P_1

3D finite-element simulations of cellulose nanocrystal alignment dynamics

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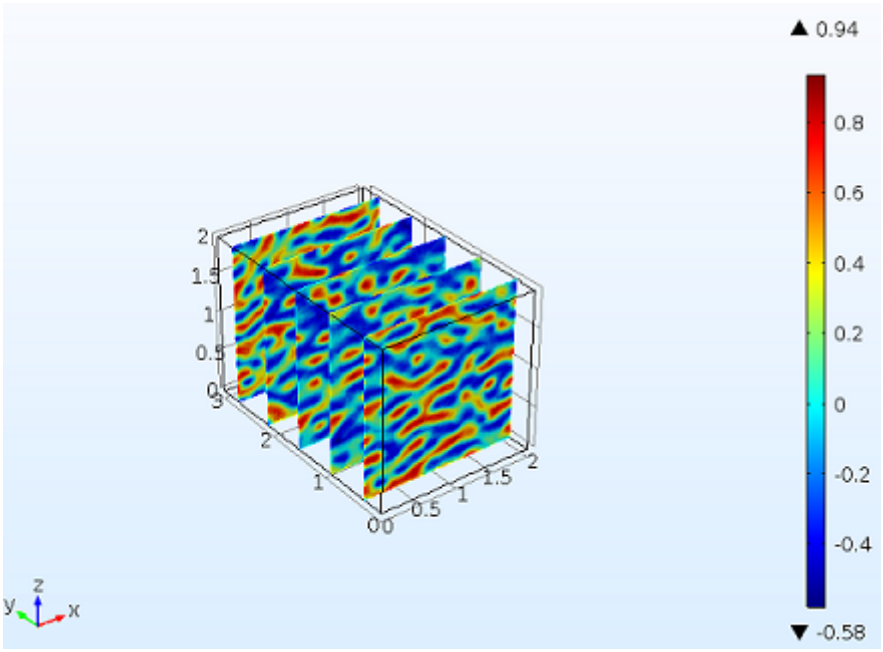
In order to study the formation of chiral structures in cellulose nanocrystal (CNC) suspensions, we develop a 3D finite element model that incorporates the Landau-de-Gennes equation for the orientation dynamics of chiral nematics. This model allows a clear comparison of chiral strength, short range intermolecular interactions, and long-range Frank elasticity. In conjunction with the experimental results of Davis et al., our system focuses on structural dynamics after the cessation of flow where the system relaxes from an aligned state and forms chiral structures. Specifically, we compare optical microscopy images against simulation results (and simulated micrographs) as chiral structures are formed, and we compare pitch values as a function of composition. (Pitch is computed using spatial Fast Fourier analysis.)



P_2

Cellulose nanocrystal films' new photonic properties

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Cellulose nanocrystals' (CNCs) solid films present remarkable optical properties as iridescence, as well as selective light reflection derived from its cholesteric organization. [1] Within its structure one can find different cholesteric domains [1], that reflect different colours, and also some micrometer-gaps [2]. If these micro-scale planar gaps, observed perpendicular to the CNCs films' cross-section between two different lefthanded films' cholesteric domains, are impregnated with a nematic liquid crystal (LC), a new photonic structure is produced (Figure 1). The LC layer acts as a half-wave retardation plate and the new composite system of CNC iridescent film/nematic LC reflects both right circularly polarized (RCP) and left circularly polarized (LCP) light [3] as observed in certain beetles cuticula, ex. the Plusiotis resplendens [4]. This CNC's new photonic structure is reversibly tuned by the application of, for instance, an electric field or a temperature variation. The same phenomenon was observed for devices derived from cellulose nanocrystals/biocompatible polymer composite films filled with a LC.

