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39. Arbeitstagung Flüssigkristalle

GERMAN LIQUID CRYSTAL CONFERENCE 2011
- Book of Abstracts -

Hamburg
30th March to 1st April 2011

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Final Program:

Wednesday 30th March:

14:00 Welcome Remarks

Chair: Günter Lattermann

14:15 - 15:00 Self-assembly of Bolaphospholipids in Water: Formation of Nanoparticles; Nanofibers and Hydrogels.
Alfred Blume, A. Meister, G. Graf, M. Bastrop, S. Drescher and B. Dobner (Halle)

15:00 - 15:30 Self-assembly of Nanoparticles.
Horst Weller (Hamburg)

15:30 - 15:50 pH- and Salt-Dependent Aggregation Behaviour of Symmetric Single-Chain Bolaphospholipids.
Gesche Graf, S. Drescher, A. Meister, B. Dobner and A. Blume (Halle)

15:50 - 16:10 Ferroelectric and Antiferroelectric Phases of Bent Mesogens with Large Opening Angle.
Martin Kirchhoff , U. Kornek, S. Stern, A. Eremin, R. Stannarius, C. Zhu and C. S. Park (Magdeburg)

16:10 – 16:40 Coffee Break

Chair: Yo Shimizu

16:40 - 17:10 Beam Characteristics of Liquid Crystal Lasers.
Jürgen Schmidtke, C. Mowatt and H.J. Coles (Paderborn)

17:10 - 17:30 Polar Order in Free-Standing Fibres of the B7-Phase.
Ulrike Kornek, S. Stern, R. Stannarius, A. Eremin, F. Araoka, L. Guo, H.Takezoe, A. Jákli, H. Nádasi and W. Weissflog (Magdeburg)

17:30 – 17:50 Orientational Order Parameters of a de Vries-Like Ferroelectric Liquid Crystal: Experimental Comparison Using Polarized Raman Spectroscopy and X-Ray Diffraction.
Alberto Sanchez-Castillo, M. A. Osipov, S. Jagiella, M. Kašpar, V. Hamplovǎ and F. Giesselmann (Stuttgart)

17:50 – 18:10 Influence of Solvent Quality on the Self-Organization of Archetypical Hairy Rods-Branched and Linear Side Chain Polyfluorenes: Rod like Chains Versus “Beta sheets” in Solution.
M. Knaapila, **Vasyl Haramus**, F. B. Dias, L. Almasy, F. Galbrecht, H. D. Burrows, U. Scherf and A. P. Monkman (HC Geesthacht)

18:10 – 18:30 Nematic Textures in Micro fluidic Environment.
Anupam Sengupta, U. Tkalec, and Ch. Bahr (MPI Göttingen)

18:30 - 19:00 Alfred-Saupe-Award

The Alfred-Saupe Price of this year goes to **Günter Baur**, Freiburg.
More about the award at:

http://www-e.uni-magdeburg.de/liquidcr/honours.shtml

19:00 - 20:00 Possibility to have a first look at the posters

19:00 - 20:00 Mitgliederversammlung der DGFK, Room 105

20:00 - 22:00 Get-together in the Foyer of the Chemical Institutes

Thursday, 31st March

Chair: Heinz Kitzerow

9:00 - 9:45 New Materials for Polymer-Stabilised Blue Phase.
Norihiko Tanaka, M. Wittek, M.C. Wu, M. Bremer, D. Pauluth and K. Tarumi (Merck, Darmstadt)

9:45 - 10:15 Design Strategies for Ionic Liquid Crystals.
Koen Binnemans, K. Lava, K. Goossens and T. Cardinaels (Leuven/Belgium)

10:15 - 10:35 New 2D-Correlated Structure of a Lyotropic Liquid Crystalline Diol.
Johanna Bruckner, D. Krueerke, and F. Giesselmann (Stuttgart)

10:35 - 10:55 Comparative Study of the Equilibrium Phase Diagrams of Propylene-glycol-Diacrylate / Liquid Crystal Blends
Yazid Derouiche, F. Dubois, R. Douali, C. Legrand, L. Méchernène and U. Maschke (Villeneuve d’Ascq/France)

10:55 – 11:30 Coffee Break

Chair: Sabine Laschat

11:30 - 12:00 Ordering Transitions of Liquid Crystalline Thin Films Driven by In-Situ Enzyme-Induced Hydrogel Degradation.
I-Hsin Lin, L. S. Birchall, R. V. Ulijin, S. B. Webb (Manchester/UK)

12:00 - 12:20 Analysis of the Formation of Polymer/Liquid Crystal Systems Prepared by Ultraviolet and Electron Beam Curing
Ammar Elqidrea, R. Meziane and U. Maschke (Villeneuve d’Ascq/France)

12:20 - 12:40 The Simplest Two-Dimensional Anisotropic Fluids Flow Orientation Coupling in Free-Standing SmC Films.
Kirsten Harth, A. Eremin and R. Stannarius (Magdeburg)

12:40 – 14:00 Lunch

Chair: Carsten Tschierske

14:00 - 14:30 On a Three-Phase Coexistence of Isotropic Phases in the Phytantriol/Water/Ethanol System.
Pawel Pieranski and L. Latypova (Paris-Sud/France)

14:30 - 15:00 Hekates – from the Formation of LC Nano-Structures and Functional, Multichromophore Star Mesogens.
Matthias Lehmann, St. Gloza and M. Jahr (Würzburg)

15:00 - 15:20 Fluorescent Mesogens Based on Rod-Shaped Aromatic Hydrocarbon Cores.
J. Buchs, H. Sawade and **Dietmar Janietz** (Potsdam-Golm)

15:20 - 15:40 Liquid Crystalline Crown Ethers: Effect of Crown Size and Complexation.
Martin Kaller and S. Laschat (Stuttgart)

15:40 -16:00 Photon-controlled isothermal phase transitions among Colr, SmA and Isotropic phases accompanied with the alternative change of molecular anisotropy
D. Tanaka, H. Ishiguro, K. Ohnishi, K. Uchida and **Yo Shimizu**, AIST-Kansai, Japan

16:00 – 19:00 Coffee Break and Poster Session

20:00 - ?? Conference Dinner at the Restaurant "Parlament" in the City Hall

Friday 1st April

Chair: Klaus Brandenburg

9:00 - 9:45 The B4 Banana Phase for Organic Photovoltaics
David. M. Walba, N.A. Clark, E. Korblova, R. A. Callahan, J. M. Richardson, E. Tsai, M. Moran, T. M. Rochelle, R. K. Shoemaker, D. K. Yoon, J. Maclennan, M. Glaser, C. Zhu, D. Chen, R. Shao, D. Coffin, and G. Rumbles

9:45 - 10:15 Structural Assembly of Hydrated Synthetic Glycolipids.
Patrick Garidel, S. Gerber, M. Wulf, M. Roessle, J. Howe, T. Gutsmann, V. Vill and K. Brandenburg (Halle)

10:15 - 10:35 Lysyl-Phosphatidylglycerol Confers Resistance of Staphylococcus Aureus to Antimicrobial Peptides and Impairs Interaction of Peptides with Model Membranes.
J**örg Andrä**, T. Goldmann, C. Ernst, A. Peschel and T. Gutsmann (Borstel)

10:35 - 10:55 Interactions of Small Polyphilic Molecules with Lipid Membranes.
Bob-Dan Lechner, A. Kerth, C. Tschierske and A. Blume (Halle)

10:55 - 11:30 Coffee Break

Chair: Regine Willumeit

11:30 - 12:00 Synchrotron Light for Characterizing the Formation of Curved Membranes and Membrane Fusion Processes.
Michael Rappolt (Trieste/Italy)

12:00 - 12:20 Neutralization of Endotoxins by Antimicrobial Peptides.
Yani Kaconis, I. Kowalski, M. Rössle, T. Gutsmann and K. Brandenburg (Borstel)

12:20 - 12:40 Evaluation of Lipopolysaccharide, a Major Bacterial Glycolipid, as a Target for Antimicrobial Peptides and Lipopeptides.
Susana Sanchez-Gomez, I. Moriyón, J. Leiva-León, K. Lohner, K. Brandenburg, R. Jerala, S. E. Blondelle, J. Andrä and G. Martínez de Tejada (Pamplona/Spain)

12:40 – 14:00 Lunch

Chair: Thomas Gutsmann

14:00 – 14:30 Critical Role of Lipid Composition in Membrane Permeabilization by Antimicrobial Peptides
Karl Lohner, D. Zweytick, G. Deutsch, E. Sevcsik, J. Andrä, K. Brandenburg, Y. Shai, S.E. Blondelle, S. Sánchez-Gómez and G. Martínez de Tejada (Graz)

14:30 – 15:00 Possibilities for Biological Nanoscience at the EMBL BioSAXS Beamline at PETRA-III.
Manfred Roessle, V. Haramus, R. Willumeit, D. Svergun and Th. Schneider (Hamburg)

15:00 - 15:20 Organisation of Amphiphilic Liquid Crystals at the Air Water Interface.
Christian Schwieger, S. Reuter, C. Tschierske, J. Kressler and A. Blume (Halle)

Speakers are indicated in bold.

15:20 - 16:00 Young Scientist‘s Award

16:00 End of Conference, Concluding Remarks.

17:00 - ? Excursion

Poster Session:

The posters can be mounted beginning Wednesday morning.

Comparative Study on New Chiral, Lactic-Acid Containing Liquid Crystals
F. Brombach and **Dirk Blunk** (Köln)

Swelling Equilibria in Mixtures of Isotropic Gels in Anisotropic Solvents
L. Bedjaoui, F. Semdani, N. Bouchikhi, **Tewfik Bouchaour** and
U. Maschke (Villeneuve d'Ascq/France)

Polymer/Cristal Liquid Blends Prepared by Electron Beam and UV Radiation : Correlation Between Rubber Elasticity and Phase Separation
A. Berrayah, A. Olivier, L. Zair, **Tewfik Bouchaour** and U. Maschke
(Villeneuve d'Ascq/France)

Mixtures of 'De Vries' Liquid Crystals with First- and Second-Order SmA – SmC Phase Transitions
Andreas Bogner, J. C. Roberts, N. Kapernaum, R. P. Lemieux and
F. Giesselmann (Stuttgart)

Conformational and Vibrational Studies of 2-Ethylhexyl Acrylate / Liquid Crystal Systems
O. Belaidi, **Tewfik Bouchaour** and U. Maschke (Villeneuve d'Ascq/France)

Liquid Crystalline Guanidinium Ion Pairs
Martin Butschies, S. Sauer and S. Laschat (Stuttgart)

Cruciforms with a Pyrazine Centre – Discotic Liquid Crystals and Acidochromic Fluorophores
S. Moschel, V. Schmitt and **Heiner Detert** (Mainz)

The Synthesis of Novel Phenylene-Modified Bolaamphiphiles: How Does the Substitution Pattern Influence the Aggregation Behaviour and the Miscibility with Phospholipids?
Simon Drescher, A. Meister, S. Sonnenberger, S. Becker, G. Hause, B. Dobner and
A. Blume (Halle)

Novel Mesophases Formed by X-Shaped Bolaamphiphiles with Oligo (Phenyleneethinylene) Central Core
Helgard Ebert , M. Prehm, F. Liu, X. Zeng, G. Ungar and C. Tschierske (Halle)

Morphological and Electro-Optical Properties of Methacrylate-Based Polymer/Liquid-Crystal Films
F. Z. Elouali, M. Elouali, **Idriss Moundoungou** and U. Maschke (Villeneuve d'Ascq/France)

Polymer/Liquid Crystal Materials Containing Diamond Nanoparticules
M. Elouali, F. Z. Elouali, C. Beyens, Guy-Joël **Fossi-Tabieguia**, O. Yaroshchuk and
U. Maschke (Villeneuve d'Ascq/France)

Lyotropic Quasicrystals with 12- and 18-Fold Symmetry
S. Fischer, **Alexander Exner**, K. Zielske, J. Perlich, S. Deloudi, W. Steurer, P. Lindner and S. Förster (Bayreuth)

Structures at Liquid-Crystal/Liquid Interfaces: Variation of the Liquid Phase
Xunda Feng and Ch. Bahr (Göttingen)

Liquid-crystalline Polymorphism of Symmetrical Azobananas:
Bis(4-(4-alkyloxyphenyl) azophenyl)2-nitroisophtalates
Zbigniew Galewski and K. Żygadło

Design of Nematogenic Bent-Core Mesogens
Karina Geese, M. Prehm and C. Tschierske (Halle)

Self-Assembly Properties of Β-Glycolipids with Different Types of Alkyl Chains
Sven Gerber, V. Vill, G. Milkereit, K. Brandenburg, P. Garidel, V.M. Haramus and R. Willumeit (Hamburg)

Synthesis and Structure-Property-Relationships of Donor-Acceptor Substituted Star-Shaped Mesogens - A New Design Concept for Photovoltaic Materials?
Steffi Gloza, M. Jahr and M. Lehmann (Würzburg)

Synthesis of Calamitic Liquid Crystals with Laterally Substituted Core and Their Mesomorphic Properties
Frantisek Hampl, M. Cigl, R. Jurok, J. Svoboda, V. Novotná, M. Glogarová and Podoliak (Prague/Czech Republic)

Modified Electroluminescence of an Organic Light Emitting Diode Incorporating a Columnar Perylene Derivative and a Si_3N_4/SiO_2 Bragg Reflector
Olga Kasdorf, B. Ohms, H. Bock, U. Hilleringmann and H.-S. Kitzerow (Paderborn)

Interaction Mechanisms Between Mycobacteria and Antimicrobial Peptides
Max Koistinen, A. Böhling, G. Helms, S. Willcocks, U. Schaible and
Th. Gutsmann (Borstel)

New Class of Synthetic Peptides (Salps) Show Protection Against Septic Shock
Ina Kowalski, Y. Kaconis, G. Martínez de Tejada, T. Gutsmann and
K. Brandenburg (Borstel)

Cubosomes and Phase Behavior of the Phytantriol/Water/Ethanol System
Larisa Latypova and P. Pieranski (Paris-Sud/France)

Polar Order in Orthogonal Phases Formed by 4-Cyanoresorcinol Derived
Bent-Core Mesogens
Anne Lehmann, C. Keith, M. Prehm, J. K. Vij, Y. P. Panarin and C. Tschierske (Halle)

