

Johanna R. Bruckner

Cholesteric Liquid Crystals and Structural Color

The majority of colors which we encounter in everyday life stem from pigments or dyes. These colorants absorb part of the visible spectrum, which corresponds to the energy required to create electronically excited states, and reflect the rest of the spectrum, which we observe as their color. Additionally, there is structural color which we perceive as especially vibrant or even iridescent, e.g. on the wings of butterflies, certain beetle shells (Figure 1a), peacock feathers or selected plants, and which originates from a different underlying mechanism. Materials exhibiting structural color consist of microstructures with alternating refractive indices whose periodicity is in the same order of magnitude as the wavelength of visible light (Figure 1b). This structure gives rise to a photonic band gap which prevents the propagation of certain wavelengths, resulting in intense, angle-dependent colors. Such materials are called photonic crystals and are of great interest for both, fundamental research as well as applications, e.g. in optics, sensor technology or as colorants. The microstructures required for photonic crystals may be fabricated by photolithography or etching techniques, however, a more convenient and

cost-efficient way is to utilize self-assembly e.g. of liquid crystals, which readily form complex microstructures without further ado.

The story of structural color in liquid crystals is as old as liquid crystal research itself. Otto Lehmann already described its observation in his seminal work of 1889 [2] when he noticed a violet-blue color twice while cooling the chiral compound cholesteryl benzoate (cf. text box). As we know today, the origin of the first color appearance was a liquid crystal blue phase and of the second a cholesteric phase with a short helical pitch. Even though, blue phases are prime examples of 3D photonic crystals, we will focus on cholesteric structures (Figure 2a) in this article due to inevitably limited length of the article.

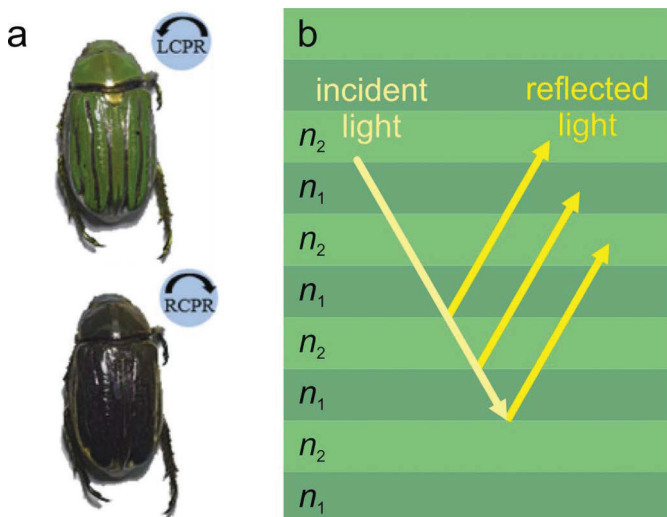


Fig. 1: (a) Images of scarab beetle *Chrysina gloriosa* illuminated with left-handed circular polarized (LCPR) and right-handed circular polarized (RCPR) light, respectively. Reprinted with permission from ref. [1]. Copyright 2021 Optica Publishing Group. (b) Sketch of a 1D photonic crystal with alternating refractive indices n_1 and n_2 , a so-called Bragg reflector, with indicated reflection of incident light.

„Die Substanz zeigt zwei Schmelzpunkte, wenn man sich so ausdrücken darf. Bei $145,5^\circ$ schmilzt sie zunächst zu einer trüben, jedoch *völlig flüssigen Flüssigkeit*. Dieselbe wird erst bei $178,5^\circ$ plötzlich völlig klar. Lässt man sie nun auskühlen, so tritt zunächst eine violette und blaue Farbenercheinung auf, die aber rasch verschwindet, worauf die Masse milchig trübe, aber flüssig bleibt. Beim weiteren Abkühlen tritt dann abermals die violette und blaue Farbenercheinung auf und gleich darauf erstarrt die Substanz zu einer weissen, krystallinischen Masse.“

O. Lehmann, excerpt from ref. [2]

First theoretical considerations on the color phenomenon of certain cholesteric liquid crystals were published in 1911 by Maugin [3]; later refined theories followed by Oseen [4], de Vries [5] and others. The bottom line is that the helical modulation of the director \mathbf{n} along the helix axis \mathbf{m} with the pitch p in the cholesteric phase (Figure 2a), results in a likewise modulation of the refractive index n , which varies between n_{\parallel} , i.e. the refractive index parallel to the director, and n_{\perp} , i.e. the refractive index perpendicular to the director (Figure 2b). This gives rise to a photonic band gap of width $p \cdot (n_{\parallel} - n_{\perp}) = p \cdot \Delta n$ centered around $\lambda = p \cdot \bar{n}$ with λ being the wavelength of the incident light propagating parallel to the helix axis and $\bar{n} = \sqrt{(n_{\parallel}^2 + n_{\perp}^2)}/2$ being the average refractive index. However, this band gap only holds for circular polarized light with the same handedness as the cholesteric structure. Consequently, light with this wavelength range and handedness is completely reflected, while light with the opposite handedness propagates unhindered through the cholesteric structure. For oblique incidence of light, the selectively reflected wave lengths may be calculated according to Bragg's law $N \cdot \lambda = p \cdot \bar{n} \cdot \cos \theta$, with θ , the