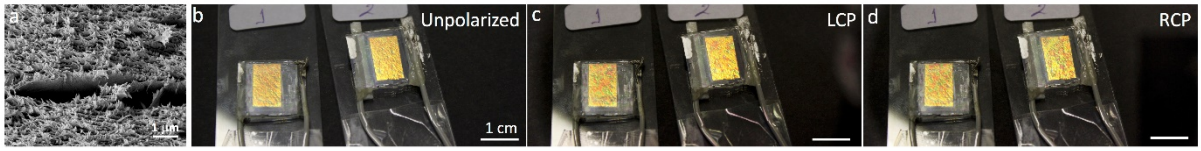

Figure. a) Cross-section image of a microgap present in a CNC/polymer composite film; Photographs of composite system observed with white light b), and circularly polarized light (c-d).

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References

[1] J. P. F. Lagerwall, et al., NPG Asia Materials, **6**, e80 (2014).
[2] D. Gray and X. Mu, Materials, **8**, 7873-7888 (2015).
[3] S. N. Fernandes, et al., Adv. Mater., **29**, 1603560 (2017).
[4] J. Hwang, et al., Nature Materials, 2005, **4**, 383-387 (2005).

P_3

The chiral nematic phases formed by hard helices

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We have investigated the phase diagram of hard helical particles using an Onsager-like theory and Monte Carlo simulations and we have found a rich polymorfism, which includes two different nematic phases with helical order. One is the *cholesteric*, where the director, i.e. the average alignment direction of particles, rotates around a perpendicular axis with a perodicity that is orders of magnitude longer than the helical pitch of the particles [2]. In the other chiral nematic phase, that we have denoted as *screw*, it is the two-fold symmetry axis of particles that spirals around the director, with periodicity equal to the particle pitch [3]. Several examples of the cholesteric phase can be found in natural and synthetic systems (see [4,5] for recent reviews); the only requirement for its formation is that the microscopic constituents are chiral. On the contrary, the screw-nematic phase requires that its constituents have a helical shape and, to our knowledge, the only experimental evidence of this phase is in suspensions of helical flagella [6]. Here we will discuss the origin of the two different chiral nematic phases and we will illustrate the relationship between the features (pitch and handedness) of these phases and the morphology of the constituent helical particles.

References

[1] H.B. Kolli, E. Frezza, G. Cinacchi, A. Ferrarini, A. Giacometti, T.S. Hudson, C. De Michele, F. Sciortino, Soft Matter **10**, 8171 (2014); H.B. Kolli, G. Cinacchi, A. Ferrarini, A. Giacometti, Faraday Disc. **186**, 171, (2016).

[2] E. Frezza, A. Ferrarini, H.B. Kolli, A. Giacometti, G. Cinacchi, Phys. Chem. Chem. Phys. **16**, 16225 (2014).

[3] H.B. Kolli, E. Frezza, G. Cinacchi, A. Ferrarini, A. Giacometti, T.S. Hudson, J. Chem. Phys. **140**, 081101 (2014).

[4] S. Pieraccini, S. Masiero, A. Ferrarini, G.P. Spada, Chem. Soc. Rev. **40**, 258 (2011).

[5] N. Katsonis, E. Lacaze, A. Ferrarini, J. Mater. Chem. **22**, 7088 (2012).

[6] E. Barry, Z. Hensen, Z. Dogic, M. Shribak, R. Oldenbourg, Phys. Rev. Lett. **96**, 018305 (2006).

P_4

Influence of structural properties of cellulose nanocrystals on the formation of the liquid crystalline phase

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The increasing interest in alternative materials to fossil fuels has been the driving force for many research efforts towards biodegradable, renewable materials. Particular attention is paid to cellulose, partially because it is the most versatile and abundant biopolymer in nature, but even more because of the possibility to isolate and utilize novel forms of cellulose that have at least one dimension in the nanometer range.[1] Full utilization of the intrinsic properties of the stiff, rodlike cellulose nanocrystals, which form a chiral nematic liquid crystalline phase with interesting optical behaviour, requires a better understanding of their properties and behaviour for controlling their assembly over several length scales.[2]

We have studied the packing of different aspect ratio CNCs obtained from wood[3] and cotton sources in the chiral nematic phase. The inherent structural properties have been investigated by small angle X-ray scattering and their influence on the formation of the liquid crystalline phase will be discussed.