V-Shaped Benzodithiophenes and Their Nematic Mesomorphism
Matthias Lehmann, J. Seltmann and K. Müller (Würzburg)

Step-Index Silica Fiber with Parallel Liquid-Crystal-Filled Micro-Channel
Alexander Lorenz, H.-S. Kitzerow, M. A. Schmidt, H. Tyagi, N. Joly,
M. Scharrrer, S. Rammler and P. St. J. Russell (Paderborn)

Triphenylene-Silanes for Direct Surface Anchoring in Binary Mixed Self-Assembled Monolayers
Markus Mansueto, G. Tovar, J. Pflaum and S. Laschat (Stuttgart)

Self Assembly of Nanoparticles in Linear Arrangements Using Optical Storage Media for Nanoimprint Lithography
Isabell Mattern, J. Perlich and A. Meyer (Hamburg)

Generation of Membrane Curvature and Multibudded Tubules Mediated by the Coat Protein Complex II on Artificial Liposomes
Annette Meister, D. Glatte, S. Daum and K. Bacia (Halle)

Fabrication of Magnetic Nanodot Arrays Using Diblock Copolymer Micelles as Templates
Andreas Meyer, N. Franz, H.P. Oepen, S.V. Roth, G. Carbone and T. Metzgerd (Hamburg)

Measurement of the Tension of Freely-Suspended Liquid Crystal Filaments
Michael Morys and R. Stannarius (Magdeburg)

Investigation of Environnemental Hazards: Characterization of Commercial LCD Blends
Idriss Moundoungou, G.-J. Fossi Tabieguia, Y. Derouiche and
U. Maschke (Villeneuve d'Ascq/France)

Thermotropic and Lyotropic Phase Behaviour of Spacered Alkoxy Disaccharide Glycolipids
Ariane Munk, S. Raabe and V. Vill (Hamburg)

Preparation of Defined Micro- and Nanometer-Sized Structures from Liquid Crystalline Elastomers
Christian Ohm, R. Rix, D. Wenzlik, C. Serra and R. Zentel (Mainz)

Freely Suspended Smectic Films in Aqueous Environment
Karthik Reddy Peddireddy and Ch. Bahr (Göttingen)

Reaction-Diffusion Model for Holographic Polymer-dispersed Liquid Crystals Utilizing NMR Data of the Diffusion Coefficients
Andreas Redler, A. Hoischen, M. Tang, C. Schmidt and H.-S. Kitzerow (Paderborn)

Tristriazolotriazines with π-Conjugated Branches – Fluorescent Discotic Liquid Crystals
S. Glang, D. Borchmann, **Thorsten Rieth** and H.Detert (Mainz)

Chirality-Induced Changes of Micellar Shapes
S. Glässel, **Florian Schörg** and F. Giesselmann (Stuttgart)

Influence of a Facial Amphiphile on Lipid Model Systems
Peggy Scholtysek, A. Achilles, S. Drescher, C.-V. Hoffmann, B.-D. Lechner, A. Meister, S. Reuter, C. Tschierske, J. Kreßler, K. Saalwächter, K. Edwards and A. Blume (Halle)

Effects of Counterions on Photoconductivity in Columnar Mesophases
Peter Staffeld, M. Kaller, S. Laschat and F. Giesselmann (Stuttgart)

Ionic Liquid Crystals with 5-Phenylpyrimidine Building Block
Gundula Starkulla and S. Laschat (Stuttgart)

The Role of Ester Group Orientation on Mesomorphic Properties of Bent-Core Liquid Crystals: From Lamellar to Nematic Phases
Jiri Svoboda, M. Kohout, V. Kozmík, V. Novotná and M. Glogarová (Prague/Czech Republic)

Plateau Borders of Smectic Liquid Crystalline Films
Torsten Trittel, R. Aldred and R. Stannarius (Magdeburg)

Microscopic Study of the Fréedericksz Transition in a Liquid Crystal Embedding a Microdisk Resonator
Martin Urbanski, K. A. Piegdon, C. Meier and H.-S. Kitzerow (Paderborn)

Nanocomposite Materials for Optical and Sensor Devices
M.V. Yakemseva and **Nadezhda V. Usol'tseva** (Ivanovo/Russia)

Incorporation of Inorganic Nanorods into Cholesteric Liquid Crystals
Daniel Wenzlik, C. Sönnichsen and R. Zentel (Mainz)

ω-Nitrogenfunctionalized Glycolipids -Thermotropic and Lyotropic Phase Behavior -
Matthias Wulf, V. Vill, K. Brandenburg, P. Garidel, S. Hauschild and S. Förster (Hamburg)

Presenting persons are indicated in bold.

SELF-ASSEMBLY OF BOLAPHOSPHOLIPIDS IN WATER: FORMATION OF NANOPARTICLES; NANOFIBERS AND HYDRGELS.

O - 01

A. Blume, A. Meister, G. Graf, M. Bastrop, S. Drescher, B. Dobner

Institute of Chemistry – Physical Chemistry,
Martin-Luther-Universität Halle-Wittenberg, von-Danckelmann-Platz 4, D-06120 Halle, Germany

Amphiphilic molecules with one polar group and a hydrophobic alkyl chain form a variety of well-studied aqueous lyotropic phases. The most common ones are the normal and inverted micellar phases, the normal and inverted hexagonal phases consisting of cylinders packed in a hexagonal lattice, and the lamellar phases, where bilayers of the amphiphilic molecules are separated by water layers. Amphiphilic molecules with two polar headgroups connected by one or two long alkyl chains are called bolaamphiphiles [1]. Depending on the size of the polar groups in relation to the cross-sectional area of the connecting alkyl chains, these bolaamphiphiles form either the already known lyotropic phases or a completely new type of aggregate structure, namely very long and stiff nanofibers with a diameter similar to the length of the molecules [2,3]. These nanofibers lead to a gelling of the aqueous solution due to a physical cross-linking of the nanofibers via hydrophobic contacts and due to entanglements. These nanofibers can be converted into micellar-like aggregates upon heating. This process is connected with a "melting" of the hydrocarbon chains and can be followed by a different methods, such as DSC, FT-IR, WAXS, SANS, ESR, NMR, and electron microscopy [3-7]. The re-formation of the nanofiber network at low temperature is time and concentration dependent. Variation of the length of the hydrocarbon chain and the size of the headgroup leads to changes of the existence range of these nanofibers and micellar aggregates. When the headgroups of the bolaamphiphiles become too small, the fibers can convert to lamellar sheets [8]. Variation of the chemical structure of the bolalipid headgroup leads to pH-sensitive hydrogels. The nanofibers can also be used for binding Au-nanoparticles leading to linear arrays of Au-nanoparticles [9] and for templating to produce networks of hollow silica tubes.

Acknowledgements: This work was supported by grants from the Deutsche Forschungsgemeinschaft

References

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[3] Köhler, K., Förster, G., Hauser, A., Dobner, B., Heiser, U.F., Ziethe, F., Richter , W., Steiniger, F., Drechsler, M., Blume, A. *J. Amer. Chem. Soc.* **126**, 16804-16813 (2004)
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[7] Bastrop, M., Meister, A., Metz, H., Drescher, S., Dobner, B., Mäder, K., Blume, A. *J. Phys. Chem. B*, **115***,* 14–22 (2011)
[8] Meister, A.; Drescher, S.; Karlsson, G.; Hause, G.; Baumeister, U.; Hempel, G.; Garamus, V. M.; Dobner, B.; Blume, A. *Soft Matter* **6**, 1317-1324 (2010)
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O - 02

SYNTHESIS AND SELF-ASSEMBLY OF SEMICONDUCTING AND MAGNETIC PARTICLES

Horst Weller

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This talk describes recent developments in the synthesis and characterization of semiconductor and metal nanoparticles. Results on the growth kinetics and the control of size, shape and surface chemistry will be addressed. We present Monte Carlo simulations of an ensemble of growing particles showing that optimal conditions for the synthesis of highly luminescent semiconductor nanoparticles are maintained if the exchange rate of monomers at the particles' surface is high during the growth. Polarized absorption and emission is observed in quantum-dot-quantum-rod hybrid systems, which consist of a spherical CdSe particle coated by a rod-like CdS shell. Examples for 2D and 3D self-assembly of nanoparticles are given. We report on the formation of colloidal crystals from semiconductor and magnetic nanoparticles. Self-assembly of ZnO nanoparticles in solution leads to the formation of single crystalline nanorods via oriented attachment. During this process the nanoparticles align in a chain-like structure and fuse under conservation of their crystallographic orientation. In the case of PbS nanocrystals oriented attachment leads to the formation of ultrathin 2D sheets. Finally we report on bio-functionalisation of nanoparticles and their use in medicine.

PH- AND SALT-DEPENDENT AGGREGATION BEHAVIOR OF SYMMETRIC SINGLE-CHAIN BOLAPHOSPHOLIPIDS

<u>G. Graf</u>[1], S. Drescher[1, 2], A. Meister[3], B. Dobner[2], A. Blume[1]
[1]*Institute of Chemistry, Martin-Luther-University Halle-Wittenberg*
[2]*Institute of Pharmacy, Martin-Luther-University Halle-Wittenberg*
[3]*HALOmem, Martin-Luther-University Halle-Wittenberg*

Long-chain bolaphospholipids with a single alkyl chain and two phosphodimethylethanolamine headgroups (Me_2PE-C32-Me_2PE) self-assemble in water into fibers and spherical micelles depending on the temperature, the pH value and the salt concentration of the suspension. They gel water very efficiently by the formation of a three-dimensional network of nanofibers that are built up by stretched bolaphospholipid molecules with an all-*trans* conformation of the alkyl chain [1-3].

The Me_2PE headgroup is zwitterionic at pH 5 (Fig. 1) and can be deprotonated at higher pH values. This results in negatively charged headgroups leading to repulsive interaction between the molecules. pH-dependent DSC measurements were carried out that suggest a significant destabilization of the fiber aggregates and no gelation at ambient temperature above pH 10. TEM images supported this assumption. Further DSC and rheological measurements were performed at pH 11 with different salt concentrations (NaCl, KCl, $MgCl_2$ or $CaCl_2$) to examine the influence of mono- and divalent cations on the bolalipid system. It was shown that the cations were able to shield the electrostatic repulsion of the headgroups enabling the formation of nanofibers and a viscoelastic gel at ambient temperature.

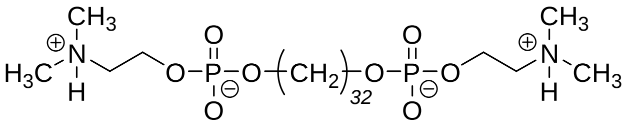

Fig. 1: Chemical structure of Me_2PE-C32- Me_2PE at pH 5

References

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[2] A. Meister, *et al.* J. Phys. Chem. B 112, 4506 (2008)
[3] S. Drescher, *et al.* Biophys. Chem. 150, 136 (2010)

O - 04

FERROELECTRIC AND ANTIFERROELECTRIC PHASES OF BENT MESOGENS WITH LARGE OPENING ANGLE

*M. Kirchhoff, *U. Kornek, *S. Stern, *A. Eremin, *R. Stannarius, §C. Zhu, §C. S. Park

*Otto-von-Guericke Universität Magdeburg, Abt. Nichtlineare Phänomene
§Colorado University, Liquid Crystal Institute, Boulder (USA)

A variety of polar smectic phases have been found in liquid crystals formed by achiral bent-core mesogens. The extent of the polar packing is largely attributed to the opening angle of the mesogen. Large opening angle reduces the tendency to polar packing resulting in occurrence of conventional SmA and SmC phases. Still, due to long range polar correlations, the behavior of such materials is unusual and poorly understood.

In this contribution we discuss the behavior of a bent-core mesogen with a large opening angle showing the conventional SmA phase as well as the polar SmCP phase [1]. These phases possess several interesting features, e.g. a field-induced tilt (quadratic electroclinic effect) in the SmA phase [2], and chirality flipping in the $\mathrm{SmCP_A}$ phase [3]. The behavior in free-standing films is particularly interesting: Two types of SmC subphases could be distinguished: a low-temperature antiferroelectric $\mathrm{SmCP_A}$ phase and a high-temperature ferroelectric $\mathrm{SmCP_F}$ phase showing a modulated ground state. Spontaneous polar order was found in free-standing film geometry but could not be detected in glass cells. In thin films, 2π inversion walls occur in the electric field, indicating the ferroelectric order in the $\mathrm{SmCP_F}$ phase (Fig. 1). The transition into the $\mathrm{SmCP_A}$ phase is marked by the splitting of the 2π walls into pairs of π walls along with a change of the switching character. Using various experimental techniques like polarizing microscopy, second harmonic generation and synchrotron X-Ray, we try to get insight into the polar behavior of the phases which lie at the boundary between the conventional calamitic and "banana" phases and the couplings between the tilt and polarization.

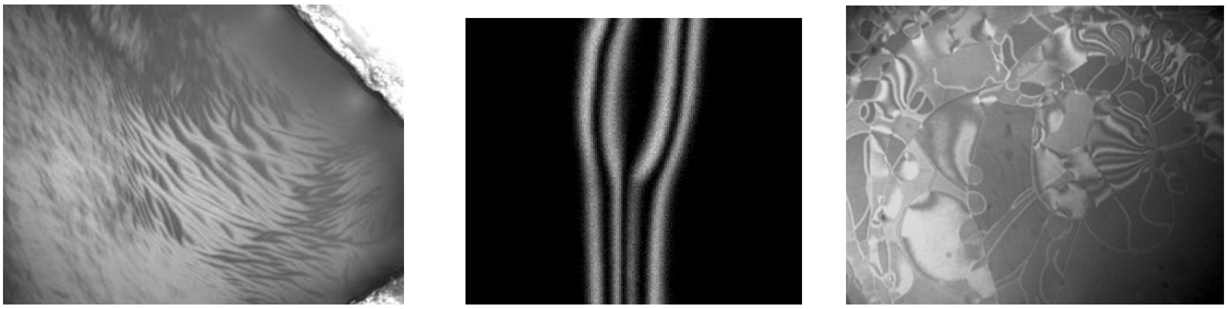
a) b) c)

Fig. 1. a) SmA-SmCP transition in thin film geometry, director modulation (T=128°C); b) splitting of π-walls at the SmCP-SmC transition (T=107°C), and c) odd-even switching of the number of layers generates different textures under DC electric field due to being $\mathrm{SMCP_A}$ phase at T=102°C

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BEAM CHARACTERISTICS OF LIQUID CRYSTAL LASERS

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During the past decade, photonic band edge lasers based on dye-doped cholesteric liquid crystals (CLCs) have attracted considerable interest as self-organized, microscopic, tunable laser sources. Different applications require different characteristics of the emitted laser beam. We have analyzed the spatial intensity distribution and temporal fluctuation of CLC laser emission in the far field, and how it depends on parameters like film thickness, pump spot area, and pump energy.

