



45. Arbeitstagung Flüssigkristalle
45th German Liquid Crystal Conference

21-23.03.2018, University of Luxembourg (LU)

Book of Abstracts and Conference Program



Häerzlech Wëllkomm zu Lëtzebuerg!

Welcome to Luxembourg!

On behalf of the organizing committee, it is our pleasure to welcome you to the 45th German Liquid Crystal Conference (45. Arbeitstagung Flüssigkristalle), held here at the University of Luxembourg.

Founded in 2003, the University of Luxembourg is a young university that has been quickly developing into a vibrant research institution, pioneering cutting-edge research in a variety of fields such as informatics, biosecurity, and condensed matter. Here at the Physics and Materials Science Research Unit, in the past few years, we have been developing robust facilities for fundamental and applied study of soft matter, particularly including liquid crystals.

Keeping with the international character of Luxembourg, a country located at the crossroads between three different cultures and languages, this conference is not just limited to participants from Germany and Luxembourg, but has grown to encompass many neighboring countries and includes presentations from institutions based as far away as the United States and South Korea.

We wish you a very fruitful and productive experience at the conference and a pleasant stay in Luxembourg!

GLCC/e@ $(LC)^2$ Schedule

Day 1: Wednesday, 21 March 2018

e@ $(LC)^2$: Focus Session on Liquid Crystal Elastomer Research in Europe

8:00	–	8:50	e@ $(LC)^2$ Registration	
8:50	–	9:00	Welcome	Jan Lagerwall
9:00	–	10:40	e@ $(LC)^2$ Part A	Chair: Anshul Sharma
9:00	–	9:30	E01: Nathalie Katsonis, "Muscle-like adaptability from liquid crystal networks"	
9:30	–	10:00	E02: Rudolf Zentel, "Actuating Liquid Crystalline Particles"	
10:00	–	10:20	E03: Danqing Liu, "Morphing surfaces formed in liquid crystal network under the electric field"	
10:20	–	10:40	E04: Irena Drevenšek-Olenik, "Peculiar Behaviour of Holographic Gratings in Light-Sensitive Liquid-Crystalline Elastomers"	
10:40	–	11:00	Coffee Break	
11:00	–	12:50	e@ $(LC)^2$ Part B	Chair: Anshul Sharma
11:00	–	11:30	E05: Verena Görtz, "Structure, function, and responsiveness in liquid-crystalline elastomer particles"	
11:30	–	12:00	E06: Arri Priimägi, "Autonomous self-regulating liquid-crystal elastomer photoactuators"	
12:00	–	12:20	E07: David Ditter, "MEMS analogous micro-patterning of liquid crystalline elastomers using a fluorinated photoresist"	
12:20	–	12:50	E08: Dirk J. Broer, "Oscillatory Dynamics in Liquid Crystal Network Films and Coatings"	
12:50	–	13:50	Lunch for e@ $(LC)^2$ Participants	

45th German Liquid Crystal Conference

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14:00	–	14:30	I01: Linda S. Hirst, "Self-mixing and Topological entropy in a biological active nematic"	
14:30	–	14:50	C01: Andreas M. Menzel, "Active microswimmers in nematic liquid crystals and liquid-crystalline order in crowds of microswimmers"	
14:50	–	15:10	C02: Alexey Eremin, "Photo-manipulation of the director field in nematic and twist-bend nematic droplets"	
15:10	–	15:30	C03: Christian Bahr, "Disclinations, Hedgehogs, and Other Structures in Flowing Liquid Crystals"	
15:30	–	16:00	Coffee Break	
16:00	–	17:00	Session 1: Living Liquid Crystals and Collective Behaviour, Part B	Chair: Kirsten Harth
16:00	–	16:20	C04: Anupam Sengupta, "Nematic microfluidics reveals topological tête-à-tête across disparate material fields"	
16:20	–	16:40	C05: Marco G. Mazza, "Hydrodynamic cavitation in Stokes flow of anisotropic fluids"	
16:40	–	17:00	C06: Andraž Rešetič, "Thermomechanical functionalization of conventional rubber"	
17:00	–	20:00	Session 2: Poster presentations (plus Reception)	
17:15	–	18:15	Poster competition judging for <u>odd</u> -numbered posters (P01, P03, P05...)	
18:15	–	19:15	Poster competition judging for <u>even</u> -numbered posters (P02, P04, P06...)	

Day 2: Thursday, 22 March 2018

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9:00	–	9:30	I02: Paul van der Schoot, "Line Tension of Carbon Nanotube-Based Lyotropic Liquid Crystal Microdroplets on Solid Surfaces"	
9:30	–	9:50	C07: Sonja Dieterich, "Gelled Lyotropic Liquid Crystals-Impact of gelator on liquid crystalline self-organization"	
9:50	–	10:10	C08: Dharmendra Pratap Singh, "Orientation of 4-n-octyl-4'-cyanobiphenyl molecules on graphene oxide surface"	
10:10	–	10:30	C09: Margarita Kurochkina, "Behaviour of CdSe/ZnS quantum dots in LC matrix"	
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14:30	–	14:50	C14: Heinz Kitzerow, "Switchable plasmonic surfaces"	
14:50	–	15:10	C15: Maria P. De Santo, "Temperature tunable lasing from dye doped chiral microdroplets encapsulated in a thin polymeric film"	
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18:00	–	19:00	DFKG Meeting (for members)	
19:15	–	20:00	Transfer to Banquet Site	
20:00	–	late	GLCC Banquet	Big Beer Company

Day 3: Friday, 23 March 2018

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10:30	–	11:05	Coffee Break	
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			I06: Wim H. De Jeu	
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12:45	–	13:00	Closing, Prize Ceremony, and Farewell	

Sponsors

The 2018 German Liquid Crystal Conference is made possible by gracious support from these companies and organizations:



Poster Presentations

Posters will be kept up throughout the duration of GLCC and will be especially available for perusal and discussion during the coffee breaks and lunches.

However, the judging for poster prizes will take place on **Wednesday, 21 March**, during the welcome reception. Judging will be performed in two groups (to allow the poster presenters to both see the presented posters and to enjoy the reception:

Group A (all odd-numbered posters): 17:15 – 18:15

Group B (all even-numbered posters): 18:15 – 19:15

In addition, one of the poster prizes will be awarded by popular vote of all the GLCC attendees. All participants are encouraged to talk to/interact with the poster presenters during the reception and then vote for the poster presentation they find best; instructions for the voting will be provided during the event. The criteria we encourage you to look for when making your choice are:

- Scientific merit
- Presentation of the results (i.e. visual appeal of the poster)
- The presenter's presentation and responsiveness to questions

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e@LC)²: Focus Session on Liquid Crystal Elastomer Research in Europe

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e@(LC)²

Focus Session on Liquid Crystal Elastomer Research in Europe

Recent advances in soft robotics have witnessed the transition from shape morphing, to encoding adaptive mechanical responses into materials. In many biological materials and tissues such as muscle fibers, collagen or fibrin, non-linear elasticity and strain-stiffening are key features that allow the establishment of high strains, and resistance to failure. I will discuss our efforts to develop strategies towards wholly artificial molecular materials that respond to illumination actively, with such a muscle-like mechanical response.

We have reported earlier on springs of liquid crystal polymer networks, in which azobenzene photo-switches are incorporated covalently, so that their photo-isomerization is amplified across increasing length scales, and eventually results into complex and versatile motion at the macroscale [1]. We have also shown that these objects also display non-linear responses to mechanical stress [2]. Here, we evidence that these springs stiffen under illumination with UV light, *i.e.* upon disruption of the liquid crystalline order. This stiffening stands in contrast to the photo-induced softening that was reported in fully polymerized networks so far. We propose that this adaptability to light is mediated by the low molecular mass liquid crystal that is incorporated into the network, because this liquid crystal interacts differently with the polymer fibers, depending on the polarity of the latter.

Besides unraveling an unprecedented photo-stiffening effect in liquid crystal networks, these results establish phase heterogeneity as a key control parameter in the photo-mechanical response of these materials.

References

- [1] Iamsaard *et al.*, *Nature Chemistry* **2014**, 6, 229-235.
- [2] Iamsaard *et al.*, *Nature Protocols* **2016**, 11, 1788-1797.

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Liquid crystalline elastomers (LCEs) are known as smart materials. They are promising candidates for an application as artificial muscles in micro robotics. They are usually used either as a macroscopic object or as an array of jointly linked microstructures. As an alternative, actuating micron-sized particles can be made by microfluidic techniques.[1] The microfluidic process fulfills hereby two requirements at the same time. On one side it produces a multitude of equally sized, micro objects. On the other side it induces an orientation of the liquid crystalline director in these particles, which gives them a typical mode of actuation (elongation as well as contraction is possible, depending on the process parameters).[2]

Recently, we succeeded in making more and more complex LCE particles by using such a microfluidic approach. These include core-shell particles which consist of an LCE shell and a liquid core. Since the inner fluid is reversibly pumped out of the particles by heating them above the phase transition temperature, they can be seen as one-piece micro pumps.[3] Also LCE tubes with a potential application as micro pumps were produced. By heating or irradiation of one spot of these tubes, a cross-sectional tapering should be obtained which can move along the tube simultaneously to the trigger and thus enables perfusion of a liquid inside. As a third type, Janus-particles in which either only one part deforms, or both parts actuate under different conditions – like varying temperatures – were synthesized.[4] All these particles are accessible via a microfluidic double emulsion process or with a microfluidic coflow device based on two parallel capillaries.

In addition we succeeded in producing LCE particles which are photo-responsive. By incorporating azobenzenes in the mesogens of a liquid crystalline network and using a redlight initiator for photopolymerization, we obtained particles which showed a fast and strong deformation during irradiation with white (visible) light. This light-triggered actuation can be reversed either by irradiation with red light or by heating.[5,6] Recent developments focus especially on the possibility to actuate both parts of a “Janus-particles” independently and on the actuation of “Janus-particles” with light.

References

- [1] C. Ohm, et al., *Adv. Mater.*, **21**, 4859 (2009).
- [2] C. Ohm et al., *J. Am. Chem. Soc.*, **133**, 5305 (2011).
- [3] E.-K. Fleischmann et al., *Nat. Commun.*, **3**, 1178 (2012).
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- [5] L. B. Braun, et al., *Polymers*, **8**, 435 (2016).
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We propose an original approach to create oscillating surface topographies in thin liquid crystal polymer network coatings by an electric field. By applying an alternating electric field from a pre-patterned interdigitated electrodes underneath of the thin liquid crystal coating, the coating surface deforms, and pre-designed local corrugations appear. In this way, glass-like surfaces can be brought into deformation as if they were liquids.

The activation principle is based on the creation of dynamic molecular voids by decreasing the order of crystal polymer networks (LCNs) and bringing the LCN into oscillation. [1] Here, we use an AC electric field to exert an oscillatory stress on the LCN polymer main chains. The mesogenic rods are thereby continuously deviating from their initial orientation and packing. This dynamic motion in polymer network leads to the formation of free volume. In order to boost the volume generation the AC field frequencies are tuned to match the natural network frequencies. This initiates resonance-enhanced oscillatory dynamics which largely amplify the deformation effects. The deformation of the coating surface is shown in Figure 1 which demonstrates that the coating deforms in between the electrodes.

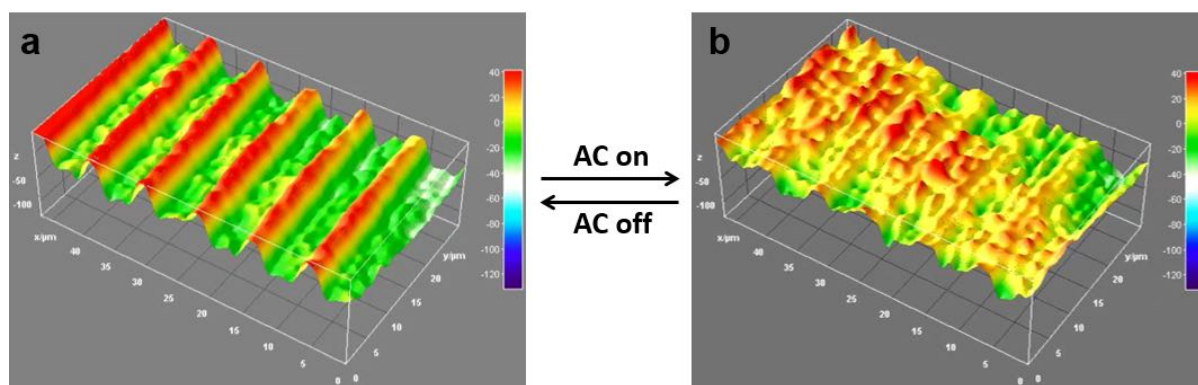


Figure 1. Surface deformations under an electric field. (a) 3D images of a coating on an electrode array in its initial state, and (b) when the electric field is on.

The response time of formation and relaxation of surface topographies in our LCN coating are on the order of 10 seconds. This is much slower than the rise and decay times of the electric field. This suggests that the deformation dynamics are dominated by viscoelastic deformation of the polymer network, rather than by dielectric properties. Related observations in azobenzene-modified LCNs support this conclusion. [2]

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Light-sensitive liquid crystalline elastomers (LS-LCEs) are optical holographic materials with many intriguing properties. Light-induced modifications of refractive index are several orders of magnitude larger than in conventional light-sensitive elastomers [1-4]. Holographic patterning process is very nonlinear, which allows an intricate control over the 3D spatial structuring. The associated effects are particularly interesting in the temperature region close to the nematic-paranematic phase transition, where phenomena, like recording of hidden holograms and hologram dark-enhancement effect can be observed [5].

LS-LCEs are also very efficient for recording of optical polarization gratings that are fabricated on the basis of the variation of polarization state of the optical field. In the vicinity of the Bragg angle such gratings exhibit an unusual splitting of the diffraction peak [6]. Very interesting behaviour appears also during mechanical stretching of the gratings, particularly along the direction of the soft elasticity, for which a synergetic correlation between the grating structure and the formation of reorientational domains can take place.

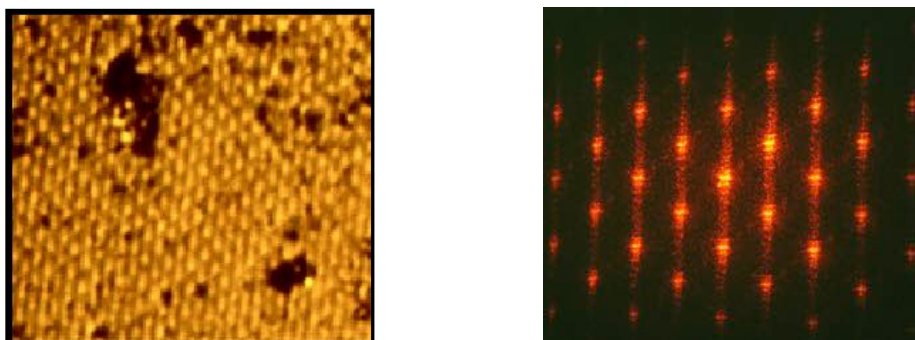


Figure 1: Optical polarization microscopy image (left) and far field optical diffraction pattern (right) of a 2D square lattice recorded in 10 μm thick LCE layer. The lattice distance is 13.5 μm .

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Structure, Function, and Responsiveness in Liquid-crystalline Elastomer Particles

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The three-dimensional topology of liquid crystal droplets in hosts such as water results in characteristic modes of self-organisation within the droplets, which are sensitive to changes in the host environment. In particular Abbott *et al* have shown ordering transitions to be triggered by the presence of a variety of biomolecules (lipids, surfactants, proteins, and viruses), and thus they provide a mechanism for sensor applications. Further, liquid crystal elastomers show remarkable mechanical properties, such as a macroscopic shape-change, or actuation, stimulated by a variety of external triggers.

In this talk, I will discuss parameters that control the confinement textures, the self-assembly, and the optical and shape responsiveness in a series of nematic and chiral nematic liquid-crystalline polymer and elastomer particles we currently investigate. We use heterogeneous polymerisation techniques to prepare particles in various size-ranges and explore their responses to external stimuli such as temperature changes, mechanical deformation, electromagnetic fields, and the uptake of guest substances.

I will discuss our findings for smaller particles (1-5 μm), produced by dispersion polymerisation, where we observed the confinement structure to most commonly correspond to either a bipolar or a radial configuration, i.e. two topologies with opposing surface anchoring (Figure 1(a) and (b)), and where we also observed a rather remarkable switch from bipolar to radial confinement upon a subtle change in monomer structure. Further, in these systems distinct and reversible optical transitions can be triggered by changes in the host environment, by mechanical deformations, or the uptake of guests.

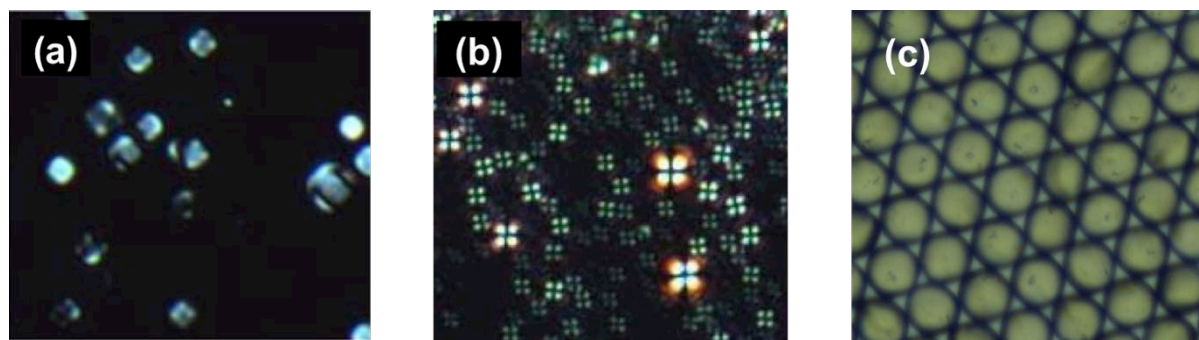


Figure 1: POM images of (a) bipolar, (b) radial particles ($\times 100$, 2-5 μm) obtained by dispersion polymerisation and (c) actuating LCE particles obtained by microfluidics.

I will further report on the preparation of larger nematic elastomer particles (20-50 μm , Figure 1 (c)) via microfluidics methods which provided surface rather than flow induced control of the alignment, good control of the monodispersity, as well as the optical and actuation properties of the obtained LCE particles.

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Natural systems act as an endless source of inspiration for scientific research. Recently, stimuli-responsive liquid-crystalline polymers have been used to mimic diverse motions of biological species. One of the grand challenges in biomimetic research is to mimic the autonomy of living systems, that is, self-action in response to certain environmental changes. Two prominent examples of self-acting systems in Nature are Venus Flytrap and mammalian iris. The flytrap exhibits a fast snapping motion when meeting a specific target, being capable of distinguishing prey from random dust. Irises, in turn, as found in many animal species, can self-regulate their aperture size in response to varying incoming light intensities, in order to stabilize light transmission into retina.

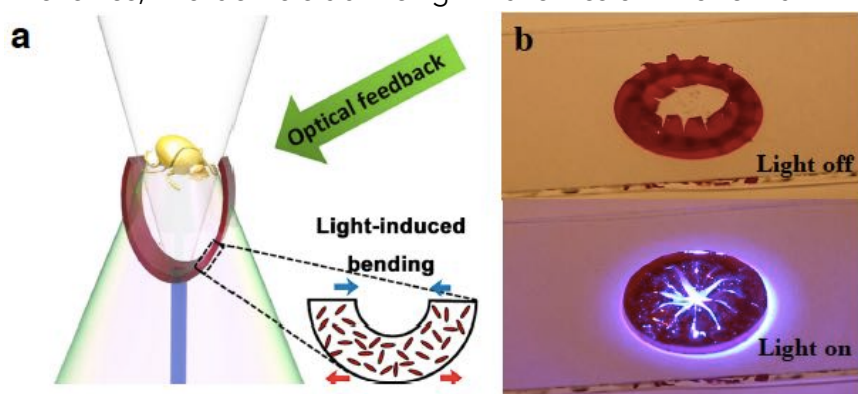


Figure 1: a) The optical “flytrap” closes when an object enters its field of view. Reflected light induces bending of the liquid-crystal elastomer, thus capturing the object. b) Soft liquid-crystal elastomer iris in the open state (top, no light) and closed state upon light illumination (bottom, illuminated with a 470 nm LED).

Here, we present our recent results on a flytrap-inspired autonomous gripping device [1] and a self-regulating iris [2]. The gripper comprises a liquid-crystal elastomer actuator fabricated onto the tip of an optical fiber. This optical ‘flytrap’ mimics the Venus Flytrap not only by autonomously gripping approaching objects, but also by distinguishing between different targets based on their optical feedback (reflectance) (Fig. 1a). The self-regulating iris is fabricated by utilizing photoalignment technique in combination with anisotropic thermal expansion of liquid crystal elastomers, devising a system that reduces symmetrically the aperture size in response to light intensity (Fig. 1b). The self-regulation demonstrated in these devices provides a new design tool for intelligent soft robotics and for tunable photonics.

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MEMS analogous micro-patterning of liquid crystalline elastomers using a fluorinated photoresist

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Liquid crystalline elastomers (LCEs) combine the properties of polymeric elastomers with the self-organization of liquid crystals. Their actuation capacities through the anisotropy-to-isotropy change of macromolecular chains make them a unique class of shape memory materials.[1] In this work, we present a method to pattern LCEs in the micrometer range without using any mechanical processing steps to prepare micron sized LCE actuators compatible with MEMS technology.

For this purpose we developed a multi-layer spin-coating process. A water soluble sacrificial layer to remove LCE actuators in the end, a photoalignment layer to align LC monomers and a LCE precursor that is polymerized and crosslinked through UV-irradiation are spin-coated successively on substrates to synthesize 300-3500 nm thick LCE films. Films up to 700 nm thick are structured with oxygen plasma using a fluorinated photoresist that is orthogonal to all other layers. For patterning of thicker films a hard mask process using hydrogen silsesquioxane as a hard mask is used. Polarized optical microscope (POM) and profilometry images of a structured LCE film are shown in Figure 1. A resolution of 1.5-2.0 microns could be achieved with the described patterning methods.[2]

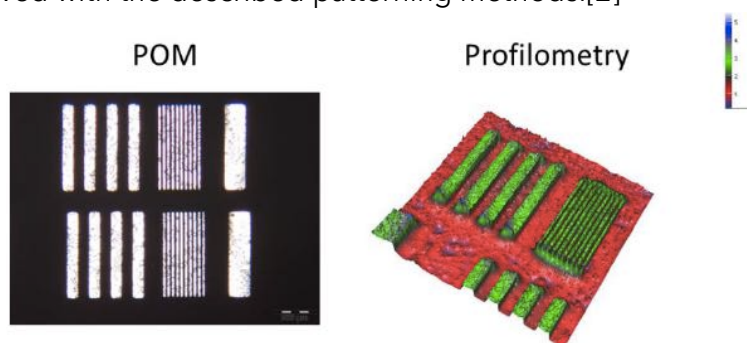


Figure 1: POM (left image, scale bar: 200 μm) and profilometry (right image, scale bar: 5 μm) images of a patterned LCE film using a hard mask process.

Structured LCEs show director dependent and reversible two-dimensional shrinkage and elongation and three-dimensional bending and twisting actuation motions. The described procedure makes it possible to pattern LCEs in every shape and with variable director fields and thus LCEs can be processed like classical MEMS. This shows the potential of LCEs in MEMS devices and encourage us to develop new kinds of micro devices in the future.[2]

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Since the development of the reactive mesogens (RM's) in the late 80's of last century they have proven their utility for a wealth of applications. The molecular liquid crystal order frozen in a polymer network brought a new dimension to liquid crystal technology. Initially developed for their use as low shrinkage, low thermal stress coatings, the RM's soon demonstrated their advantages also for optical applications. The large, temperature-stable and adjustable birefringence proved to be a useful instrument for the display industry which adopted the RM's for many purposes, varying from viewing angle enhancement to optical-retarder based 3D imaging optics. Presently, advanced optical applications for augmented reality and astronomy lenses are drawing much attention as well their use to stabilize special liquid crystal effects for smart windows and dedicated display types.

The use of RM's for soft robotics applications is nowadays studied by many academic and industrial institutes. Typically, they are polymers that change their shape, their surface structure or their porosity. At Eindhoven University, we developed self-sustaining oscillators and micro-transport devices responding to triggers as heat, light and/or electrical fields. Films may deform from a flat to a complex, but pre-designed, shape with prospects to light-triggered origami and self-folding plastic elements. A completely new development relates to coatings that switch their surfaces from basically flat to corrugated with a controlled topography, thus controlling properties as friction and grip. The lecture will discuss our newest developments, giving a preliminary view on the future of RM's with advanced applications in the fields of smart coatings, soft robotics and haptics.

