Discrete supermolecular ring assembly
From nanoscale physics to metamaterials science

Filling liquid crystals into nanopores results in properties that do not naturally occur in these materials. We show by optical birefringence, X-ray diffraction and Monte Carlo simulations that using disc-shaped molecules in nanopores leads to a temperature-tuneable nanoscale ring formation in combination with 1D charge carrier pathways. The peculiar optical properties and mechanical stability of the macroscopic confining porous matrix renders our system particularly interesting as an electronic and photonic metamaterial. Metamaterials derive their mechanical and functional properties not from the properties of the base materials, but from their newly designed, often multi-scale structures, in terms of precise shape, geometry, size, orientation, and elastic properties.

In general, liquid crystal molecules have the tendency to align along one direction called the director $n$. This characteristic behaviour gives rise to temperature dependent anisotropic properties, most prominently to optical birefringence [1, 2]. Discotic (disc-shaped) liquid crystals consisting of aromatic hydrocarbons substituted by alkyl side chains tend to stack up into 1D columns, which then arrange in a 2D hexagonal lattice. The liquid character along the columnar axis results from the melting of the alkyl chains, while the $\pi-\pi$-bonding of the conjugated hydrocarbons promotes crystalline properties. Due to the unique combination of these two states, discotic liquid crystals exhibit long-range self-assembly and self-healing mechanisms in combination with high one-dimensional charge mobility along the columnar axes [3].

To study spatial confinement effects on a discotic liquid crystal a macroscopic transparent monolithic silica membrane is synthesized by thermal oxidation of black nanoporous silicon, see inset in Fig.1 [4]. Embedding a discotic liquid crystal by capillary action into such a membrane results in interesting features of the optical properties, see Fig. 1a. At high temperature in the isotropic phase, i.e. the disordered state, the optical retardation vanishes. Upon decreasing temperature the molecules closest to the pore wall start to orient edge-on and with the in-disc direction parallel to the long pore axis due to specific surface conditions, see Fig. 1b. Resulting from the cylindrical confinement they form a bent columnar concentric ring [5]. Surprisingly, upon further cooling, the collective molecular order does not evolve in a continuous manner. Subsequently five pronounced changes in the optical retardation occur resulting from the formation of five concentric columnar rings as seen in the snapshots extracted from Monte Carlo simulations in Fig. 1b–c. Their curvature and geometric frustration is highest in the centre of the pores. Due to this fact, the disordered high-temperature phase is nucleated in the pore centre resulting in a pronounced temperature hysteresis between cooling and heating.

By analysing the thermodynamics of the confined system, we found that the dominant mechanism contributing to the free energy is given by the strong bend of the columns. Extracting
Figure 2
Temperature dependence of the (10) Bragg ring for a cooling/heating cycle. The optical retardation from Fig. 1 serves as a guide to the eye. Insets: (Right) X-ray diffraction pattern of the liquid crystals confined in nanopores focusing on the (10) Bragg ring. (Left) Enlarged reciprocal space assuming a randomization of the (10) reflections with regard to the mean pore axis direction. The red arrow indicates the beam direction, the black dashed line the pore axis and the large green section a part of the Ewald sphere.

the supercooling temperature differences between subsequent rings provides the otherwise hard to determine bend elastic constant $K_3$ of 2.7 pN. This material constant is a measure for the stiffness of the columns, i.e. how easy they bend. It is in reasonable agreement with values reported for chemically closely related discotic liquid crystals.

The optical measurements are only sensitive to the orientational order. Important complementary insights into the translational order are achieved by temperature-dependent X-ray diffraction experiments in transmission geometry at beamline P08 at PETRA III (see Fig. 2). The scattering geometry is chosen to be sensitive to the molecules’ translational order in cross-sections aligned parallel to the long nanopore axes. Resulting from the hexagonal columnar arrangement, and in agreement with the molecules dimensions, an intensity ring at a wave vector transfer $q_{10} = 0.3445 \, \text{Å}^{-1}$, typical of the leading (10) Bragg reflection, is detected. The temperature evolution of the (10) ring follows remarkably well the optical retardation, both in the onset and in the hysteresis width. However, the staircase behaviour is only marginally detectable. This results from defect healing and reorientation mechanisms during the phase transition as shown in parallel-tempering Monte Carlo simulations. The optical experiment is not sensitive to these processes that smear out the phase transition in the X-ray diffraction experiment.

In summary, we have found a near-room-temperature phase transition discretization in a discotic liquid crystal confined in cylindrical nanopores. Our study shows in a remarkable manner how geometrical confinement can alter the physics of liquid crystals. It also highlights how versatile soft matter can adapt to extreme spatial constraints. From a materials science point of view we provide a fine example that solids traversed by pores smaller than the wavelength of visible light can be fine-tuned with regard to their effective optical properties by infiltration of soft, liquid-crystalline fillings. Here, the resulting soft-hard metamaterial exhibits an optical birefringence that can be adapted step-wise by external temperature control.

Author contact: Kathrin Sentker, kathrin.sentker@tuhh.de; Patrick Huber, patrick.huber@tuhh.de

References

Original publication

Kathrin Sentker1, Arne W. Zantop2, Milena Lippmann1, Tommy Hofmann3, Oliver H. Seeck4, Andriy V. Kityk3, Arda Yildirim6, Andreas Schönthal5, Marco G. Mazza2 and Patrick Huber1

1. Institut für Materialphysik und -technologie, Technische Universität Hamburg, Germany
2. Max-Planck-Institut für Dynamik und Selbstorganisation, Göttingen, Germany
3. Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany
4. Helmholtz-Zentrum für Materialien und Energie, Berlin, Germany
5.Faculty of Electrical Engineering, Czestochowa University of Technology, Poland
6. Bundesanstalt für Materialforschung und -prüfung, Berlin, Germany