The main results are: Beam divergence increases with increasing pump spot area – obviously, emission is not diffraction limited, contrary to expectations. The beam divergence is not significantly affected by the film thickness. The far field is composed of a broad central spot and a surrounding system of concentric rings. The ring pattern becomes more pronounced with increasing pump spot size. The radial periodicity of the ring pattern is not affected by the pump spot size, but depends on the film thickness: obviously, the radial intensity modulation is not due to simple diffraction effects. Instead, it can be related to the angular dependency of the sample's optical properties, i.e. the angular dependence of the photonic stop band and location of the Fabry-Perot interference fringes. Statistical analysis of a time series of far field patterns reveals fluctuations in the light field (fluctuating speckle pattern), which probably originate from thermally driven director fluctuations disturbing the cholesteric order. With increasing pump spot size, these fluctuations diminish. This can be explained by a more efficient averaging over the local structural fluctuations with increasing laser-active sample volume.

Several conclusions with respect to applications can be drawn: For efficient coupling into fiber-optical systems, a small pump spot yielding an almost Gaussian beam profile (unperturbed by pronounced fringe pattern) might be favorable. On the other hand, applications requiring a stable spatial field distribution (e.g. holography) would benefit from large pump spot sizes. Simple integration into miniaturized optical systems might benefit from a small pump spot size, as the resulting small divergence of the emitted beam might render light collecting optics unnecessary.

Thanks are due to Dr. Tim Wilkinson (University of Cambridge) for providing sample cells, as well as Alps Electric UK Ltd (Chiralase project) and the German Research Foundation (Graduiertenkolleg 1464 – *Micro- and Nanostructures in Optoelectronics and Photonics*) for financial support.

O - 06

POLAR ORDER IN FREE-STANDING FIBRES OF THE B_7-PHASE

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The discovery of novel liquid crystalline (LC) phases made of bent-core molecules [1] opened up a new field in LC-science. Spontaneous emergence of polar order and chirality in materials of achiral mesogens induces a rich diversity of microscopic structures. One of these is the polarization-modulated phase of bent-core mesogens, which exhibits a variety of the most beautiful textures in polarizing microscopy [2]. More interestingly it is able to form free-standing filaments made of cylindrically arranged smectic layers [3].

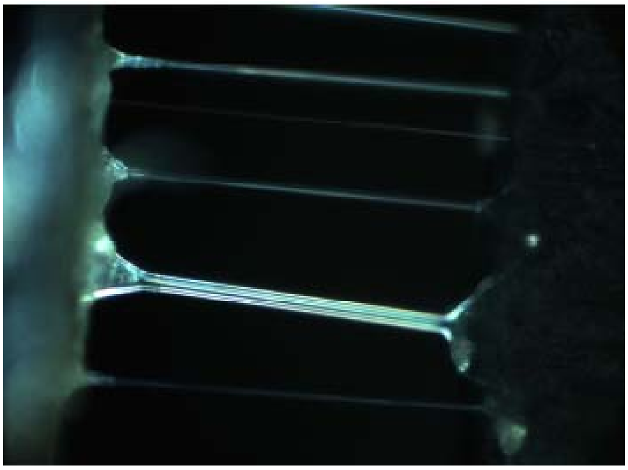

Fig. 1 Freely-suspended filament in PM-SmCP phase.

These objects can reach diameter-to-length-ratios above 1000, the Rayleigh-Plateau instability is suppressed. Their local structure is different from the bulk, resulting in a broken up-down symmetry along the long filament axis. This leads to a distinct ferroelectric order of single fibers which is connected to the high stability of the geometry in the compound discussed. Here, we present evidence for this structural stabilization using microscopy, nonlinear optics (Second Harmonic Generation, SHG), and SHG-microscopy techniques. We also discuss the evolution of the polar structure during the $SmCP_A \rightarrow$ PM-SmCP transition and how the polar order affects the stability of the filaments.

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ORIENTATIONAL ORDER PARAMETERS OF A DE VRIES-LIKE FERROELECTRIC LIQUID CRYSTAL: EXPERIMENTAL COMPARISON USING POLARIZED RAMAN SPECTROSCOPY AND X-RAY DIFFRACTION.

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We carried out a study on the (*S*)-hexyl-lactate ferroelectric liquid crystal 9HL (Fig. 1) using confocal polarized Raman spectroscopy (PRS) as well as X-ray scattering. This material, showing a second order SmA*-SmC* phase transition, exhibits characteristics of de Vries-like materials [1].

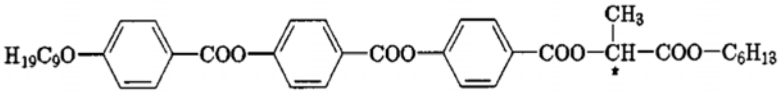

Figure 1: Molecular structure of the ferroelectric liquid crystal 9HL

Hayashi *et al*. [2] have previously used PRS to obtain the orientational order parameters of a de Vries-like material (TSiKN65) which shows a first order phase transition. We followed the same experimental procedure for 9HL as described there. In particular, the phenyl stretching mode (1606 cm^{-1}) of the core part of the molecule was studied for a homogenously aligned sample of 4 µm thickness. Then, the apparent orientational order parameters, $\langle P_2 \rangle_{app}$ and $\langle P_4 \rangle_{app}$, were calculated for the SmA* and SmC* phases. On the other hand, the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ were evaluated from X-ray scattering measurements as described in ref. [3]. Surprisingly, the values obtained in the uniaxial SmA* phase using X-ray scattering (e.g $\langle P_2 \rangle = 0.6$) are lower than those obtained from the Raman experiments (e.g $\langle P_2 \rangle = 0.8$) measured at the same temperature *T*.

The discrepancies between both experimental techniques could be explained in terms of the effective part of the molecule that each of these two methods really probes. Indeed, taking into account the angle between the particular Raman axis of vibration and the rotation axis of the molecule we found that the data from Raman and X-ray experiments are in better agreement.

In conclusion, we observed that our material possesses in any case positive order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ and although the experimental techniques yielded different values, they could be interconnected via the molecular model. With the comparison of the order parameters from both experimental techniques, very precise information about the real orientational order could be achieved.

Financial support from the CONACyT and DAAD is gratefully acknowledged.

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O - 08

INFLUENCE OF SOLVENT QUALITY ON THE SELF-ORGANIZATION OF ARCHETYPICAL HAIRY RODS-BRANCHED AND LINEAR SIDE CHAIN POLYFLUORENES: RODLIKE CHAINS VERSUS “BETA-SHEETS” in SOLUTION

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We report on the nanoscale structure and solvent-induced phase behavior of two, nearly similar π-conjugated hairy-rod polymers, branched side chain poly[9,9-bis(2-ethylhexyl)fluorene-2,7-diyl] (PF2/6) and linear side chain poly[9,9-dioctylfluorene-2,7-diyl] (PFO or PF8), in good and bad (or poor) solventssdeuterated toluene and deuterated methylcyclohexane (MCH)sat 20 °C. Small-angle neutron scattering (SANS) measurements exploiting contrast variation with side chain deuterated PFO polyfluorene have been employed and complemented by optical absorption measurements. In toluene both PF2/6 and PFO adopt an elongated (rodlike) conformation containing predominantly only a single polymer chain (diameter of the order of 1 nm), which indicates dissolution down to the molecular level. In contrast, in MCH, PF2/6 shows an elongated structure while PFO forms sheetlike structures (characteristic thickness of 2-3 nm), thus dissolving down to the “colloidal” level. The elongated structure of PFO consists of individual polymer chains adopting dominantly a conformational isomer C_α. The thickness of sheetlike PFO particles corresponds to that of around two polymer layers and side chain contrast variation gives an evidence for an even distribution of the backbones within the sheets. These sheets are potentially an initial stage of PFO crystallization and also contain conformational isomer C_α of those chains observed in the so-called beta-phase (or beta-sheets) in the solid state. The observed phenomena were not found to depend on concentration over the concentration range 5-10 mg/mL.

NEMATIC TEXTURES IN MICROFLUIDIC ENVIRONMENT

O - 09

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Novel colloidal systems consisting of colloidal particles dispersed in nematic liquid crystals have recently attracted large interest [1]. In these systems, the colloidal pair interaction is not of the van der Waals or electrostatic type, but stems from the elastic distortion of the director field of the nematic host. A direct manipulation of these systems can be achieved by means of optical tweezers. A different manipulation approach could be the use of forces which are present when the systems flow through an appropriate microfluidic device.

In the present study, we investigate the flow of a nematic liquid crystal through microchannels possessing degenerate planar anchoring conditions on the channel walls. Depending on the channel dimensions and the flow rate, the formation of different textures and topological defect structures is observed and studied using polarizing optical microscopy and fluorescence confocal polarizing microscopy. The observed structures comprise π-walls, disclination lines pinned to the channel walls, disclination lines with one pinned and one freely suspended end, and disclination loops freely flowing in a chaotic manner. We focus on the controlled creation, evolution and morphology of different kinds of π-walls and pinned disclinations. Such defects and textures of the nematic matrix can potentially be applied for guiding the transport of colloidal particles or assemblies using an appropriate microfluidic device.

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O - 10

NEW MATERIALS FOR POLYMER-STABILISED BLUE PHASE

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Division Performance Materials, BU Liquid Crystals - Research & Development, Merck KGaA

Compared to other liquid crystalline mesophases the Blue Phase exhibits extremely fast switching via induced birefringence by an external field. However, the pure Blue Phase is characterized by a rather narrow temperature range on the order of a few K. For display applications, one very promising way to broaden the stable temperature range is achieved by polymer-stabilization of the Blue Phase. A crucial prerequisite for efficient stabilization is the optimal material selection/matching of reactive mesogens (RMs) and the chiral host. New material concepts will be introduced and discussed.

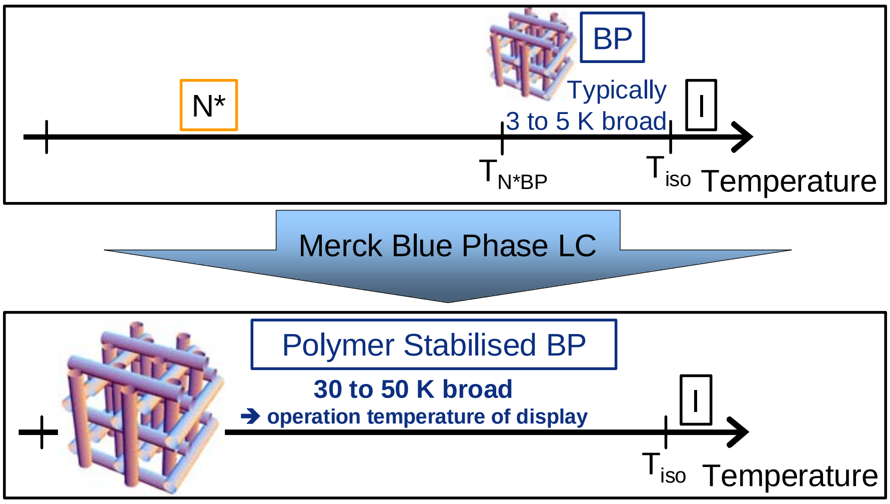

Figure 1: Schematic drawing of broaden the stable temperature range of Blue Phase with polymer stabilisation.

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DESIGN STRATEGIES FOR IONIC LIQUID CRYSTALS

O - 11

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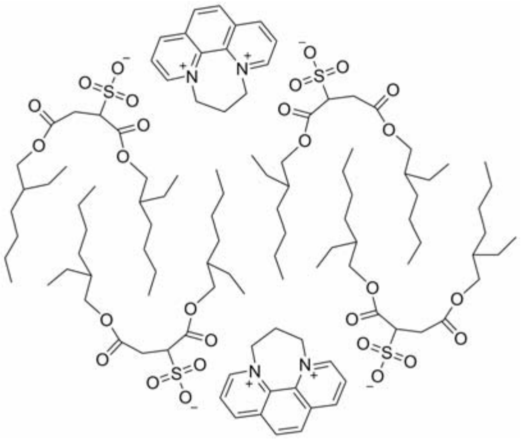
The aim of this presentation is to give an overview of different approaches for obtaining ionic liquid crystals. *Ionic liquid crystals* (ILCs) are a fascinating class of molecular materials: they combine the characteristics of liquid crystals (anisotropy of physical properties) with those of ionic liquids (electric conductivity, 'tuning' possibilities, thermal stability …) [1]. While most liquid crystals are neutral organic compounds, ionic liquid crystals consist of cations and anions. Due to the ionic character, their properties may differ significantly from those of conventional liquid crystals. Typical for the ionic compounds is the ion conductivity. A common approach towards ionic liquids crystals starting from ionic liquids is to extend the length of the alkyl chain. 1-Alkyl-3-methylimidazolium salts [$C_n$mim][X] exhibit mesophase behavior for long alkyl chains. The minimum chain length depends on the type of anion. However, there exist other strategies to transform ionic liquids into liquid crystals. These include the terminal or lateral attachment of mesogenic groups via a flexible spacer, or incorporation of the cationic core within rigid part of the mesogen. The choice of the cationic is also of importance. Imidazolium salts have a delocalized positive charge and form in general only smectic A phases. Pyrrolidinium salts, on the other hand, have a localized positive charge and form highly ordered smectic phases. A smectic T phase has been observed for these compounds [2]. An usual new class of ionic liquid crystals are 1,10-phenanthrolinium cations combined with dodecyl sulfate or dioctyl sulfosuccinate anions. These compounds form smectic A and E phases.