References

[1] Moon, R. J.; Martini, A.; Nairn, J.; Simonsen, J.; Youngblood, J., Chem. Soc. Rev., **40**, 3941–3994 (2011).

[2] Lagerwall, J. P. F.; Schütz, C.; Salajkova, M.; Noh, J.; Hyun Park, J.; Scalia, G.; Bergström, L., NPG Asia Mater., **6**, e80 (2014).

[3] Schütz, C.; Agthe, M.; Fall, A. B.; Gordeyeva, K.; Guccini, V.; Salajková, M.; Plivelic, T. S.; Lagerwall, J. P. F.; Salazar-Alvarez, G.; Bergström, L., Langmuir, **31**, 6507–6513 (2015).

P_5

Fractionation of cellulose nanocrystals

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Cellulose nanocrystals (CNCs), nanorods produced by acid hydrolysis of cellulosic sources, are emerging as a new class of functional biomaterial. CNCs present a broad range of uses, for example in composites, cosmetics, security paper and medical devices [1]. The fascinating ability of CNCs to self-organize into a cholesteric liquid crystal phase, with a helical arrangement of the nanorods, is attracting substantial interest across different research fields [2].

A critical problem from an analytical, and likely also from an applied perspective, is the high length polydispersity of as-produced CNC samples. In this study, we introduce a method for fractionating the CNC nanorods, utilizing the spontaneous phase separation between isotropic and liquid crystalline phases, allowing us to shift the length distribution diagram. The aspect ratio has a strong effect on the period of the cholesteric helix and the volume fraction. We present how this affects the self-assembly process, and consequently the color formation in such bio-derived structural films.

References

[1] J.H. Park et al., ChemPhysChem, **15**, 7, pp. 1477-1484 (2014).
[2] Lagerwall, J. P. F. et al. Cellulose nanocrystal-based materials: from liquid crystal self-assembly and glass formation to multifunctional thin films. NPG Asia Mater. **6**, e80 (2014).

P_6

Simulations of helical Yukawa rods as a model for cholesteric liquid crystals

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Cholesteric liquid crystals show a rich phase diagram, including the usual isotropic, nematic and smectic phases, and the special cholesteric (chiral nematic) phase. Especially biological materials show this cholesteric phase, e.g. *fd* viruses and cellulose nanocrystals [1].

Our aim is to explore the complex phase diagram of helical Yukawa rods, which are an example of simple model chiral mesogenes, by Monte Carlo simulations. The rods are hard spherocylinders with a helical distribution of discrete charges on their surface, which interact via a Yukawa (screened Coulomb) potential. A similar model has already been studied analytically by Wensink and Jackson [2]. Of special interest is the simulation of equilibrium cholesteric pitches. For this, we introduced a new method including soft walls and self- determined boundary conditions [3].

We study the dependence of the maximum density after isobaric compression of an isotropic system on a number of parameters: surface charge, added salt concentration and internal pitch of the charge helix. By decreasing the internal pitch, the local alignment of rods is reduced, resulting in a lower maximum density. The internal pitch also determines the strength of twist in (pancake-like) membranes of helical Yukawa rods.

The influence of aspect ratio on the isotropic-cholesteric transition and the cholesteric pitch is another part of our investigation.

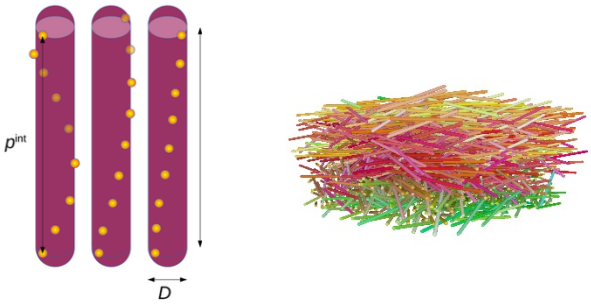

Figure. Left: Sketch of helical Yukawa rods used as model for cholesteric liquid crystals with length L, diameter D and internal pitch p^{int}. Right: Cholesteric phase of the model system (color shows orientation).

