Experimental Report

14/01/2014

Proposal:	**6-05-928**	**Council:**	10/2012

Title: Vibrations and molecular dynamics of a discotic liquid crystal confined to channels with an ultra-low diameter

This proposal is continuation of: 6-05-882

Researh Area: Soft condensed matter

Main proposer: **SCHOENHALS Andreas**

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Local Contact: FRICK Bernhard

Samples: C54_H84_O6
Anodic Aluminium Membrane, Al2O3

Instrument	Req. Days	All. Days	From	To
IN6	4	5	07/06/2013	12/06/2013

Abstract:

Discotic liquid crystals (DLC) are soft-matter materials which organize into columns that further assemble into two-dimensional arrays with a hexagonal mesophase. Highly ordered columnar structures were found to be very promising as active semiconductors in organic field-effect transistors and photovoltaic devices. The charge transport in these systems is controlled by their molecular mobility. Confining DLCs to the unidirectional channels of nanoporous anodic aluminium (AAO) can be regarded as model system for nanoscaled wires. To investigate the influence of a nanoscaled confinement on the vibrational density of states and the molecular mobility it is proposed to carry out Time-of-Flight experiments on a triphenylene based DLC embedded to the 25 nm wide pores of AAO at IN6.

EXPERIMENTAL REPORT

EXPERIMENT N°6-05-928 INSTRUMENT IN6

DATES OF EXPERIMENT 07/06/2013-12/06/2013

TITLE

Vibrations and molecular dynamics of a discotic liquid crystal confined to channels with an ultra-low diameter

EXPERIMENTAL TEAM

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Date of report 13/01/2014

Discotic liquid crystals (DLC) are self-assembled materials where self-assembly is driven by noncovalent intermolecular interactions [1]. DLCs consist of a flat and rigid aromatic core substituted by flexible aliphatic side chains. The former is responsible for the π-stacking and the latter for the increased solubility, processability, and rich thermotropic behavior. The disc-shaped molecules organize into columns that further assemble into two-dimensional arrays with a hexagonal mesophase. The alkyl chains fill the intercolumnar space giving rise to a nanophase separated state.

To have an overview about the influence of a nanoscale confinement on the vibration densities of states (VDOS), incoherent inelastic neutron scattering experiments are carried out at IN6 for Hexakis [n-hexaoxy]triphenylene (HAT6) embedded to the pores of commercially available anodic aluminum membranes (AAO) (Smart Membranes, Pore diameter 25nm, 40nm, 80 nm). For preparation the empty aluminium membrans were treated in vacuum to remove impurities and after that they were transferred under vacuum into a glove box filled with Argon. The pores were filled by melting the DLC on the top of the membrane at a temperature above the clearing temperature by capillary wetting. The filling degree was estimated by TGA measurements. The experiments were done on IN6 (λ=5.12 Å). All spectra were corrected for the scattering of the empty host membrane sealed under Argon and the empty can. The measurements were carried out at 80 K where the bulk discotic liquid crystal is in the plastic crystal state.

Fig. 1 shows the VDOS of nanoconfined HAT6 (Pore Sizes 80nm, 40nm, 25nm) for the frequency range of the excess low-energy excitation (Boson peak, BP) normalised to that what is expected from the Debye theory of sound waves which gives $g(\omega)\sim\omega^2$. HAT6 shows a boson peak in the bulk as well as in the confined state. Because a BP seems to be characteristic for a glassy behaviour one can conclude that this class of discotic liquid crystals undergoes a glass transition. As hydrogen is a strong incoherent scatterer, mainly the vibrations of the hydrogen nuclei are monitored, that means the vibrations in the intercolumnar space. Therefore this glassy dynamics have to be related to the intercolumnar space.

With decreasing pore size the maximum of the BP shifts to lower frequencies and gains in intensity. This can be understood as a disturbance of the plastic crystalline phase by the nanoconfinement. A disordered (quasi-amorphous) boundary layer is formed close to the walls of of the channels. With decreasing pore size the amount of this disordered boundary layer increases. Moreover the VDOS for the smallest pores size shows a dependence on the orientation of the pores with respect to the Q-vector of the incident neutron beam. This is is also in agreement with the existence of a boundary layer.

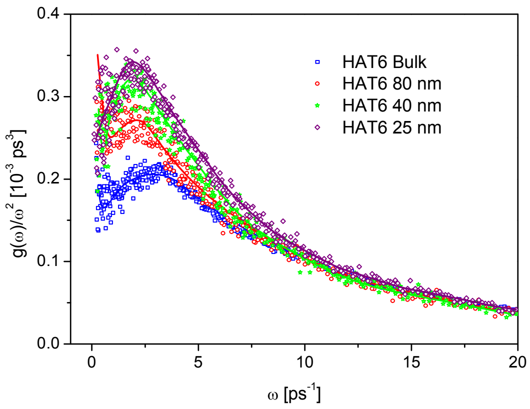

Fig. 1: VDOS at T= 80 K for HAT6 in the bulk and confined to the channels of AAO for the labelled pore sizes. Lines are guides for the eyes.

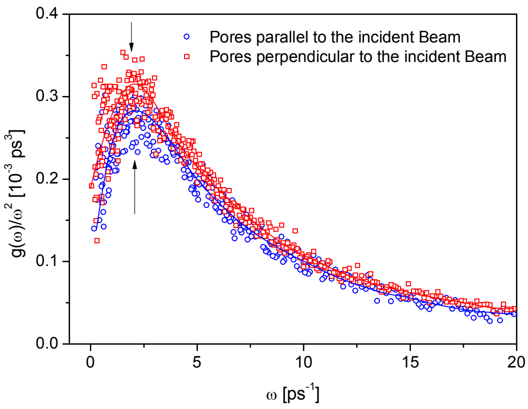

Fig. 2: VDOS at T= 80 K for HAT confined to the 25 nm wide channels of AAO for the labelled pore orientations.

[1] J. Wu, W. Pisula, and K. Müllen, Chem. Rev. **107**, 718 (2007)
[2] C. Krause, R. Zorn, B. Frick, and A. Schönhals, Colloid Polymer Science (in preparation)