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O - 12

NEW 2D-CORRELATED STRUCTURE OF A LYOTROPIC LIQUID CRYSTALLINE DIOL

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The lyotropic liquid crystalline 5-[4-(5-*n*-heptylpyrimidine-2-yl)-phenyloxy]-pentane-1,2-diol (HPPOPD) has formerly been reported to exhibit a nematic, a lamellar L_α- and a quite uncommon lamellar tilted (SmC-analog) mesophase [1]. In search of lyotropic SmC-analog phases, we were now able to show by detailed X-ray investigations, that the tilted lamellar phase is indeed a rather complex 2D-correlated structure.

The sharp small-angle reflections of this 2D-correlated phase (Figure 1 a), which were obtained by good alignment of the sample, were indexed on an oblique lattice belonging to the plane group *p*2. The molecules in this lattice ($a = 12.1$ nm, $b = 7.4$ nm, $\alpha = 90°$ at 70 °C and 7 wt.% H_2O) are organized in ribbons, forming a so far not reported liquid crystalline phase, in which a stacking of three staggered ribbon-layers occurs (Figure 1 b). Next to this phase we were able to make out not only the nematic and the lamellar L_α-phase, but also two more lyotropic mesophases. Increasing the concentration of H_2O leads to the formation of a hexagonal phase at high temperatures and to a further liquid crystalline phase at lower temperatures. This phase not only shows a very interesting texture, but also a complex diffraction pattern indicating a 2D-correlated structure.

In conclusion, the supposed SmC-analog lyotropic phase of HPPOPD turned out to be a new 2D-correlated lyotropic structure. Thus, this is another striking example of the unresolved problem why tilted fluid structures – even though quite common in thermotropics – are rarely found in lyotropics.

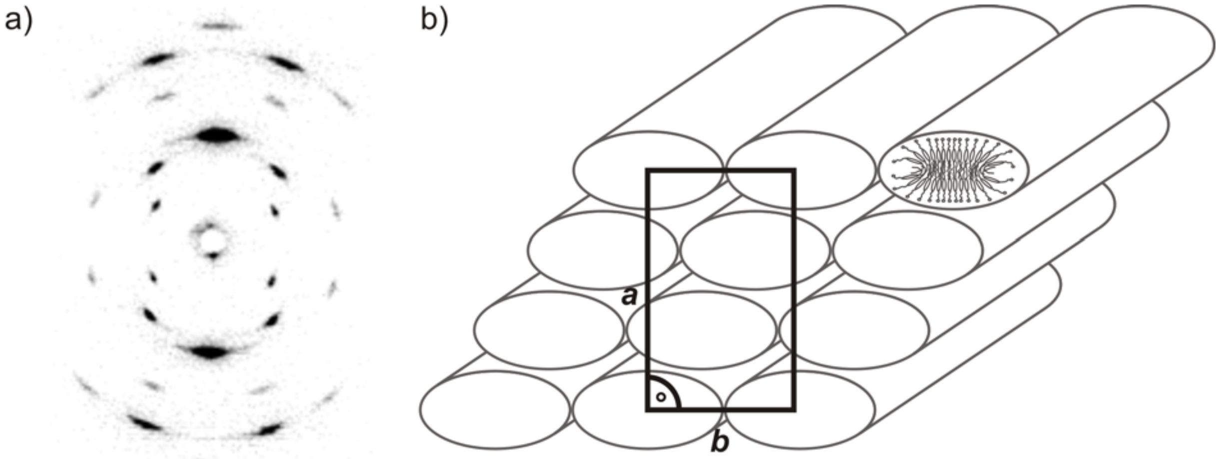

Figure 1: a) X-ray pattern of the *p*2-phase; b) Structure of the *p*2-phase, the ribbons are pictured in grey and the unit cell in black.

Financial support by the Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged.

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COMPARATIVE STUDY OF THE EQUILIBRIUM PHASE DIAGRAMS OF PROPYLENEGLYCOL-DIACRYLATE / LIQUID CRYSTAL BLENDS

O - 13

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A comparative study of the equilibrium phase diagrams of poly (propylene glycol) diacrylate (PPGDA)/ liquid crystal mixtures before and after UV polymerization was performed. The PPGDA monomers used here differ only by their molecular weights between the two reactive chain ends, giving the formation of chemically cross-linked polymer networks with varying distances between two cross-linking points. The chain length of the monomeric species was determined by ^{1}H-NMR measurements, giving molecular weights M_n of 350 g/mol for TPGDA, 520 g/mol for PPGDA540 and 870 g/mol for PPGDA900. E7 was employed as nematic eutectic LC mixture.

Equilibrium phase diagrams were obtained from observations made by polarizing optical microscopy (Fig. 1). The uncured systems exhibit a single isotropic phase in the upper part of the phase diagram which covers an important area in the temperature/composition frame and expresses the high miscibility of the monomeric systems. In the nematic+isotropic (N+I) phase, where the miscibility is strongly reduced at lower temperatures, the monomer in its isotropic phase coexists with a nematic phase of almost pure LC. The (N+I/I) transition temperature decreases rapidly with addition of monomer to pure E7.

The cured systems show completely different phase diagrams which will be discussed together with the dependencies of the polymer glass transition temperature on LC concentration (Fig 2).

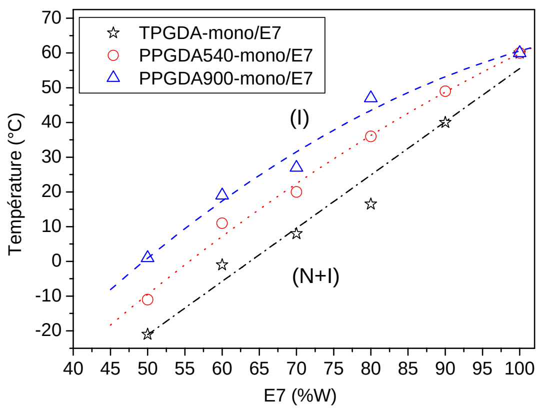

Fig.1: Phase diagrams of PPGDA/E7 systems

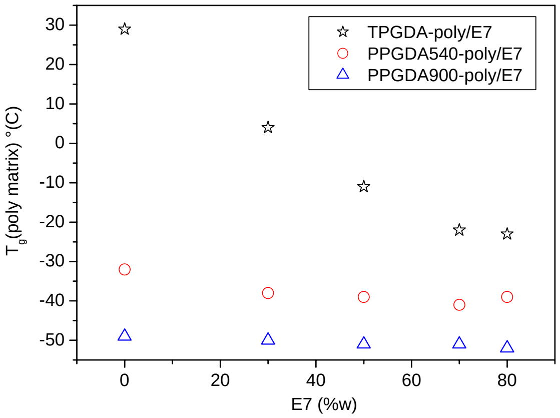

Fig.2: Variation of T_g (polymer) with LC concentration

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O - 14

ORDERING TRANSITIONS OF LIQUID CRYSTALLINE THIN FILMS DRIVEN BY *IN-SITU* ENZYME-INDUCED HYDROGEL DEGRADATION

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Stimuli-responsive hydrogels have unique biocompatibility, with enzyme-responsive molecular hydrogels in particular showing great promise as responsive components in medical devices and biomaterials for detecting disease-specific molecular signals. Here we describe a general and novel procedure that utilizes liquid crystal (LC) ordering transitions to report on enzyme-induced hydrogel degradation. Gel degradation associates with planar-to-homeotropic LC anchoring transitions, leading to diagnostic bright-to-dark optical readouts without requiring complex instrumentation.

Aromatic peptide amphiphiles were chosen as the hydrogelators, as they self-assemble into gel fibrils that combine β-sheet and π-stacking motifs. In-situ hydrogelation at the LC/gel interface caused the LC to adopt planar anchoring. A phospholipid containing-hydrogel was then assembled over the first hydrogel, preserving LC planar anchoring (Fig. 1A). Addition of an enzyme that cleaves a target sequence in the hydrogelator resulted in hydrogel degradation, liberating phospholipid into the bulk solution. Spontaneous phospholipid adsorption at the LC/aqueous interface then induced the LC ordering transition from planar to homeotropic, leading to a bright-to-dark optical readout under crossed polars (Fig. 1B-C). Enzymes that do not initiate hydrogel degradation cannot liberate phospholipid, and the LCs preserve the planar anchoring under the robust hydrogel layers. The results presented here show that this hydrogel/LC composite allows label-free monitoring of dynamic hydrogel degradation, and shows potential for the diagnostic screening of hydrolytic enzymes.

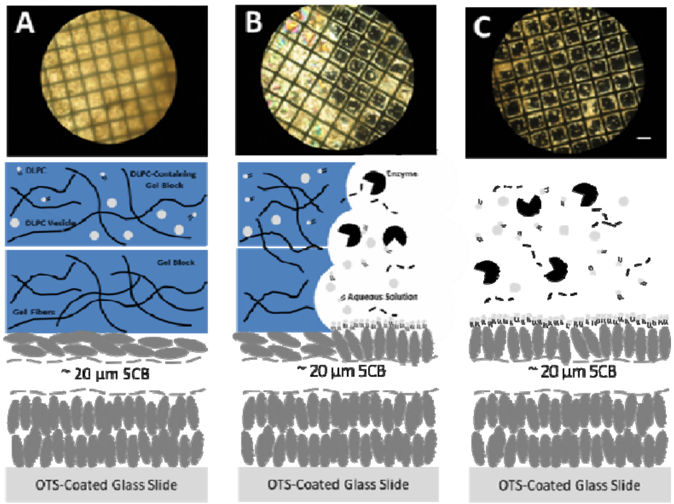

Fig. 1 *In situ* subtilisin-induced Fmoc-TL-OMe hydrogel degradation at 5CB-gel interfaces. (A-C) Optical images of 5CB anchoring at the 5CB-gel interface upon subtilisin addition for (A) 0hr, (B) 6hr, and (C) 7hr at 25ºC. The 5CB reveals dynamic anchoring transition from planar to homeotropic alignment in parallel to the subtilisin-induced Fmoc-TL-OMe degradation at interfaces. Cartoon representation for the 5CB anchoring transition upon subtilisin-induced Fmoc-TL-OMe degradation. Scare bar is 200 µm.

ANALYSIS OF THE FORMATION OF POLYMER/LIQUID CRYSTAL SYSTEMS PREPARED BY ULTRAVIOLET AND ELECTRON BEAM CURING

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Polymer/liquid crystal composite materials of the type PDLC (for Polymer Dispersed Liquid Crystals) are usually employed in the field of electro-optical applications. Their properties depend mainly on the polymer structure and on the morphology of the segregated LC domains.

In this work, films were elaborated by polymerization under ultraviolet (UV) and electron beam (EB) radiation of the monomer 2-ethylhexylacrylate in absence and presence of nematic LC 4-cyano-4'-pentylbiphenyl (5CB). The Fourier Transform InfraRed Spectroscopy (FTIR) technique was employed to investigate the progress of the reaction of radical polymerization and to calculate the monomer/polymer conversion ratio.

Characterization of the obtained samples by Gel Permeation Chromatography (GPC) made it possible to obtain informations on the molar mass as well as on the distribution of the chain length of the obtained polymer. NMR (Nuclear Magnetic Resonance) spectroscopy analysis was carried out to get knowledge about the polymer structure. As the glass transition temperature of the polymer (T_g) is an important parameter in the study of these composite materials, calorimetric experiments were conducted by DSC (Differential Scanning Calorimetry) in order to characterize the evolution of T_g of the polymer and other parameters as function of the concentration of LC.

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O - 16

THE SIMPLEST TWO-DIMENSIONAL ANISOTROPIC FLUIDS˜ FLOW ORIENTATION COUPLING IN FREE-STANDING SmC FILMS

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Free-standing films of thermotropic smectic tilted phases (smC, smC*) represent the simplest quasi two-dimensional liquids. Due to their layered structure, stable films of two to thousands of molecular layers in thickness can be prepared. Distortions of the c-director (local tilt-azimuth of the mesogens) generate elastic forces and torques. Such features are unique to anisotropic liquids. As the material flow is confined to a very thin sample, the coupling between flow and reorientation can be explored in a quasi two-dimensional geometry.

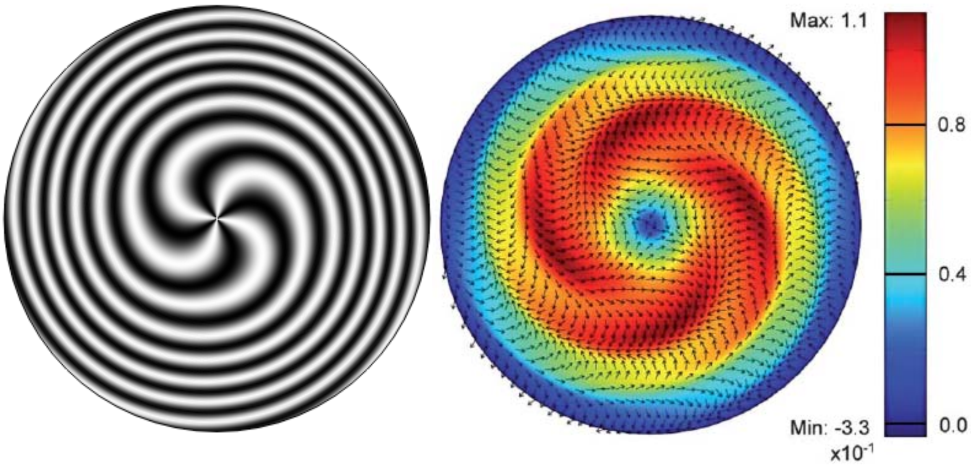

Fig. 1: Calculated texture between crossed polarizers (left) and corresponding tangential flow (right, colour, in μm/s) and director fields (right, arrows) in a relaxing spiral around a –1-defect [3].

By means of external electric or magnetic fields, non-equilibrium director configurations can be prepared. Their relaxation dynamics provide direct access to viscoelastic material properties. We examine simple geometries (circular films) with textures of the director field in the form of targets or spirals in polarised light (Fig. 1, left). The relaxation dynamics have been described earlier within a linear model neglecting material flow and elastic anisotropy. However, this approach leads to large quantitative and even qualitative errors in the fit of the rotational viscosities. Actually, induced flow contributes to an accelerated relaxation of the orientational distortions. We solve the full 2D dynamic equations - the incompressible anisotropic Navier-Stokes equation and torque balance - numerically with standard finite element methods (COMSOL package). Comparison with experiments provides quantitative data of shear-viscosities of the smectic, which are very difficult to access otherwise. In the simplest model, five independent shear and rotational viscosity coefficients enter the hydrodynamic equations. We discuss general aspects, such as the flow field structure (Fig. 1, right) and the coupling of flow field and director, and we demonstrate the influence of individual viscosity coefficients and of elastic anisotropy on the relaxation dynamics.

