed by a Dimension 3100 Atomic Force Microscope in tapping mode. The measured topographic micrographs were analysed using non-commercial software NanoScope Analysis (version 1.50 R2Sr2.111746). Transmission electron microscopy (TEM) were conducted on a FEI Tecnai G2S-Twin with a field emission gun operating at 200 kV. Tensile strength measurements were carried out on 25×5 mm strips using a Dynamic Mechanical Analysis Q800 (T.A. Instrument) at 50% relative humidity. UV-visible spectra were measured through a Cary 5000 UV-Vis/NIR spectrophotometer in reflection mode, with an integrating sphere. The surface of the samples was mounted perpendicular to the beam path. Angular dependent UV-Vis spectra was conducted on the same spectrophotometer. The sample surface was mounted with varying angles to the beam path. The LCP and RCP spectra reflectance measurements were performed by illuminating the samples with a broadband lamp and collecting the reflected light by an optical fiber, coupled to a monochromator. The polarization of the incident light was controlled by using a linear polarizer and a quarter waveplate. The optical set-up for angular-resolved scattering measurements was based on previous reports,[1] which composed by a broadband Deuterium-Halogen light source (mod. DH-2000, Ocean Optics) coupled to a multimode optical fibre. The optical and AFM surface profile data of the beetle Chalcothea smaragdina were collected from the previous report[2] through a non-commercial software (GetData Graph Digitizer 2.24) and re-plotted by Origin 8.5. Zeta potential of the colloidal suspension was measured on Malvern Zetasizer Nano-ZS90.

2. Experimental Section

The preparation process of patterned PDMS sheet was based on our previous report.[3] PDMS film was prepared by mixing silicone elastomer with curing agent at a weight ratio of 10:1. 5.0 g of the mixture was poured into a Petri dish (diameter 60 mm) with the thickness of PDMS layer about 2 mm. After that the mixture was degased in vacuum oven at room temperature for 20 min and cross-linked in an oven at 70 °C for 3 hour. The resulting PDMS sheet was cut into a rectangle shape and mounted onto a home-made sample holder with a uniaxial pre-stretch of 10%. Then, the strained PDMS sheet was placed into a plasma vacuum chamber (Harrick Plasma, PDC-32G) for an oxygen plasma treatment at a pressure of 250 mTorr with high power input for a certain time duration (t=10 min and 20 min, respectively). This treatment can convert the topmost layer of PDMS into a hydrophilic silica coating. Finally, the pre-strain was relieved slowly and periodic oriented wrinkles spontaneously formed on the surface of PDMS to resist thermal shrinkage upon cooling the PDMS to room temperature.

The preparation of chiral nematic patterned film (CNPF) was mainly based on the soft lithography process as we demonstrated before.[3] In a typical experiment, an aqueous CNC suspension (5 g, 5.0 wt%) was mixed with varying amount of PVA powder (0.025 g, 0.102 g and 0.208 g) and stirred at room temperature for 3 h to allow the formation of a homogeneous mixture, which used as CNC-PVA ink. Then, the ink was transferred onto the surface of the prepared PDMS mould (ε=10%, t=10 min) with the mould embedded into a PDMS coated Petri dish (60 mm, plasma treated) and the ink was fully spread onto the surface of PDMS. This mixture was allowed to evaporate under ambient conditions until solid films had formed on the surface of PDMS (typically ca. 2 days), generating CNC-PVA composite with chiral nematic ordering. Finally, the CNC-PVA films were carefully peeled off from the PDMS mould with the surface gratings imprinted onto the bottom surface of the film, giving rise to free-standing chiral nematic patterned films (CNPFs). Depending on the CNC-to-PVA ratio, the resulting composites were donated as CNPF1-3. The corresponding pattern-free composites were termed as the reference sample (REF1-3), which were prepared in the same condition by casting the CNC-PVA ink onto the plasma treated PDMS sheet with a smooth surface.

As a comparison, a surface patterned CNC-PVA composite film without chiral nematic ordering was prepared by casting CNC-PVA-NaCl ink onto the patterned PDMS mould in a similar process as above described. Typically, the ink was prepared by mixing PVA (0.319 g) with aqueous CNC suspension (5 g, 5.0 wt%) through vigorous stirring for 1 hour, and then NaCl was added into the mixture with the final concentration of 5 mM. After that, this CNC-PVA-NaCl ink was casted onto PDMS sheet for two days to generate a chiral nematic-free patterned composite film.