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Self-mixing and Topological entropy in a biological active nematic

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Over the past few years, the surge of research into "active matter" systems has been one of the most important and exciting developments in soft condensed-matter physics. In an active fluid, the constituent particles are not simple passive tracers---instead the constituents consume energy and move relative to one other in a defined way. In such fluids, both local and global order can develop, persist, and evolve as the constituent particles propel themselves. This talk focuses on an active fluid with nematic order, inspired by biology. The fluid constituents are microtubules (components of the cytoskeleton) that are propelled tangent to one another via molecular motors (kinesin) powered by the consumption of ATP. Energy is thus injected on the microscale, through ATP hydrolysis, but produces unsteady laminar flow with structure on larger (millimeter) scales.

The microtubules exhibit a local nematic ordering with isolated topological defects; these defects wind around one another in a complex choreography. The net affect of the defect motion is an enhanced mixing of the fluid, which exhibits the classic stretch and fold patterns indicative of chaotic dynamics. A better understanding of this mixing mechanism could elucidate transport within the cytoskeleton and provide important insights for bioengineering and microfluidic applications, where efficient mixing in Stokes flows can be a challenge. However, despite this importance, the mixing properties of active nematic flows is understudied. Our work attempts to address this deficiency using both experiment and theory to investigate transport and mixing properties in active nematics.

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Active, self-propelled microswimmers can be generated artificially in the form of colloidal Janus particles that are self-driven by phoretic effects, or they are found in nature in the form of living bacteria or algal cells featuring an active propulsion mechanism [1].

Introducing reduced minimal models of such objects, we, on the one hand, study their swimming behavior in well-aligned nematic liquid crystals by analytical calculations [2]. Depending on the viscosity ratios of the nematic liquid crystal and the propulsion mechanism, we find alignment parallel or perpendicular to the nematic director, see figure 1 (a). Consequently, by adjusted director configurations or switching of the nematic director, individual microswimmers can be guided along a requested path.

On the other hand, we analyze the collective behavior and liquid-crystalline ordering in crowds of many interacting self-driven microswimmers [3,4]. Particularly, we concentrate on a situation in which these swimmers are spherically confined. As a consequence of selfpropulsion, each swimmer sets the surrounding fluid into motion, which affects all other swimmers. Remarkably, this so-called hydrodynamic coupling can lead to polar alignment of the microswimmers by spontaneous symmetry breaking, implying induced net fluid flows and also collective motion, see figures 1 (b) and (c). Additionally, we have studied the collective dynamics when the swimming trajectories show a persistent bending in the case of biaxial microscopic circle swimmers, resulting in collective chiral behavior [4].

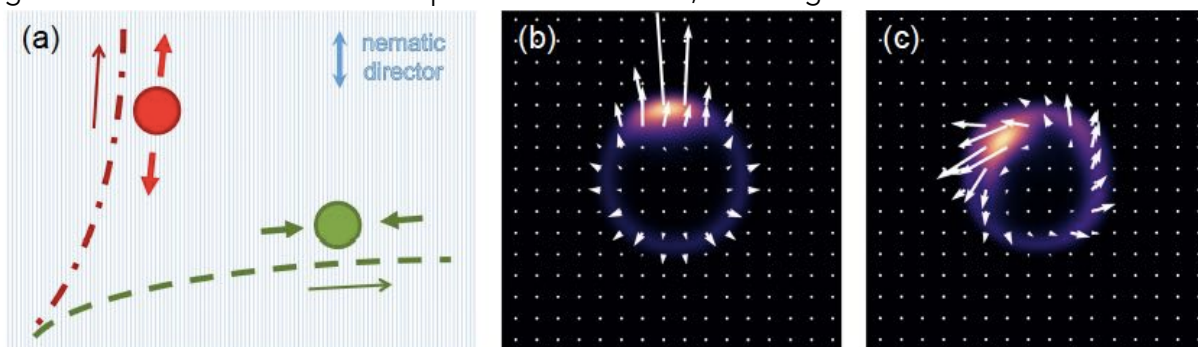


Figure 1: (a) Simplified active model microswimmers in an aligned nematic liquid crystal. Depending on the viscosity ratios and propulsion mechanism, the swimmers either align parallel to or propagate perpendicularly to the nematic director [2]. (b) Interacting microswimmers in an isotropic fluid under spherical confinement show polar ordering of their self-propulsion directions as a result of hydrodynamic interactions (brighter color reflects higher density, while white arrows indicate local swimmer orientations) [4]. (c) Increasing the active drive of self-propulsion, collective motion of the polarly ordered microswimmers around the confinement arises [4].

The next step shall be to combine these two situations and analyze the collective behavior and emergent liquid-crystalline order in crowds of active microswimmers suspended in aligned nematic liquid crystals.

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Photo-switchable surfactants enable manipulation of the anchoring conditions at water/LC and glass/LC interfaces using exposure to UV light. The anchoring condition can be reversibly switched from the orthogonal to a degenerated planar one. In our previous studies, we demonstrated light-driven reconfiguration of the director field and even the light-driven motion of the inclusions in a 5CB liquid crystal. Here, we investigate the behaviour of LC droplets of compound M (a mixture provided by Merck GmbH) exhibiting the nematic (N) and the twist-bend nematic (NTB) phases. We demonstrate that in contrast to 5CB, the droplets of M prefer a disclination loop to a hedgehog defect in the nematic state with an orthogonal anchoring condition. In the NTB phase a weak modulation of the director is observed which can be removed by changing to the planar condition under UV. We discuss these observations in the light of differences in the elastic anisotropy of 5CB and compound M. We also discuss and compare the NTB materials with bent-core nematics. Adjusting the anchoring energy by balancing the UV and VIS exposure opens new opportunity for fine tuning the optical properties of the LC droplets in LC emulsions.

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We report new results concerning the influence of anchoring, electric field, and flow on the director field and topological defect structures in nematic liquid crystals employing two experimental systems: microfluidic channels and self-propelling nematic droplets.

Recently, we reported a method to connect and disconnect nematic disclination lines in microfluidic channels [1]. Here, we report a more fundamental study of structural transformations of disclination lines in microchannels. In particular, we show how the interplay between anchoring, flow, and electric field can be used to switch between different configurations corresponding to wedge, linear twist, and zigzag-shaped twist disclination lines.

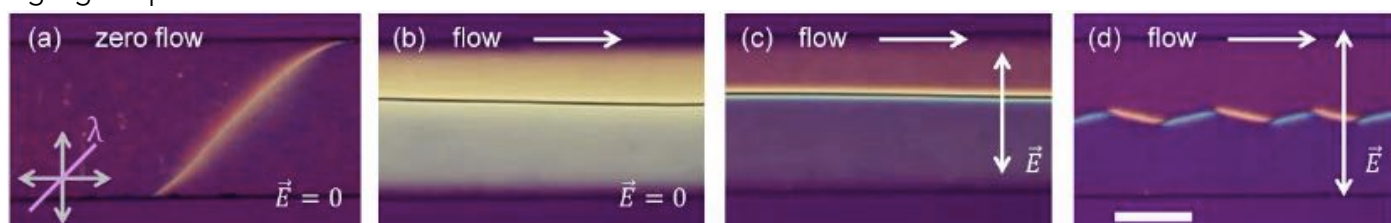


Figure 1: Micrographs showing structural transformations in microfluidic channels. (a) Wedge disclination. (b) Flow-stabilized twist disclination. (c) Twist disclination spatially quenched by electric field. (d) Field-induced zigzag-shaped twist disclination. Scale bar corresponds to 100 μm .

The second system under investigation consists of nematic droplets in aqueous surfactant solutions which show a self-propelled motion under certain conditions [2, 3]. The Marangoni flow in the droplet surface, which causes the self-propelled motion, leads also to a convective flow within the moving droplet. Here, we study the effect of the internal convection on the director field in the nematic droplet. An obvious effect is the shift of the central point defect (radial hedgehog) towards the droplet surface. Comparison between experimental micrographs and calculated micrographs based on model director fields reveal additional structural features resulting from the internal convection. We report also first results concerning the internal structure of self-propelling nematic shells.

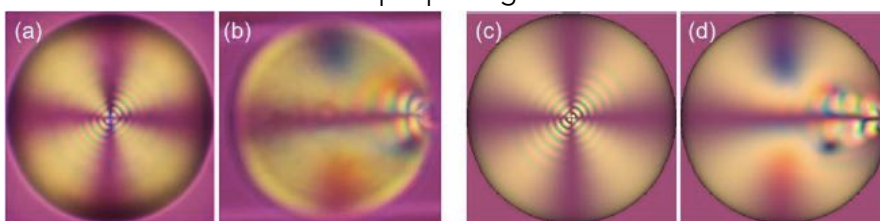


Figure 1: (a), (b) Experimental micrographs (crossed polarizers with diagonal λ plate) of a 5CB droplet (diameter 46 μm) in the resting (a) and self-propelling (b, motion from left to right) state. (c), (d) Calculated micrographs (Jones matrix method) for model director fields. While the resting droplet possesses a simple radial hedgehog defect, the active droplet shows a shifted hedgehog and additional deformations in the director field.

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Nematic microfluidics reveals topological tête-à-tête across disparate material fields

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Topological defects are singularities in material fields that play a defining role across range of systems: from cosmic microwave background polarization to superconductors, and living matter. Despite significant advances in our understanding of topological defects and their mutual interactions, little is known about the formation and interaction of defects across different material fields embedded within the same system. Using nematic microfluidics as a test bed, we report how topological defects in two different material fields – the hydrodynamic flow field, and the nematic orientational field – co-emerge and cross-talk with each other [1]. To do so, we generate hydrodynamic stagnation points of different topological charges at the center of star-shaped microfluidic junctions, as shown in Figure 1, which then interact with emergent topological defects in the orientational field of the nematic director. Supported by analytical and numerical calculations, these experiments demonstrate that a hydrodynamic singularity of given topological charge can nucleate a nematic defect of equal topological charge, which we corroborate by creating -1, -2, and -3 topological defects in 4-, 6-, and 8- arm junctions. Finally, we characterize the coupling between the orientation and the flow fields, and propose this as tunable parameter for designing multi-field topology in nematic microfluidic systems. Our work is an attempt toward describing materials that are governed by distinctly multi-field topology, and although discussed in a nematofluidic context, has potential ramifications on both equilibrium and non-equilibrium systems.

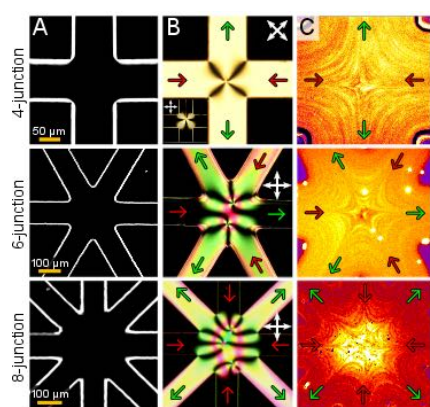


Figure 1: Emergence of nematic defects and hydrodynamic singularities at microfluidic junctions. (A) Star-shaped microfluidic junctions, with 4- 6- and 8- arms (from top to bottom). (B) Emergent topological defects at the microfluidic junction visualized using polarization optical microscopy. (C) Concomitant fluorescent imaging of flowing tracers reveal hydrodynamic stagnation points at the geometric center of each microfluidic junction.

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C05 Hydrodynamic cavitation in Stokes flow of anisotropic fluids

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Cavitation, the nucleation of vapour in liquids, is ubiquitous in fluid dynamics, and is often implicated in a myriad of industrial and biomedical applications. Although extensively studied in isotropic liquids, corresponding investigations in anisotropic liquids are largely lacking. We reveal flow-induced cavitation in liquid crystals at low Reynolds numbers [1]. We combine liquid crystal microfluidic experiments, nonequilibrium molecular dynamics simulations and theoretical arguments to identify the mechanism underpinning LC cavitation. The cavitation domain nucleates due to sudden pressure drop upon flow past a cylindrical obstacle within a microchannel. The inception and growth of the cavitation domain ensued in the Stokes regime, while no cavitation was observed in isotropic liquids flowing under similar hydrodynamic parameters. Using simulations we identify a critical value of the Reynolds number for cavitation inception that scales inversely with the order parameter of the fluid. Strikingly, the critical Reynolds number for anisotropic fluids can be 50% lower than that of isotropic fluids.

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C06 Thermomechanical functionalization of conventional rubber

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The method of dispersing additional material into a polymer network can enhance or introduce new properties to elastic materials, thus broadening its applicability and adaptability to various industrial needs. We have therefore adopted this idea to introduce a novel method of thermomechanically functionalizing conventional rubber. By producing a composite material consisting of magnetically oriented liquid crystal elastomer particles incorporated in a cured PDMS matrix, we have transferred thermomechanical properties from the particles onto the composite, meaning that the material experiences reversible contraction in the particle's alignment direction upon thermal activation. Such composites, termed polymer-dispersed liquid crystal elastomers or PDLCE's [1], are no longer restricted by the limitations of the 2-step LCE synthesis procedure [2] so they can be molded into arbitrary shapes and sizes. By spatially modulating the particle's director orientation throughout the specimen using an external magnetic field, it is also possible to achieve complex reversible thermomechanical deformations (Figure 1).

The amount of thermomechanical deformation of PDLCE's strongly depends on the particle's concentration and elastic moduli of PDLCE constituents, as well as on the degree of particle's orientational order, which we successfully assessed by means of deuterium perturbed ²H-NMR. By controlling these parameters, the PDLCE's thermomechanical and elastic properties can be custom tailored to user's preferences, while the lack of mechanical manipulation of the specimen and the liquid nature of the pre-polymerized PDLCD melt, makes the material well suited for implementation into additive manufacturing techniques, such as 3D-printing.

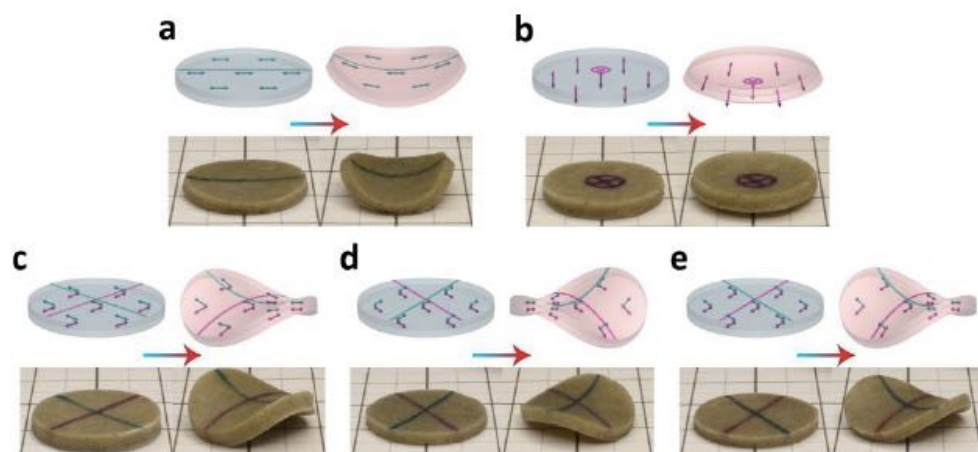


Figure 1: Determined PDLCE's orientational order parameter.

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Line Tension of Carbon Nanotube-Based Lyotropic Liquid Crystal Microdroplets on Solid Surfaces

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Dispersions of long, rod-like particles such as carbon nanotubes are known to form spindle-shaped, cylindrically symmetric elongated nematic liquid crystalline droplets in coexistence with the isotropic phase. Their shape and director field structure depends on the size of the drops, the interfacial tension, anchoring strength and elastic constants. In contact with a wall, the droplets lose their cylindrical symmetry and flatten. By visualising hundreds of droplets of carbon nanotubes dissolved in chlorosulfonic acid and applying elasticity theory to fit the data, we find that the ratio of the line tension and the interfacial tension for this particular system equals $-0.84 \pm 0.06 \mu\text{m}$. This ratio is 2 orders of magnitude larger than what has been reported for conventional fluids, in agreement with theoretical scaling arguments.

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Gelled lyotropic liquid crystalline phases are soft materials in which the anisotropy of a lyotropic liquid crystal (LLC) is combined with the mechanical stability of a gel. Here we present results obtained by a systematical investigation of the preparation and the phase behaviour of this new class of complex fluids. We will discuss how the monomeric gelator as well as the gel network influence structures and properties of the lyotropic liquid crystalline phases.

The studied LLC system consists of sodium dodecylsulfate (SDS) as surfactant, decanol as co-surfactant and water. At constant temperature (25°C) and fixed water content (70 wt.%) various liquid crystalline phases (lamellar L_α , nematic N_d and N_c , hexagonal H_1) are formed depending on the decanol to SDS ratio. Using the low molecular weight organogelator 12-hydroxyoctadecanoic acid, we developed a procedure for the simultaneous formation of the LLC phase and the gel network which leads to anisotropic and highly viscous gels (see Figure 1a).

The coexistence of gel network and lamellar L_α phase was demonstrated by freeze-fracture electron microscopy (FFEM). Twisted gel fibers and lamellar layer steps were observed side by side (Figure 1b). Small angle X-ray (SAXS) scattering results indicate a higher translational order for gelled than for non-gelled lamellar phases. Additionally, an arrested lamellar layer spacing was found in the gelled state, as can be seen in Figure 1c).

Gelled nematic phases however could not be observed since the surface active gelator is monomerically integrated into micelles acting partly as co-surfactant which reduces the micelle curvature and thereby leads to a widening of the lamellar regime.

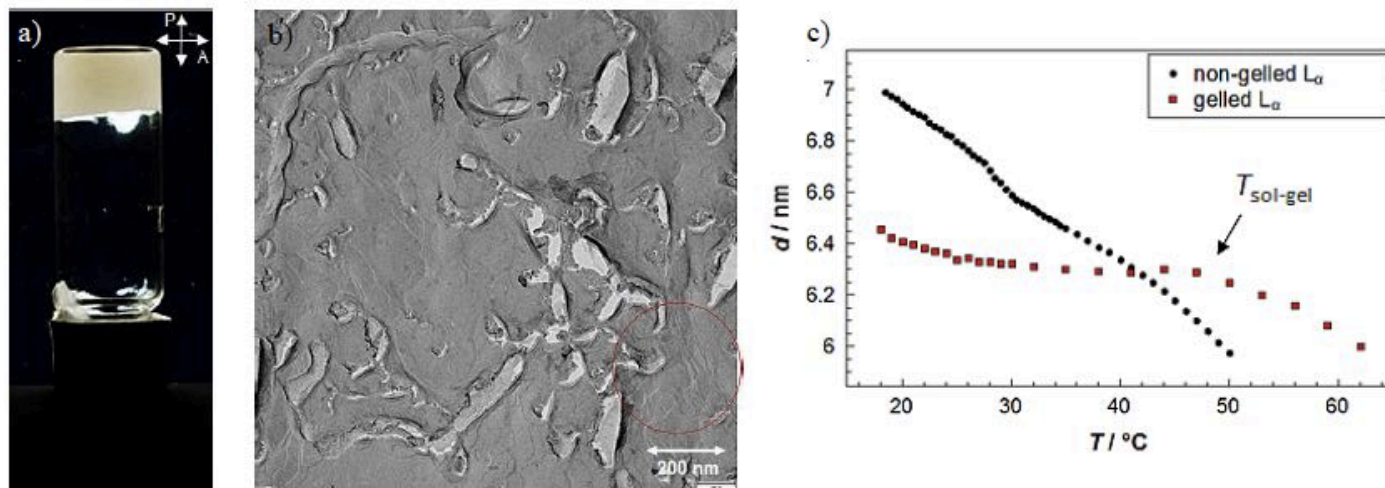


Figure 1: a) Picture of the gelled lyotropic lamellar phase between crossed polarizers. The gel shows no flow but strong optical birefringence. b) Freeze-fracture electron microscopy picture of the gelled L_α phase. A helically twisted gel fiber and lamellar layer steps (highlighted by the red circle) were found next to each other. c) Lamellar layer spacing of the non-gelled and the corresponding gelled L_α phase versus temperature measured by small angle X-ray scattering. For the gelled L_α phase an arrested layer spacing was observed below the sol-gel transition temperature $T_{\text{sol-gel}}$.

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Orientation of 4-n-octyl-4'-cynobiphenyl molecules on graphene oxide surface

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Graphene oxide (GO) flakes [1] were introduced in anisotropic medium of 4-octyl-4'-cynobiphenyl (8CB) to investigate the long range molecular interaction of 8CB molecules with that of the GO surface. It is observed that 8CB molecules always vertically adsorb on the surface of GO flakes but observed polarized optical micrographs reveal the random orientation of GO flakes with bulk 8CB molecules. As the concentration of GO in 8CB matrix is varied, the molecular orientation successively progressed towards the homeotropic alignment in bulk. This molecular orientation is attributed to electron-phonon interaction taking place between the electrons present on CN functional group of 4-octyl-4'-cynobiphenyl with that of the phonons of GO. The investigated results are supported by the Raman spectroscopy, Fourier transformed infrared spectroscopy and polarized optical microscopy.

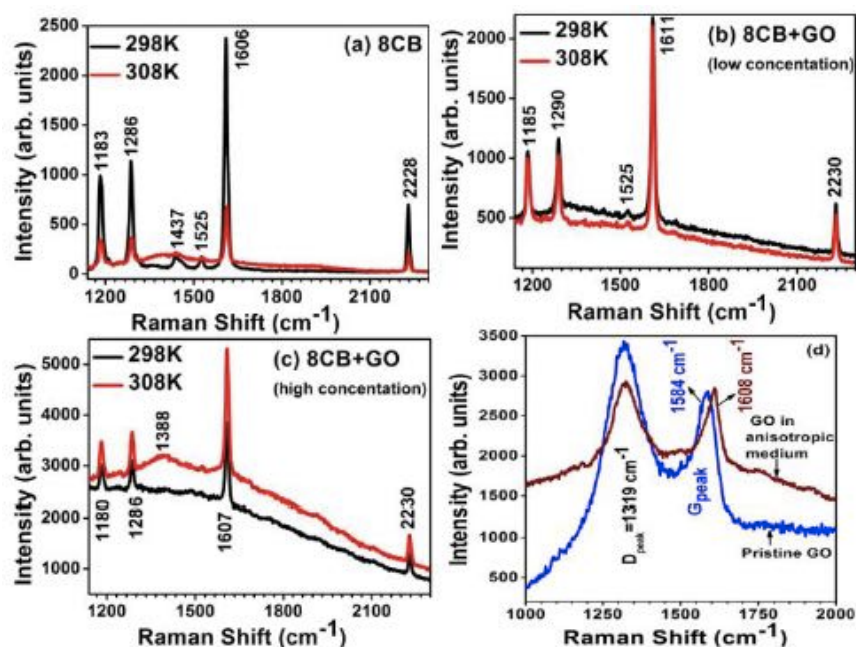


Figure 1: Experimental Raman spectra of (a) 4-n-octyl-4'-cynobiphenyl (8CB), (b) 8CB+graphene oxide (GO) hybrid material for low concentration of GO (wt% ≤ 0.1), (c) 8CB+ GO hybrid material for high concentration of GO (wt% > 0.1), whereas (d) shows the Raman spectra of GO in pristine form and in the anisotropic (8CB) medium.

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Over the past decade the optical properties of hybrid structures based on liquid crystals (LCs) and semiconductor nanoparticles have attracted increasing attention of scientists [1]. To control the properties of quantum nanoparticles they are introduced into various matrices [2], which can be conditionally divided into 2 types - passive and active. Using liquid crystals as active matrix opens new possibilities to control of quantum dots (QDs) luminescence by means of an electric field [3]. The absence of a general theory describing the mechanisms of interaction of LCs and semiconductor nanoparticles, explaining the observed changes in luminescent properties of LCs and QDs, makes it urgent to conduct detailed studies of their composites. We studied the optical properties of semiconductor CdSe/ZnS QDs in a nematic LC matrix under action an external electric field.

The composites were prepared by adding a sample of dry hydrophobic CdSe/ZnS QDs with a core diameter of 3.5 nm and 5 nm to a nematic liquid crystal LC-1289 with a positive dielectric anisotropy. The LC cells of the sandwich type assembled from two quartz substrates coated with indium-tin oxides layers and a planar orienting polyimide layers. The composites were obtained using ultrasonication process during from 30 minutes to 4 hours. The LC structures with 1 wt. % QDs have a homogeneous orientation after filling the cells.

The enhancement of the CdSe/ZnS QDs photoluminescence (PL) in LC has been observed with an increase in the electric field applied to the LC cell. The maximum of the PL intensity was found about 0.125 V/ μm . That is associated with passivation of centers of recombination of QDs in the LC matrix and also with energy transfer from liquid crystals to semiconductor nanoparticles. A further increase in the electric field strength led to a significant quenching of the PL intensively of the QDs. This could be explained by a decrease in the probability of recombination of the electron-hole pair as a result of a decrease in the overlapping of the wave functions of the electron and hole in the excited nanoparticle and an increase in the size of QDs aggregates as a result of the reorientation of the nematic director in electric field.