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ON A THREE-PHASE COEXISTENCE OF ISOTROPIC PHASES IN THE PHYTANTRIOL/WATER/ETHANOL SYSTEM

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The phase behavior of the ternary system phytantriol/water/ethanol is very complex (see the communication of L. Latypova). In particular it involves the coexistence of three isotropic phases - L1, L2 and L3 – occurring during the transition L1/L2 → L1/L3.

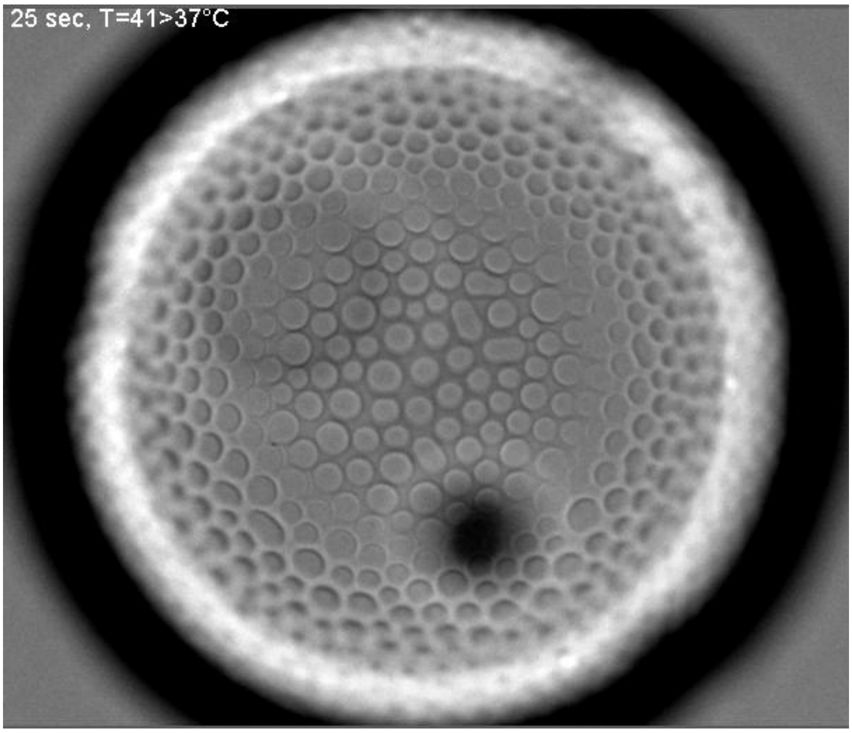

Figure: Droplets of the sponge phase L3 growing at the L2/L1 interface in the phytantriol/water/ethanol ternary system.

We will focus on experimental results and on theoretical aspects of this transition.

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O - 18

HEKATES – FROM THE FORMATION OF LC NANO-STRUCTURES AND FUNCTIONAL, MULTICHROMOPHORE STAR MESOGENS

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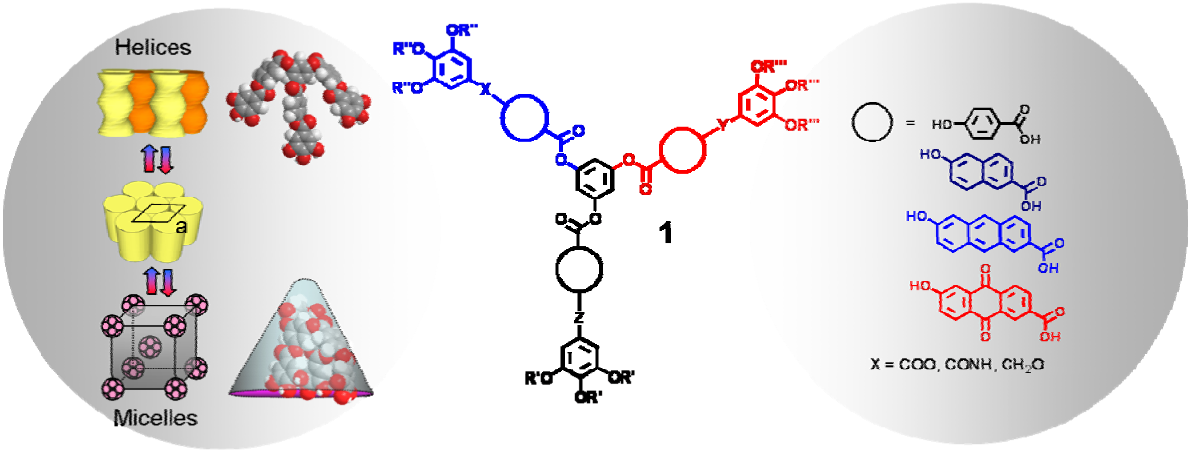
Hekates are star-shaped mesogens with up to three different arms. In the family of semi-flexible oligobenzoate stars, nano-segregation and folding to wedge or cone shaped conformers control the formation of helical and micellar nanostructures and thus, the symmetry of the soft crystalline and liquid crystalline phases.[1,2,3] Micelles are enormously stable and can be visualised even by AFM techniques.[4] The understanding of the self-assembly should enable us to control also the structure formation of Hekates with functional units such as chromophores. First attempts with the small chromophore naphthalene revealed no different mode of self-organisation compared with the parent oligobenzoate mesogens, but afforded materials with promising charge carrier mobilities.[5] This encouraged us to synthesise more complex structures with larger and different chromophores, like pyrene, anthracene and anthraquinone. Mesogens with donor and acceptor chromophores are especially attractive with respect to photovoltaic applications.



Beside the structure formation of the parent and naphthalene containing Hekates, we present here the challenging preparation of the appropriately substituted chromophore building blocks, the arm units and the synthesis of stars **1** with up to two different functional units, e. g. donor and acceptor chromophores. The structure is studied by polarised optical microscopy, differential scanning calorimetry and X-Ray scattering. The photophysical properties are determined by UV/Vis and fluorescence spectroscopy in solution and solid state.

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FLUORESCENT MESOGENS BASED ON ROD-SHAPED AROMATIC HYDROCARBON CORES

O - 19

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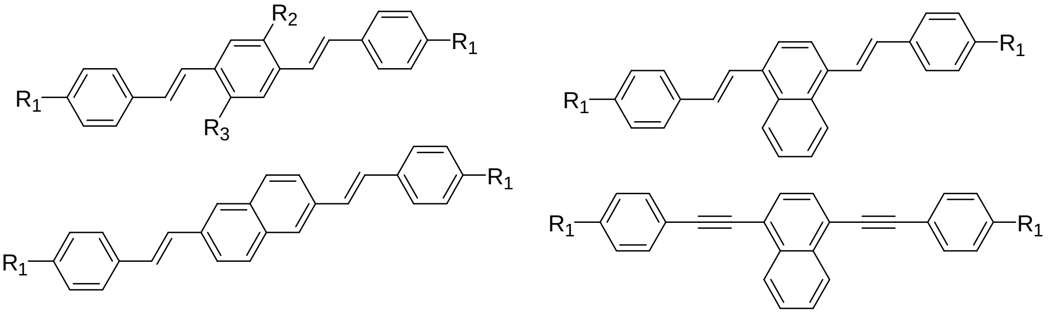
Certain device applications require the generation of polarized light which can be achieved with fluorescent dichroic dyes. If reactive mesogens are used as nematic orientation matrix it is preferable that the dye displays a nematic phase as well to ensure an efficient miscibility. However, the design of emissive calamitic mesogens is still challenging since the design principles for achieving highly efficient luminophores and those for developing rod-like liquid crystals are not always consistent with each other [1].

We present here our approach towards calamitic luminophores based on an elongated aromatic hydrocarbon core. These are composed of a central benzene or naphthalene unit substituted with either phenylethenyl of phenylethinyl moieties. The terminal and lateral substitution pattern were systematically modified.



Chemical structure of the investigated compounds.

The compounds display nematic and/or smectic liquid crystalline phases. The mesomorphic behaviour will be discussed as a function of the core structure and the incorporated substituents.

The fluorescence properties were studied in solution and in the solid state. The compounds show photoluminescence in the blue region, Thereby, the emission maximum can be tuned by the structure of the chromophoric core and by the substituents attached to it.

Acrylate substituted naphthalene-bis-tolanes and naphthalene-bis-phenylene-vinylenes were investigated in mixtures nematic reactive mesogens. Uniaxial orientation of the mixed systems was achieved by annealing of spin-coated films on polyimide orientation layers within the liquid crystalline temperature range. The film anisotropy was stabilized by subsequent photocrosslinking. The films show linear polarized photoluminescence. The fluorescence intensity can be enhanced with films containing both chromophores due to radiationless energy transfer from the acetylene to the ethylene.

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LIQUID CRYSTALLINE CROWN ETHERS: EFFECT OF CROWN SIZE AND COMPLEXATION

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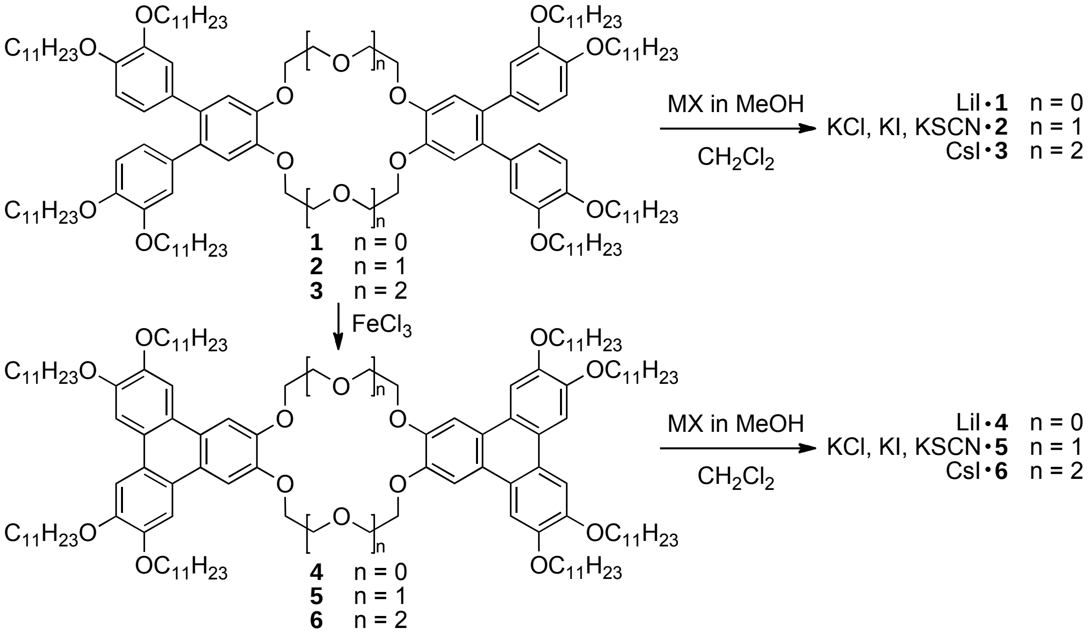
Liquid crystalline crown ethers are interesting hybrid materials combining the properties of crown ethers such as selective ion complexation and the ability to form ion channels [1] with the electronic properties of extended aromatic substituents, e.g. photoconductivity [2]. Recently, we synthesized and investigated crown ethers with twisted *o*-terphenyl (**1**–**3**) and flat triphenylene (**4**–**6**) substituents with regard to the size of the central crown ether and the presence of various salts (Scheme 1) [3-5].



Scheme 1: Synthesis and complexation of crown ethers **1**–**6**.

Three main trends were observed comparing the different crown ether compounds:

1) Triphenylene-substituted derivatives **4**–**6** possess higher clearing temperatures compared to their *o*-terphenyl-substituted precursors **1**–**3** due to increased π-π-stacking.
2) Clearing temperatures and phase widths depend on the diameter of the crown ether and increase with decreasing ring size, most evident for the series **4**–**6**.
3) Complexation with salts possessing hard counterions (e.g. KCl) leave the mesomorphic properties virtually unchanged. Salts with soft counterions (e.g. LiI, KI and KSCN) lead to a significant increase in the mesophase range due to the presence of tight ion pairs.

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PHOTON-CONTROLLED ISOTHERMAL PHASE TRANSITIONS AMONG COL$_R$, SmA AND iSOTROPIC PHASES ACCOMPANIED WITH THE ALTERNATIVE CHANGE OF MOLECULAR ANISOTROPY

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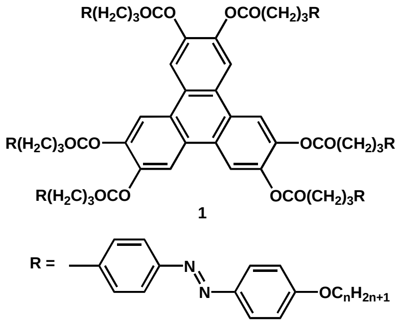

1a : $C_{10}H_{21}$
1b : $C_{12}H_{25}$
1c : $C_{14}H_{29}$
1d : $C_{16}H_{33}$

Liquid crystal is a supramolecular system exhibiting dynamic behaviour as molecular aggregations. This characteristic nature is subjected to external fields and perturbations such as electric and magnetic fields. In particular, photon flux is one of the most attractive sources of external forces to control such a dynamic state of matters and isothermal phase transistion is one of the most interesting issues in terms of the generation of new functional materials, especially which could be remote-controlled without any physical touch to the systems [1]. Once it was found that a triphenylene mesogen possessing six decyloxyazobenzene (***1a***) exhibits kinetically controlled phase transition between calamitic smectic A and discotic hexagonal columnar mesophases, probably accompanied with the alternative change of molecular shape between a rod-like and disc-like ones [2]. This sort of peculiar behaviour of shape-changeable mesogens is also expected to give the similar phase transition behaviour by photo-irradiation to reversibly cause the molecular shape change of the azobenzene moieties.

In this work, the homologues were synthesized and studied on the mesomorphism. In particular, the tetradecyloxy homologue, ***1c*** was investigated on the mesomorphic behaviour under photo-irradiation to find a sequence of enantiotropic phase transitions among Col$_r$, SmA and Iso phases.