3. Supporting Figures

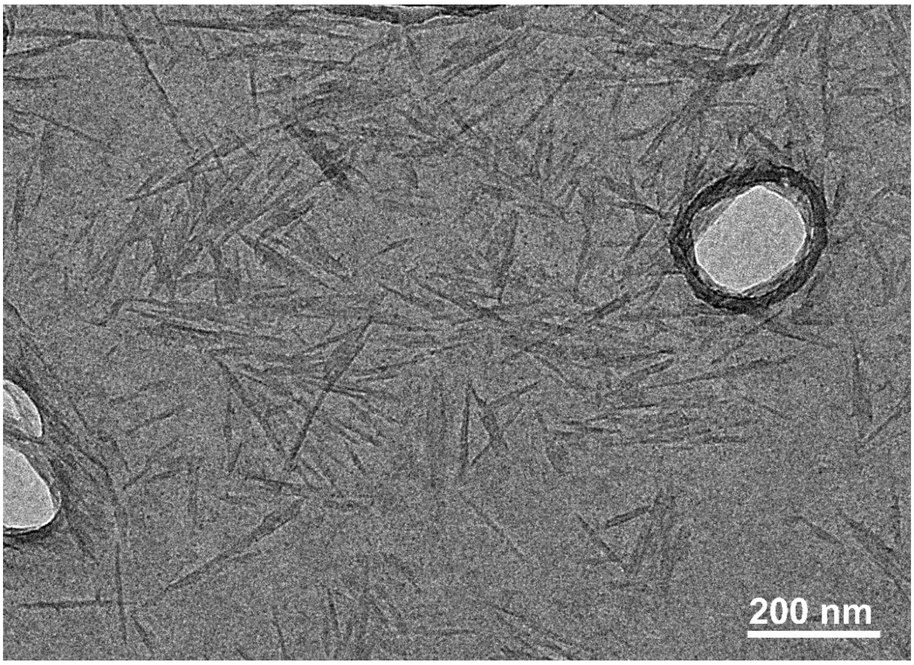

Fig. S1 TEM image of CNC nanorods. The sample was prepared from fast evaporation of a dilute CNC suspension which shows individual crystallites.

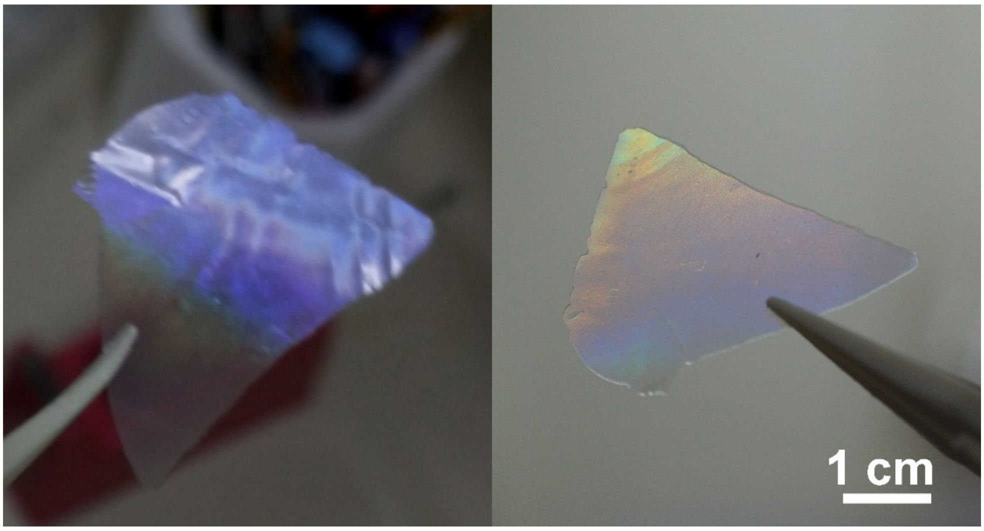

Fig. S2 Photographs of a piece of CNPF1 with different orientations, showing vivid iridescent colour.