References

[1] J. Lagerwall et al., NPG Asia Materials **6**, e80 (2014).

[2] H. Wensink, G. Jackson, J. Phys.: Condens. Matter **23**, 194107 (2011).

[3] A. Kuhnhold, T. Schilling, J. Chem. Phys **145**, 194904 (2016).

P_7

Biaxial shapes and nematic liq1uid crystal phases: towards twist-bend nematics

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We investigate the infl uence of the shape of hard biaxial particles on the formation of prolate, oblate, and biaxial nematic liquid crystal phases. The biaxiality and polarity of the phase and the particles is included through a general formulation of Onsager-Parsons-Lee theory. For a given particle shape, the angular dependence of the excluded volume is expanded in Wigner matrices and the corresponding coeffcients are calculated using Monte Carlo. We construct phase diagrams for different types of hard biaxial particles, including bricks and boomerangs, as a function of packing fraction and particle anisometry. The resulting phase diagram for boomerangs is shown in the figure. In addition, we show that this general framework can be readily extended to include the spatial modulation of the nematic director in a chiral or twist-bend nematic phase.

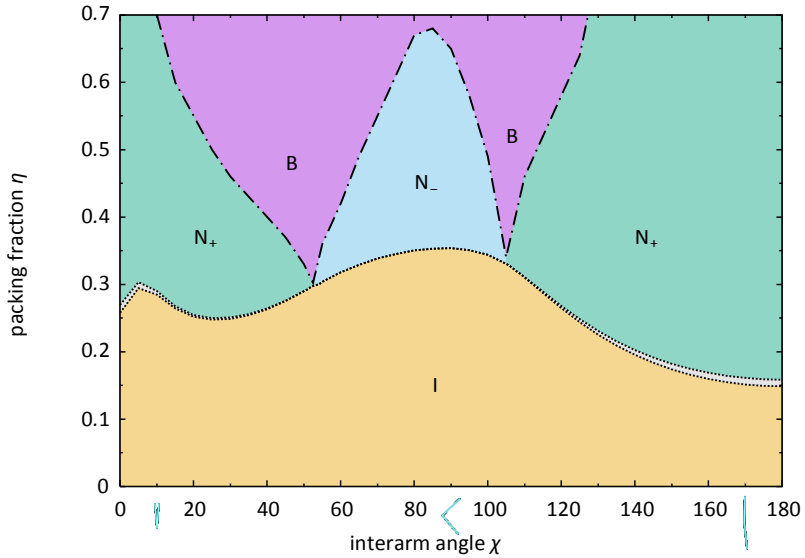

Figure. Phase diagram for boomerang particles with equal length arms ($L_1 = L_2 = 10D$) as a function of the angle χ and the packing fraction η. At low packing fraction, an isotropic phase (I) is found, while at higher packing fractions oblate (N_-), prolate (N_+), and biaxial (B) nematic phases are found, with two Landau points at approximately $\chi = 52{:}5$ and $\chi = 105$.

P_8

Beyond Buckling: Humidity-Independent Measurement of the Mechanical Properties of Cellulose Nanocrystal Films