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Dissipative versus Reversible Contributions to Macroscopic Dynamics: Time-reversal Symmetry and Entropy Production

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We discuss the time-reversal behavior of dynamic cross-couplings among various hydrodynamic degrees of freedom in liquid crystal systems. Using a standard hydrodynamic description including linear irreversible thermodynamics we show that the distinct thermodynamic requirements for reversible and irreversible couplings lead to experimentally accessible differences. We critically compare our descriptions with those of existing standard continuum mechanics theories [1-3], where time-reversal symmetry is not adequately invoked. Despite the common belief, there are subtle differences between the two schools of describing the dynamics, even for simple liquid crystal. The motivation comes from recent experimental progress allowing to discriminate between the hydrodynamic description and the continuum mechanics approach.

This concerns the dynamics of Lehmann-type effects in chiral liquid crystals [4]. If both, the direct and the inverse Lehmann effect [5] is measured for the same system, one can verify that these effects are based on the irreversible, rather than the reversible part of the dynamics. A second example is the dynamic magneto-electric response in ferronematics and ferromagnetic nematics [6], a liquid multiferroic system. Here, the different behavior under time reversal of the nematic director and of the magnetization leads to characteristic, experimentally detectable features that have not been found by a continuum mechanics approach.

In addition, we discuss the consequences of time-reversal symmetry for flow alignment of the director in nematics (or pretransitional nematic domains) and for the dynamic thermomechanical and electro-mechanical couplings in textured nematic liquid crystals.

With the advent of ever more complicated liquid crystal and soft matter systems, like bentcore nematics or smectic liquid crystals, systems involving tetrahedral order [7], polar and magnetic liquids, polymers or elastomers, and of ordered active matter, it has become obvious that a thorough theoretical description based on thermodynamics is inevitable. Time reversal symmetry is an important element of that.

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Self-Assembly of Discotic Rings and Nanowires in a Liquid Crystal Confined in Nanopores

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Discotic Liquid Crystals (DLC) tend to stack up into linear columns creating charge carrier pathways along the stacking direction due to overlapping π -electrons. Embedding DLCs into nanoporous membranes enables the preparation of organic molecular nanowires or nanorings. Combining high-resolution optical birefringence, measuring orientational order [1,2], and synchrotron-based X-ray diffraction, measuring translational order, we found a pore size and anchoring condition dependent orientational transition from the circular (nanoring) to axial (nanowire) orientation in anodic aluminum oxide nanopores. Thereby, for nanopores smaller than 20 nm, an additional component to the pore size dependent phase transition temperature shift following the Gibbs-Thomson mechanism is found [3]. Additionally, and in combination with Monte Carlo simulations, we show that confining the same thermotropic DLC in cylindrical silica nanopores induces a quantized formation of annular layers consisting of concentric circular bent columns, unknown in the bulk state, see Fig. 1. Starting from the walls this ring self-assembly propagates layer-by-layer towards the pore center. By establishing a Gibbs free energy phase diagram the phase transition quantization is traced back to the discreteness of the layers' excess bend deformation energies in comparison to the thermal energy allowing the determination of the otherwise hard to access bend elastic constant [4].

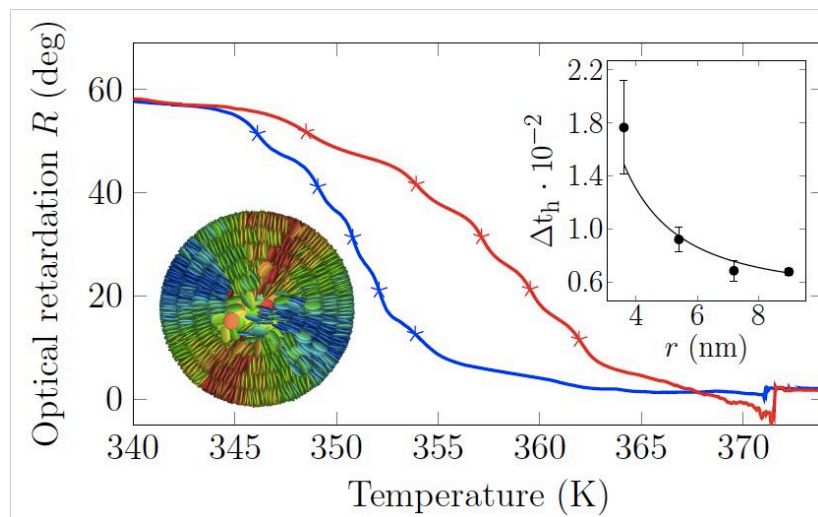


Fig. 1: Measured temperature evolution of the optical retardation R of HAT6 in confinement. Inset: Normalized supercooling temperature for the isotropic-columnar transition of each annular layer and snapshot from Monte Carlo simulations.

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It has long been known that suspensions of ferromagnetic nanoparticles in a nematic liquid crystal could induce a ferromagnetic liquid crystal phase [1]. Only recently this phase was successfully experimentally realized [2]. In Refs. [3] and [4], the measurements of the statics and the dynamics were modeled using the existing theory first presented in [5].

The ordering in a ferromagnetic nematic liquid crystal is described by two fields: the director field \mathbf{n} , which describes an average orientation of the molecules of the liquid crystal and the magnetization field \mathbf{M} , describing an average orientation of the magnetic moments of the magnetic particles. Unlike for usual nematics, the ferromagnetic phase is sensitive to very small magnetic fields.

To understand the complete dynamic behavior of a ferromagnetic nematic one needs to measure rheological properties of the system. An interesting phenomenon, well-known in usual nematics, is flow alignment, where under the influence of a simple shear flow the director is tilted by a finite angle with respect to the velocity field. Certain liquid crystals nevertheless show a tumbling behavior. Flow alignment can be in these cases restored with a sufficiently strong electric field [6]. We show that in a ferromagnetic nematic the boundary between flow alignment and tumbling can be shifted by using small magnetic fields.

Generally, the measured viscosity of the system depends on the magnitude of the shear rate. To circumvent this dependence, simple experiments were proposed in [7], where the orientation of the molecules is fixed by an external electric or a strong magnetic field. This way, one can introduce in an ordinary nematic liquid crystal three different Miesowicz viscosities. In a ferromagnetic nematic the presence of the magnetization leads to additional dynamic cross-couplings [5]. As a result, the three Miesowicz viscosities for an ordinary nematic are replaced in a ferromagnetic nematic by nine viscosities.

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C13 Efficient ferronematic coupling with polymer brush particles

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The ability to control nematic phases in thermotropic liquids by external fields is of great importance for their application, e.g. in optical devices. While it is common to use electric voltage in such devices, the employment of magnetic fields is less straight forward due to the low magnetic anisotropy of the mesogens.

However, as already predicted by deGennes and Brochard in 1970, the incorporation of dipolar magnetic particles is expected to result in nematic phases that are readily manipulable at moderate magnetic field strength.[1] Nonetheless, one of the main challenges for the experimental realization is strong tendency to agglomerate of the nanoparticles, as a consequence of the strong molecular interactions of the mesogens and the dipolar interactions between the particles.[2] Thus, up to now, experimental evidence for such coupling is rare.

Our new approach to circumvent this problem, and to achieve ferromagnetically doped liquid crystals with enhanced volume fraction and stability, is based on nanoparticles that are surface-modified with a side-chain LC polymer brush. Thereby, a variation of shell thickness, mesogen density and the spacer length is possible. With this approach, a higher compatibility between the particle surface and the mesogenic matrix, and an effective steric stabilization of particles against agglomeration is obtained.

The impact of the doped particles on the phase behavior of 5CB ($B_{th} = 250$ mT at a layer thickness of $d = 25$ μ m) is investigated with respect to particle concentration. Up to a concentration to 0.2 vol% particles can be stabilized in 5CB. By addition of 9OCB-PHMS functionalized magnetic particles, the order parameter of the system increases, indicating an effective coupling between the particles and the LC matrix. The magnetic response of the ferronematic phases is investigated by capacitance measurements in a magnetic field (Figure 1b). As compared to 5CB, the critical field strength and the shape of the Fréederickzs transition is strongly is affected by the particle volume fraction. In fact, at a field as low as 20 mT, 5CB doped with 0.1 vol% magnetic particles can readily be manipulated.

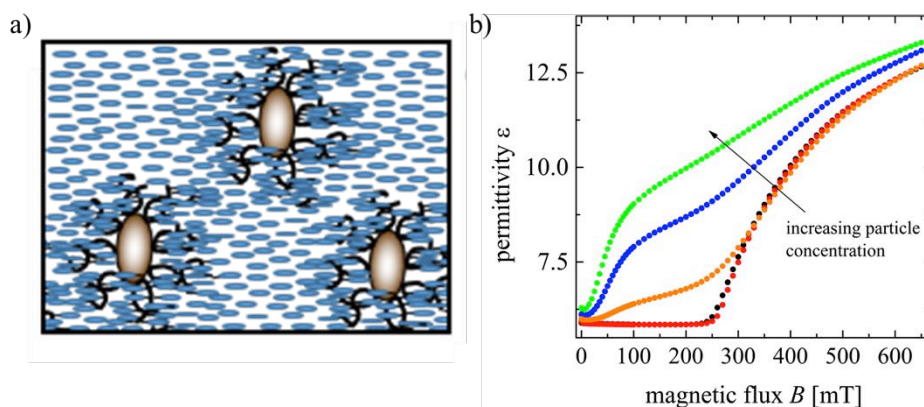


Figure 1:a) Scheme of LC polymer brush particle, b) Capacitance measurements with parallel B and E field for pure 5CB(black) and 5CB doped with a) 9OCB-PHMS@CoFe₂O₄ and in volume fractions from 0.01 vol% up to 0.1 vol%..

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Complex periodic liquid crystal structures by holographic photo-alignment

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Photo-alignment is a novel method to define the anchoring direction for liquid crystal by illumination a photosensitive polymer with polarized UV light. Using two interfering UV laser beams with opposite circular polarization, a periodic alignment pattern is obtained (Figure 1 left). A liquid crystal cell in which the two substrates have periodic photo-alignment patterns with orthogonal periodicity, provides complex 3D director patterns without disclinations (Figure 1 middle). The period of these patterns is twice that of the photo-alignment and symmetry breaking leads to two equivalent states. The resulting 3D director pattern depends on the cell thickness and the periodicity of the photo-alignment.

The director pattern can be identified by performing numerical simulation with a Q-tensor finite element method. The simulation results can be verified by polarization optical microscopy (Figure 1 right) or by observing the diffraction properties of the structure. The director pattern can be deformed continuously by applying a potential difference between the two substrate electrodes [1]. At high voltages, the director is mainly homeotropic, except near the substrates. At low voltages, the director remains perpendicular along diagonal lines. The periodic structures have interesting diffraction properties with a small number of diffraction orders if the period of the UV illumination is small.

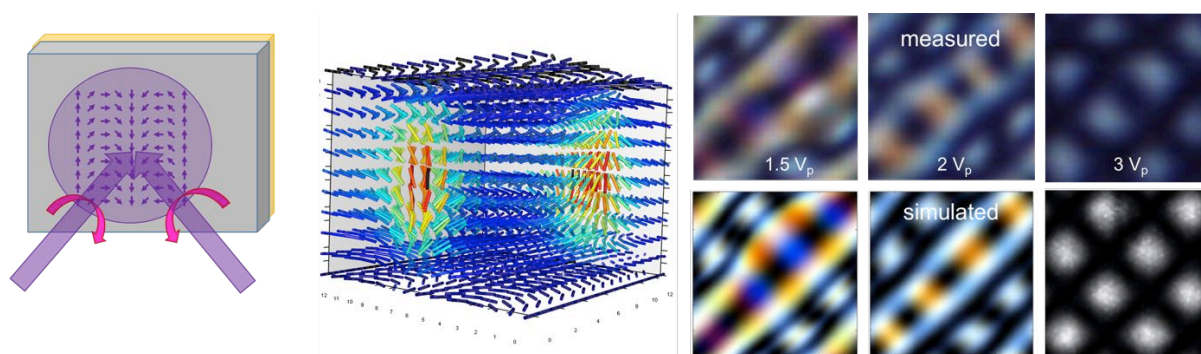


Figure 1: Left: Periodic photo-alignment by two circularly polarized UV laser beams. Middle: simulated 3D director distribution. Right: measured and simulated patterns in polarization optical microscopy.

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Metamaterials and metasurfaces can interact with waves in extremely unusual ways. They are composed of three- or two-dimensional arrangements of objects that are smaller than the wavelength under consideration. Their effective material parameters are not only governed by the bulk properties of the compounds composing them, but depend to a large extent on the geometry of these objects with subwavelength size. Previous studies on tunable metamaterials containing liquid crystals have mainly focused on utilizing the calamitic nematic phase. Here, a switchable metasurface composed of plasmonic split ring resonators and a polymer-stabilized liquid crystal blue phase is presented (Fig. 1) [1]. Also the applicability of liquid crystals for switchable holograms with high diffraction efficiency based on geometrical metasurfaces [2] was investigated. Preliminary results [3] will be shown.

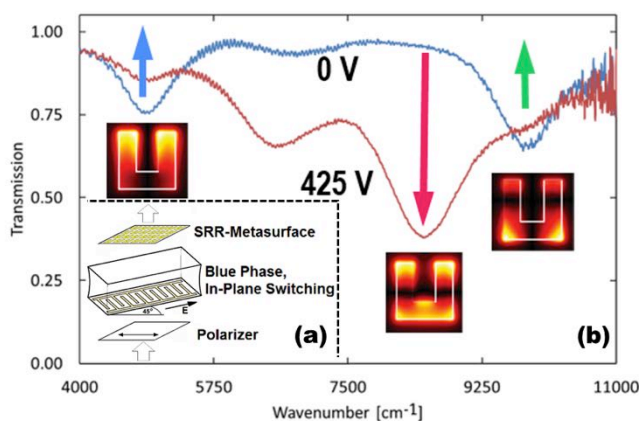


Figure 1: (a) Experimental setup: A metasurface composed of split ring resonators (SRR) is exposed to infrared (IR) radiation transmitted through an in-plane switching (IPS) cell filled with a polymer-stabilized blue phase. The latter controls the state of polarization. (b) IR transmission spectra at different voltages. (Inset: spatial distribution of the field amplitudes of the respective resonant modes of the SRR) [1].

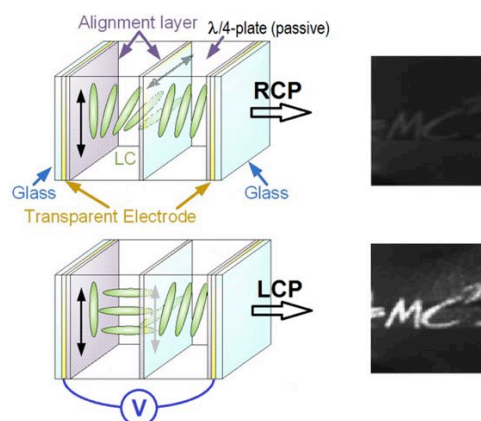


Figure 2: Liquid crystal cell transforming linearly polarized light to right circularly polarized light (RCP) if no voltage is applied or to left circularly polarized light (LCP) if a voltage of a few volts is applied. To the right: Reconstruction of a hologram from a geometric metasurface as described in Ref. [2] by means of the integrated RCP/LCP electro-optic switch at 0V (RCP) and 10 V (LCP), respectively [3].

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Cholesteric liquid crystals (CLC) are one of the most promising materials in the field of soft-matter photonics, that may be the key elements for the development of compact laser sources. From a practical point of view, as opposite to semiconductor lasers, using CLC any wavelength can be obtained, from ultraviolet to near infrared simply by adjusting the position of the photonic band gap and properly selecting the luminescent dopant for the desired wavelength range.

3D laser emission from dye doped cholesteric liquid crystals confined inside micro-droplets paves the way for many applications in the field of sensors or tunable photonics [1]. Several techniques can be used to obtain small micro-resonators, as an example, dispersing a liquid crystal inside an immiscible isotropic fluid to create an emulsion [2]. Here, we report on the possibility to obtain a thin free standing film starting from an emulsion having a mixture of water and poly vinyl alcohol as isotropic matrix. Following water evaporation, a free-standing polymeric film in which the micro droplets are encapsulated is obtained (Figure 1a). Bragg type stimulated laser emission can be obtained from the emulsion as well as from the thin film. Using a chiral dopant, with temperature dependent solubility, the emitted laser wavelength can be tuned in a range of 40nm in a temperature of 17°C (Figure 1b). The proposed device can have applications in the field of sensors and for the development of anti-counterfeiting labels.

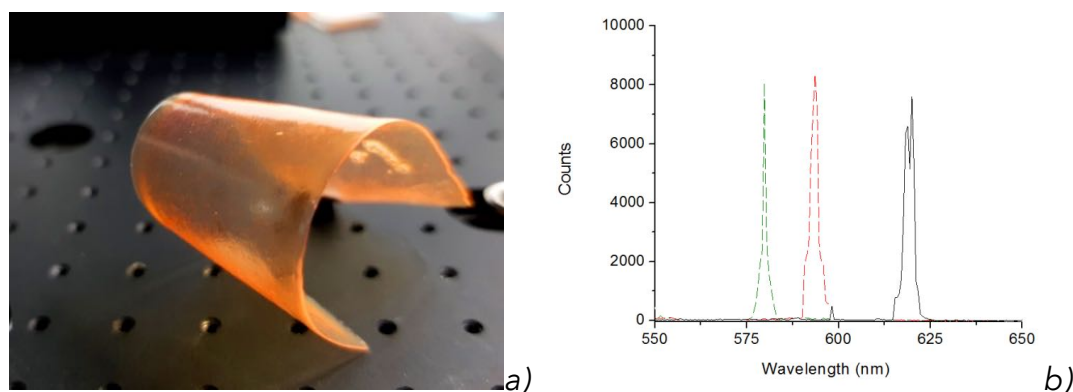


Figure 1: a) free standing polymeric film containing DD-CLCs micro-droplets; b) blue shift of the laser emitted wavelength, measurements acquired at 28°C (black solid line), at 40°C (red dashed line) and at 46°C (green dotted line), respectively.

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Localized, field induced defect formation and manipulation in hybridized LCs

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Highly responsive LC test cells were assembled with photovoltaic substrates (iron doped lithium niobate windows). In these hybridized samples, the LC was driven by exposure with a tightly focused laser beam, which caused locally high photovoltaic surface fields (generated within the substrates). Field induced director orientation, defect creation, lensing, manipulation of the film edge, and interaction of defects were studied [1-3] in experiments and simulations. Samples were investigated with rotated crossed polarizers [1,3] in order to learn about defect strength and sign of the field induced topological charges. In a nematic LC, umbilic defects and interactions of point and line defects were seen. Defect-free director realignments with radial symmetry were found, if these samples were assembled with an indium tin oxide coated cover glass. In samples with chiral nematic (N*) LCs, rewritable patterns (Figure 1) were created. A uniformly standing helix texture was seen in the initial state. Exposure with a scanned laser beam locally resulted textural transitions (Frank-Pryce defects) and bistable responses: Such a hybridized N* LC can be used as rewritable canvas for index modulations and micron scale textural transitions – no dye doping is required + a diode laser beam has just the right intensity for writing and erasing patterns. Small, field generating iron doped lithium niobate particles, functionalized with surface grafted surfactants [4] are promising candidates to fabricate photo responsive LC dispersions.

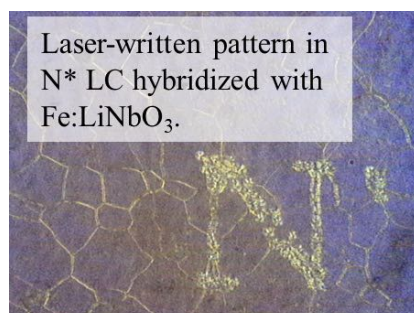


Figure 1: Pattern in a N* LC sample (no doping, no dyes), written with a scanned laser beam.

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Complete solid-state cholesteric liquid crystal (CLC_{solid}) droplets and shells are fabricated using microfluidics after UV curing and chiral-dopant extraction of monodispersed CLC droplets, which consist of a reactive nematic LC mesogen mixture and a nonreactive chiral dopant [1, 2]. The helical pitch of the CLC_{solid} droplet and shell is reduced by removing the chiral dopant in proportion to the extracted volume. The CLC_{solid} droplet and shell exhibits a coloured reflection spot at the centre, with cross-communication dots and central concentric rings. These photonic colours indicate that the helical photonic CLC structure is well-maintained even after UV curing and dopant extraction. The pitch of the well-defined helical photonic structure depends on the solvent quality, temperature, and humidity, giving rise to a reversible change of the reflection colour of the CLC_{solid} droplet and shell under external stimuli. The CLC_{solid} droplets and shells are extremely stable for a long time, even in a good solvent. This smart solid-state molecular-spring photonic droplet eliminates the obstacles to CLC-droplet application caused by the fluidic LC state, and thus introduces a new avenue for CLC applications.

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C17 Tailoring Columnar Self-Assembly by Soft Sulfur Interactions

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Disk-shaped polycyclic aromatic compounds forming columnar mesophases display various interesting properties such as 1D charge carrier mobility, photoconductivity and self healing of defects. However, from a practical point of view mesophase ranges are often above ambient temperature and clearing transitions are in many cases close to the decomposition temperature, thus limiting potential applications [1]. We anticipated, that incorporation of sulfur groups might solve the problem, because it is known from calamitic liquid crystals that sulfur improved both mesomorphic properties and charge carrier mobilities and led to decreased HOMO-LUMO gaps [2, 3]. However, for discotic liquid crystals this issue was less explored. Therefore we initiated a case study employing triphenylene crown ethers and derivatives thereof, where we could demonstrate, that successive replacement of alkoxy side chains by thioethers not only shifted the columnar mesophase to room temperature, but also affected the redox potential in a beneficial way [4]. The influence of the sulfur units was even more pronounced as compared to the introduction of branched side chains [5], suggesting the sulfur-sulfur interactions promote columnar self-assembly.

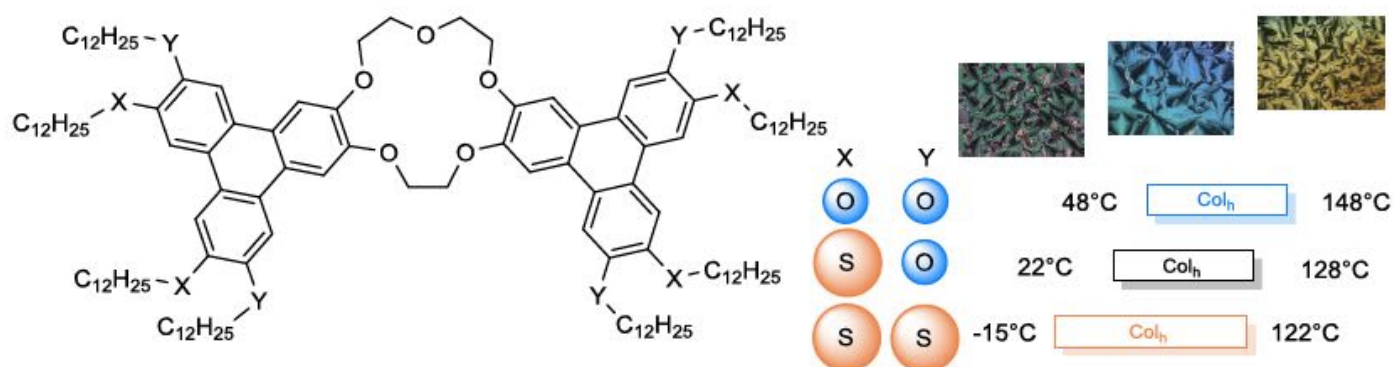


Figure 1: Effect of sulfur- vs. oxygen-containing side chains on mesophase behaviour

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In the last decade hybrid materials from donor chromophores and Fullerenes as acceptors have been attracted great interest for the application in photovoltaic devices.[1,2] However, even the best materials reveal only low efficiencies owing to structural defects, low quality of alignment, moderate relative permittivity, fast recombination and the macroscopic separation of the components among others. Liquid-crystalline covalent bound dyads may introduce important advantages over other materials, because they can in principle be well aligned and reveal often rather highly ordered and well nanosegregated structures.[2,3]

Recently, our group focused the research on star-shaped, shape-persistent mesogens **1** and **2** with 1,3,5-benzene or Phthalocyanine cores and conjugated oligomers as arms decorated with aliphatic or oligo(ethyleneoxy) chains (R).[4,5] The intrinsic void can be filled with Fullerenes, which were attached to one or more arms using spacers of various lengths (n). The stacking of these mesogens has been studied by comprehensive X-ray scattering methods and simulation.