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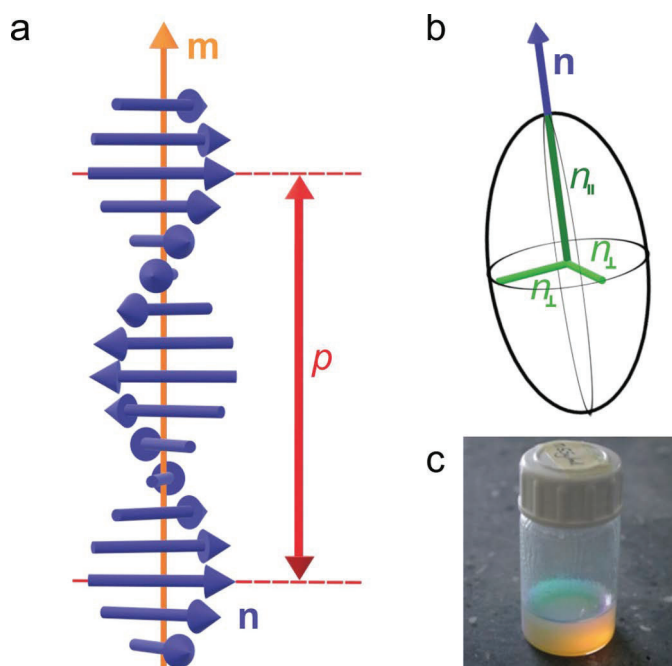


Fig. 2: (a) Sketch of the cholesteric phase, with the director \mathbf{n} , which is defined by the average mesogen (molecule) orientation, rotating along the helix axis \mathbf{m} . The distance along \mathbf{m} required for a 360° turn of the director \mathbf{n} is called pitch p . (b) Uniaxial positive indicatrix illustrating the value of the refractive index n with respect to the director \mathbf{n} . (c) Cholesteric phase with angle dependent selective reflection of visible light.

angle between the incident light and the helix axis \mathbf{m} , and N , an integer which may only be larger than unity for $\theta > 0$ (Figure 2c).

The particular beauty of photonic materials based on cholesteric liquid crystals lies in their easy manipulation and simple processability, which is inherent to soft matter, leading to a constant interest from researchers. They found, that, hand in hand with the pitch, the selective reflection depends amongst others on the chemical composition, the temperature, the pressure, and the presence of applied electric or magnetic fields. Yet, research in this field only really got going, when the vast potential for applications of selectively reflecting cholesterics became manifest. Already in the 70's and early 80's, researchers suggested their use as temperature sensors [6] and circular polarizers [7]. The interest in this field was further boosted by the possibility to stabilize the fluid state either by direct polymerization of the liquid crystal, embedding in a polymer network (polymer-stabilized) or encapsulation in a polymer binder (polymer-dispersed), which made the photonic materials easier to handle and thus more versatile (Figure 3a). Taking advantage of the strong light scattering, polymer-stabilized cholesterics find application in smart windows for privacy protection [8] or energy saving [9], while polymer-dispersed cholesterics are studied for reflective displays [10]. When adding dyes to the cholesteric, it can serve as active lasing material for tunable, mirrorless lasers [11]. Current research branches study the combination of photonic properties and actuation of cholesteric elastomers, making use of the fact that every stimulus, which changes the pitch and thus the reflection color, simultaneously changes the spatial extension of the material along the helix axis. This enables e.g., the fabrication of programmable materials, soft robotics, smart wearable devices and fabrics, optical cloaking and tunable color filters [12].

In recent years, sustainability and eco-friendly processes became increasingly important, together with the industrial need for low production costs, which incited researchers to move away from petrochemical liquid crystals towards biologically sourced compounds. Most prominently, cellulose nanocrystals (CNCs), which form a cholesteric phase in aqueous suspensions at single-digit mass fractions and may be produced from any kind of cellulose by acidic hydrolysis, are currently under intensive investigation [13]. Although the pitch of the liquid crystal phase is too large to reflect visible light, CNC suspensions are exquisite parental materials for the production of photonic films. Evaporating water from these suspension causes a reduction of the interparticle distances, while the self-assembled helical structure of the CNCs is maintained, leading to a shrinkage of the pitch to the sub-micrometer regime. Thus, photonic CNC films combine the easy processability and facile structural tuning of liquid crystals with the sustainability, non-toxicity, light weight and low cost of the omnipresent biopolymer cellulose. Dried CNC films and composites exhibit vast potential for applications, e.g., as sensors [14], actuators [15], smart wearables [16] or for encrypting [17], and are suitable for large-scale production [18].