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Precise knowledge of the mechanical properties of nanomaterials and nanocomposites is crucial to match their performance with suitable applications. While methods to characterize mechanical properties exist, they are limited by instrument sensitivity, sample requirements and, in the case of bio-based nanomaterials, extreme humidity dependence. We present a new approach, based on buckling mechanics, to determine the elastic modulus of cellulose nanocrystal (CNC) thin film composites or aligned CNC films, in a humidity-independent manner. Composite films were prepared using layer-by-layer (LbL) assembly with CNCs and water-soluble polymers on pre-stressed polystyrene substrates. Aligned CNC films were solvent cast on pre-stressed polystyrene substrates which had been plasma treated to change the wettability. Chiral nematic, radial alignment and parabolic focal conic defect textures were reproducibly achieved depending on the drying parameters. Films on the pre-stressed polystyrene were shrunk by heating above the polymer glass transition temperature. The compression during shrinking led to wrinkled films with hierarchical structures and characteristic topographies. Films were found to have humidity-independent elastic moduli (calculated from FFT analysis of SEM images) that varied with the composition and degree of CNC alignment. This structuring method is straightforward and amenable to a wide range of supported thin films, and fills an existing gap in the available methods to measure nanomaterial mechanical properties.

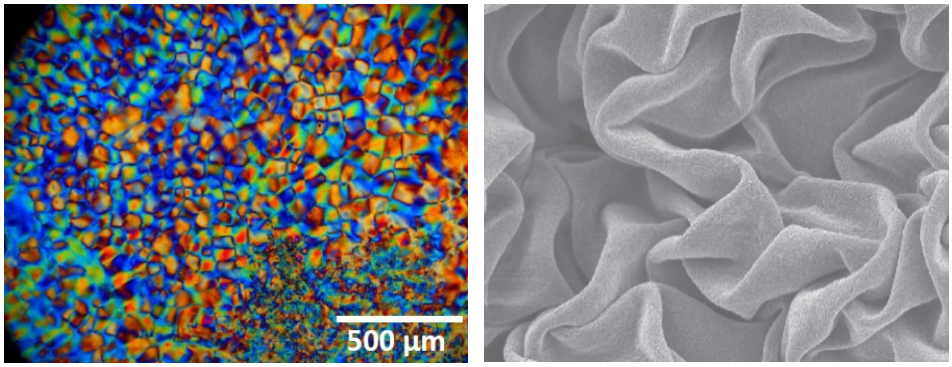

Figure. (Left) Parabolic focal conic defect texture of a CNC film on pre-strained PS substrates imaged by polarized optical microscopy; and (right) CNC films after shrinking, imaged by SEM, size: 10 µm across.

P9

Liquid Nanocrystalline Cellulose Aqueous Suspensions: Rheological Effects

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The rheological properties and microstructure of nanocrystalline cellulose (NCC) aqueous suspensions have been investigated at different concentrations. The suspension is isotropic up to 3 wt.%, and phase separates to liquid crystalline and isotropic domains at higher concentrations where the samples exhibit a fingerprint texture and the viscosity profile shows a three-region behavior, typical of liquid crystals. The suspension behaves as rheological gel at even higher concentrations where the viscosity profile shows a single shear thinning behavior over the whole range of shear rates investigated [1,2]. The effects of ultrasound energy and temperature on the rheological properties and structure of these suspensions were studied using polarized optical microscopy and rheometry [1]. Our results indicate that the amount of applied ultrasound energy affects the microstructure of the suspensions, and the pitch of the chiral nematic domains. The viscosity profile is changed significantly at low shear rates, whereas the viscosity of biphasic suspensions at intermediate and high shear rates decreased with increasing temperature. This suggests that between 30 and 40 ºC, structural rearrangement takes place. At higher concentrations of about 10 wt.%, the temperature has no significant effect on viscosity, however, a marked increase in viscosity has been observed at around 50 ºC. Finally, the Cox-Merz rule was found to fail after a critical concentration, thereby implying significant structural formation. This critical concentration is much higher for sonicated compared to unsonicated suspensions.

References

[1] S. Safiei-Sabet, W. Hamad and S.G. Hatzikiriakos, Langmuir, **28**, 17124-17133 (2013).
[2] S. Safiei-Sabet, W. Hamad and S.G. Hatzikiriakos, Rheologica Acta, **52**, 741-751 (2013).