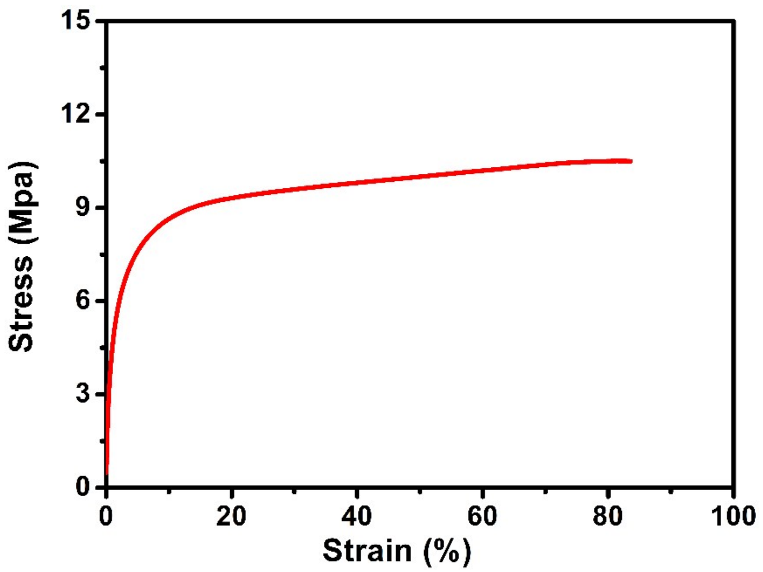

Fig. S3 Stress-strain curve for the sample of CNPF3.

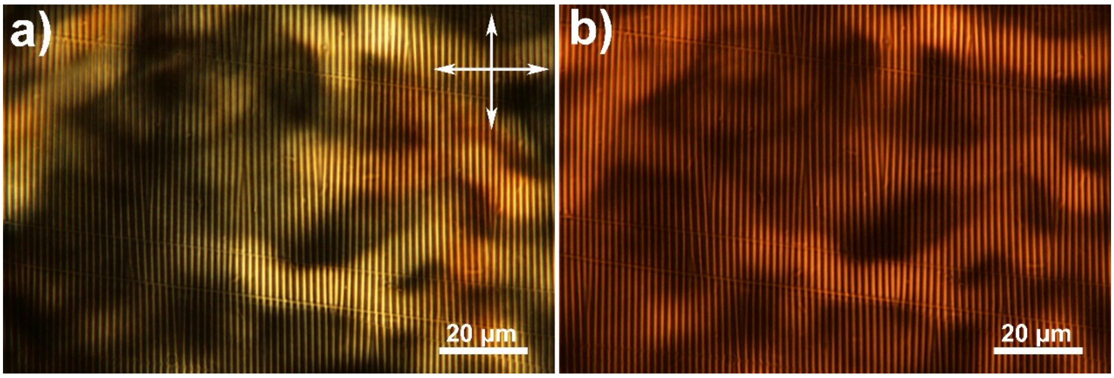

Fig. S4 Optical images of CNPF3 that captured in transmission mode with crossed polarizers (a) and without crossed polarizers (b), showing the same alternately dark and bright stripes.

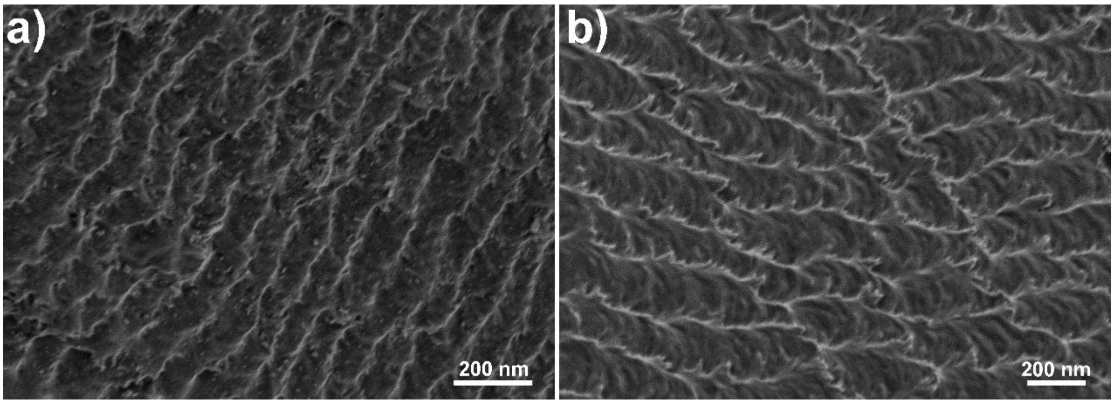

Fig. S5 SEM images of the sample of CNPF1 (a) and CNPF2 (b) with increasing helical pitch.