This contribution will highlight the beautiful hierarchical self-assembly in double-nanosegregated helical columns, which can be fine-tuned by the spacer length for molecules **1c**. Even mixtures of Fullerene containing non-LC compounds (**1b**, **2b**) with the parent stars without Fullerene (**1a**, **2a**) self-organize in such donor-acceptor stacks. For the Phthalocyanine derivatives **2** a limited range of mixtures of components **2a** and **2b** can be aligned and result in n-stacked columns, in which the Fullerenes are nanosegregated at the periphery of the columnar stacks. Only derivatives **2** can be decorated with oligo(ethyleneoxy) chains without loss of mesomorphic properties. The optimization of these mesogens for the development as possible new LC photovoltaic materials will be discussed.

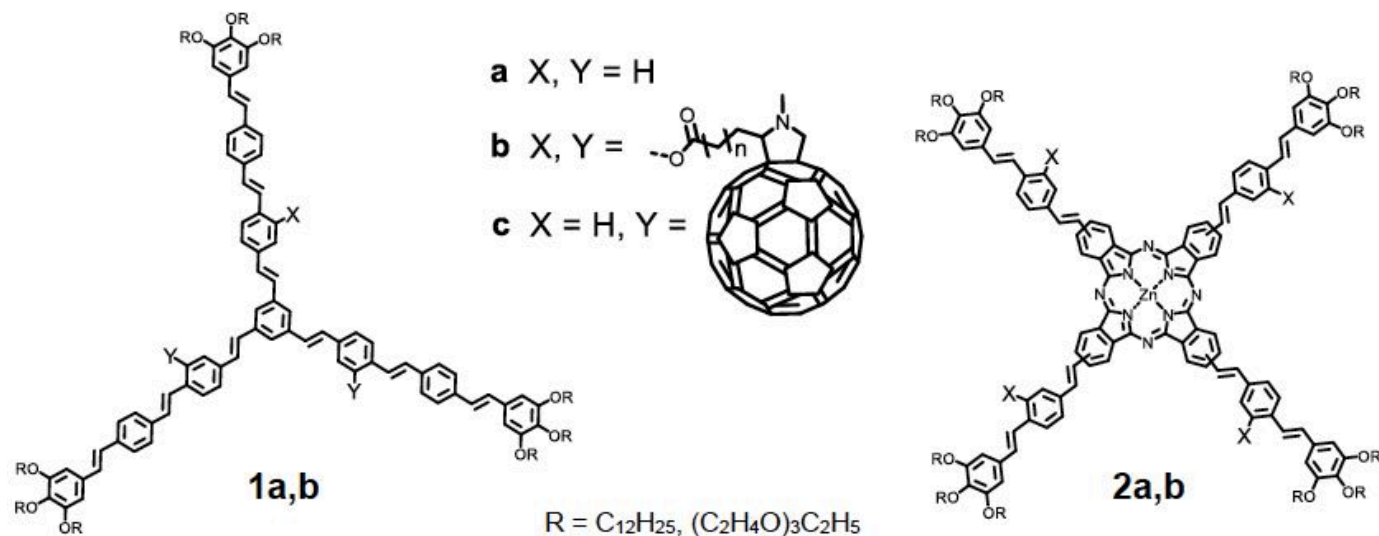


Figure: Donor-acceptor dyads under investigation.

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Mesomorphic properties and structures of two mix-substituted phthalocyanine (Pc) derivatives of the A₃B type, with a different ratio of electron-donating (hexadecyloxy-) and electron-withdrawing (Cl-) substituents on the isoindol fragments 'A' and 'B', correspondingly (Figure 1), were studied by polarising optical microscopy [1, 2], differential scanning calorimetry and small-angle X-ray scattering [3]. Both compounds display columnar mesophases, and the type of organisation of the columns in the mesomorphic state was found strongly depended on the number of peripheral chlorine substituents in the molecule.

The Pc columns of the dichloro-derivatives associate three-by-three into approximately cylindrical bundles with the chlorine substituents in the core, and these bundles arrange in turn according to a large-size hexagonal columnar lattice. No association in bundles on the contrary occurs for the tetrachloro-derivative, and columns hence stay isolated and irregularly spaced by the asymmetry of the periphery, so that only orientational long-range order is kept and a nematic columnar (N_{Col}) mesophase is displayed at any temperature. The reason for this different self-assembling is discussed.

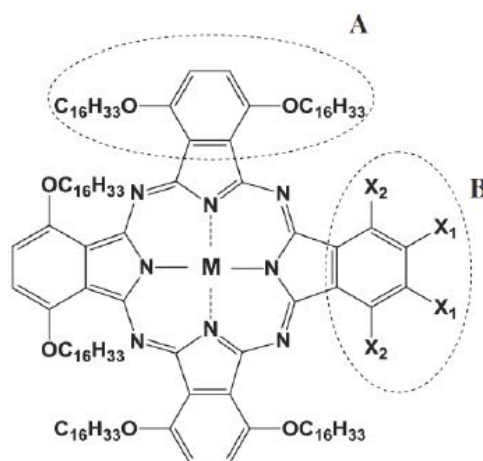


Figure 1. Structural formula of the studied mix-substituted phthalocyanines of A₃B type: I (H₂-Pc(OC₁₆H₃₃)₆-Cl₂): M = 2H⁺, X₁ = Cl, X₂ = H; II (H₂-Pc(OC₁₆H₃₃)₆-Cl₄): M = 2H⁺, X₁ = X₂ = Cl.

The work was supported by the programme of the Ministry of Education and Science of the Russian Federation (Grant No. 16.1037.2017/4.6) and the Russian Foundation for Basic Research (Grant No. 16-03-00883a). BD and BH thank the CNRS and the Université de Strasbourg for support.

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X-shaped bolapolyphiles combining benzothiadiazole with fluorinated aromatics for organic semiconductors

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Liquid crystal molecules gained a lot of attention for semiconductors due to their special properties such as self-organization and high charge carrier mobility. Especially molecules with benzothiadiazole (BT) have shown its high potential characteristics as an excellent acceptor [1] and fluorination of aromatic groups lead to lower HOMO-LUMO gaps [2]. Furthermore, liquid crystals forming nano-segregated columnar phases such as X-shaped molecules [3] can form well-ordered donor-acceptor system due to its driving forces from amphiphilicity, which is critical for semiconductor applications [4].

Herein we designed and synthesized new X-shaped molecules based on BT unit. These compounds were characterized by differential scanning calorimetry, polarizing microscopy and X-ray diffraction. Depending on the chain length and temperature, different phases were observed. Compounds with short branched chains show a hexagonal columnar phase ($\text{Col}_{\text{hex}}/p6mm$) with triangular honeycomb structure. The shortest derivative with linear chains exhibits a rectangular columnar phase ($\text{Col}_{\text{rec}}/c2mm$) and on increasing the chain length and volume by using branched chains, square columnar phases ($\text{Col}_{\text{sq}}/p4mm$) replace $\text{Col}_{\text{hex}}/p6mm$. Due to the importance of aromatic fluorination and BT unit in lowering HOMO-LUMO gap values, UV-vis and fluorescence spectra were conducted for a selected sample. The result was compared to parent compounds without fluorinated aromatics and BT unit. The result shows that both, fluorination of aromatic groups and BT units, have the effect of lowering the HOMO-LUMO gap.

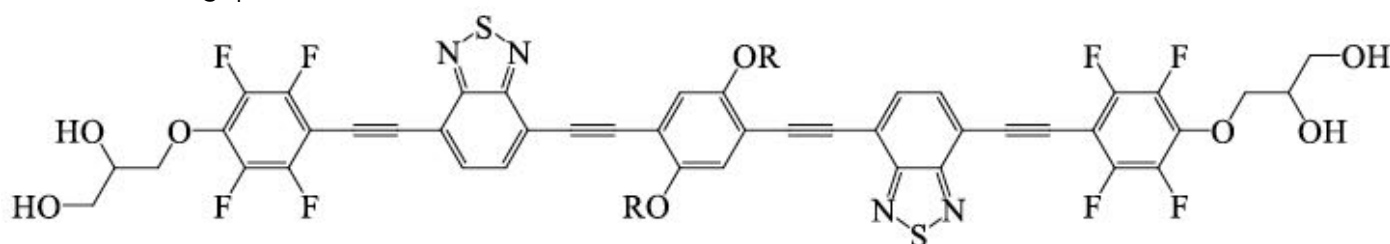


Figure 1. Molecular structure of the reported X-shaped molecules with BT and fluorinated aromatic units (R = linear or branched alkyl chains)

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Quasi-one dimensional fluid structures are commonly found in nature, but may be formed from any material that can suppress the Rayleigh-Plateau instability, which prohibits many isotropic Newtonian fluids from achieving a length-to-diameter ratio greater than π . Some liquid crystal phases, such as the B7 mesophase, can overcome this instability and achieve length-to-diameter ratios over 1000. An interesting feature of these materials is not only how they form so-called fibers, but also their response when exposed to external mechanical, thermal, acoustical or electrical perturbations. It was shown that quasi-one dimensional fibers formed in the PM-SmCP and B7 liquid crystal phases could be electrically and acoustically plucked, with the decay time of their oscillations proportional to their length [1]. Additionally, fibers formed in the B7 liquid crystal phase can assemble into quasi-*three* dimensional structures when sheared (Figure 1) [2]. Fiber stability could also be maintained through liquid crystal phase transitions for liquid crystals composed of star-shaped oligobenzoates [3]. Knowledge of these dynamic responses and the causes find relevance in technological applications, where materials are subjected to a variety of external stimuli, which may (or may not) be desired or useful.



Figure 2: "Seashell" structure formed along a liquid crystal fiber dilated with velocity $\geq 7.1 \mu\text{m/s}$ [2].

Here, I will discuss our most recent results on the dynamic responses of free-standing liquid crystal structures using a modified force sensing technique. We investigate the strain- and strain rate-dependent stress response of liquid crystalline fibers [4], including the formation of quasi-three dimensional structures along the fibers. We also found that slight variations in temperature could actuate the fiber, with an oscillation period proportional to the temperature fluctuations. A viscoelastic model that takes into account the fiber's structure is necessary in order to fully establish the complex interplay between the material's molecular self-assembly and the fiber's macroscopic features. We hope to further elucidate this complex interplay such that it may be harnessed for applications in soft electronics and robotics, and open new avenues in theoretical fluid dynamics.

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Disclinations in liquid crystals bear striking analogies to defect structures in a wide variety of physical systems, they are excellent models to study fundamental properties of defect interactions. Freely suspended smectic C films behave like quasi 2D polar nematics and are thus an ideal model system for studying defect dynamics in quasi 2D systems. However, despite its generality, experiments so far only addressed with defects dynamics in nematics, which are more complicated as they are always 3D systems.

One crucial difference between diffusive defect motion and liquid crystals is the presence of (back)-flow interactions. This reduces the annihilation time and introduces an asymmetry between the motion of the positive and negative defects: the flow driven by the director reorientation drives a flow which accelerates the motion of the positive defect. These phenomena predicted in simulations [1] have been confirmed in experiments with nematics, e.g. in Refs. [2]. Svnsek and Zumer predicted similar effects in a simulation of free-standing smectic C films [3], albeit limited to the very late stages of annihilation.

We analyze defect dynamics in free-standing smC films experimentally. An experimental procedure is introduced to capture high-strength disclinations in localized spots, see Fig. 1a. After they are released in a controlled way, the motion of the mutually repelling topological charges is studied, see Fig. 1. We demonstrate that the classical models, based on elastic one-constant approximation, fail to describe their dynamics correctly. In realistic liquid crystals, the models work only in ideal configurations. In general, additional director walls modify interactions substantially [4].

Finally, we present a novel method to prepare isolated $+1 - (-1)$ defect pairs and present first experimental conclusions on their annihilation dynamics. We find the predicted asymmetry of defect velocities. The defects' dynamics is strongly influenced by the orientation of the -1 defect with respect to the connecting axis, disorientation inducing strong orbital motion of the defect pairs.

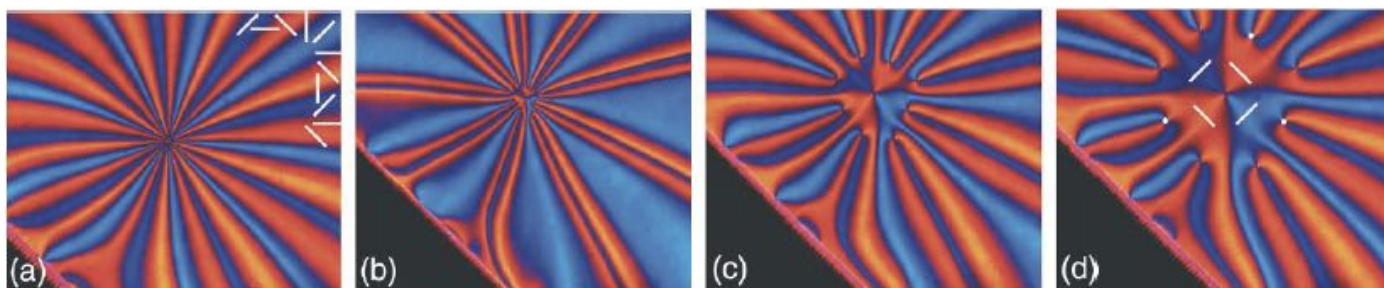


Figure 1: (a) Nine trapped defects in a hole of approximately $10\ \mu\text{m}$ diameter. (b) Exploding configuration immediately after the hole was extinguished. (c) 1.8 s and (d) 5 s after release. Dimensions are $475\ \mu\text{m} \times 400\ \mu\text{m}$.

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Hydrodynamics of droplet lattices in quasi 2D free-standing liquid crystal films

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In an experiment on ISS, we prepared nearly regular triangular droplet lattices on free-standing liquid crystal films to investigate the diffusion and vibration dynamics on these lattices [1]. The layered structure in smectic A phases allows the preparation of thin and homogeneous macroscopic films. We record the motion of the droplets and calculate their diffusion characteristics. The experiments are compared to numerical simulations of droplet arrangements assuming specific repulsive interaction potentials. The mean-square displacement of the droplets reveals mobilities in the lattice and information on the strength of the potential.

The study was supported by NASA, DFG and DLR within the OASIS project.

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The recent discovery of a new lyotropic liquid crystal phase, the structure and properties of which are analogous to the chiral ferroelectric smectic C-phase (SmC*) in thermotropics, was based on a tailored structure of the amphiphile **G10** (fig. 1a) in which a tilt-promoting 2-phenylpyrimidine core was linked to a chiral diol-headgroup via a hydrophilic ethylene glycol spacer [1]. However, so far there is only one example of this general amphiphile structure known to form the new lyotropic SmC* phase in mixtures with water and with formamide.

In an attempt to systematically elucidate the molecular requirements for the formation of lyo-SmC* phases [2] we here report three new amphiphiles leading to lyotropic SmC* phases. These amphiphiles are derived from the parent amphiphile structure by (i) an elongation of the hydrophilic ethylene glycol spacer, (ii) the inversion of the original 2-phenylpyrimidine core and (iii) its exchange by an even more tilt-promoting fluorenone core. The probably most striking effect was found in the case of the new amphiphile **G10inv** (fig. 1b), where the simple inversion of the 2-phenylpyrimidine core direction in the original **G10** structure led even in the neat **G10inv** material to a 30 K wide thermotropic SmC* phase, which is fully preserved in the lyotropic state up to formamide concentrations of at least 35 wt%.

Even though we were successful to enlarge the existing library of lyo-SmC* amphiphiles, our investigations also reveal that the formation of the lyotropic SmC* phase is highly sensitive to even minor changes in the molecular amphiphile structure.

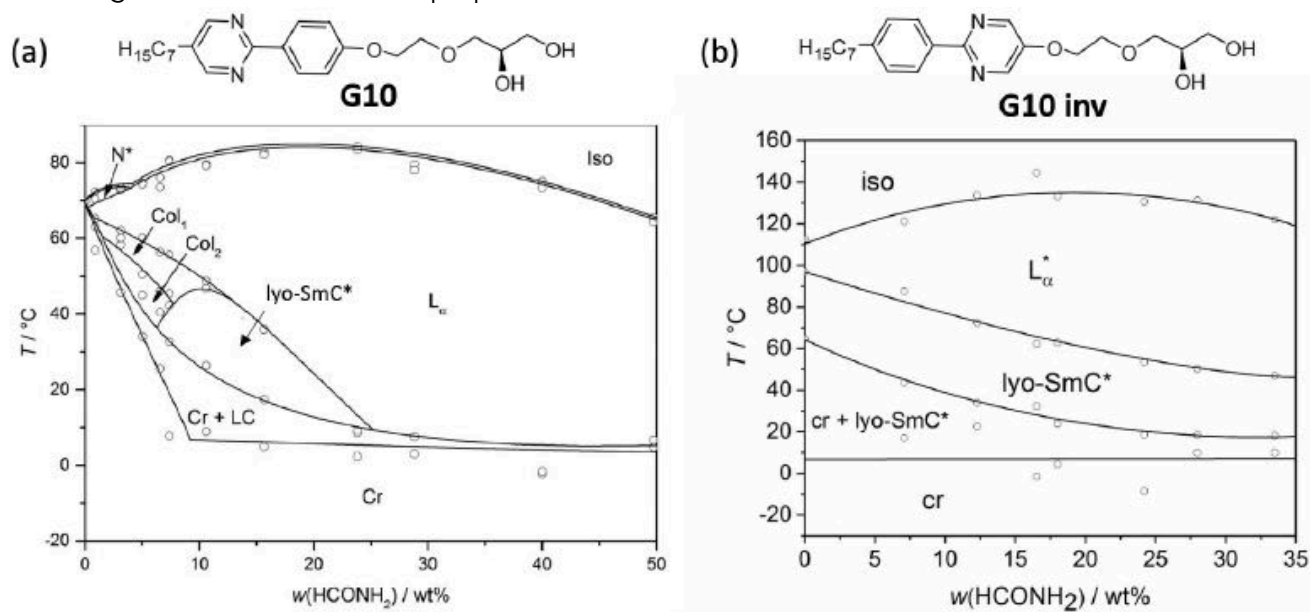


Figure 1: Phase diagrams of G10 with formamide on the left [2] and on the right the lyotropic system G10 inv with formamide. The chemical structures of G10 and G10 inv are shown above.

We thank the *Deutsche Forschungsgemeinschaft* for financial support (DFG Gi243/4).

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This year, the German Liquid Crystal Society (Deutsche Flüssigkristall-Gesellschaft) has the pleasure of awarding the Saupe prize to Prof. Dr. **Wim H. de Jeu** (RWTH Aachen).

The Saupe Prize will be awarded and the *laudatio* given by Dr. Frank Giesselmann (University of Stuttgart).

The characterization of the interfacial properties of liquid crystals, particularly of liquid crystals against water, can be challenging to undertake with existing techniques due to the reliance of current techniques on additional data about the liquids in contact, typically the densities and/or viscosities, which may be difficult to determine with precision [1–3]. To overcome this major limitation, we present a microfluidic approach based on the production and aspiration of droplets into a channel. Inspired by the technique of micropipette aspiration on living cells to determine membrane tension [4], our technique generates droplets *in situ* and immediately aspirates them, allowing for interfacial tension data to be obtained from a modified Young-Laplace equation by simply observing the radii of the undeformed and the deformed droplet and measuring the applied pressure necessary to induce such a deformation [5], as shown in Figure 1. We demonstrate that this technique can be applied to measure both dynamic and equilibrium interfacial tensions of liquid crystals, allowing for rapid measurement of interfacial tension with a minimum of material and with a high degree of precision.

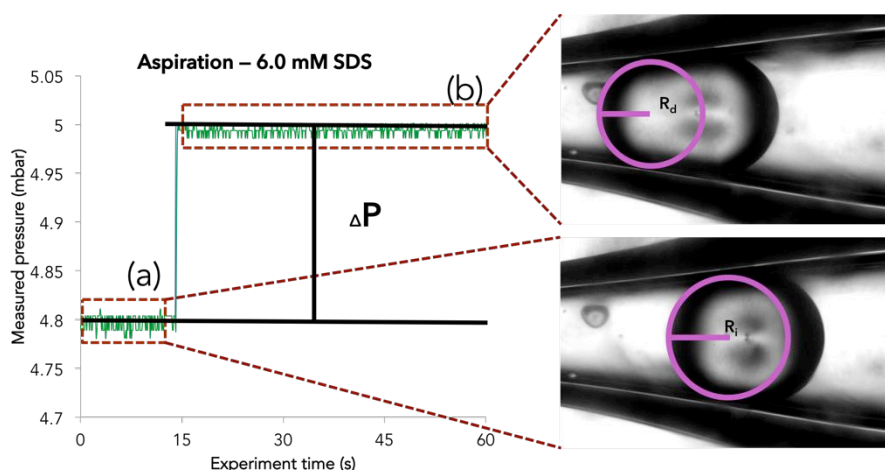


Figure 1: Aspiration of a 5CB droplet in a 6.0 mM SDS (aq) solution. The difference in pressure between the aspirated (b) and unaspirated (a) states, combined with the radii of the corresponding droplets, is used to determine the interfacial tension between the liquids.

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Smectic C* layer buckling and fast electro-optics of a LC confined in anodic aluminium oxide nanochannels

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The ferroelectric liquid crystal 2MBOCBC confined inside the nanochannels of anodic aluminium oxide (AAO) is investigated concerning its structural and electro-optical properties and their change as a function of temperature.[1] The AAO nanochannels of different pore diameters from 20 nm up to 42 nm are coated with a polymer in order to force a tangential alignment of the liquid crystal molecules at the channel walls.

Neutron diffraction experiments reveal a fully reversible, hysteresis-free smectic C* layer buckling towards a chevron-like structure during the temperature course in AAO membranes with 42 nm channel diameter (see Figure 1). This chevron formation is accompanied by a drastic reduction of the linear electro-optic response, as a result of the structural reorganisation of the smectic layers.

The phason relaxation frequency, investigated by electro-optical measurements, is found to be two orders of magnitude higher in the nanoconfinement compared to the bulk liquid crystal. It possesses a temperature behaviour following an Arrhenius law (see Figure 2) and its magnitude varies proportionally to the inverse of the squared channel radius.

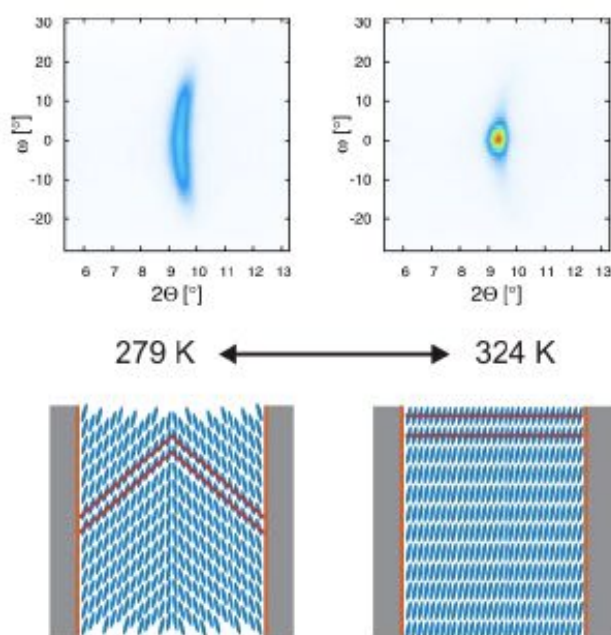


Figure 1: Neutron diffraction data show the reversible formation of a chevron-like smectic layer structure.

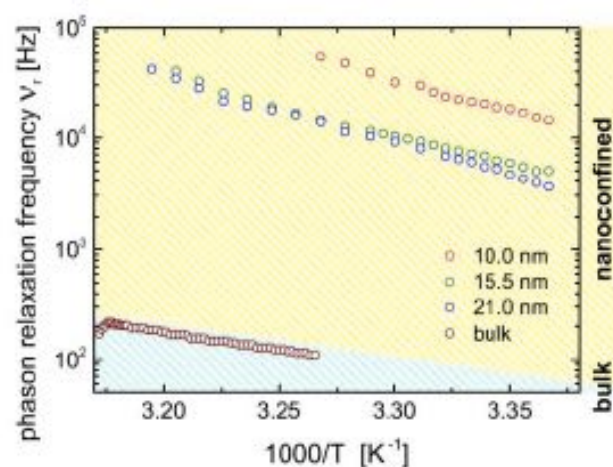


Figure 2: Arrhenius-type temperature behaviour of the phason relaxation frequency of the bulk and the nanoconfined liquid crystal.

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Formation of complex LC phases by catechol based bolapolyphiles

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T-shaped and X-shaped bolapolyphiles are able to form a wide variety of new LC phases, among them various liquid crystalline honeycomb structures with prismatic cells of different shapes ranging from triangular to hexagonal and beyond [1,2]. Recent simulations show that T-shaped bolapolyphiles with a swallow-tail lateral chain can form different cubic phases [3], in agreement with previous experimental evidences[4,5].