Fig. 1 shows the phase diagram on the photo-intensity change at 375 nm. The phase transition temperatures are decreased as the intensity increases for both clearing and SmA-Col$_r$ phase ones. Interestingly the setting-up of system at 203-202 °C leads to the observation that the transitions continuously take place with the change of photo-intensity in a reversible way. This is a first example of mesogen exhibiting photo-controlled isothermal phase transitions among three phases, Col$_r$, SmA and Iso phases and these are probably by way of alternative change of molecular shape between rod and disc.

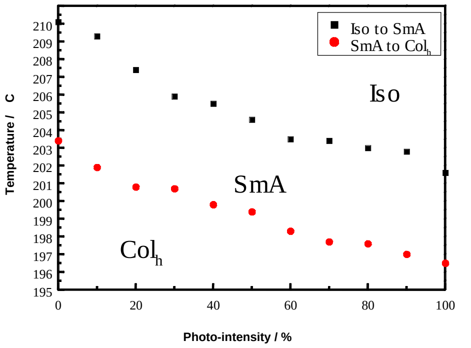

Fig.1 A phase diagram on the photo-intensity change (365 nm) for ***1c***.

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O - 22

THE B4 BANANA PHASE FOR ORGANIC PHOTOVOLTAICS

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Considerable work aimed at elucidation of the structure of the B4 banana phase has recently allowed characterization of the phase as a unique hierarchical assembly of smectic layers possessing spontaneous negative curvature [1]. These layers stack to form helical filaments, or twisted nanorods self-limiting in size in two dimensions (Fig A, B). For a classic double benzylideneaniline bent-core, these cylindrical nanorods are ~30nm in diameter, with no constraints on their length. In addition, due to the twist, half of the surface area of the rods is composed of exposed layer edges, where aromatic core sublayers makes direct contact with the local environment. Based upon many considerations, including solid state NMR [2], it appears that the individual B4 layers are crystalline, though the rods are not crystalline.

Here we describe a new B4 material lacking benzylideneaniline moieties, and additional NMR evidence for the crystalline nature of the B4 layers.

The unique B4 structure, where the aromatic semiconductor sublayer in each smectic layer has an unobstructed path to the edges and ends of the rods, suggests application of B4 in molecular electronics and photovoltaics. The latter is especially interesting given the tendency of B4 to entrain other compounds, forming seemingly “uniform” nanoscale heterojunction materials [3]. In this regard preliminary characterization of a benzylideneaniline B4 material using time-re-solved microwave photoconductivity measurements [4] on a planar hetereojunction composed of a thin film of B4 contacting a thin evaporated layer of C60, shows a large signal diagnostic of efficient exciton splitting and/or high hole carrier mobility, and long-lived carriers. Finally, recent experiments demonstrating excellent alignment of B4 (Fig C) will be described.

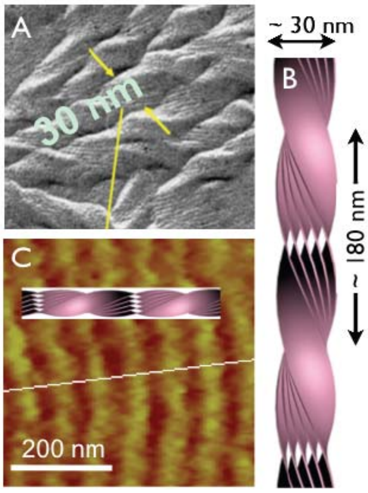

Figure: A) TEM image of B4 nano-rods showing exposed layer edges. B) Illustration of the structure of the rods. C) AFM image of aligned B4 indicating orientation of the rods (not to scale).

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STRUCTURAL ASSEMBLY OF HYDRATED SYNTHETIC GLYCOLIPIDS

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Glycolipids, conjugates of lipids with carbohydrates, play central roles in a number of biological processes, like cell recognition and cell adhesion or immune stimulation. However, also in the field of material science they are of relevance. Namely, amphiphiles derived from carbohydrate structures are suitable sources for the formation of monophilic liquid crystals, because they have strong chirality fixed in rigid rings inducing unusual chirality effects of the mesophases [1,2]. Due to the fact, that sugars show up big variability's in their chemical structures, e.g. the formation of diastereomers, the design of synthetic glycolipids allow an efficient fine-tuning of their physico-chemical properties [3].

In the last years [2, 4-6], we have designed and synthesised a large variety of synthetic glycolipids by varying the carbohydrate structure (e.g. mono-, disaccharides), the hydrocarbon chains (e.g. mono, di, saturated, unsaturated) as well as the linker (e.g. eher, amide) between the polar and apolar part of the amphiphiles. The formed supermolecular structures were characterised using microscopic, calorimetric, X-ray or spectroscopic techniques. Selected examples are presented to illustrate that tiny changes in the chemical structure have a strong impact on the structural properties and on the formed phases of the self-assembled systems [4-6].

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LYSYL-PHOSPHATIDYLGLYCEROL CONFERS RESISTANCE OF STAPHYLOCOCCUS AUREUS TO ANTIMICROBIAL PEPTIDES AND IMPAIRS INTERACTION OF PEPTIDES WITH MODEL MEMBRANES

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Modification of membrane phosphatidylglycerol (PG) of *Staphylococcus aureus* by addition of a L-lysine residue changes the net charge of this lipid from -1 to +1 and confers resistance to cationic antimicrobial peptides (AMPs) such as the human defensins [1]. AMPs are part of the innate immunity and provide the first line of defence against pathogenic microorganisms. Due to their unique mode of action, they have gained high interest as new drugs to overcome bacterial resistance to classical antibiotics. The primary target of AMPs is the cell membrane of bacteria. Peptides cover the bacterial membrane and induce the formation of transient or stable pores. Their precise mode of action, however, as well as the significance of the natural lipid composition are still a matter of debate.

We investigated the ability of different AMPs and derivatives thereof to inhibit the growth of a clinical isolate of *S. aureus,* wild type strain SA113, and, since PG lysination is done by the membrane protein MprF, mutants lacking the MprF gene. Moreover, we visualized ultrastructural changes by electron microscopy and correlated the biological activity with peptide insertion, analyzed by Förster resonance energy transfer (FRET) spectroscopy, and pore formation in planar lipid bilayers composed of PG and lysyl-PG to mimic the lipid compositions of the cytoplasmic membranes of various *S. aureus* strains. The studied peptides were: i) NK-2 [2], an α–helical fragment of mammalian NK-lysin, ii) arenicin-1 [3], a lugworm cyclic β–sheet peptide, and iii) bee venom melittin.

For all peptides, bacterial growth inhibition and biophysical data obtained from the model systems were consistent, suggesting that peptide-membrane interaction is crucial for killing *S. aureus*. The ability of NK-2 to inhibit the growth and to kill *S. aureus* was strongly dependent on the amount of lysyl-PG in the membrane. Furthermore, an impaired antibacterial activity was paralleled by a reduced capacity to insert into liposome membranes and to form pores in planar lipid bilayers, demonstrating that PG lysination strongly affect membrane interaction of the cationic peptide NK-2 and effectively protects bacteria against the action of this peptide. In contrast, the biological activity of melittin as well as its interaction with model membranes was only marginally affected by lysination of PG, suggesting that interaction of NK-2 is primarily driven by electrostatic forces and melittin interaction is not. Arenicin-1 was also affected by lysination, however, was still considerably active against *S. aureus* strains which expose lysyl-PG and is thus the most promising lead structure for drug development.

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INTERACTIONS OF SMALL POLYPHILIC MOLECULES WITH LIPID MEMBRANES

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Interactions of peptides or proteins with membranes have been intensively studied in the past decades to understand the mechanism of pore formation and diffusion processes through membranes[1]. To reduce the complexity of the systems model membranes have been usually used. Even though many studies concerning function and dynamic properties have been performed, the principles of structure formation of foreign molecules in membranes and the underlying mechanism of pore formation are still not completely clear.

The aim of this study is to determine the interaction and resulting morphology of polyphilic molecules (fig1) [2], which show in bulk thermotropic liquid-crystalline behaviour, with lipid model membranes. These polyphilic molecules bear hydrophilic and hydrophobic as well as fluorinated moieties and consist of rigid and flexible domains. Incorporation of these molecules into lipid model membranes can cause perturbation of the membranes and structural changes such as break-down of vesicles or, possibly, induction of pores.

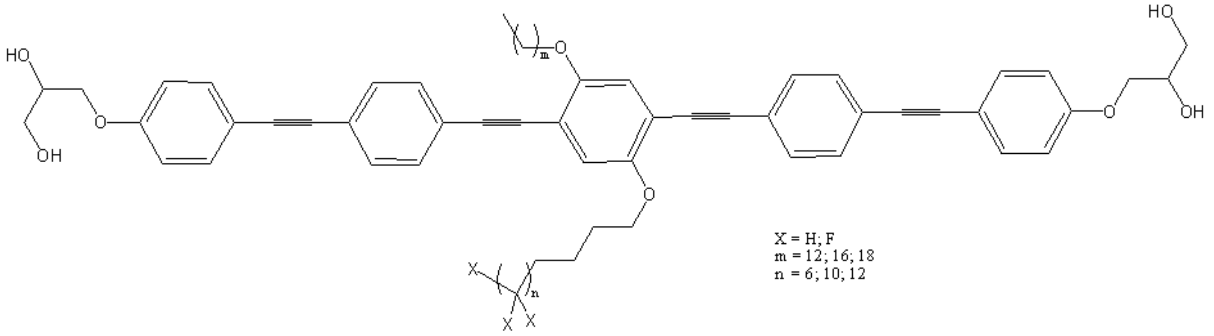

Fig. 1: Chemical structure of polyphilic molecules used in this study

The interaction of these molecules and their incorporation into membranes was studied using differential scanning calorimetry (DSC), the morphological changes were followed by atomic force microscopy (AFM), electron microscopy (EM), and the structural changes by X-ray diffraction, respectively. It was found that the interaction of these molecules with phospholipids in water leads to a break-down of vesicular structures and the formation of lamellar sheets or hexagonal phases as well as filaments.

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SYNCHROTRON LIGHT FOR CHARACTERIZING THE FORMATION OF CURVED MEMBRANES AND MEMBRANE FUSION PROCESSES

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Lamellar to non-lamellar membrane transitions play an important role not only in cell life (e.g. cell communication), but also in the efficacy of membrane active drugs. Therefore a great share of research studies is dedicated to understanding the formation and stability of lipidic model membrane systems, which are mimicking biomembranes in a simple manner. Using especially time-resolved synchrotron X-ray scattering techniques fundamental questions and formation pathways of theses nanostructures can be elucidated. After a brief introduction into fusion models, an overview on several lipid mesophases that are believed to take part in membrane fusion processes is given [1]. This includes to present prominent examples on the bicontinuous cubic phases, the columnar H_2 phase as well as the rhombohedral $R\underline{3}m$ phase, which is known to “host” a stalk-like fusion intermediate. Second, in-situ investigations of fast structural transitions of diluted DOPG/MO vesicles into well-ordered lipidic domains at low salt concentrations are presented. The strong binding of divalent cations to the negatively charged DOPG molecules causes a rapid collapsing of the vesicles and the reorganization of the lipid molecules to form within few milliseconds various non-lamellar phases (inverse cubic, hexagonal and sponge phases were observed) [2,3]. Finally, the described results will be discussed with respect to mechanism of action of a special class of antimicrobial peptides that induce inverted cubic phases in the cytoplasmatic bacterial membranes.

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EUTRALIZATION OF ENDOTOXINS BY ANTIMICROBIAL PEPTIDES

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Antimicrobial peptides play an important role in the immune system. The mode of action of antimicrobial peptides interfering within the process of inflammation is not yet identified. Understanding the mode of action of antimicrobial peptides can help to prevent septic shock and sepsis by their clinical application as a future therapeutic. The inhibition of an uncontrolled general inflammation is the major target of our investigation of the interaction between synthetic anti-LPS peptides (SALP) and endotoxins. Here, we report of a possible mode of action on the molecular level concerning structural changes of lipopolysaccharides (LPS) caused by the interaction with SALP in that LPS aggregates undergo a structural change converting the active conical conformation into an inactive cylindrical shape [1], [2]. AFM experiments depict a multilamellarization of LPS when interacting with antimicrobial peptides. SAXS experiments also show a change from cubic aggregates into a multilamellar form [2]. The investigation of the lipid A anchor by Fourier-Transform-Infrared-Spectroscopy (FTIR) reveals a fluidization of acyl chains [1]. The degree of the structural changes of the LPS aggregates caused by antimicrobial peptides corresponds strongly with their neutralizing capacity of LPS.

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EVALUATION OF LIPOPOLYSACCHARIDE, A MAJOR BACTERIAL GLYCOLIPID, AS A TARGET FOR ANTIMICROBIAL PEPTIDES AND LIPOPEPTIDES

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Lipopolysaccharide (LPS, endotoxin), a high molecular weight glycolipid, is the only lipid present on the outermost surface of Gram-negative bacteria thus being in close contact with the extracellular milieu. LPS plays a key role in bacterial cell homeostasis since many of the cell permeability properties depend on the integrity of the LPS layer. This molecule is also involved in providing the surface attachment necessary to form the sophisticated bacterial aggregates called biofilms. Moreover, LPS has a very high pro-inflammatory activity when released from the cell and LPS dependent overstimulation of the immune system may lead to a multiorganic failure called sepsis. This glycopeptide is therefore an attractive target for the development of antimicrobial agents.

Peptides and lipopeptides derived from the LPS-binding region of human lactoferrin were synthesized and the following activities were tested: (i) ability to bind to LPS *in vitro* as measured by the displacement of a fluorescence probe (BODIPY TR cadaverine) bound to LPS; (ii) *in vivo* antiendotoxic activity in a mouse model of acute sepsis caused by injection of LPS, (iii) permeabilizing activity on bacterial cells measured by the decrease of the antimicrobial activity of novobiocin, an antibiotic excluded by intact cells; (iv) anti-biofilm activity determined by crystal violet staining and measurement of respiratory rate after peptide treatment.

In general, peptides and their acylated derivates were able to bind to LPS, but their antimicrobial and antiendotoxic activities differed very significantly. Whereas lipopeptides were able to neutralize endotoxic shock in mice, peptides were more effective as permeabilizing compounds and as antimicrobial agents against cells grown in biofilms. Although further experimentation is needed to elucidate the contribution of the acyl chains in the different activities tested, the optimization of these compounds may form the basis of an effective antimicrobial therapy.