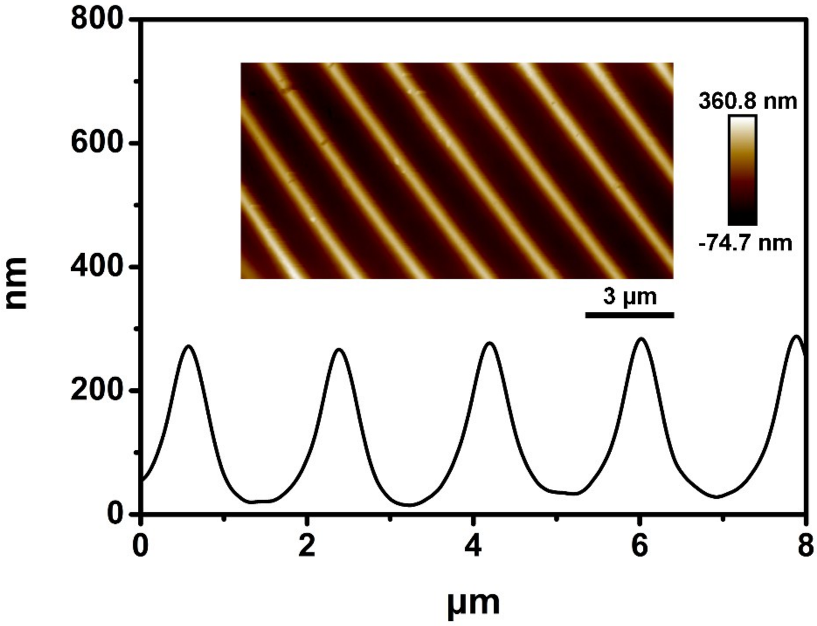

Fig. S6 Two-dimensional AFM image and numerical analysis of the CNPF2 surface profile.

Table S1 Wavelength and amplitude of the surface patterned PDMS mould with varying plasma treatment time.

Time	Wavelength	Amplitude
10 min	2.4 µm	260 nm
20 min	3.2 µm	290 nm

Table S2 Comparison of CNPF2 that imprinted with different PDMS mould (plasma treatment for 10 min and 20 min, respectively) for their wavelength and amplitude.

Sample	Wavelength	Amplitude
CNPF2-10 min	2.5 µm	275 nm
CNPF2-20 min	3.1 µm	302 nm

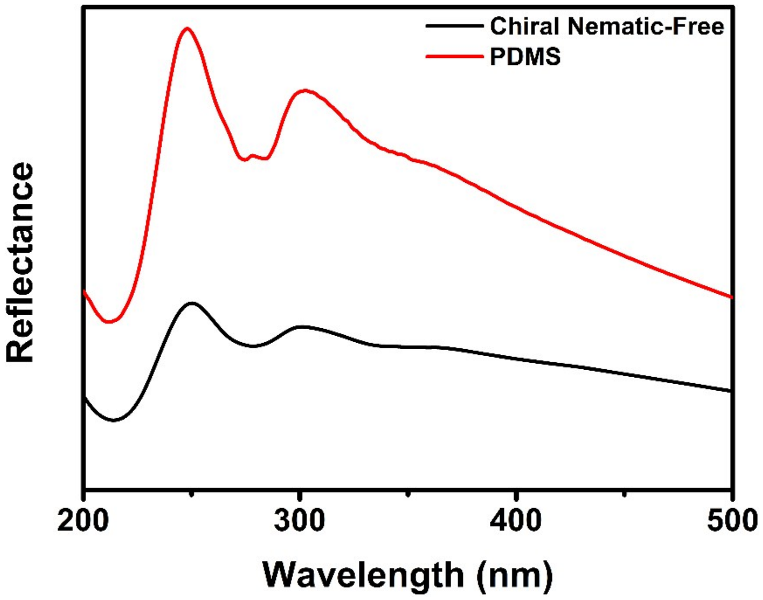

Fig. S7 UV-Vis spectra of patterned PDMS template and chiral nematic-free CNC-PVA composite, which show a double peak structural at the UV-blue range.