Herein we report a new type of catechol based *n*-shaped polyphilic molecules with two linear alkyl or semiperfluorinated chains which are located at the central benzene ring of the *p*-terphenyl based rigid core (Figure 1). The compounds were synthesized, their mesophase behaviour fully characterised by XRD, DSC and polarizing microscopy (POM) and the phase sequences compared with related compound with a single swallow tailed lateral substituent. Depending on the chain length and side chain structure, a series of very different and highly complex LC phases was observed. Besides the polygonal honeycomb phases, either with square, hexagonal or rectangular lattice, two different types of cubic phases, and also correlated lamellar phases were found. The rectangular columnar phase represents a honeycomb composed of octagonal and pentagonal prismatic cells in a ratio 1:2, leading to a tiling pattern resembling that of BIK type zeolites [2]. With longer chains two cubic phases, formed by longitudinal rod-bundles, one with *la3d* lattice (double gyroid) [4], and the other with *Fd3m* lattice were found. The latter is a single diamond phase adding to the previously reported double diamond phase (*Pn3m*) [5]. The lamellar phases occurring besides these new types of *tricontinuous* cubic phases represent layers with the rod-like unit arranged parallel to the layer planes. Thus the overall phase sequence on increasing the lateral chain volume is from polygonal honeycombs via longitudinal rod-bundle networks to longitudinal rod-layers. The correlation between adjacent rod-layers leads to the observed *p2mm* symmetry of the correlated lamellar phases for compounds with alkyl chains and *c2mm* symmetry for compounds with semiperfluorinated chains.

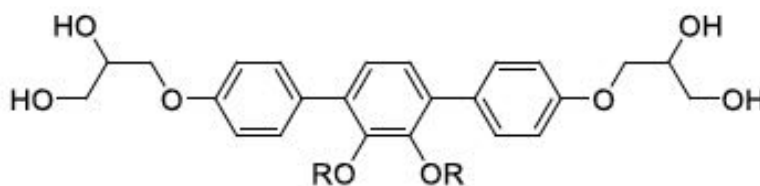


Figure 1: Structure of discussed catechol based bolapolyphiles ($R = C_nH_{2n+1}$ or $(CH_2)_nC_mF_{2m+1}$).

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Posters

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Microfluidic processes have become a popular approach for the fabrication of liquid crystalline elastomer (LCE) actuators. This production in flow, not only enables the production of particles with shapes and morphologies which aren't accessible by other syntheses, but also induces an orientation of the liquid crystalline director in these particles, which gives them a typical mode of actuation [1]. The orientation, which is inalienable for a strong actuation, is caused by the shear rates between a high viscous continuous phase and the droplets of the monomer mixture.

In LCEs the mesogens of a liquid crystal are connected to the slightly crosslinked polymer network of an elastomer and thus combine properties of both materials. Due to their macroscopic deformation during the nematic-to-isotropic phase transition, they are promising candidates for an application as artificial muscles in micro robots. [2]

We recently succeeded in producing more and more complex LCE particles like core-shell and Janus particles by modifying the microfluidic setups.

Here we present the fabrication of photoresponsive particles that change their shape by irradiation. Therefore, we use an azo-group containing LC-monomer and a LC-crosslinker which are polymerized by a VIS-photoinitiator in a microfluidic device. These photo actuating particles show a fast and reversible elongation of up to 24% during irradiation with white light. [3,4] In addition we present the synthesis of LCE tubes with a potential application as micro pipelines. By heating or irradiation of one spot of these tubes, a cross-sectional tapering should be obtained which can move along the tube simultaneously to the trigger and thus enables perfusion of a liquid inside. Currently we work on the fabrication of Janus-particles containing both, a temperature actuating as well as a photo responsive part.

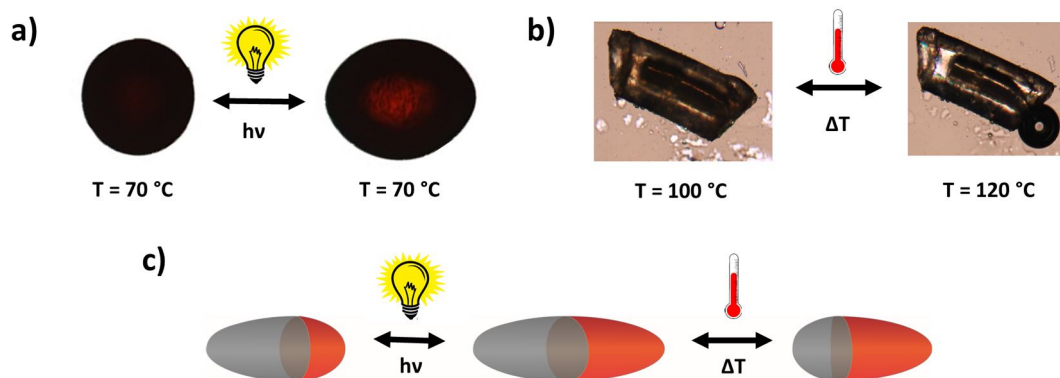


Figure 1: a) Photo actuating particles showing a deformation of 24%; b) a thermo actuating LCE micro tube releasing air during actuation; c) a scheme of a Janus particle responding to light and temperature.

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Liquid crystal elastomers are interesting materials that possess some remarkable features that are of great interest to scientific community and also to the industry. By incorporating some nanomaterial, the liquid crystal elastomers can be further improved.

Polymer nanocomposites are a novel class materials where a small amount of the added nanomaterial drastically changes the overall properties of such material. Incorporating super-paramagnetic nanoparticles into the liquid crystal elastomer matrix, obtained nanocomposite becomes responsive to the external magnetic field. Nanoplatelets in our case were chemically bound into the main-chain liquid crystal elastomer (MLCE). Final crosslinking was done with and without the presence of external magnetic field. The samples that were prepared in the presence of external magnetic field exhibit permanent magnetization which was locked-in during the polymerization process. Samples that were not prepared in the presence of external magnetic field exhibit polydomain structure and their net magnetization is zero.

Chemically coupling super-paramagnetic nanoparticles to the MLCE backbone contributes to some interesting features.

With external magnetic field, one can orient magnetic nanoplatelets inside the MLCE, thus making the whole sample magnetized. The MLCE matrix can accommodate for such changes and the particles remain orientated even without the external magnetic field. By heating the sample above N-I phase transition and below Curie-Weiss temperature the sample reverts magnetization and shape change to the starting conditions.

When exposing such material to the external magnetic fields that are capable of switching the domain orientation in the nanoplatelets we observe magneto elastic effect of 2.5% but the change is not completely reversible.

This mechanism also works in reverse so with mechanical stretching the samples become orientated and magnetized.

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The formation of lyotropic liquid crystalline (LC) phases from rigid-rod objects as a result of anisotropy in form is well understood [1]. Theoretically, anisotropic in form nanoparticles with high aspect ratio can act directly as mesogens to form LC phases. The formation of LC phases requires the mobility at high concentration. Thus, a neat material of highly anisotropic nanometer-sized objects does not usually form LC phases above a certain threshold concentration owing to lack of mobility and a "solubilization" of the nanometer-sized objects is required. The concept of "hairy rods", originally developed for stiff main-chain LCs, is promising [2]. In this model, a stiff insoluble core is solubilized by long alkyl chains (the hairs) on its surface. Our group has already demonstrated the applicability of this concept and the investigation of LC phases for various anisotropic in form nanoparticles [3].

Here, we present the surface functionalization of anisotropic in form ferri-magnetic Fe_3O_4 -nanorods (NRs) with a diblock copolymer, consisting of a PMMA- or PDEGMEMMA- solubilizing block and a dopamine anchor block. The successful surface functionalization of the Fe_3O_4 NRs with the diblock copolymer was monitored using TGA, IR, TEM and SEM measurements. Furthermore, NRs functionalized with polymer exhibit a high dispersibility in organic media, showing the applicability of this functionalization concept.

During solvent evaporation, the anisotropic in form Fe_3O_4 -NRs functionalized with polymer align spontaneously into birefringent domains. The self-assembly into lyotropic LC structures could be observed in PEG 400 as a non-evaporating solvent. Thereby, the anisotropic in form NRs align themselves along a director without the loss of mobility, as observed in POM, TEM and SEM images. Magnetic fields have a strong influence on the LC phases formed. They not only lead to macroscopic orientation, but also to phase separation into highly concentrated LC phases and an isotropic phase, mostly free of NRs. In addition, this alignment can be reversed by demagnetizing the nanoparticles and dispersed NRs without macroscopic orientation are observed again [4].

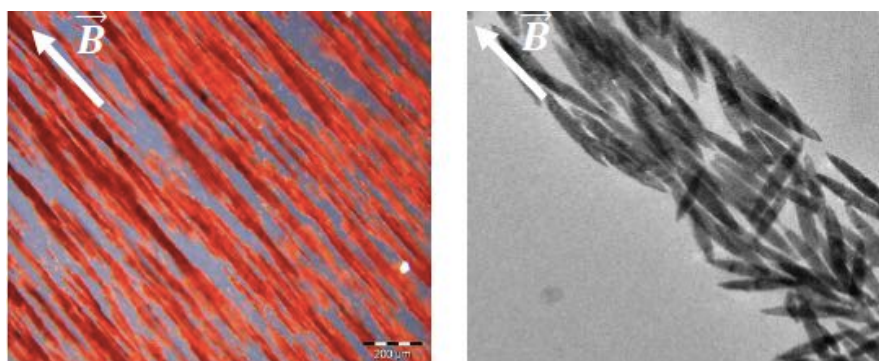


Figure 1: (left) Polarized optical microscope and (right) TEM images showing self-assembly of functionalized Fe_3O_4 -nanorods into wire-like LC structures upon applying an external magnetic field.

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Microfluidic production of liquid crystal elastomer shell actuators

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Liquid crystal elastomer (LCE) actuators are rapidly gaining attention in many applications ranging from biomedical devices [1] to soft robotics [2]. The actuation of LCE is dictated by the alignment of the network and can be triggered by either by electricity [3], heat [4], humidity [5], light [6] or pH [7]. So far, the alignment of the LCE has achieved either in a 2D film shape by surface orientation [8] or 3D objects of sphere or shell shape by shear-induced alignment in microfluidic geometries [9]. Here, in this report, we show the osmosis driven LCE alignment shell actuators produced using glass-based microfluidics. In detail, we use commercially available components such as reactive mesogen RM257 and thiol monomers dissolved in a solvent along with photoinitiator for room temperature LCE precursor shell production. The solvent removal, osmosis driven shell stretching, and the combination of catalyst addition and UV crosslinking steps lead to various ground state aligned LCE shell actuators. This method of synthesizing LCE shells allowed us to realize unconventional LCE shell actuators with ground state director can be tuned from planar, homeotropic with positive birefringence to homeotropic negative birefringence shells.

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Liquid crystal elastomers (LCEs) are elastic solids that have properties of liquid crystals and of a polymer rubber with anisotropic response to various stimuli such as heat or light. An LCE network consists of liquid crystal monomers chemically bonded by a lightly crosslinked network that maintains a predefined molecular orientation. Several methodologies of LCE design and techniques to control molecular orientation with different structures of the main chain and side chain polymer networks have been explored. The main areas of application of LCEs are actuators, artificial muscles, and scaffolds for tissue regeneration along with many more applications [1-2]. Recently, methods such as melt extrusion and wet spinning assisted by a microfluidic set up have been used to obtain oriented LCE fibers [2 and references there in]. There has been significant amount of work done to incorporate liquid crystal into polymer fibers using electrospinning and air-brush techniques [2-4]. Here, we present electrospinning as a robust method to obtain oriented core-sheath fibers with a nematic LCE core and polymer sheath. The core material during spinning is a suitable precursor mixture consisting of reactive mesogen, crosslinking agent, photoinitiator and solvent, and the polymerization/cross-linking is done after fiber formation. The role of two different sheath polymers is studied with respect to degrees of actuation, morphology and optical response using scanning electron microscopy (SEM) and polarizing optical microscopy (POM) measurements.

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Over the last few decades discotic liquid crystals became a continuously expanding field of liquid crystal research. Due to an efficient π -overlap of the rigid cores in columnar phases, discotic LC's are enabled to 1D charge and ion transport in the columnar mesophase, which qualifies them as organic semiconductors, field effect transistors and light emitting diodes [1].

A particularly interesting subclass of discotic LC's are shape-persistent hekates. These star-shaped mesogens consist of three rigid arms attached to the central core. The void between the arms can be filled either by backfolding of the long alkoxy chains [2] or by rotating the neighbouring mesogens along the columnar axis, whereby helices can be formed [3]. Recently, our group published a series of liquid crystalline triphenylbenzenes **1**, where the propeller-like structure led to the formation of triple 61 helices in the columnar hexagonal mesophase [4]. For dendrimeric triphenylbenzenes with bulky lateral groups attached to the core, two different Col_h-phases were observed: one with a helical structure and another with a zick-zack arrangement in the mesophase [5]. In a further approach we enlarged the substituents on the end of the side chains, as shown in Figure 1, to gain further insight in the mesophase arrangements of triphenylbenzenes [6].

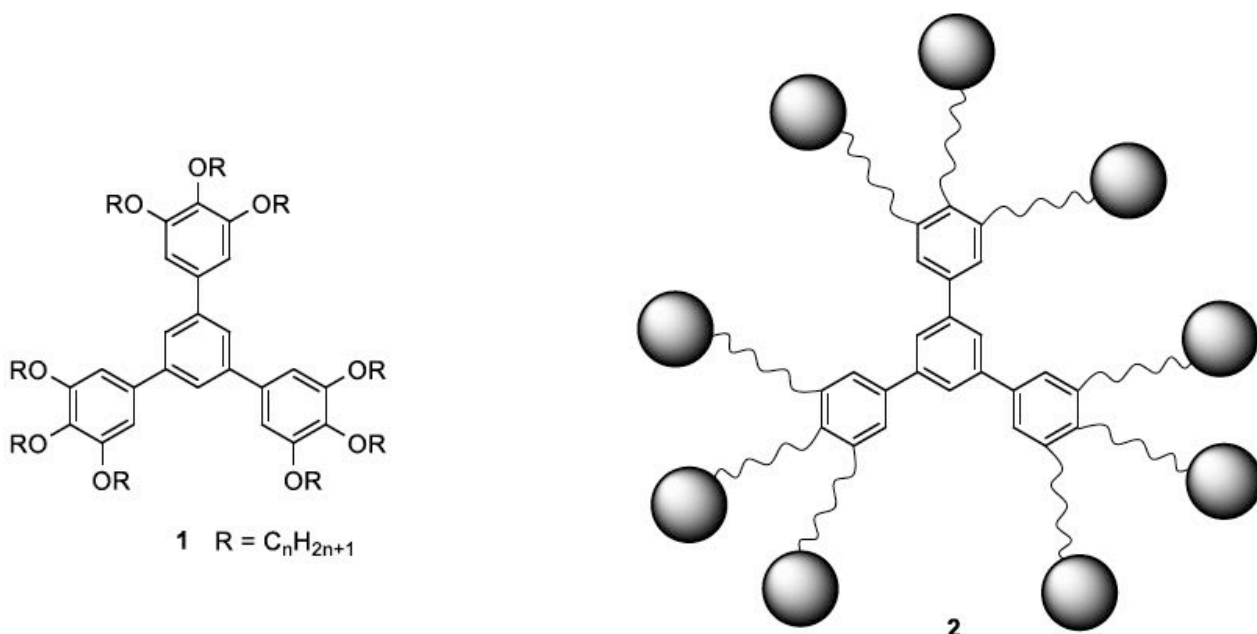


Figure 1: Known helical triphenylbenzene **1** [4] and novel triphenylbenzene **2** with bulky end-groups [6].

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Donor-Acceptor Phthalocyanine-Dyads: The Right Complex LC Nanostructures For Organic Photovoltaics?

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Phthalocyanines are highly interesting substances for the application in organic photovoltaic cells due to their strong absorption in the red- and infrared range and their flat and broad π -system, which allows efficient p-stacking along columnar assemblies.[1,2]

Therefore, it is highly attractive to convert these chromophores to star-shaped mesogens **A1-A3** and fill the intrinsic free space with Fullerenes by simple physical mixing with Fullerene derivate **A4**. The mixture in the right ratio reveals an extraordinary hierarchical self-assembly in a quadruple Helix of Fullerenes.[3] Such nanostructures might become interesting for the application in photovoltaic cells.

In order to optimize the potential for this application, the light sensitive oligo(*p*-phenylenevinylene) units are replaced by oligothiophene units (**B1-B4**), which are already commonly used as good electron donors in organic electronics owing to their fast charge carrier mobility.[4]

Besides the challenging synthetic procedures, the investigation of the highly ordered, liquid-crystalline structures by means of polarized optical microscopy, differential scanning calorimetry and comprehensive X-ray scattering will be presented.

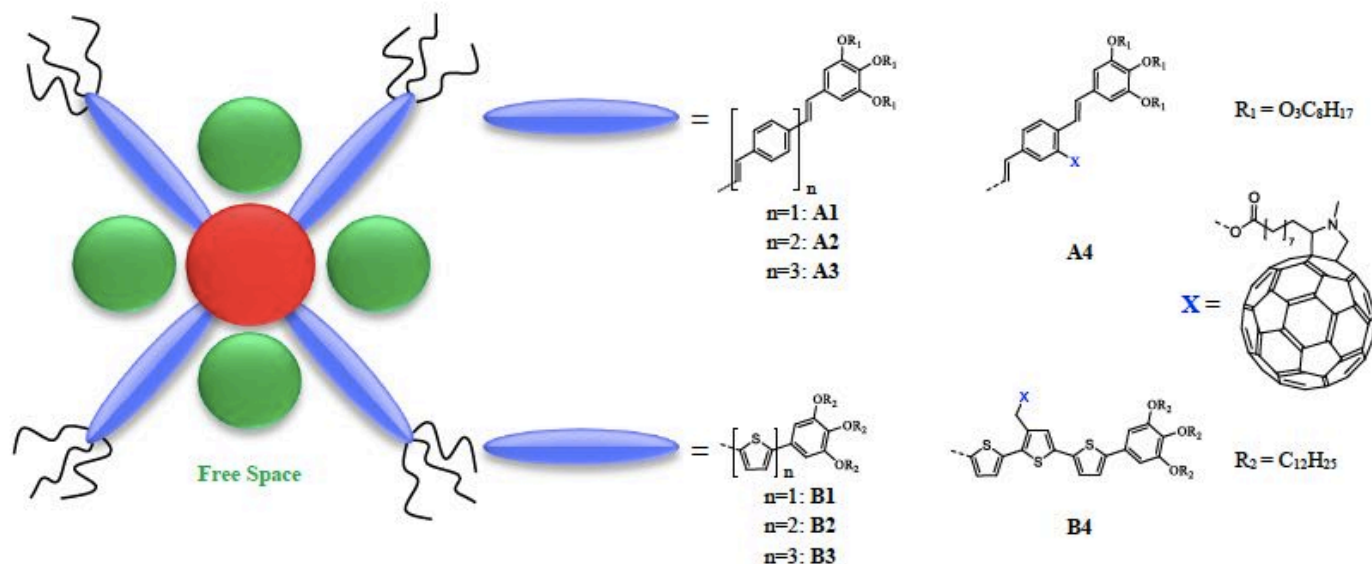


Figure 1: Schematic structure of the star-shaped phthalocyanines **A1-A4** and **B1-B4**.

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The threefold Huisgen reaction[1] of cyanuric chloride and alkoxyphenyl tetrazoles gives tristriazolotriazines **1a-h**, fluorescent p-conjugated molecules. The phenyl rings are tangentially attached to the tristriazolotriazine core, the torsion angles between triazole and phenyl are 12 – 82°, [2] giving a paddle-wheel structure to these discotic molecules. The melting point of triphenyl-TTT is above 300 °C, but two or three alkoxy chains of medium length result in the formation of broad mesophases, typically with a hexagonal columnar structure [3, 4] and often a complex superstructure. [5] Contrary to earlier reports, [3] these DLCs are not thermostable. A rearrangement of the TTT unit occurs in three successive steps, bringing the phenyl substituents from the tangential positions in **1** to radial positions as in **2**. The new *r*-TTT is nearly planar, dihedral angles are 6° or less. The extension of the molecular diameter and the planarization have a huge impact on the thermotropic properties: higher melting points are typical, complete destruction of mesomorphism, but also the transformation of non-mesomorphous *t*-TTTs to discotic liquid crystals have been observed.

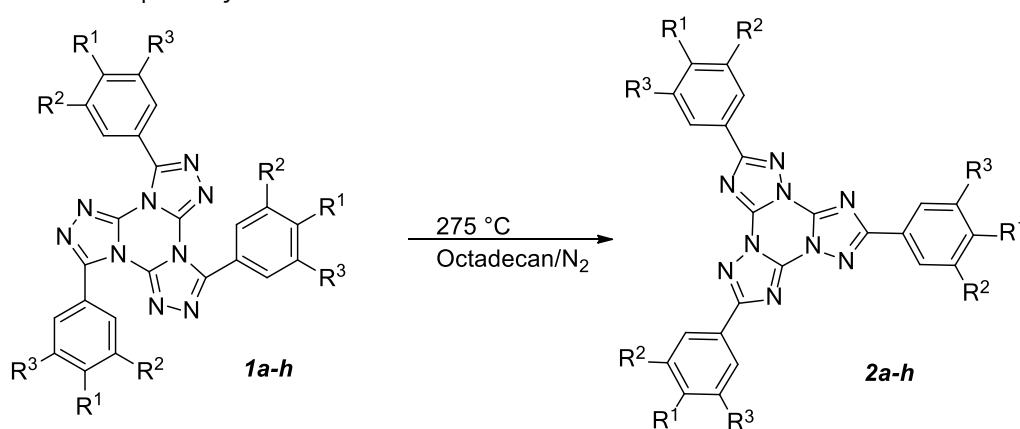


Figure 1: Thermal tangential-radial isomerisation of tristriazolotriazines

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Anthocyanins are the biggest class of water-soluble natural colorants [1]. Due to their hydroxy and alkoxy substituted flavylum backbone they exhibit a pH-depending chemical reaction network of different colored species ranging from bright red in acidic solution to a deep blue in an alkaline environment. Anthocyanidins are promising candidates for dye sensitized solar cells (DSSC) as reported by Grätzel *et al.* [2]. The nearly planar structure with bearing a central ionic group and the property of flavylum salts to form vertical aggregates in solution made us curious if flavylum salt could form liquid crystalline phases.

Here we want to present the first results for the novel alkoxy-substituted flavylum based liquid crystals [3]. We used a modular concept starting from alkoxy substituted aldehydes **1** providing in three further steps both building blocks for the acid cyclisation reaction forming the corresponding flavylum salts. All synthesized derivatives were examined by POM, DSC and X-ray diffraction as well as UV/Vis and fluorescence spectroscopy in solution. A broad variety of mesophases like SmA, Col_r and Col_h. The mesophase widths ranges from 50 K up to over 200 K and one derivative even showed liquid crystallinity at room temperature.

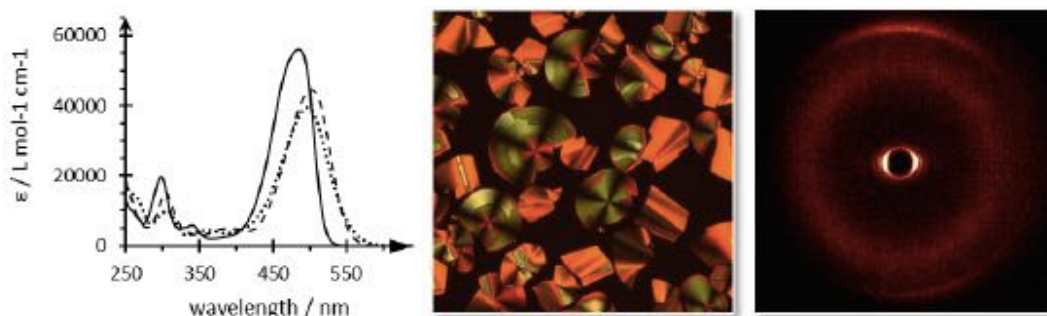


Figure 1: Absorption spectra for different substitution patterns (left) and a typical POM texture and the corresponding diffraction pattern of a Col_{ro} mesophase (middle and right) of synthetic flavylum salts.

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Liquid Crystalline Dithienothiophene Derivatives for Organic Electronics

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Organic semiconductors (OSC) have a high potential for applications on flexible substrates and for low-cost production based on roll-to-roll techniques [1]. In particular, OSCs that are liquid crystals (LC) show a high degree of order in nanofilms, which is beneficial for charge carrier transport. Defects, which appear during the manufacturing process can be removed by heating the nanofilms into the LC phase and slowly cooling them down again. This process is commonly referred to as self-healing [2].

