EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

	Experiment title: Characterization of the thermotropic phase behavior and microscopic structure of a confined discotic liquid crystal	**Experiment number**: SC 4703
Beamline:	**Date of experiment**: from: 04 Apr 2018 to: 07 Apr 2018	**Date of report**: 09.09.2020
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Report:

K. Sentker, A. Yildirim, M. Lippmann, A. W. Zantop, F. Bertram, T. Hofmann, O.H. Seeck, A. V. Kityk, M. G. Mazza, A. Schönhals and P. Huber, Self-assembly of liquid crystals in nanoporous solids for adaptive photonic metamaterials, Nanoscale 11, 23304 (2019).

Nanoporous media exhibit structures significantly smaller than the wavelengths of visible light and can thus act as photonic metamaterials. Their optical functionality is not determined by the properties of the base materials, but rather by tailored, multiscale structures, in terms of precise pore shape, geometry, and orientation. Embedding liquid crystals in pore space provides additional opportunities to control light– matter interactions at the single-pore, meta-atomic scale. Here, we present temperature-dependent 3D reciprocal space mapping using synchrotron-based X-ray diffraction in combination with high-resolution birefringence experiments on disk-like mesogens (HAT6) imbibed in self-ordered arrays of parallel cylindrical pores 17 to

160 nm across in monolithic anodic aluminium oxide (AAO). In agreement with Monte Carlo computer simulations we observe a remarkably rich self-assembly behaviour, unknown from the bulk state. It encompasses transitions between the isotropic liquid state and discotic stacking in linear columns as well as circular concentric ring formation perpendicular and parallel to the pore axis. These textural transitions underpin an optical birefringence functionality, tunable in magnitude and in sign from positive to negative via pore size, pore surface-grafting and temperature. Our study demonstrates that the advent of large-scale, self-organised nanoporosity in monolithic solids along with confinement-controllable phase behaviour of liquid-crystalline matter at the single-pore scale provides a reliable and accessible tool to design materials with adjustable optical anisotropy, and thus offers versatile pathways to fine- tune polarisation-dependent light propagation speeds in materials. Such a tailorability is at the core of the emerging field of transformative optics, allowing, e.g., adjustable light absorbers and extremely thin metalenses.

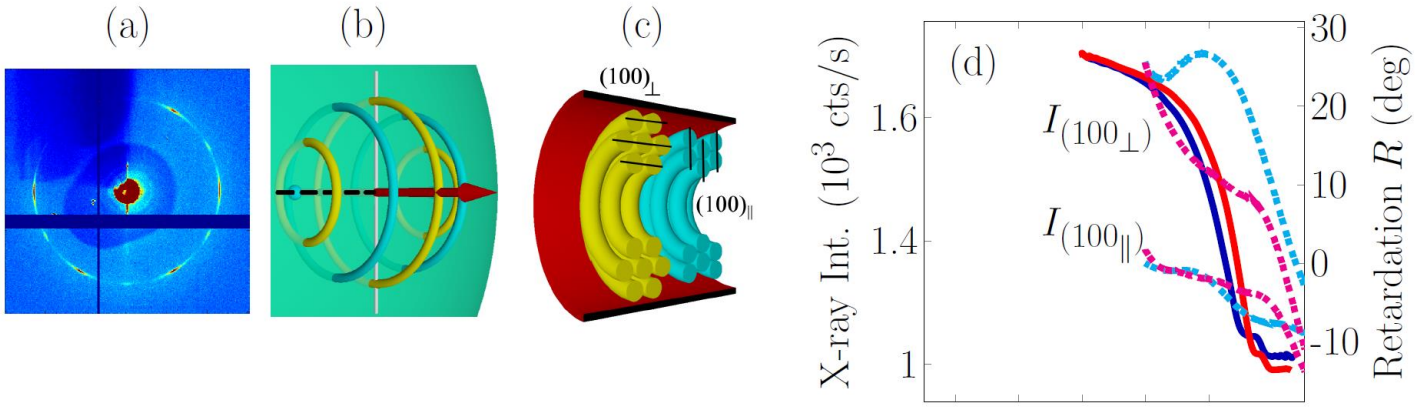

Figure 1 (a) Small angle diffractogramm of HAT6 confined in cylindrical pores with a diameterof 86 nm and resulting molecular configurations in (b) reciprocal and (c) real space. (d) Temperature dependence of the scattering intensities (dashed lines) of both (100) domains oriented perpendicular and parallel to the long pore axis compared to optical birefringence (retardation) measurements (straight lines).

Additional comments:

We performed SAXS measurements at ID31 on the discotic liquid crystal confined in nanoporous AAO membranes, see abstract and Fig. 1. During the beamtime it was at first challenging to detected the small angle peak at q = 0.34 $Å^{-1}$ due to shadows from the large beamstop, see Fig. 1(a). In addition, only small intensities were detected due to the high X-ray beam energy of 70 keV, see Fig. 1(d). To increase the scattering cross section energies not higher than 30 keV are necessary for this type of sample for future beamtimes.