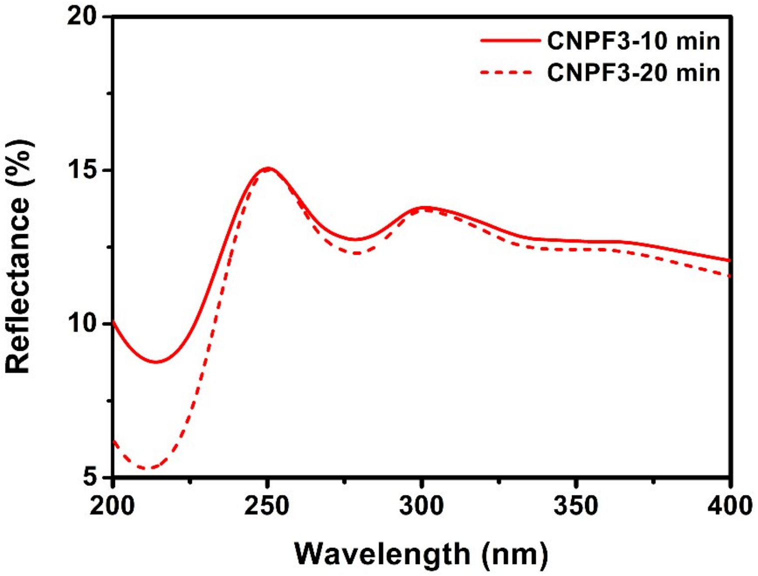

Fig. S8 UV-Vis spectra of the sample of CNPF2 that imprinted from different PDMS mould with varying plasma treatment (10 min and 20 min, respectively), demonstrating a similar spectral features at UV-blue range.

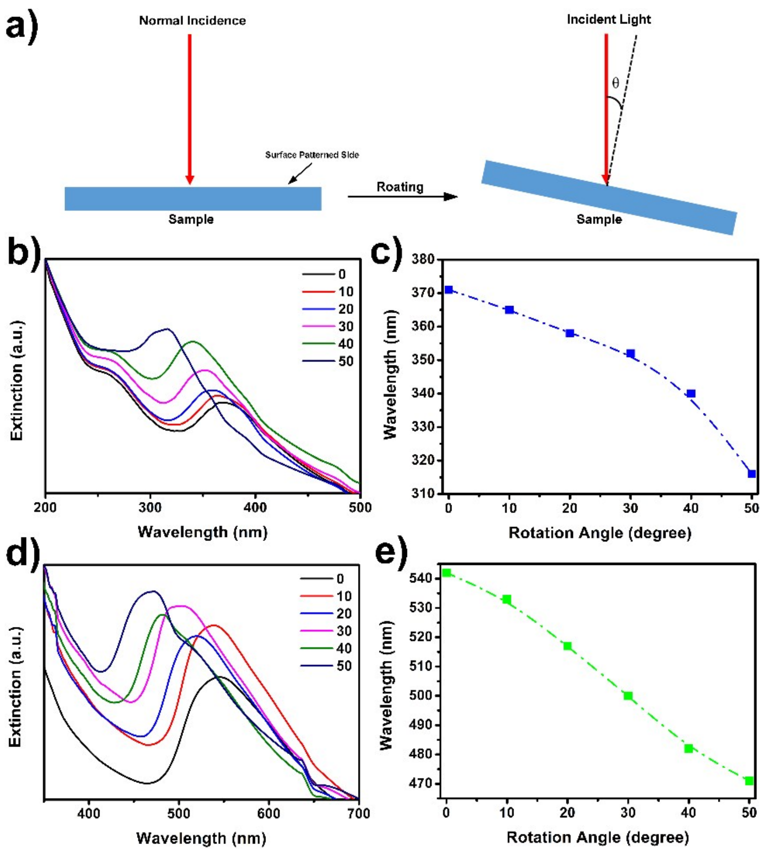

Fig. 9 (a) Schematic description of the angular-dependent spectra measurement. (b), (d) Angle resolved UV-visible spectra of the sample of CNPF1 and CNPF2, respectively. (c), (e) Plot of the photonic band-gap peak wavelength as a function of rotation angle for CNPF1 and CNPF2, respectively. The peak wavelength blue shifts as the rotation angle increased from 0° to 50°.