In this study, dithienothiophene derivatives with a bent core (**1**, **2**) were investigated [Figure 1 (a)]. Their LC properties were characterized via polarized optical microscopy, differential scanning calorimetry and small angle x-ray scattering. UV-vis spectroscopy, fluorescence spectroscopy and cyclic voltammetry were used to elucidate the band gap, Stokes-shift, and the HOMO/LUMO-energies. The performance of organic light emitting diodes (OLED) with a perylene derivative as emitter material [Figure 1 (b)] indicate that compounds **1** and **2** are viable hole transporting materials. One of these OLEDs and its electroluminescence spectrum are shown in Figure 1 (c). Their current versus voltage and luminance versus voltage characteristics are comparable with earlier studied OLEDs, which contained TPD as a hole transporting layer [3].

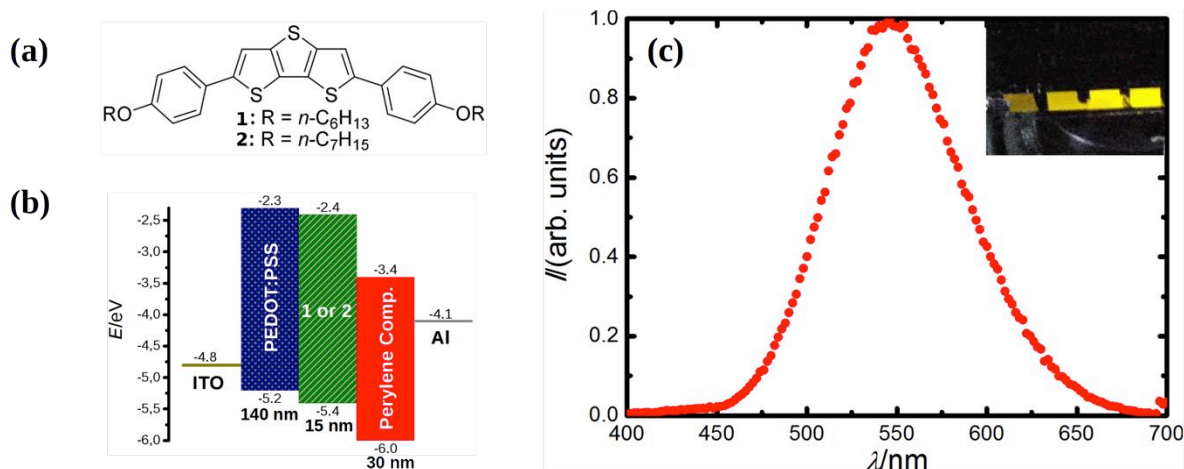


Figure 1: (a) Chemical structure of the studied compounds. (b) Relevant energy levels, layer sequence and thickness of the studied OLEDs. (c) Electroluminescence spectrum of an OLED (inset: image of working device).

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Structure and electro-optic behaviour of non-symmetric azobenzene-based bent-core ferroelectrics

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Azobenzene-based liquid crystalline materials, exhibiting reversible trans/cis isomerization upon irradiation with light can be used for many applications in diverse fields, such as flat panel displays, photonics, and photodriven devices [1, 2]. Therefore, combining the ferroelectric LCs phases formed by BCLCs and the photoswitchable nature of the azobenzene units could lead to potential new multifunctional materials in which the polar response can be modified with light. For this reason, azobenzene-based BCLCs attracted the attention of many researchers in recent years. 4-cyanoresorcinol-based bent-core liquid crystals are distinguished for their formation of switchable orthogonal phases [3,4]. In our research, a new class of non-symmetric BCLCs derived from 4-cyanoresorcinol central core connected to non-symmetric rod-like wings was designed. These compounds exhibit a high temperature SmA phase followed by a series of random- and switchable tilted antiferroelectric phases. It appears that with increasing the chain lengths a paraelectric phase is formed first with small polar domains which increase in size with decreasing temperature then changes to the antiferroelectric switching phases. In particular, we demonstrate a complex optical switching behaviour where an analog V-switching observed at low voltages and a threshold behaviour at higher fields. The polar switching characteristics and the dielectric properties of the materials were studied using non-linear optics and dielectric spectroscopy.

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The self-assembly of shape-persistent star mesogen **1** (Figure) has been recently shown to be tunable by guest molecules, which fill the void space between the oligo(*p*-phenylenevinylene) arms [1,2]. Thereby the mesogens with bound "pseudo" guests (**2a-c**) reveal the highest mesophase stability, since the guests cannot escape from the intrinsic cavity.[2] This prompted us to study the impact of guests, which will not naturally incorporate by supramolecular interactions. Therefore, we synthesized mesogens **3a-d** with oligopeptide building blocks. With these hybrid materials, we aim to control the nanostructure of a segmented LC column. The synthesis of these new materials will be presented. The mesophase properties as a function of the peptide size and structure are studied by means of polarized optical microscopy, differential scanning calorimetry and x-ray diffraction.

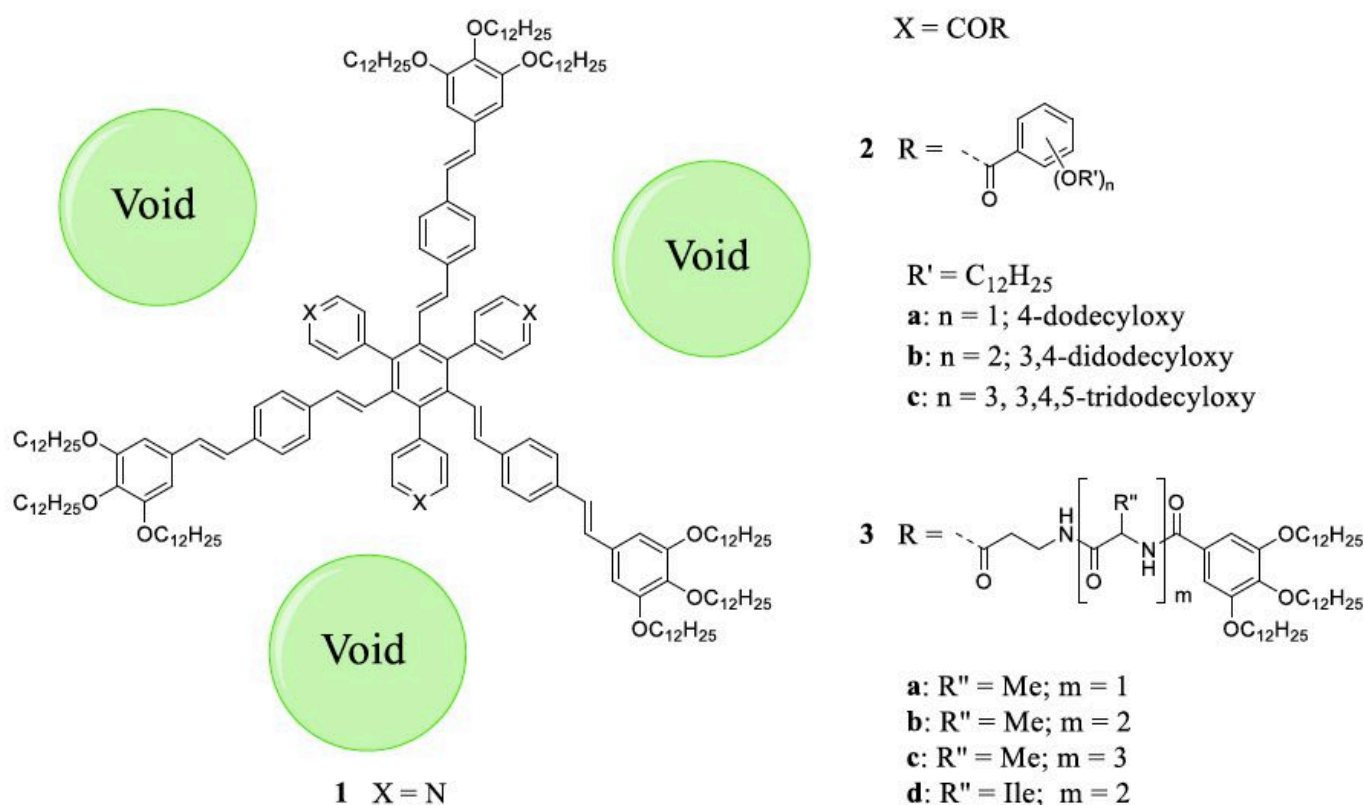


Figure 1: New hybrid Peptide/OPV star mesogens.

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In the recent years, molecular photoswitches have gained much attention due to their wide range of possible applications in material sciences. For instance, photoswitchable thermotropic liquid crystals could be used as optical storage devices [1, 2]. A simple light induced change of molecular structure can have dramatic effects on properties of the material. Most notably, the change of the order parameter of the material can result in a phase transition. Both increase and decrease in the order parameter were observed with various phase transitions [3]. Several photoswitches have already been used, such as azobenzenes [2, 4], naphthopyrans [3] and spiropyrans [5, 6, 7].

Spiropyran moiety can be converted into a zwitterionic merocyanine dye using UV irradiation, while the reverse reaction requires visible light irradiation or heating. The change of the order parameter during photoswitching is anticipated to be significant since the spiropyran form can be described as two planar aromatic rings perpendicular to each other, while the whole system is planar in the merocyanine form.

The aim of this work is to systematically study the effect of spiropyran substitution and photoswitching on the mesomorphic properties. In order to achieve this, several molecules were designed (Figure 1). **R**₁ substituents were designed as promesogenic groups inducing liquid crystallinity, while **R**₂ groups are different electron withdrawing groups which stabilize the merocyanine form of the material and facilitate the photoswitching process.

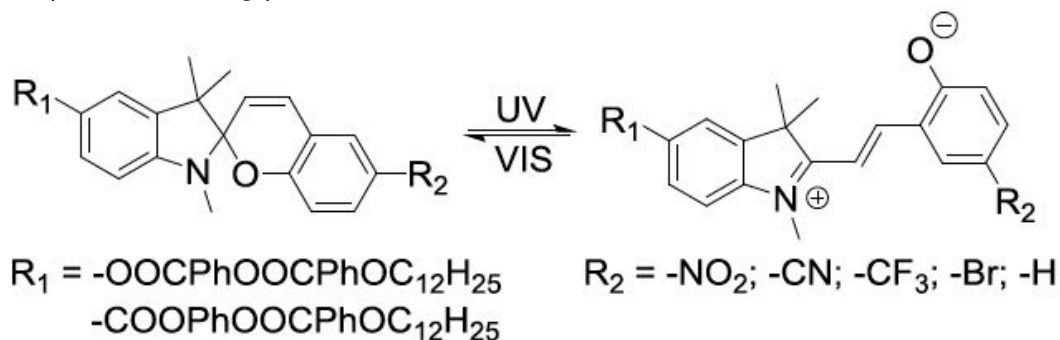


Figure 1: Designed materials and photoswitching.

Acknowledgement

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Towards the Synthesis of Hybrid Mesogens with a Fluorinated Azobenzene-Core and Oligopeptide Tails

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Azobenzene containing liquid-crystalline elastomers have recently attracted an enormous interest owing to their application as actuators, i.e. artificial muscles.[1,2] Although linear polymers have been successfully studied,[2] supramolecular polymers were not investigated so far. Therefore, we aim the synthesis of linear azobenzenes **1** and **2** (Figure) with two oligopeptide sequences attached to either of the two termini via aliphatic spacers. Similar structures with only one peptide building block are already known to form stimuli-responsive hydrogels [3].

We assume that the hydrogen bonding network of **1** and **2** may lead to new hydrogels and lyotropic liquid crystals. The synthesis of the new target compounds will be presented. Their supramolecular properties are studied by polarized optical microscopy, Differential scanning calorimetry and X-ray scattering.

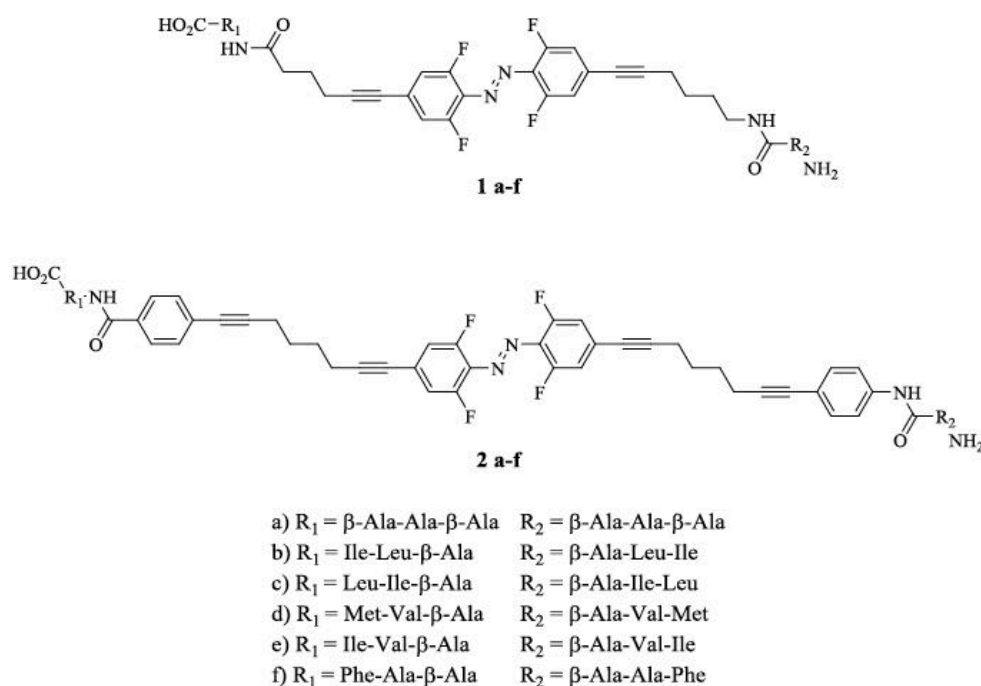


Figure 1: Various Azobenzene-Peptide Target Structures

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Over the last few decades, the field of discotic liquid crystals have been studied intensively. To find specific application possibilities in electronics (e.g. air-stable semi-conductors) and optoelectronics (e.g. organic light-emitting devices, photovoltaic devices), it is important to tailor the self-assembly behaviour. [1] Columnar crown ethers provide a variety of opportunities to design the chemical and physical properties by the choice of peripheral units, ring sizes, counterions and side chain lengths. To modify the peripheral units the introduction of heteroatoms is an easy way. Due to the interesting properties of sulfur-containing organic compounds in electronic and optoelectronic organic devices the introduction of sulfur atoms to the side chains offers the possibility of promising results. [2]

We synthesized and investigated liquid crystalline crown ethers with *ortho*-terphenyl groups as mesogenic sub units. [3] We studied the effects of side-chain polarity, chain length, core crown size, and the use of metal salt ion pairs on the mesomorphic properties. Recently, we examined the influence of the sulfur atoms within the side chain on the mesomorphic behaviour. Crown ethers with sulfur substituted side chains were prepared and studied by polarised optical microscopy (POM), differential scanning calorimetry (DSC), and small- and wide-angle X-ray diffraction (SAXS/WAXS) and compared with the known crown ethers carrying only alkoxy side chains. The synthesized compounds showed liquid crystalline properties at room temperature and the temperature range of the liquid crystalline phase was increased. [4]

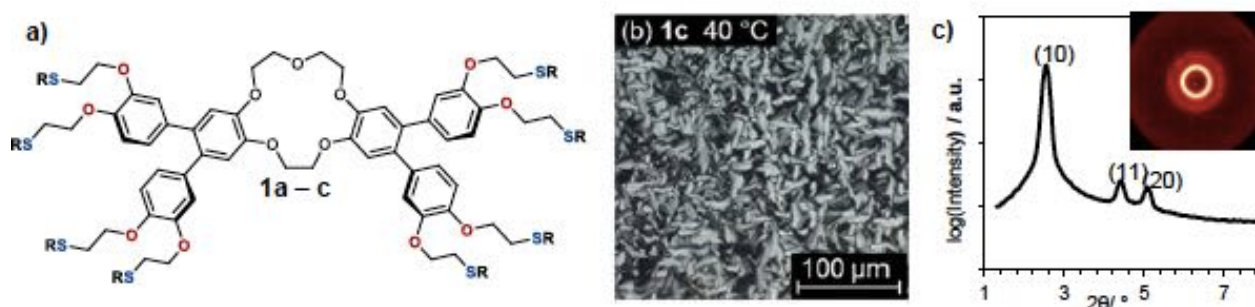


Figure 1: a) chemical structure of crown ethers with sulfur substituted side chains; b) focal conic texture of **1c** at 40°C (cooling rate 10 K min⁻¹, magnification '200); c) Characteristic SAXS profile and SAXS diffraction pattern (inlay) of **1c**. [4]

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Synthesis, Optical and Thermotropic Properties of Tetrakis(oxadiazolylphenyl)pyrazines TOPPs

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Four-armed liquid crystalline pyrazines are rarely studied. [1] We report new discotic pyrazines with broad mesophases showing the characteristic textures of a columnar arrangement observed by polarisation optical microscopy.

Cyclisation of 4,4'-bis(methoxycarbonyl)benzoine with ammonium acetate followed by oxidation with iodine leads to 2,3,5,6-tetraphenylpyrazines. [2] Those pyrazine centered π -systems were enlarged by additional Huisgen[3] reaction which leads to mesomorphic alkoxyaryl-substituted 2,3,5,6-tetrakis-(4-(1,3,4-oxadiazol-2-yl)phenyl)pyrazines (TOPP). Majority of prepared TOPPs containing 3,4-alkoxyphenyl-substitutes. Furthermore 3,4,5- trialkoxyphenyl-substituted derivatives were synthesized and studied. Additionally biphenylene and naphtalene were insert in TOPPs to increase the aromatic system.

Characterization has been done by NMR-, IR- and mass spectroscopy. Liquid crystalline behavior has been studied via polarization microscopy and differential scanning calorimetry. Further investigations were done by optical spectroscopy, single crystal X-ray scattering, wide- and small-angle X-ray scattering on orientated fibers.

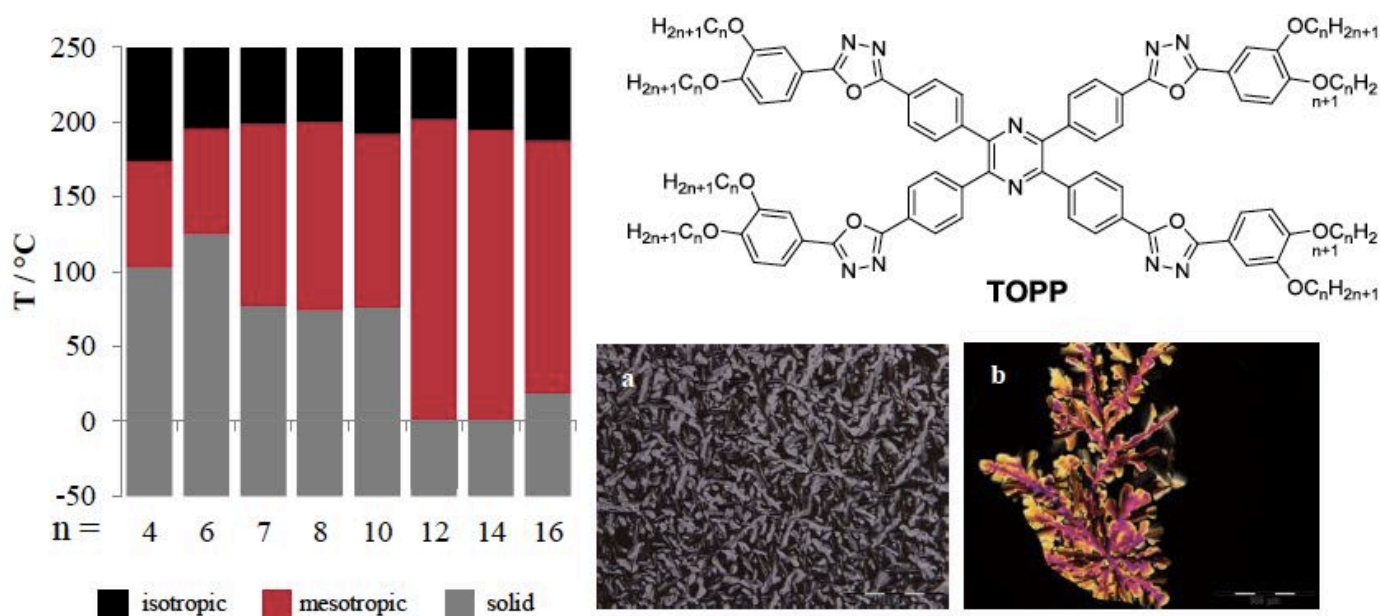


Figure 1: left: aggregate state of TOPPs with various n -alkylchains. right: textures (POM) a) tetradecyl substitution (203°C , 1K/min) b) hexadecyl substitution (234°C , 5K/min)

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Confinement-enhanced chiral induction in lyotropic liquid crystals

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Recently the phenomenon of spontaneous chiral symmetry breaking under capillary confinement was reported for chromonic liquid crystals [1] and for a classical micellar lyotropic liquid crystal [2]. The appearance of chiral symmetry broken configurations (twisted-escaped radial (TER) and twisted polar (TP)) was attributed to the twist elastic modulus which is known to be unusually small in the case of chromonic liquid crystals. Strong splay and/or bend deformation can energetically escape into twisting which leads to equilibrium helical structures. Hence, these systems are quite sensitive towards chiral perturbations.

We have studied the lyotropic system in [2] consisting of disc-shaped micelles formed by *N,N*-dimethyl-*N*-ethyl-hexadecylammoniumbromide in water with 1-decanol as co-surfactant. In the achiral case the volume fractions of left- and right-handed TP domains are balanced (50:50). When for example adding a small amount of (*R*)-mandelic acid as chiral dopant the left handed domains grow on the expense of the right handed ones. Already after adding a minute amount of 0.03 Mol-% of (*R*)-mandelic acid (one out of 3000 molecules is chiral) the whole macroscopic sample, on a centimetre length-scale, is driven into homochirality (Fig.1). Thus, the TP configuration, characterized by a double helix of two half unit twist disclination lines, provides a highly sensitive system to observe chiral amplification in lyotropic liquid crystals.

This could be regarded as a prime example of a confinement-enhanced sergeant and soldiers effect and opens new possibilities in chirality detection and sensing.

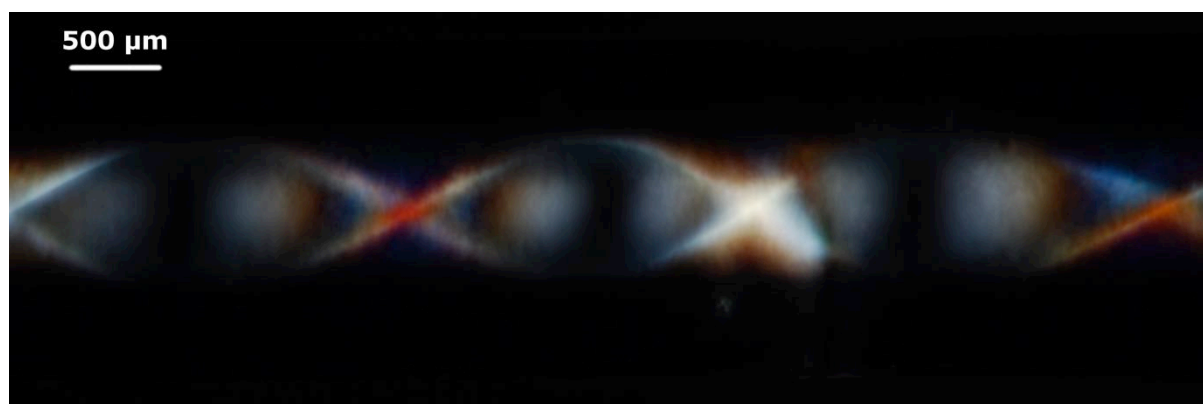


Figure 1: POM image of the homochiral twisted polar configuration of the host phase doped with 0.03 Mol-% of (*R*)-mandelic acid.

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Interface tensions of liquids in water play a dominant role in microfluidics, they determine deformations of micro-droplets and their relaxation, droplet coalescence and pinch-off, the rupture of thin films, capillary forces and various other static and dynamic features of multiphase systems. During the last decade, microfluidic methods have been extensively applied to liquid-crystalline materials, e.g. in the production of LC droplets and shells.

Whereas surface tensions of LC materials to air have been studied quite extensively, very little is known about LC interface tensions to other fluids. Such measurements are complicated, e.g., by the small density difference of LCs to aqueous environments or by long equilibration times. Consequently, only an order of magnitude is known.

We introduce a new, simple and accurate method to measure the interface tension of smectics to a surrounding fluid. The only prerequisite is the possibility to prepare a stable smectic bubble. We employ the buoyancy of an air bubble trapped underneath the film to deform the smectic bubble to a Delaunay surface. The measurement of few simple geometric quantities near the contact line is sufficient for an explicit calculation of the smectic interface tension. We will apply our method to measurements of the static and dynamic interface tensions of a mixture of phenylpyrimidines to ionic surfactant solutions of different concentrations.