CRITICAL ROLE OF LIPID COMPOSITION IN MEMBRANE PERMEABILIZATION BY ANTIMICROBIAL PEPTIDES

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Although multidrug antibiotic resistance is an increasingly global health problem, the number of novel antibiotics on the market declines. In addition, the threat that bacteria such as Enterococcus being resistant to vancomycin, a drug of last resort, will pass its resistance gene to more dangerous pathogens further emphasizes the need of novel antibiotics. One promising strategy is based on antimicrobial peptides (AMPs), effector molecules of innate immunity. AMPs do not target single defined molecular structures, but act on the cell membrane killing bacteria rapidly within minutes, which reduces the likelihood of induced resistance. Understanding the mechanism(s) of membrane damage is a critical need to design efficient AMPs [1].

As the main difference between bacterial and mammalian cell membranes is their net charge, the focal point of consideration in many membrane mimetic experiments with AMPs is lipid headgroup charge. Therefore, we studied the interaction of a number of antimicrobial peptides of various origin and derivatives thereof using membrane model systems of single or binary lipid components of the predominant lipids in cytoplasmic membranes. Our biophysical studies have demonstrated a complex behaviour in terms of membrane perturbation at the molecular level, whereby the mode of interaction strongly depends on the nature of the lipids. In binary lipid mixtures one lipid generally governs the mode of lipid/peptide interaction, which is not necessarily the charged one. Thus, our results show that lipid net charge is not necessarily the decisive factor determining the membrane-perturbing mechanism of such peptides, but only one of several parameters.

Furthermore, linking a hydrophobic moiety to the N-terminal part of an AMP resulted in a different mode of bilayer perturbation as compared to its non-acylated parent peptide. Massive membrane damage was only observed in the presence of N-acylated AMPs, visualized by incorporation of the cationic dye SYTOX green, which can only enter cells, when its membrane is disrupted. This behaviour was also reflected in a stronger degree of membrane destabilization of *E. coli* and *S. aureus* as well as increased vesicle leakage in the presence of N-acylated AMPs. However, these findings did not necessarily correlate quantitatively with the antimicrobial potency, which in several cases was similar for the N-acylated and its parent peptide. This suggests that both types of AMPs interact also differently with other targets such as lipopolysaccharides in case of Gram-negative bacteria or lipoteichoic acid in case of Gram-positive bacteria. Electron micrographs support this notion showing formation of extrusions of lipid material, presumably from the outer membrane, in the presence of N-acylated peptides. Both types of peptides though induced membrane ruffling and detachment of the inner and outer membranes clearly indicating a membrane-based mode of action that leads to bacterial killing.

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O - 30

POSSIBILITIES FOR BIOLOGICAL NANOSCIENCE AT THE EMBL BIOSAXS BEAMLINE AT Petra-III

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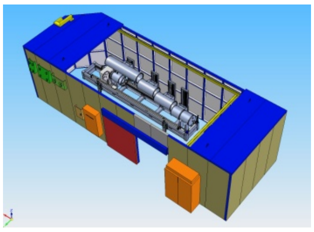
SAXS is a versatile tool for investigation of biological particles such as protein and large macro-molecular complexes in solution. It is a unique method for studying structures at low resolution and of structural transitions between individual states.

The projected BioSAXS beamline at the upgraded PETRA-III storage ring will allow challenging experiments, which are currently being carried out at the limit of existing SAXS stations in terms of sensitivity and sample consumption. The beamline combines a high brilliance X-ray beam with low scattering background and energy tunability (4keV to 20keV) for anomalous SAXS experiments on metals such as Calcium up to Molybdenum. The beamline is positioned in sector 8 of the PETRA-III on a straight section of a 2m canted undulator. The focal point is at 87 m (focus on the detector) and the optical layout permits beamsizes of 200 x 60 μm^2 and a beam divergence of 40 x 10 μrad^2. The standard mode operates a Si 111 double crystal monochromator and a pair of bimorph mirrors in Kirkpatrick Baez geometry. Further options such are high flux multilayer monochromator and a white beam option are under planning.



The optical hutch construction is finished and installation of optical elements is scheduled for autumn 2009. The experimental hutch is planned to be ready for late summer.

Figure 1: BioSAXS experimental hutch. An area of 11 x 4 m^2 is prepared for installing different sample environments such as automated sample handling and future nano focusing possibilities

A 5 m detector stage is constructed in collaboration with the Helmholz research center Geesthacht. This stage allows recording of different scattering angular regimes by changing the sample to detector distance. The device is automated and widens the BioSAXS applications towards biological soft condensed matter such as lipid membranes, fibres and biological nanoparticles.

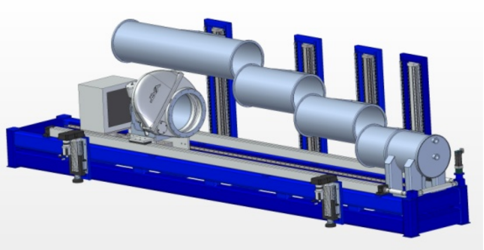


Figure 2: Automated BioSAXS detector stage. Sample to detector distances are possible of: 0.5m, 1m, 2m, 3m and 5m. The stand alone device is highly automated, no manual user interaction is necessary. Image provided with friendly permission of GKSS .

For future SAXS experiments in ultra-small sample volumes (< 1 nano liter) microfluidic sample environments are under development. Cutting-edge experiments, such as kinetic experiments on an ultra-short time scale and pilot experiments for future X-FEL applications biological samples will be possible.

ORGANISATION OF AMPHIPHILIC LIQUID CRYSTALS AT THE AIR WATER INTERFACE

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Amphiphilic liquid crystals do not only show a thermotropic polymorphism but often also form stable Langmuir films at the air/water interface. Under compression these films show an interesting phase behaviour. One characteristic feature that was observed for such systems is a wide pseudo-plateau in the surface-pressure/area isotherm [1]. This was explained with the formation of a stable triple layer by “roll-over collapse” of a monolayer [2].

We studied p-terphenyl derivates, terminally substituted with two hydrophobic n-alkyl chains and laterally substituted with a hydrophilic oligo-oxyethylene unit [3]. Variation of the n-alkyl chain length gives rise to very different phase behaviour at the air/water interface.

Molecules with long terminal n-alkyl chains (C_{16}) crystallize in two steps under compression of a monolayer. This was concluded from the shape of Langmuir isotherms and Brewster angle microscopy and clearly shown by monitoring the CH_2-streching vibrations by Infrared-Reflection-Absorption-Spectroscopy (IRRAS).

Molecules with shorter n-alkyl chains (C_{10}) do not crystallize upon compression. Instead they show a pronounced pseudo-plateau in the Langmuir isotherm. From the beginning to the end of this plateau the mean molecular area (mmA) is reduced by a factor of 1/3. It was concluded that a triple layer formation by roll-over collapse was induced. Indeed, AFM measurements on transferred Langmuir-Blodgett films show a layer thickness increase by a factor of 2.5, which fits the model of an interdigitated triple-layer. However, also tilting of the molecules would explain the decrease in mmA as well as the increase on layer thickness [4]. We used IRRAS to monitor the ordering of the alkyl chains, to measure the layer thickness increase directly at the air/water interface and to determine the orientation of the liquid crystal cores in the region of the pseudo-plateau. The results indicate that at the beginning of the pseudo-plateau the liquid crystals are organized in a monolayer of 1.5 nm thickness. The molecules are oriented parallel to the air/water interface. Upon compression a multilayer with a thickness of 3.7 nm is formed. However, the orientation of the molecules is lost and at the end of the plateau the molecules are isotropically distributed. Thus, the mechanism of the multilayer formation is not a well defined roll-over collapse, which should preserve a flat orientation of the molecules. Likewise, a tilting up of the molecules as explanation for the pseudo-plateau could be excluded by the IRRAS experiments. We conclude that the multilayer formation is a much less defined process, which produces disorder within the layer.

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COMPARATIVE STUDY ON NEW CHIRAL, LACTIC-ACID CONTAINING LIQUID CRYSTALS

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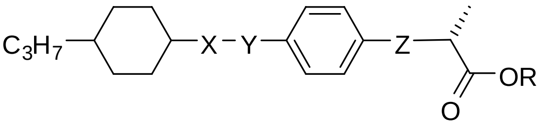
P - 01

Chiral liquid crystalline (LC) materials have gained increasing importance over the last few decades. In many mesogens of this kind the chirality is allocated in the aliphatic side-chain, which is connected to the core via an ester or ether function. Most commonly enantiomerically pure secondary alkyl alcohols are used as starting material which have the disadvantage that they are comparatively expensive due to their difficult production.

A reasonable approach for synthesizing chiral, enantiomerically pure low-cost materials is the use of chiral-pool materials like naturally occurring alcohols, amino-acids or e.g. bifunctional lactic-acid. The latter is the approach which we follow here. The principal use of lactic acid in mesogenic structures is not completely new,[1-3] but still the field is wide open and interesting to be explored.

The aim of the present work is to compare different mesogens which all contain a lactic-acid moiety as chiral motif which is attached to the molecular core either as ester or ether. Additionally, the orientation of the central ester group is varied. The bicyclic substructure of the mesogenic core is either a bicyclohexyl- or a cyclohexylphenyl moiety. Their general structure is shown in Figure 1. Apart from the analyses commonly applied in organic chemistry, polarization microscopy, differential scanning calorimetry and X-ray scattering studies have been performed, that latter for a selection of the new compounds. The purity of all materials was proven by elemental analysis.



X= CHex, Ph
Y= COO, OOC
Z= COO, O
R= C_nH_{2n+1}, n=2, 4, 6, 8, 10

Figure 1: General structure of the investigated compounds.

Substances with Z=COO have already been published previously by our group. [4]

Acknowlegments

We would like to thank Dr. E. Poetsch, Merck KGaA, Darmstadt, Germany for providing us with valuable starting-materials as well as Prof. Dr. Giesselmann for giving us access to his SAXS- and WAXS-equipment.

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P - 02

SWELLING EQUILIBRIA IN MIXTURES OF ISOTROPIC GELS IN ANISOTROPIC SOLVENTS

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Blends of polymers and low molecular weight liquid crystals (LCs) are being actively studied from fundamental and applied points of view. Polymer Dispersed Liquid Crystals in short PDLCs represent systems that consists of micron-sized LC inclusions dispersed in a polymer matrix, possessing a considerable potential for electro-optical applications for example in display technologies [1].

Electro-optical properties of these polymer/LC blends depend particularly on the size, shape, number density and spatial distribution of LC inclusions. These properties are influenced by the kinetics of phase separation, hence it is important to precisely determine their phase behavior. In recent years, several studies have been reported along these lines, which were conducted by polarizing optical microscopy (POM), differential scanning calorimetry (DSC), and light scattering (LS) techniques.

The phase diagrams were established in the case of photochemically crosslinked poly (butyl acrylate) (PABu) gels swollen in smectic A and nematic LCs. Polyacrylate networks were prepared by ultraviolet (UV) irradiation of reactive formulations including a monomer (n-butyl acrylate), and a crosslinking agent (hexane diol diacrylate, HDDA) [2].

The obtained dry polymer networks were immersed in an excess of 4-n-octyl-4'-cyanobiphenyl (8CB), 4-n-octyloxy-4'-cyanobiphenyl (8OCB) and nematic LC E7. The swelling behavior was investigated and the corresponding phase diagrams were established by POM and analyzed theoretically with the prediction of the Flory-Rehner theory of isotropic mixing and the Maier-Saupe theory of nematic order extended by Mc Millan to include smectic A order [3]. The calculated phase diagrams displayed isotropic network + smectic solvent (I+S), network + nematic solvent (I+N), isotropic network + isortropic solvent (I+I), and isotropic swollen network (I) coexistence regions. A good agreement between theory and experiments was observed.

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POLYMER/CRISTAL LIQUID BLENDS PREPARED BY ELECTRON BEAM AND UV RADIATION : CORRELATION BETWEEN RUBBER ELASTICITY AND PHASE SEPARATION

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This investigation reports on static and dynamic mechanical properties of Poly (tripropyleneglycoldiacrylate) (Poly-TPGDA) / liquid crystal (LC) systems, elaborated via radical polymerization processes induced by Electron Beam (EB) and Ultraviolet (UV) radiation. During exposure to radiation, the initial reactive TPGDA/LC blends will be transformed into three-dimensional chemically cross-linked polymer networks which can be characterized for example by their glass transition temperatures and their average distance between two neighboring cross-linking points.

The choice of the curing conditions, like radiation dose and dose rate, influence strongly on the kinetics of the polymerization/cross-linking processes, and thus create an impact on the formation of the polymer network. Ultraviolet (UV) induced radical polymerisation processes require the presence of a photoinitiator absorbing in the emission spectrum of the employed UV source. The electron beam technique has the advantage that the curing process can be carried out in the absence of any initiating species and is not sensitive to UV-absorbant materials like pigments.

Pure polymerized/crosslinked TPGDA networks prepared by EB radiation show a high modulus indicating low elasticity and short average distances between two neighboring cross-linking points. Dilution of the initial monomeric material with a LC like the commercial mixture E7 leads to a significant weakening of the mechanical strength of the obtained cured films. This decrease is essentially due to a plasticizing effect of the LC molecules randomly dispersed in the polymer network. Above 30 wt.-% LC, radiation induced crosslinking polymerization of TPGDA/LC leads to heterogeneous systems consisting of segregated LC domains dispersed in the polymer host. In particular, a strong correlation was observed between polymer elasticity and phase separation effects of the polymer/LC blends.

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MIXTURES OF ‘DE VRIES’ LIQUID CRYSTALS WITH FIRST- AND SECOND-ORDER SmA – SmC PHASE TRANSITIONS

P - 04

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Typically, the phase transition from the orthogonal smectic A (SmA) into the tilted smectic C (SmC) phase is associated with a substantial shrinkage of the smectic layer thickness due to the emerging tilt of the mesogenic molecules within the smectic layers. In some rare cases however, smectic A – C transitions with little or no layer contraction in the SmC phase were observed. The first important contribution to the understanding of how it is possible that some materials do not show layer contraction in SmC goes back to the early ideas of Adriaan de Vries [1] who recognized that the non-perfect orientational order present in all SmA phases is associated with a substantial molecular tilt of about 20 – 30 degrees on average. The tilting-transition to SmC can, in the „de Vries‟ model, occur simply through a long-range ordering of the molecular tilt *directions*. De Vries also claimed that this order-disorder-type transition is first order. During the last years however, examples of „de Vries‟-type materials with second-order smectic A – C transitions were found [2] and the nature of the „de Vries‟ transition thus remained to be a controversial issue.