P_{10}

Influence of the Particle Concentration and Marangoni Flow on the Formation of Cellulose Nanocrystal Films

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Cellulose nanocrystals, rod-like crystalline nanoparticles, are a bio-based material that can be a great alternative to obtain films with tunable optical properties. Iridescent and light diffracting films can readily be obtained via the drying of a suspension of these cellulose nanocrystals. The characteristics of the particle deposition process together with the self-assembly in the precluding suspension has a direct effect on the optical properties of the obtained films. Particle deposition onto a substrate is affected by the flow dynamics inside sessile droplets and usually yields a ring shaped deposition pattern commonly referred to as the coffee-ring effect. We started to investigate this deposition process. [1] Being able to control it will enable to generate the desired deposition pattern. We therefore set out to measure and describe the drying kinetics under different conditions and used the developed expertise to control the deposition patterns of the cellulose nanocrystal films. Iridescent films with a uniform thickness were obtained by exerting control over the relative magnitude of Marangoni flow and the colloidal stability of the nanoparticles.

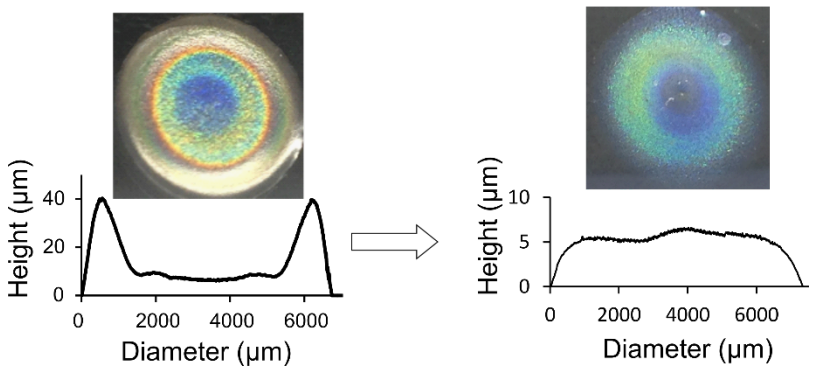

Figure. Photographs of cellulose nanocrystal films and uniform deposition by the means of Marangoni flow

References

[1] Gençer, A.; Schütz, C.; Thielemans, W., Influence of the Particle Concentration and Marangoni Flow on the Formation of Cellulose Nanocrystal Films. Langmuir, **33** (1), 228-234 (2017).

P_{11}

Self-assembly in Confined Spaces –Towards Functional Hybrid Materials

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Molecular self-assembly has attracted much attention as a bottom-up method for new functional nano-materials.[1] The supramolecular approach is especially attractive, since it facilitates synthetic routes and yields dynamic functional aggregates combining properties of the individual building units with properties induced by the formation of the supramolecular entity.[2],[3] The present work investigates the self-assembly of hydrogen-bonded liquid crystals[4] in the confinement of chiral-nematic mesoporous silica films derived from cellulose nanocrystal (CNC) templating. The obtained hybrid materials[5] revealed fast and reversible thermo- and photo-responsive switching of the photonic properties as proven by polarizing optical microscopy (POM), UV-vis and CD-spectroscopy.