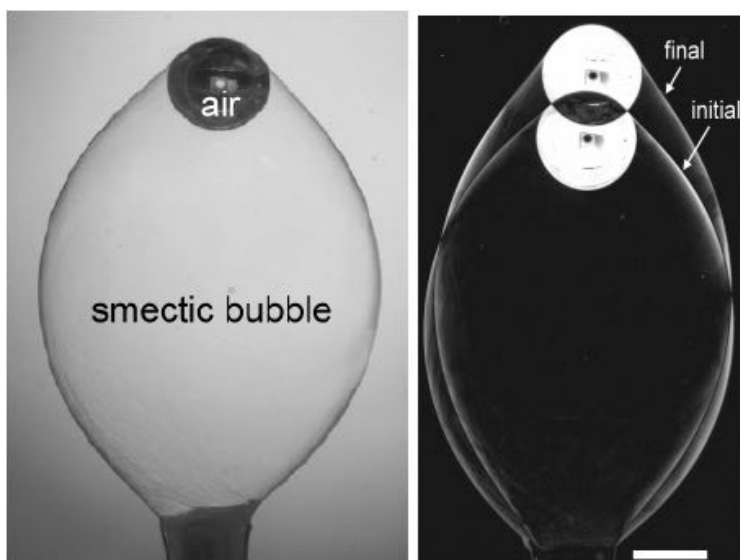


Figure 1: Left: Smectic bubble submerged in a surfactant solution, a small air bubble is trapped underneath the smectic film. Right: Difference image between initial and final bubble shapes during a measurement of the dynamic interface tension of an unsaturated surfactant solution.

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It is now known that certain liquid crystal phases, namely the ferroelectric SmC_sP_f (B7) phase formed by certain bent-core liquid crystals (BLCs), are capable of spontaneously forming stable microfibers under uniaxial extension [1,2]. These fibers, which possess a complex, layered structure, are capable of suppressing the Rayleigh-Plateau instability by means of a smectic layer compression modulus [3]. Previous studies focused on measuring the static tension of both single fibers and fiber bundles to better understand their structure and stability [4]. However, their dynamic properties were not investigated in detail until a recent publication reported on their rupture and recoil behavior [5].

For the present work, a modified force sensing technique using specially designed glass capillaries, piezo positioning, a custom heat stage and specialized imaging and control software was developed and assembled into a compact extensional rheometer. Experiments to investigate the strain- and strain-rate dependent stress response and the induced structural (phase) changes of these fibers are conducted alongside theoretical work to develop a viscoelastic model. With an improved understanding of the interplay between the fluid and elastic properties of these fibers, we hope to exploit their complex internal geometry to achieve actuation in the form of controlled length contraction and dilation in the presence of external fields. In addition, polymer stabilization and the use of BLCs containing an azo group to enhance the stability and actuation behavior under UV irradiation, respectively, are being investigated. We expect that such soft, self-healing fiber actuators will provide a key advancement in the fields of robotics, biomedical and cybernetic engineering.

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Measuring the anchoring energy of nematic liquid crystal on carbon nanotubes: a nontrivial problem

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Carbon nanotubes (CNTs) sheets pulled from suitable vertically-grown forests can be employed as multifunctional layers for liquid crystals (LCs) [1], [2]. These sheets can be used for applying an electric field to reorient LC molecules due to their excellent electrical properties and, at the same time, for promoting LC alignment [3]. The abilities to align and switch the LC are key properties for a successful implementation of new materials in display technology. Achieving this would allow to abandon the expensive indium tin oxide (ITO), and focus on future developments in flexible and fast switching displays.

Understanding the interaction between the liquid crystal and the CNTs sheet is an important task since the LC anchoring strength influences the LC behavior and, in particular, the switching performance. In this work, we investigate the switching behavior of the LC in an in-plane switching configuration for the evaluation of the anchoring energy. Special cells are made with the glass substrate coated with in-plane electrodes having the CNT sheets on top and with the LC in contact with the CNTs. Between the CNT sheets and the electrodes, we introduce a thin polymer layer to insulate the CNTs from the electrodes and to achieve a good adhesion of the sheets onto the substrates. LC align planarly on the surface of CNTs and along the CNT orientation; thus, changes in the orientational order parameter of the CNT sheets can be expected to affect the alignment of the LC. In order to monitor the CNT sheet alignment, we have measured the anisotropic absorption of the CNT sheets, deriving the order parameter that turns out to vary according to the choice of the polymer used underneath the CNT sheet [4].

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Over the past few decades, research into the use of thermotropic liquid crystal (LC) films as sensors [1,2] has attracted significant interest worldwide. Here, we investigate the sensitivity and stability characteristics of thermotropic LC films (that respond by transitioning from hybrid to homeotropic alignment) used in sensing applications [3]. We particularly focus on gaining a better understanding of the following effects that may occur during LC sensing using aqueous solutions with unknown composition [4]:

- Influence of co-solutes, such as glycine (Gly) (see Figure 1)
- Effect of pH of aqueous solutions of sodium dodecyl sulfate (SDS) on LC films
- Importance of hydrophilic-lipophilic balance (HLB) of SDS or Triton X-100 in LC sensing

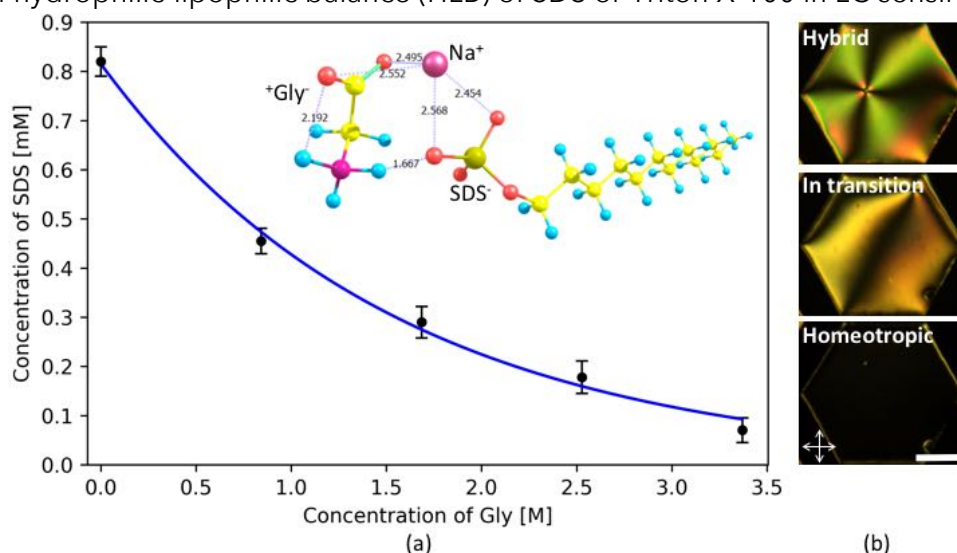


Figure 1: Increasing the sensitivity of thermotropic liquid crystal sensor towards surface-active molecules by adding amino acids to aqueous solutions:

a) The exponential fitted curve to the experimental data on the graph characterizes the response of the 5CB nematic film to SDS surfactant molecules in presence of a sensitivity adjusting co-solute (here, glycine). The optimized structure of an $\text{SDS}^- \text{Gly}^+$ complex obtained from quantum chemical simulation is shown in the inset above the curve.

b) Visualisation (from top to bottom) of hybrid to homeotropic transition of thermotropic LC films. Arrows represent the crossed linear polarizers. The scale bar represents 25 μm.

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There is an increasing demand for low-power and cost-efficient sensor elements for the detection of gaseous emissions e.g. of smoldering fires in an early stage, of drugs as well as of homemade explosives. Available devices are typically not inherently specific and require some sophisticated measurement setup. The here presented approach uses the optical properties of chiral-nematic liquid crystals (N*). The actual reaction state is thereby transduced to an optical signal which can be monitored either by an electronic system or, in some applications, even by naked eye.

Using N* to detect volatile substances is not a completely new approach [1]. There are different mechanisms for the detection of volatile compounds using liquid crystals. One is a phase transition into the isotropic state of a nematic liquid crystal when it comes in contact with the analyte. A second one is a blue- or red-shift of the selectively reflected wavelength caused by a solvating process of the analyte in a N*. The mechanism used in this work is a chemical reaction of the dopant with the analyte causing a change in the dopant's helical twisting power (HTP), like published by Han et al. [2]. A wide range of commercially available dopants and nematics enables to customize different N* for a selective detection of gaseous analytes. However, there are some drawbacks, which prevent further utilization in practical sensing elements. Two of these issues, namely the protection of the liquid crystals from mechanical or environmental influences and the choice of suitable dopants, will be discussed. In order to make these sensors more applicable and more resistant, the N* is encapsulated in a polymer fiber via coaxial electrospinning like suggested by Kim et al. [3] One of the main challenges will be the use of non-water soluble polymers for the spinning process and avoiding an immediate mixing of the sheath and core material at the same time.

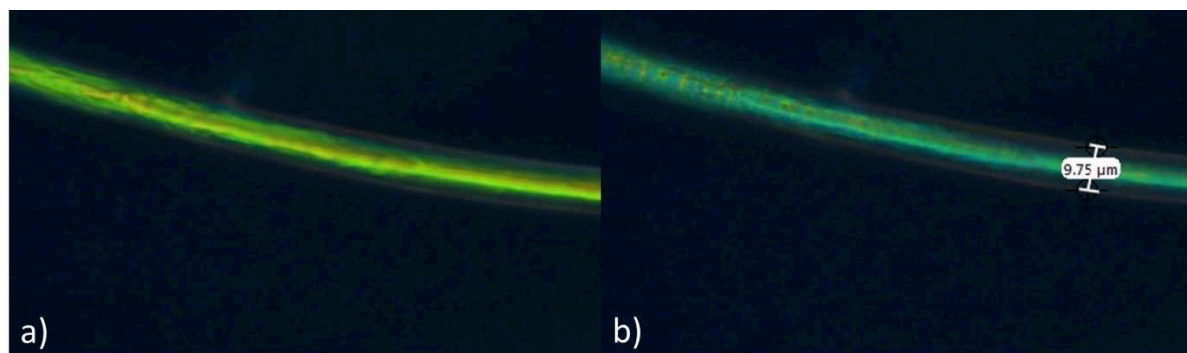


Figure 3: Polyvinylpyrrolidone (PVP) fiber filled with doped E7 a) before and b) after reaction with CO₂.

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The columnar phases of discotic liquid crystals are well known as one dimensional (1D) organic semiconductors. Since the 1D electronic charge transport along the columns is highly sensitive to structural defects, the control of alignment and defect density is a major challenge in the application of columnar LC semiconductors. More recently, the semiconducting properties of smectic liquid crystals received more and more attention. Since higher ordered smectics have the ability to transport charges in the two dimensions along the smectic layers, they avoid many problems of the 1D charge transport in columnar phases [1]. Confining higher ordered smectics in cylindrical nanopores of inorganic templates, such as alumina or silica, might be a promising way to get a stable and reproducible alignment of smectic layers for semiconductor applications (Figure 1a).

We now report a first study of the alignment of the higher ordered smectic liquid crystal 5,5''-dioctyl-2,2':5',2''-terthiophene with tilted liquid crystalline SmC, SmF and G phases [2]. The commercially available alumina membranes were fabricated with straight cylindrical pores of 170 nm in diameter and 50 μm in length [3]. The nanoporous alumina membranes were filled with the higher ordered smectic liquid crystal in the isotropic phase by capillary action. Temperature dependent 2D X-ray diffraction measurements with the primary beam along the linear pores revealed high quality radial alignment of the smectic layers suggesting homeotropic anchoring at the pore walls in all smectic phases (Figure 1b, exemplary shown for SmF). The electric conductivity across the membranes was analysed by impedance spectroscopy. Based on these results we could show that cylindrical nanoconfinement is a reliable method to achieve stable alignment of higher ordered smectic liquid crystals for semiconductor applications.

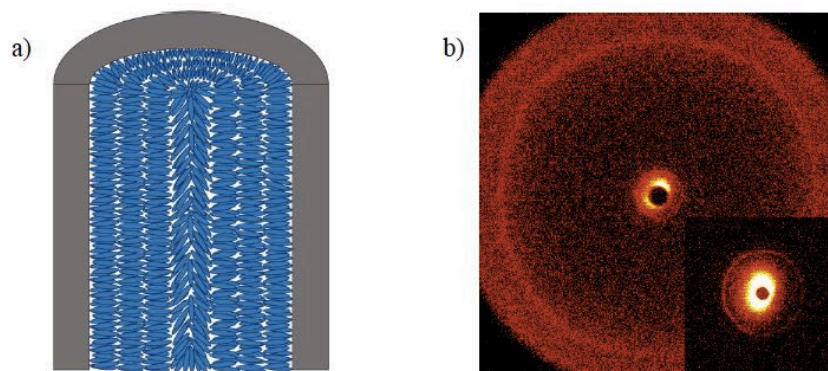


Figure 1: a) Schematic drawing of a cylindrical pore filled with a smectic liquid crystal with radial alignment and homeotropic anchoring. b) 2D X-ray diffraction pattern of the SmF phase, where the incident X-ray beam is parallel to the pore axis (inlay: enlarged view of the small angle region).

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A cholesterol biosensor was fabricated by coating 4-cyano-4'-pentylbiphenyl (5CB) in a transmission electron microscope (TEM) grid with poly(acrylic acid-b-4-cyano-4'-undecyl acrylate) (PAA-b-LCP), followed by co-immobilization of cholesterol oxidase (or glucose oxidase) and horseradish peroxidase on the PAA brushes. [1, 2] This TEM grid sensor was tested for stability and sensitivity of the immobilized enzymes to cholesterol (or glucose). Cholesterol (or glucose) was detected by a planar-to-homeotropic orientational change of 5CB at a limit of 0.8 mM (0.002 mM for glucose). The high stability, ease of preparation, and specific detection of cholesterol in a complex mixture, could provide a new and convenient method for screening cholesterol levels in a sample using a polarized optical microscope.

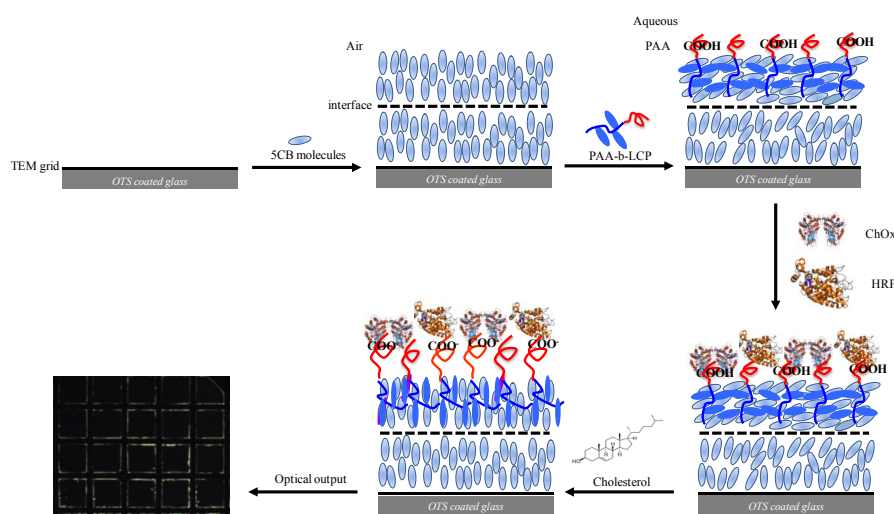


Figure 1: Responsive Polymer and Enzyme Based Method.

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Effect of relative humidity on the formation of cellulose nanocrystal films from evaporating sessile drops

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Cellulose nanocrystals (CNC) are rod-shaped nanoparticles formed by the acid hydrolysis of cellulose-rich materials like wood. From a materials science viewpoint, CNC constitute an attractive yet sustainable biomaterial, due to its exceptional mechanical and optical properties. From a fundamental point of view, aqueous CNC suspensions are fascinating because they form a chiral nematic phase above a critical concentration. The scientific and practical interests intersect in the case of films produced by drying CNC suspensions. The director helical alignment is preserved during water loss, however the pitch is shifted to sub-micrometer values. Therefore, the films display iridescence, as impinging white light is selectively reflected [1].

Even though CNC films hold great promise for utilizing them in photonic applications, controlling their optical features has turned out to be complicated. A plethora of parameters have been identified to impact the morphology and thus the optical properties of dry CNC films. Nevertheless, in almost all reports, the effects of those parameters have only been addressed by exploring the dry films [2]. Here, we focus on the poorly understood influence of relative humidity (*RH*) on the formation of films from evaporating sessile drops of CNC suspensions. We employ a combination of microscopy techniques to study the behavior of isotropic drops during drying at two extreme evaporation conditions, fast and slow drying. In particular, we utilize Laser Scanning Confocal Microscopy in drops containing a small amount of fluorescent microparticles to uncover the hydrodynamic flow patterns during drying. In parallel, Polarized Optical Microscopy is used to reveal the emergence of an anisotropic phase, as a result of the CNC concentration increase due to the water evaporation.

Our observations help us link the hydrodynamic flows and the kinetic arrest that occur during drop evaporation, to the final morphology and the photonic properties of the dry CNC deposits. We hypothesize this link is a key element for an in-depth understanding of the film formation process, which is a prerequisite for designing films with tailored optical response.

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Softening of the magnetic Fréederiksz transition in LC dispersions of magnetic nanoparticles

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Ferronematics, dispersions of magnetic nanoparticles in a nematic liquid crystal, have been intensively investigated in recent years. Such dispersions exhibit superparanematic behaviour which affects the configuration of the director field in the liquid crystal. In our study, we investigate the magnetic Fréederiksz transition in the dispersions of 15 nm CoFe₂O₄ nanoparticles and α -Fe₂O₃ spindles (60 nm width and 350 nm length) in 5CB. We demonstrate the “weak ferronematic” response, that is the Fréederiksz transition exhibits a pre-transitional reorientation of the mesogens which softens the transition. This softening is not related to the pretilt or anchoring at the substrate but it is directly related to the magnetization-director coupling. The experimental results can be explained by extending the model of Burylov and Raikher of ferronematics modified by D’Alessandro et al [1 - 3]. In this model, the quadratic coupling between the magnetic **m** and the nematic directors **n** is introduced together the pairwise couplings of the external magnetic field **H** to **n** and **m**. The resulting model exhibits a low-field plateau in the field dependence of the director deflection angle which is dependent on the coupling coefficient Ω . The values of the coupling coefficients as well as their dependences on the concentration of the magnetic nanoparticles are estimated from the experimental data.

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Gelation of Cellulose Nanocrystals Suspensions: Effect of Counterions

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Cellulose nanocrystals (CNCs), nanorods typically produced by acid hydrolysis of cellulose fibers, are emerging as a new class of functional material [1]. The intriguing ability of CNC to self-organize into a cholesteric liquid crystal phase, with a helical arrangement of the nanorods, is attracting substantial interest across different research fields. This, in combination with excellent mechanical properties, optical transparency, ease of chemical functionalization, and ability to form liquid crystal phases, renders them very attractive for the preparation of high-performance materials [2].

The isotropic-to-chiral nematic equilibrium is sensitive to the nature of the counterions present in the suspension [3], without having a significant effect on the CNC concentration at which gelation is reached. In this work we show the influence of different inorganic counterions on the onset of gelation as well as the chiral ordered phases formed above critical concentrations.

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Linear Self-Assembly of Nanoparticles Within Liquid Crystal Defect Arrays

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We represent investigation on composite films of gold nanoparticles (NPs)/liquid crystal (LC) defects as a model system to understand the key parameters, which allow for an accurate control of NP anisotropic selfassemblies using soft templates [1]. We combined spectrophotometry, with calculations of dipole coupling models and soft sphere interactions. We demonstrate that dense arrays of elementary edge dislocations can strongly localize small NPs along the defect cores, resulting in formation of parallel chains of NPs. Furthermore, we show that within the dislocation cores the inter-NP distances can be tuned. This phenomenon appears to be driven by the competition between “soft (nano)sphere” attraction and LC-induced repulsion. We evidence three extreme regimes controlled by the NPs density: (i) at low density, NPs form chains parallel to oily streak; (ii) intermediate density, leading to formation of ruban of NPs; (iii) high density, formation of monolayer of NPs. The templating of NPs by topological defects, beyond the technological inquiries, may enable creation, investigation, and manipulation of unique collective features for a wide range of nanomaterials.

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Investigation of the electrical resistance of carbon nanotubes sheets in liquid crystals

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Carbon nanotubes (CNTs) are highly electrically conductive and anisotropic nanoparticles that, when physically connected, form networks themselves conductive but at macroscopic scale. Liquid crystals can impose orientational order on isolated CNTs but they can even impose some degree of orientational order onto networks of nanotubes. In order to explore the properties of CNT networks embedded in LCs we present here investigations of the electrical properties of aligned CNT networks. Electrical resistivity is a basic material property that quantifies opposition of a material to current flow and it can affect the characteristics of a device, such as the series resistance, threshold voltage, RC time constant, and other parameters. One of the most common ways of measuring the resistivity of conductive, thin and flat materials is using a four-point collinear probe. The four-point probe technique involves bringing four equally spaced probes in contact with a material of unknown resistance measuring either current or voltage from inner electrodes while applying voltage or current onto external contacts. In this study, we have evaluated the resistance of aligned CNT sheets deposited on glass for different electrode distances. The resistance of the CNT sheets is measured initially using a two-wire configuration and then with four-wire configuration. We also report on the values of the resistance and the orientational order of CNTs when they are incorporated into LCs.

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Mixtures of liquid crystals (LCs) with nanomaterials are of high interest nowadays [1]. The addition of different magnetic nanoparticles (MNPs) as dopants to create magnetic field responsive LC materials faced the problem of MNPs non-miscibility with LC hosts or aggregation. This problem can be resolved *via* modification of the MNPs surface using different pro-/mesogenic ligands. However, the majority of the published ligands serves only as stabilizers.

In the current study, we present MNPs modified with novel functionalized promesogenic ligands. The prepared ligands contain different chiral units (lactic acid or BINOL) to induce chirality in non-chiral LC hosts and a photosensitive azo unit to tune the LC hosts supramolecular structure with UV-light (Figure 1).



Figure 1: Planar textures of a studied nanocomposite: a) without UV-light, b) under UV-light.

Optical purity of prepared chiral intermediates and ligands was verified using HPLC on a chiral stationary phase. Ligands structures were determined by ¹H, ¹³C, ³¹P NMR, IR spectroscopies, mass spectrometry and elemental analysis. Modified MNPs were qualitatively characterized using TEM and IR. The quantity of the immobilized ligands and the ligand/co-surfactant ratio were calculated from the elemental analysis data. Prepared MNPs were used as dopants in various LC hosts. The relationship between the ligands structure, miscibility of the prepared MNPs and its effect on physical properties of the used matrixes will be discussed in detail.

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P31 Investigation of orientational order in carbon nanotube sheets used as multi-functional-layer for liquid crystal display devices

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Free-standing sheets formed by strands of aligned carbon nanotubes (CNTs), easily obtained drawing the tubes from suitable forests, are an ideal system for realizing networks of CNTs in which observing and studying at macroscopic scale the exceptional properties of single CNTs [1]. Oriented CNTs can provide alignment in liquid crystal (LC) [2] but the CNT sheets can play more roles at the same time, namely of transparent electrodes and aligning layers [3]. The degree of orientational order of the nanotubes is of particular importance for the templating action since it is expected to have a direct influence on the LC order. The orientational order of CNTs is relevant also for the optical properties of the CNT sheet since it affects its optical anisotropy, which, in turn, has consequences on the state of the transmitted light. More specifically, the polarization of light results remarkably affected. We will describe our efforts in evaluating the order parameter of aligned CNT sheets and in estimating how the macroscopic order parameter affects the degree of polarization rotation of the transmitted light. Since CNT sheets are attractive for integration in cells for LCs, the assessment of the relation between orientational order of the nanotubes and its effect on light polarization is of particular importance because the state of light emerging from the CNT sheets will be experienced by LC and by the analyzer thus directly influencing the overall optical behavior.

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Experimental evidence of smectic layer distortion by X-ray scattering measurements and subsequent effect on electro-optical parameters of CdSe QDs dispersed SmC* phase

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CdSe QDs cause significant change in the physical properties of liquid crystalline materials [1]. CdSe QDs dispersed SmC* matrix is studied by X-ray scattering, polarized optical microscopy, Raman spectroscopy and atomic force microscopy to understand the molecular organization in distorted helical geometry. SAXS has confirmed that the presence of QDs causes the enhancement in smectic layer separation. The smectic order parameter for neat FLC and FLC-QDs mixtures is obtained in the range of 0.6 to 0.85. The smectic order parameter and structural tilt, both are found to be lesser for FLC-QDs mixtures as compared to neat FLC. The insertion of QDs in SmC* matrix causes a localized smectic layers distortion in such a way that spontaneous polarization remains almost same but the electro-optic switching of molecules becomes faster. The capability of electrical energy storage of FLC-QDs mixtures is also investigated and we found the mixtures to be suitable for energy storage in a more efficient manner and can be utilized in modern electronic devices [2].