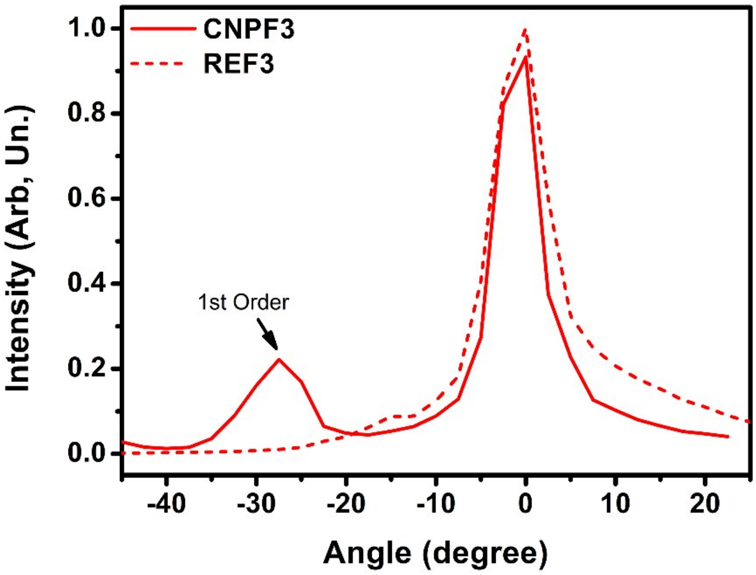

Fig. 10 Comparison of the angular dependent scattered light intensity between the sample of CNPF3 and REF3.

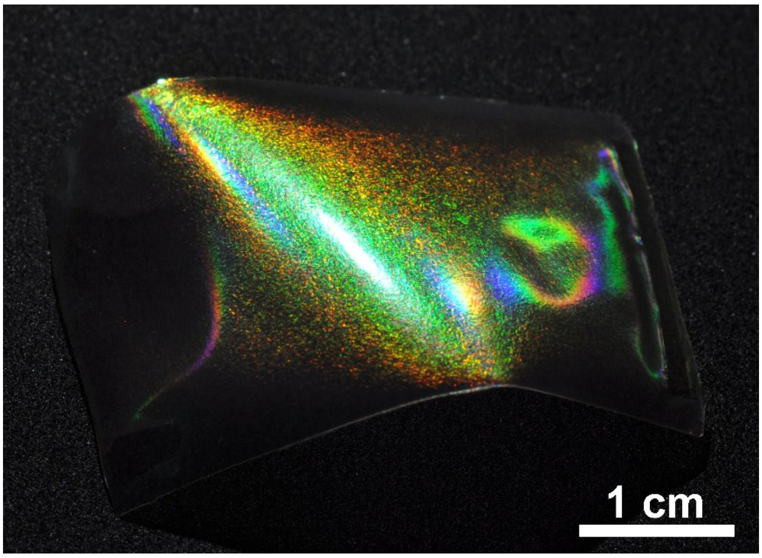

Fig. S11 Photograph of CNPF2 that reveals helical derived green structural colour and rainbow-like diffraction appearance.