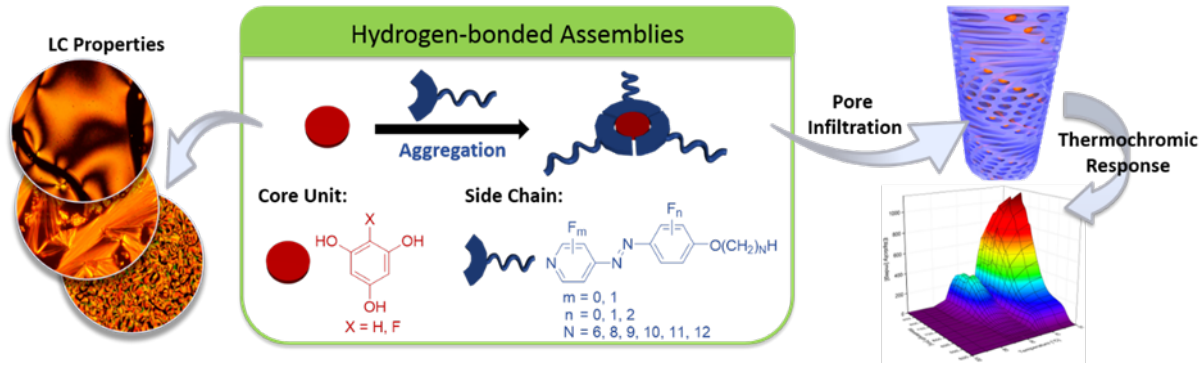

Figure 1. Modular approach towards novel functional hybrid materials with tailor-made properties.

References

[1] K. Liu, Y. Kang, Z. Wang and X. Zhang, Adv. Mater., 2013, 25, 5530-5548.

[2] X. Yan, F. Wang, B. Zheng and F. Huang, Chem. Soc. Rev., 2012, 41, 6042-6065.

[3] Z.-T. Li and L.-Z. Wu, Hydrogen-Bonded Supramolecular Materials, Springer, Heidelberg, 2015.

[4] M. Pfletscher, C. Wolper, J. S. Gutmann, M. Mezger and M. Giese, Chem. Commun., 2016, 52, 8549-8552.

[5] M. Giese, T. Krappitz, R. Y. Dong, C. A. Michal, W. Y. Hamad, B. O. Patrick and M. J. MacLachlan, J. Mater. Chem. C, 2015, 3, 1537-1545.

P_{12}

Substrate effect on the colours of films dried from liquid crystal-forming cellulose nanocrystal suspensions

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Nowadays the photonic properties of short-pitch cholesteric systems based on cellulosic biopolymers motivate innovative research for real products, targeting smart photonic applications. In this work we produce thin films using cellulose nanocrystals (CNC) suspended in water.

The characteristic of the particles deposition process together with the self-assembly in the equilibrium suspension has a direct effect on the optical properties of the films obtained by drying [1]. Preparation of the suspension (sonication, salt addition [2]), contact angle with the substrate [3] and humidity [4] also influence the optical properties.

Our experiments were conducted at ambient temperature and humidity. We investigate the film appearance on different types of substrate (hydrophilic and hydrophobic), for varying volume and concentration of the CNC suspension.

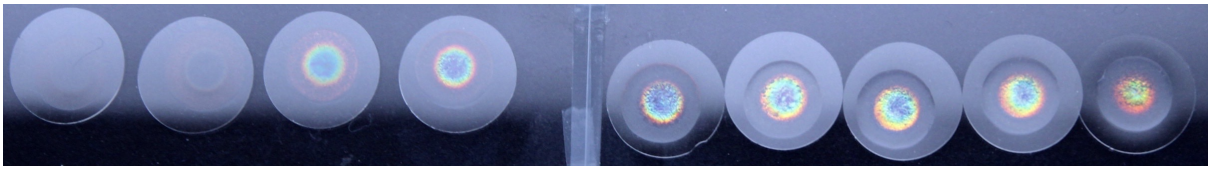

Figure. Drop casted CNC films after water evaporation, the CNC concentration increasing from 1 wt% (left) to 9 wt% (right). The volume of suspension is constant.

References

[1] X. Mu and D. Gray, Materials, 8, pp. 7873-7888, 2015; J.H. Park et al., ChemPhysChem, 15, 7, pp. 1477-1484 (2014)
[2] W. Hamad, “Photonic and Semiconductor Materials Based on Cellulose Nanocrystals”, in Adv. Polym. Sci. (Springer, 2015)
[3] T.D. Nguyen, W.Y. Hamad and M.J. MacLachlan, Chem. Commun., 49, pp. 11296-11298 (2013)
[4] A.G. Dumanli et al., Adv. Opt. Mater., 2, pp. 646-650, 2014