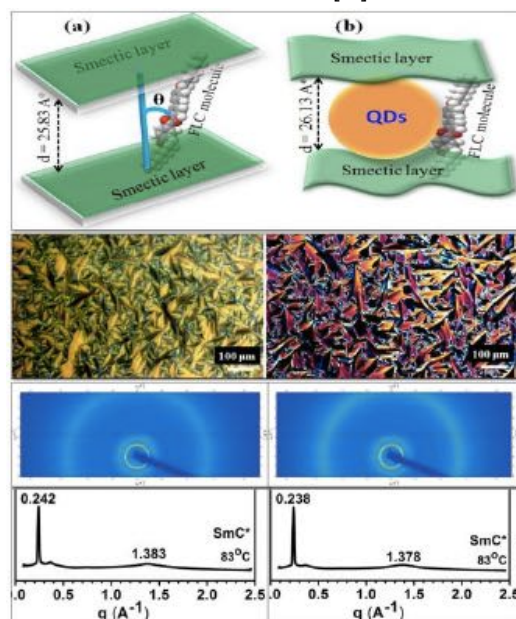


Figure 1: Schematic representation of (a) neat SmC* and (b) CdSe QDs dispersed SmC* LC matrix and corresponding POMs and X-ray diffractograms.

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P33 Liquid crystalline phase behavior of cellulose nanocrystals in different solvents and varying surface modifications as a platform for composites with thermotropic liquid crystals

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Cellulose, being the most widely found and one of the most versatile biopolymers in nature, is attracting a rapidly growing interest for novel multifunctional materials due to the possibility to extract cellulose particles in the nanometer range. Furthermore, a remarkable property of the stiff nanorods referred to as cellulose nanocrystals (CNCs) is their ability to form a liquid crystalline, specifically chiral nematic, phase [1] when dispersed in an appropriate solvent. So far, most composites and hybrids have been prepared from aqueous dispersions, whereas the exploration of non-aqueous systems is sparse. Yet this is essential for accessing the full scope of possibilities in fabricating new functional materials based on CNC. A better understanding of the behavior of CNC rods in different solvents [2], possibly after functionalization of the CNC surface, and the interactions between CNC and the matrix material, is required for tapping the full potential of this promising new nanomaterial.

This project aims to fill the gap with a systematic study of the phase diagram, with specific focus on the liquid crystal formation, of hydrophobized CNCs in non-polar solvents. Quarternary ammonium surfactants carrying varying length of carbon chains have been tested and result in altering dispersability and formation of liquid crystalline order in different solvents.

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The diffraction behavior of polymer network liquid crystal (PNLC) was studied in in-plane switching (IPS) test cells and compared to the behavior seen in a nematic liquid crystal (NLC). PNLCs are capable to result continuous optical phase modulation [1,2]. The influence of the polymer network was investigated in numerical simulations of the LC director realignments using Q -tensor approach [2,3]. Here, the polymer was modelled as phase separated, porous network. The field distributions caused by IPS electrodes were considered. The optical phase retardation profiles (Fig. 1) were calculated and, subsequently, the corresponding diffraction patterns were obtained by calculating Fourier transforms. In the case of NLC, a Gaussian-like phase modulation was obtained. Introducing polymer network led to a considerably deformation of the phase modulation profile caused by anchoring torque exerted by the porous polymer network [3].

Diffraction patterns of NLC showed near zero diffraction efficiency at second order $m = 2$ (driving voltage of $V = 6$ V). Interestingly, the PNLC also comparable behavior at an applied voltage of $V = 60$ V. Due to continuous phase modulation, PNLCs can yield voltage-dependent diffraction patterns and suppress the 0th order peak. The simulated results are in good agreement with experimental findings.

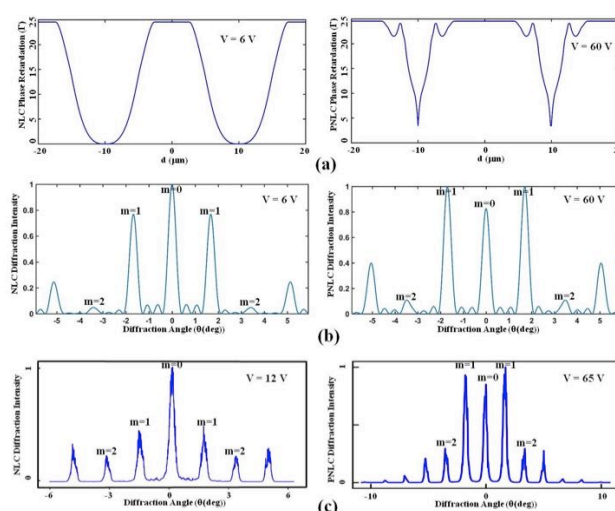


Figure 1: (a) Phase retardation profiles, (b) simulated diffraction patterns, and (c) experimental diffraction patterns of NLC (left plot) and PNLC (right plot) IPS test cells at their corresponding driving voltages.

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X-ray diffraction is one of the most important experimental techniques to study the structure and order of liquid crystal (LC) phases. We recently presented a computational tool which allows realistic calculations of 2D X-ray diffraction (XRD) patterns of fluid smectic liquid crystal phases with different shapes of a prescribed orientational distribution function (ODF) while the smectic order is assumed to be perfect [1]. In this paper, we now present the extension of our simulation tool to McMillan distribution functions [2] taking into account the impact of imperfect 1D translational (smectic) order. In addition, we studied the influence of variations in the molecular electron density distribution (or the molecular form factor thereof) on the 2D XRD pattern.

The starting configurations of the simulations were set up to follow a McMillan type distribution $p(\beta, z)$, meaning that the Gay-Berne particles were placed with their z -coordinates and their long-axis orientations according to a certain McMillan distribution with fixed values of the orientational order parameter S_2 and the mixed order parameter σ . Here β is the angle between the molecular long axis and the director and z is the z -coordinate (in the direction of the layer normal \mathbf{k}). During the simulations, the GB particles were neither allowed to change their z -coordinates nor their orientations but were allowed to translate in the x - and y -directions of the simulation box. Under these restrictions, the original McMillan distribution is preserved, while still obtaining a minimum energy configuration during the simulation. A realistic molecular electron density distribution was calculated from a Hartree-Fock minimum structure of 5-Octyl-2-(4-hexyloxyphenyl)-pyrimidine (6OPhPy8) and incorporated into each GB particle. With these simulations, we systematically analyze the impact of (i) orientational disorder, (ii) translational disorder and (iii) the molecular electron density distribution on the 2D diffraction patterns of smectic-A phases and compare the simulated diffraction patterns to experimental 2D XRD patterns.

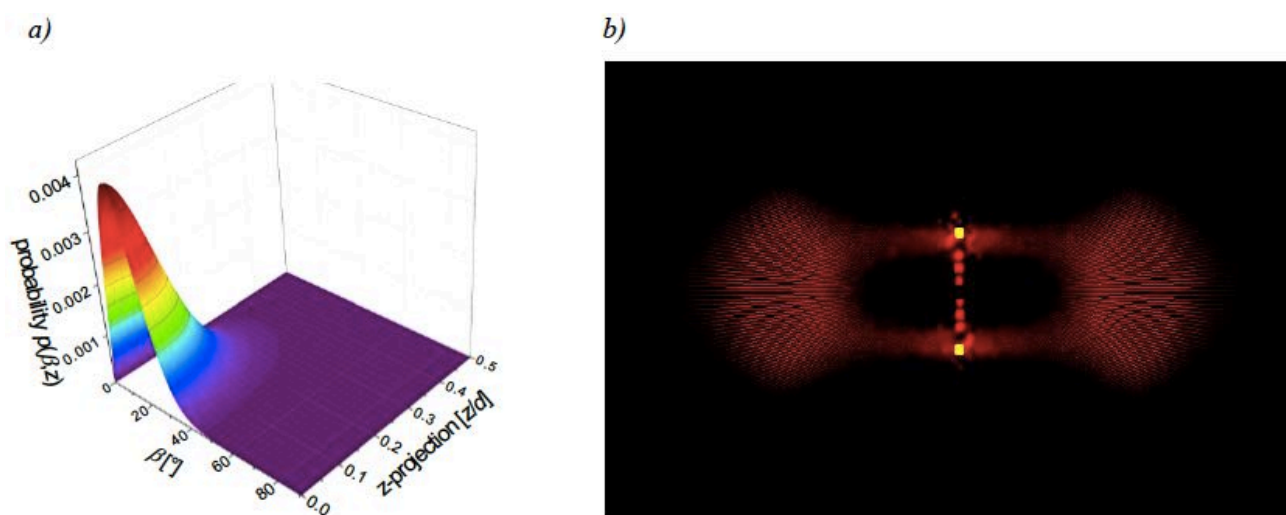


Figure 1: a) McMillan distribution with the probability of finding a particle at a certain orientation β between the director \mathbf{n} and the long axis of a molecule and at a certain displacement z from a smectic layer with spacing d . b) Diffraction pattern calculated from the simulation following the distribution in a).

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From Rafts to Ziggurats: Modelling Stacked Domains in Lamellar Bodies

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Multi-lamellar stacks of phospholipid membranes appear in many living organisms (e.g. in plant chloroplasts). These membranes can be composed of a mixture of saturated and unsaturated phospholipids, and cholesterol. When reduced to sufficient temperature, the mixture separates into liquid-disordered (containing mostly unsaturated lipids) and liquid-ordered (containing higher levels of saturated lipids and cholesterol) phases, which can coexist. [1] It has been observed that these liquid-ordered domains align across the multilayer system, resulting in columnar ordering of liquid-ordered rafts across many neighbouring membranes. [2]

These stacks of membranes can be naturally modelled as smectic liquid crystals. The nature of the liquid-ordered regions as being relatively static and much less flexible than the surrounding liquid-disordered region, invites us to consider the liquid-ordered region as an inclusion within the smectic. Inclusions such as these can deform the arrangement of layers within the lamellar body by locally fixing the spacing between neighbouring membranes. [3] We construct a general Hamiltonian for an infinite system, using the Landau de-Gennes Hamiltonian to account for the energy of the bulk. [4] This is used to determine the energy required to form stable liquid-ordered columns in the smectic and so show that columns of the kind observed can be stable, despite their locally distorting the layer spacing of the lamellae.

By exploiting the symmetry of the layer-distortion caused by inclusions, we are able to enforce a periodicity in the model. In then considering only a single period we are able to capture the characteristics of a finite slab geometry within the framework previously constructed.

This model is able to predict many of the properties of aligned liquid-ordered phases observed in lamellar stacks. In particular, size of domains relative to the dimensions of the slab, and their preference for certain positions within the stack is captured by our results.

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Analyzing and Comparison on Temperature and Wavelength Dependence of Order Parameter and Polarizability Properties in 8CB and 8OCB

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Liquid crystals are quite significant and attractive materials in point of technological applications because of their affected by external field and by exhibition of different phases depend on temperature. By decreasing temperature liquid crystals show various mesophases such as nematic, smectic A etc. and these mesophases approach to resemble solid crystal state. Nematics that are one of these mesophases have weak orientational order and also smectic A mesophases have positional and orientational order different from the nematics [1-4].

In this study, 8CB and 8OCB that are one of the alkyl based liquid crystals have been analyzed depend on temperature and wavelength along both direct phase transition and reverse phase transition processes. By using analyzed data, microscopic order parameter (S) and anisotropic polarizability parameters (α_o , α_e , α_{ave} , $\Delta\alpha$) have been given and have been compared for both materials in accordance with Vuk's approach. All results will be given.

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Liquid crystals are important materials for technical and technologic applications in thermo-optical, magneto-optical, electro-optical and accousto-optical devices. For such applications detailed and all-round information about optical properties of liquid crystalline materials are extremely important [1-4].

In this work, wavelength-temperature dependences of the refracting and birefringent properties of 8CB and 8OCB mesogens have been investigated. Behavior of the \bar{n} , n_o and n_e refractive indices vs. wavelength and temperature have been investigated. For these investigations the aligned monocrystalline with high orientation degree and non-aligned polycrystalline textures have been obtained. The correlations for the \bar{n} , n_o and n_e refractive indices as the $\bar{n}(0.625\ \mu\text{m}) < \bar{n}(0.525\ \mu\text{m}) < \bar{n}(0.465\ \mu\text{m})$, $n_o(0.625\ \mu\text{m}) < n_o(0.525\ \mu\text{m}) < n_o(0.465\ \mu\text{m})$ and $n_e(0.465\ \mu\text{m}) < n_e(0.525\ \mu\text{m}) < n_e(0.625\ \mu\text{m})$, have been found in the smectic A and nematic thermal interval. Besides, the correlation for the Δn as the $\Delta n(0.625\ \mu\text{m}) < \Delta n(0.525\ \mu\text{m}) < \Delta n(0.465\ \mu\text{m})$ has been also found.

Results of these investigations will be discussed.

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Switching dynamics and nanosegregation in carbosilane 'de Vries'-type smectics

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In smectic A (SmA) to smectic C (SmC) transitions of the 'de Vries'-type, the appearance of director tilt is coupled to a substantial increase in optical birefringence and thus in orientational order. This increase – more or less – compensates the smectic layer contraction in the SmC phase [1]. A large group of 'de Vries' materials contains nanosegregating subunits such as carbosilanes, siloxanes or perfluorinated alkyl chains [1,2].

The influence of the nanosegregating subunit on static properties such as phase sequences, birefringence, layer spacing profiles and tilt angles was recently shown to be important [3]. We now investigated a series of mesogens (Fig. 1a) all having a SmA* – SmC* phase sequence but with terminal carbosilane segments of different length. This series allows to systematically study the influence of nanosegregation on the switching dynamics of these ferroelectric liquid crystals (FLCs), namely the question whether or not a carbosilane sublayer of increasing thickness can act as kind of lubricant between the mesogen sublayers and speeds up the ferroelectric and electroclinic switching in the SmC* and SmA* phases, respectively. The analysis of detailed dielectric spectroscopy investigations however show that the soft mode relaxation is getting stronger and faster with elongation of the carbosilane segments (Fig. 1b) while the rotational viscosities are almost the same over a broad temperature range in the SmC* phase. The elongation of the terminal carbosilane group thus enhances the 'de Vries' character of the FLC materials while their switching dynamics remains almost unchanged. These findings are highly relevant for the rational design of new 'de Vries'-type materials.

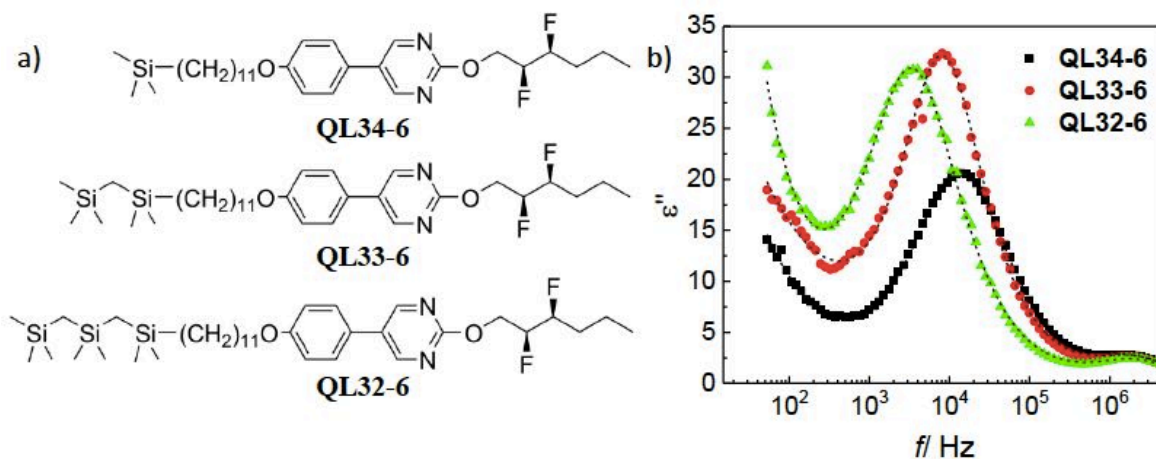


Figure 1. a) Chemical structures of the investigated smectic compounds and b) frequency dependence of the dielectric response ϵ'' at the phase transition temperature T_{AC} showing a strong soft mode relaxation.

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Due to the presence of a selective reflection band, cholesteric liquid crystals (CLCs) strongly modify the emission of fluorescent guest molecules. Emission along the helical axis – for wavelengths outside of absorption bands – has been studied both experimentally and theoretically, and is well understood. However, there still is a lack of quantitative understanding of the emission properties at oblique angles with respect to the cholesteric helix.

We present a systematic study of the angular dependent emission properties of CLC films doped with a fluorescent dye. Angular dependent measurements show a continuous blue shift of the reflection band with increasing detection angle. Furthermore, the polarizations of the eigenmodes for light propagation inside the CLC strongly depend on the propagation direction. This results in a strong angular dependence of emission intensity as well as emission polarization. An example measurement is shown in Figure 1, where the cholesteric pitch is adjusted to result in an overlap of the dye's emission spectrum with the CLC's reflection band for observation angles in an interval around 70° . Here we find a pair of photonic band gaps, one affecting only right-handed circularly polarized emission, the other completely suppressing emission of the dye; the band gaps are framed by sharp emission maxima due to the presence of photonic band edge resonances.

The experimental findings are complemented by simulation results based on the Berreman formalism.

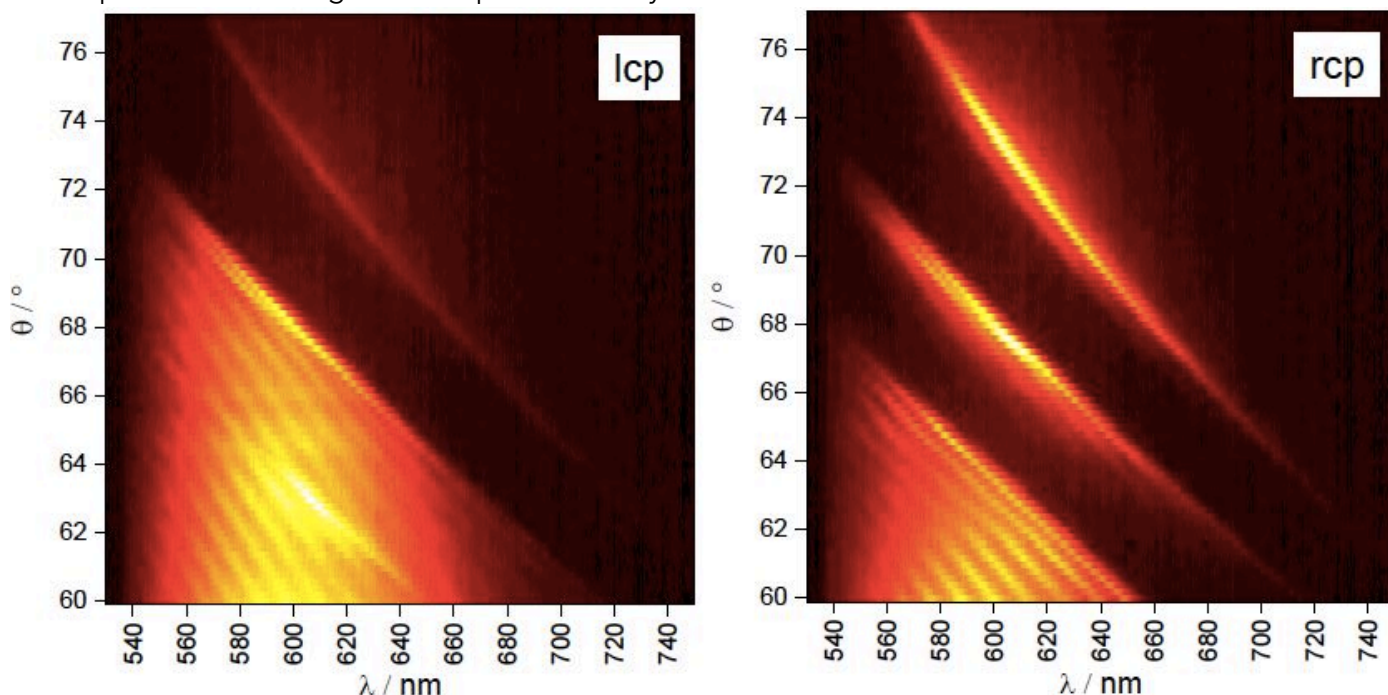


Figure 1: High resolution measurement of the angular-dependent spontaneous emission of a dye-doped cholesteric film; left- and right-handed circularly polarized ("lcp", "rcp") emission contributions are shown.

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Monolayer carbon based materials are considered as supermaterials and expected to impact dramatically different aspects of science and technologies in future because of their unlike and superior proprieties. Their applications are envisaged not only in solid phase, but also in liquid phase. It has been shown that wet chemical exfoliation of graphite can be used for large-scale production of graphene oxide (GO) flakes [1]. GO flakes because of their high aspect ratio, in aqueous suspension form liquid crystal (LC) phases. They show distinctive optical properties of LCs like birefringence, making them fascinating objects for optical applications such as liquid crystals displays. Recently, switching of GO-LCs by applying electric fields was reported and this finding raised an intense curiosity, triggering further studies on the electro-optical switching of graphene based-LCs [2-3]. In this report, we study the electro-optical switching of GO flakes in cells in which the GO suspension is confined by electrode walls, as sketched in Figure 1a. We study the electro-optical switching of GO-LCs using different electrode types monitoring in particular the effect of the different surfaces and dimensions on the GO-LC switching behavior. We observed that there are macroscopic areas with preferred order but different orientations already from the start, after filling, presumably because of the cell structure. These domains disappear when an electric field is applied and a fairly uniform texture appears as shown in Figure 1b below.

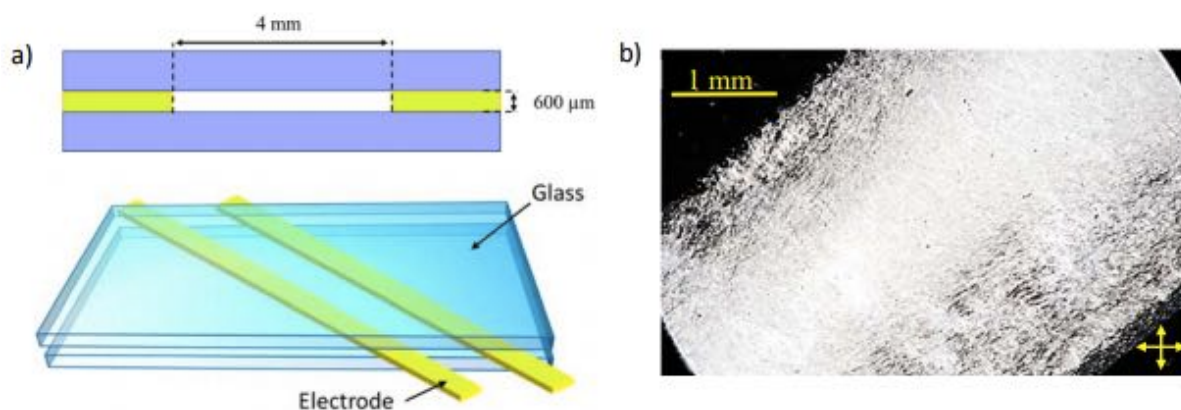


Figure 1: a) Sketch of the cells. b) Switched GO-LC under an electric field

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Advancing flexible volatile compound sensors using liquid crystals encapsulated in polymer fibers

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Until recently, organic vapor sensors using liquid crystals (LCs) have employed rigid glass substrates for confining the LC, and bulky equipment for vapor detection.[1] Previously, we demonstrated that coaxially electrospinning nematic LC within the core of polymer fibers provides an alternative and improved form factor for confinement.[2] This enables ppm level sensitivity to harmful industrial organics, such as toluene, while giving the flexibility of textile-like sheets. Moreover, toluene vapor responses of the LC-core fiber mats were visible macroscopically with the naked eye depending on the fiber morphology, and collection orientation (aligned, or random format). We identified two types of responses: one corresponds to the LC transition from nematic to isotropic, and the other we suggest is due to an anchoring change at the LC-polymer interface that influences the alignment. While we need to study the effects that the defects can have in more detail, we noted that fiber mat thickness is crucial in attempting to understand how and why we are able to visualize two responses in aligned LC-fiber mats. Ultimately, we noted that the response of the polymer sheath, via polymer softening, to repeated organic vapor exposure also affects the liquid crystal confinement in the core. From the microscopic point of view, both response of the sheath and the mat thickness will influence the threshold concentrations that fibers in a mat will respond to.

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Cover: View overlooking the Grund and N  im  nster Abbey in Luxembourg City (LU)

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