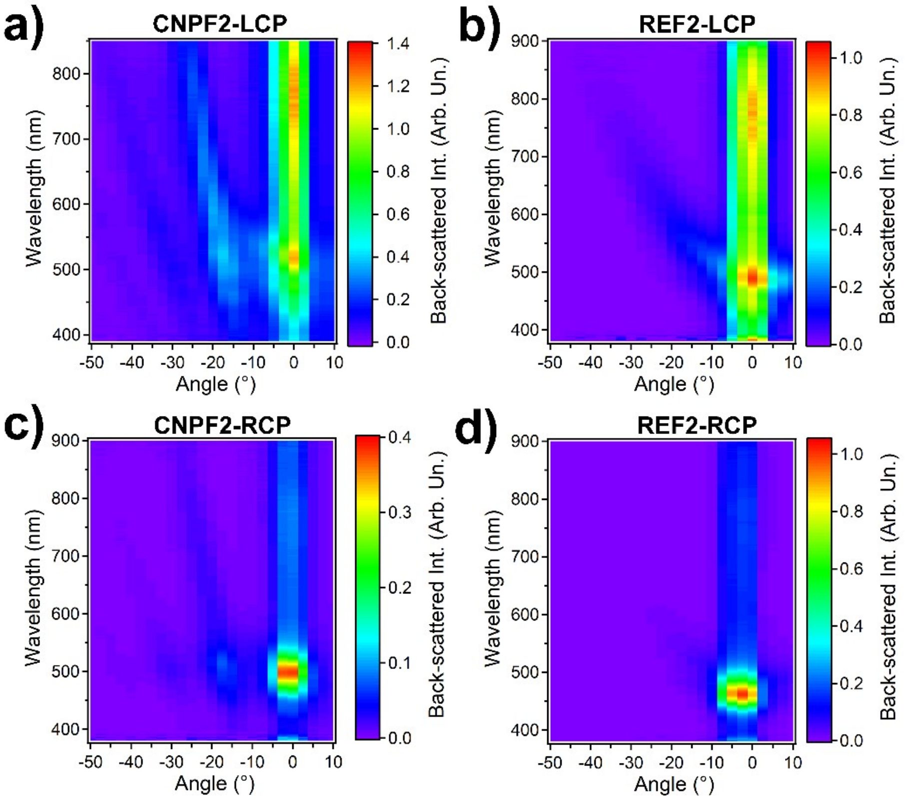

Fig. S12 (a), (b) Two-dimensional maps of CNPF2 and REF2 showing the angle-resolved scattering spectra under LCP illuminations. (c), (d) Two-dimensional angle-resolved scattering maps of CNPF2 and REF2 under RCP illuminations.

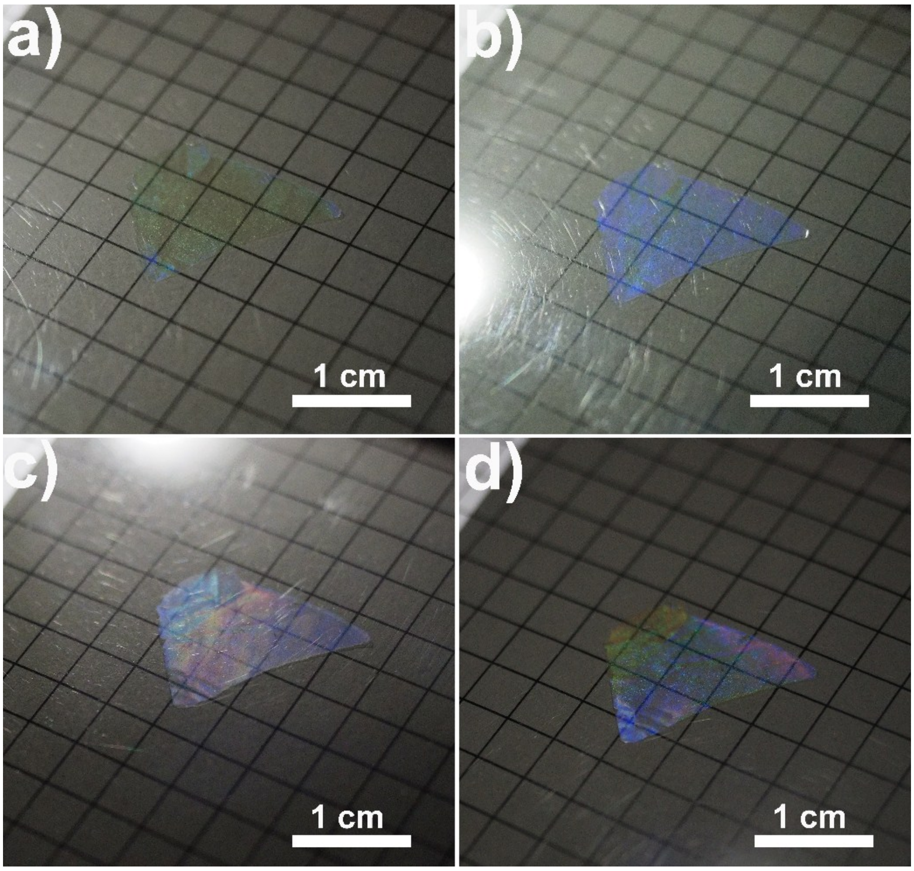

Fig. S13 (a)-(d) Photographs of CNPF1 captured under a LCP filter with different orientations of light illumination, showing strong circularly polarized iridescence which due to the coupled diffraction and photonic band-gap.

REFERENCE:

(1) Vignolini, S.; Moyroud, E.; Glover, B. J.; Steiner, U. *J. R. Soc. Interface* **2013,** *10*, 20130394.
(2) McDonald, L. T.; Finlayson, E. D.; Wilts, B. D.; Vukusic, P. *Interface Focus* **2017,** *7*, 20160129.
(3) Chu, G.; Camposeo, A.; Vilensky, R.; Vasilyev, G.; Martin, P.; Pisignano, D.; Zussman, E. *Matter* **2019**, https://doi.org/10.1016/j.matt.2019.05.005.