Next to CNCs, other naturally sourced polymers are currently investigated regarding their potential for the fabrication of photonic materials. In 2022, Narkevicius et al. showed that dried films of fungal chitin nanocrystals reflect visible light after an alkaline treatment [19]. This year, Xiao et al. demonstrated that dried

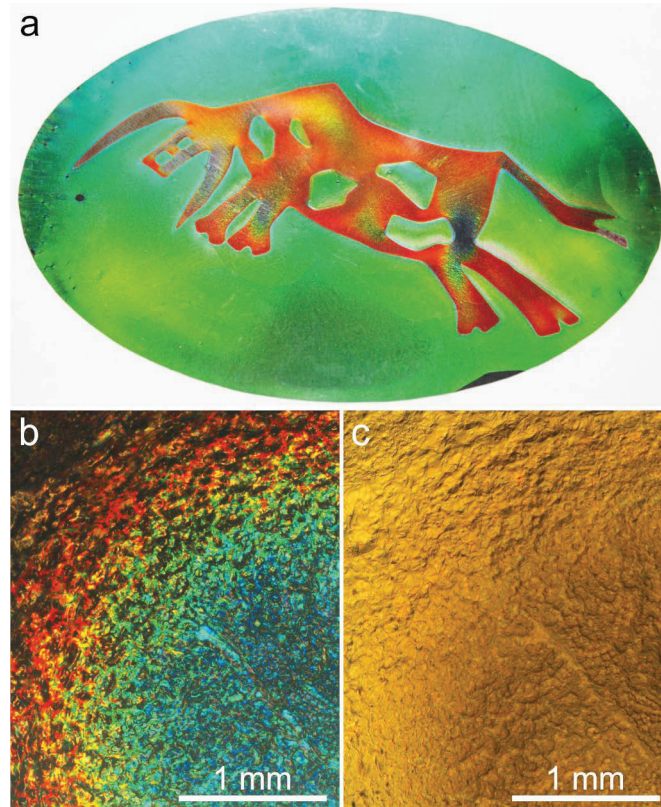


Fig. 3: (a) Polymer stabilized cholesteric liquid crystal with high optical quality. Color control was achieved by polymerization at different temperatures. Reprinted with permission from ref. [21]. Copyright 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) Eco-friendly photonic film prepared from bacterial xanthan gum, illuminated with left-handed polarized light and (c) with right-handed polarized light.

films of the bacterial polysaccharide xanthan exhibit structural color (Figure 3b and c) after depolymerization by ultrasound treatment [20]. Compared to the rigid nanocrystals, films prepared from the semiflexible xanthan are less brittle and require no chemical treatment steps, which increases their eco-friendliness even further. Investigating such additional biological sources for the production of photonic materials will help to broaden their range of application as well as economic viability, and thus help society to evolve towards a technologically advanced and sustainable future.

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Dr. Johanna R. Bruckner



Dr. Johanna R. Bruckner studied chemistry at the University of Stuttgart and pursued a doctorate in physical chemistry. In her doctoral studies, which she completed in 2015, she proved the existence of ferroelectric lyotropic liquid crystals for the first time and was awarded with the Glenn H. Brown Award of the International Liquid Crystal Society. Subsequently, she moved to Luxembourg to investigate the properties of cellulose nanocrystals in non-aqueous suspensions at the university's department of physics and materials science. After a two-year interlude in industry, where she worked as a development engineer at the Robert Bosch GmbH, Dr. Bruckner returned to the University of Stuttgart to engage in the newly founded cooperative research center (CRC) 1333 to develop highly defined ordered mesoporous materials by direct liquid crystal templating. In 2021, she received a Margarete von Wrangell fellowship, which gave her the opportunity to set up her independent research group and continue her habilitation. In 2022 she became principle investigator within the CRC 1333. Besides this her group studies the preparation and physicochemical properties of bio-derived liquid crystals. Dr. Bruckner actively engages in teaching, various aspects of university self-administration and currently chairs the German Liquid Crystal Society.

ZITATE

"The real point of honor [for a scientist] is not to be always right. It is to dare to propose new ideas, and then to check them."

Pierre-Gilles de Gennes

"Fließende Krystalle! Ist dies nicht ein Widerspruch in sich selbst – wird der Leser der Überschrift fragen –, wie könnte denn ein starres, wohlgeordnetes System von Molekülen, als welches wir uns einen Krystall vorstellen, in ähnliche äussere und innere Bewegungszustände geraten, wie wir sie bei Flüssigkeiten als „Fließen“ bezeichnen und durch mannigfache Verschiebungen und Drehungen der ohnehin schon des Wärmezustandes halber äusserst lebhaft durcheinander wimmelnden Moleküle zu erklären pflegen?"

Otto Lehmann

Über fließende Krystalle, 1889