We recently found a series of siloxinated „de Vries‟ liquid crystals where homologues with long alkyl chains show first-order, and homologues with short alkyl chains second-order smectic A–C transitions (see figure 1) [3]. We now use this system to systematically study the possible connection between the thermodynamic nature of the smectic A–C transition and the manifestation of „de Vries‟ behavior (i.e., the lack of coupling between director tilt and smectic layer contraction). In particular, we search for a mixture showing „de Vries‟ behavior and a phase transition at the crossover from first- to second-order (tricritical transition), since the first „de Vries‟-type material close to tricriticality was recently shown to have rather exceptional properties, such as a weakly temperature dependent giant electroclinic effect [4].

In order to achieve this goal, different mixtures had been investigated by means of X-ray and electro-optical measurements. First results of this study will be presented.

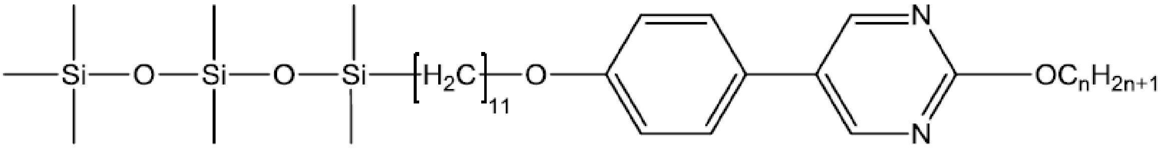

Fig. 1: Chemical structure of the homologous series of „de Vries‟ liquid crystals. Homologues with $n > 6$ have first-order smectic A–C transitions, whereas the transition is second-order in the case of $n \le 6$.

Financial support by the *Deutsche Forschungsgemeinschaft* in the “Materials World Network” program is gratefully acknowledged.

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CONFORMATIONAL AND VIBRATIONAL STUDIES OF 2-ETHYLHEXYL ACRYLATE / LIQUID CRYSTAL SYSTEMS

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Vibrational and conformational studies were performed by analyzing the monomer 2-ethylhexyl acrylate (2-EHA) as well as the nematic low molecular weight liquid crystal (LC) 4-cyano-4'-pentylbiphenyl (5CB).

Extensive experimental and theoretical research was carried out showing that monomeric acrylates exist preferentially in two heavy planar structures (s-cis and s-trans). The preferred molecular conformation of these molecules could be of considerable significance to discuss some of the properties and applications of these compounds.

Fourrier Transform Infrared Spectroscopy (FTIR) spectra of 2-EHA and 5CB, as liquid films, were obtained within a range from 4000 to 700 cm^{-1}. Calculations of harmonic frequencies from fully optimized geometries of planar s-cis and s-trans rotamers at ground state have been performed with the Density Functional Theory using B3LYP functional and extended basis sets 6-31G**and 6-311+G**. Scaled 6-311+G** anharmonic frequencies and potential energy distribution have been employed to assign the experimental spectrum over the region 4000-700cm^{-1}. A structural comparison was made between 2-ethylhexyl acrylate and methyl acrylate, which revealed a good agreement for heavy atoms. The calculated spectrum was found in excellent agreement with the experiments and confirms the co-existence of the two planar rotamers (s-cis and s-trans) of nearly equal energy.

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LIQUID CRYSTALLINE GUANIDINIUM ION PAIRS

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P - 06

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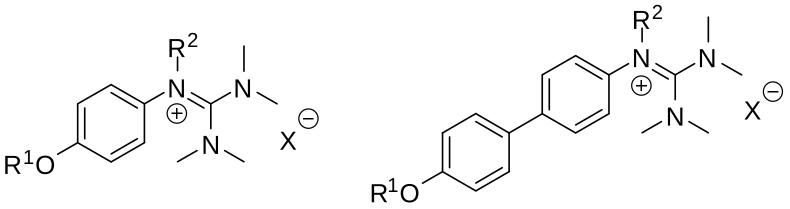
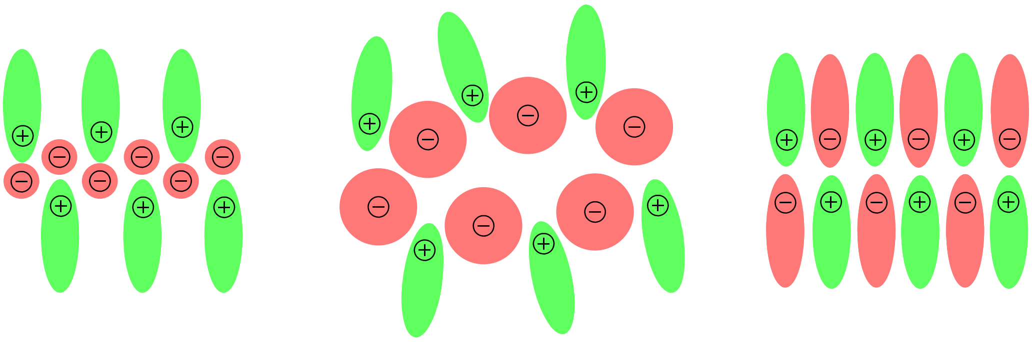
Recently we investigated calamitic guanidinium salts with thermotropic liquid crystalline properties (Scheme 1). Exchange of the anion showed a dependence between the size of the ion and the stability of the mesophase.[1,2]



R^1 = long alkyl chain
R^2 = short alkyl chain
X = spheric anion

Scheme 1

Through x-ray and POM experiments on the guanidinium salts we identified the molecular assembly as a smectic bilayer structure with the corresponding anions located between the layers (Figure 1). Increased size of the anion led to a decrease of the mesophase stabilities.



Scheme 2

To improve the mesophase widths of guanidinium salts, instead of using small anions, we synthesized new liquid crystalline ion pairs with symmetrically shaped anions and cations. So we decreased the repulsive interactions of the former spherical anion between the smectic bilayers.

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CRUCIFORMS WITH A PYRAZINE CENTRE – DISCOTIC LIQUID CRYSTALS AND ACIDOCHROMIC FLUOROPHORES

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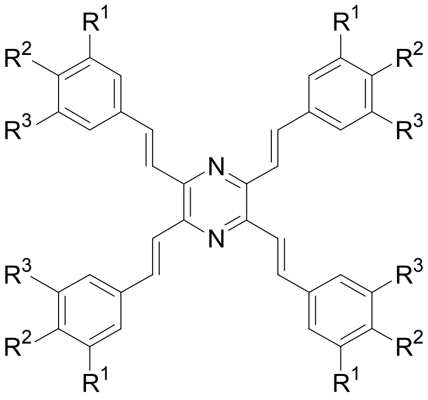
Star-shaped π-systems have been intensively investigated during the past two decades. [1] The unique combination of their electrical, optical, and non-linear optical properties with the ability to form discotic liquid-crystalline mesophases is a strong stimulus for continuously intensive investigations in this field. Recently, Bunz reported a series of cruciforms, symmetrical and unsymmetrical, [2, 3] and the tuning of their optical properties by changes of the environment. In extension of our project on fluorophores with multiple changes of absorption and emission spectra [4, 5] we used pyrazine as a central unit. An optimized synthesis enabled us to obtain cruciforms with a pyrazine centre in good to excellent yields. Though the first tetrastyrylpyrazine had been reported in 1952 [6], but the capability of these cruciforms to serve as a core for discotic liquid crystals was discovered about 40 years later.[7]

Herein we report the synthesis of tetrastyrylpyrazines with dialkylamino and with alkoxy substitution, their optical spectra depending on the environment and their thermal properties influenced by substitution pattern and chain length.



R^1 - R^3 = H, N-Alkyl$_2$, O-Alkyl

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THE SYNTHESIS OF NOVEL PHENYLENE-MODIFIED BOLAAMPHIPHILES: HOW DOES THE SUBSTITUTION PATTERN INFLUENCE THE AGGREGATION BEHAVIOUR AND THE MISCIBILITY WITH PHOSPHOLIPIDS?

P - 08

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Bipolar amphiphiles (bolaamphiphiles) are composed of two hydrophilic headgroups attached to one or two lipophilic spacers. These bolaamphiphiles originate in the membrane lipids of certain species of archaebacteria, especially in those of *methanogenes* and *thermoacidophiles*. The membrane-spanning and, hence, membrane-stabilizing properties of these lipids make them attractive candidates in vesicular drug delivery systems or for the stabilization of supported biosensor devices.

Having developed a general approach for the synthesis of symmetric polymethylene-1,ω-bis(phosphocholines) (PC-Cn-PC) with chain lengths (n) from 22 to 32 carbon atoms (Figure 1) via copper catalysed GRIGNARD coupling and subsequent phosphorylation and quarternisation [1] ongoing research focuses on the phenylene modification of the alkyl chain of the bolalipids including different substitution pattern (ortho, meta, and para) of the phenyl ring.

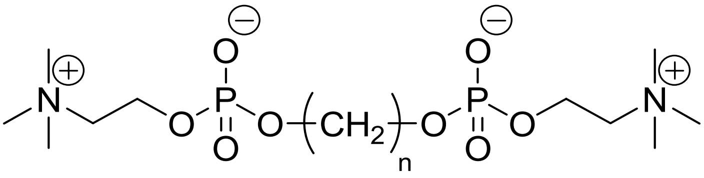

Figure 1: Chemical structure of PC-Cn-PC with n=22-32

Since the mixing behaviour of unmodified bolalipids with conventional phospholipids (DPPC, DMPC, and POPC) is very limited due to packing problems caused by the larger space requirement of the PC headgroup of PC-C32-PC compared to the small cross-sectional area of the alkyl chain [2] the question arose if an additional phenyl ring within the alkyl chain of the bolalipid could expand the cross section of the lipophilic spacer and, hence, enhance the miscibility.

In the presented work we describe two synthetic approaches for the preparation ofphenylene modified bolalipids: the copper-catalysed GRIGNARD reaction and the palladium-catalysed SONOGASHIRA cross coupling. The aggregation behaviour and the miscibility of these novel bolaamphiphiles with phospholipids (DPPC, DSPC) was investigated by differential scanning calorimetry (DSC), dynamic light scattering (DLS), and transmission electron microscopy (TEM).

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NOVEL MESOPHASES FORMED BY X-SHAPED BOLAAMPHIPHILES WITH OLIGO(PHENYLENEETHINYLENE) CENTRAL CORE

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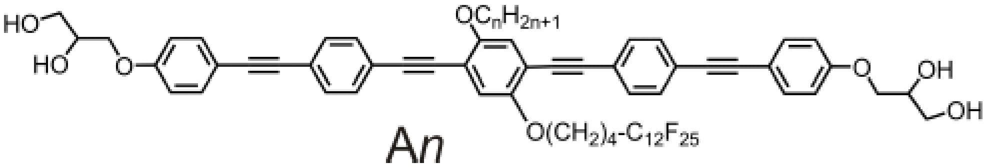
In several studies, the mesophase morphologies of T-shaped bolaamphiphiles with one lateral substituent have been investigated [1]. Such compounds exhibit different types of lamellar and columnar phases. The columnar mesophases represent honeycomb-like arrays of polygonal cylinders. More complex mesophases will be formed, if an additional substituent (R_2), incompatible with the first one (R_1), is attached in lateral position at opposite sides of the rod-like core to give X-shaped bolaamphiphiles [2]. In the recent work, one class of X-shaped bolaamphiphiles have been synthesized (**A*n***). The structure of them is shown below.



An

One serie of oligo(phenyleneethinylene) derived bolaamphiphiles are reported, where the length of the lateral alkyl chain has been variated, which lead to LC phases with rhombic, square and triangular shape of the cylinder cross section. In addition, continuous phase transitions between different cylinder structures were observed in some cases. The mesophase behaviour of the synthesized compounds was investigated by means of polarization microscopy, differential scanning calorimetry and X-ray scattering and was confirmed by electron density maps calculated from X-ray data and was compared with analogous compounds.

Acknowledgement

This work, as a part of the ESF EUROCORES Programme SONS, project SCALES, was supported by funds from the DFG and the FP6 under contract No. ERAS-CT-2003-989409.

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MORPHOLOGICAL AND ELECTRO-OPTICAL PROPERTIES OF METHACRYLATE-BASED POLYMER/LIQUID CRYSTAL FILMS

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The electro-optical properties and memory effects are of great importance for polymer/liquid crystal (LC) devices. We have studied the relationship between the nature of the chosen monomer and electro-optical as well as morphological properties of ultraviolet (UV) cured monomer/LC films. Memory-type polymer/LC films were prepared with a panel of methacrylate monomers : 2-hydroxyethylmethacrylate (HEMA), 2-hydroxypropylmethacrylate (HPMA), 2-hydroxybutylmethacrylate (HBMA), and the nematic LC 4-cyano-4'-pentylbiphenyl (5CB).

Polymer/LC samples were prepared using the polymerization induced phase separation technique, starting from blends where the LC to monomer ratio was taken as 60 weight-% (wt.-%)/40wt.-%. A small amount of photoinitiator was added to the initial blends which were exposed to a static UV irradiation source, as a function of time.

The transmission versus voltage curves exhibit good reproducibility and remarkable memory effects were observed for nearly all systems investigated. The transmittance of the memory state was preserved for a long time (weeks, months,…), after the applied electrical field was removed.

The influence of the sample composition, irradiation conditions, etc. was studied by several experimental techniques and especially by the analysis of the electro-optical response, Fourier Transform InfraRed (FTIR) and NMR spectroscopies, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), polarizing optical and scanning electron microscopies. A particular attention was paid to correlate the obtained results with sample composition and chemical nature of the monomer.

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POLYMER/LIQUID CRYSTAL MATERIALS CONTAINING DIAMOND NANOPARTICULES

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Nanoparticles have attracted great interest in recent years because of their unique mechanical, electrical, optical and magnetic properties. These properties are strongly related to the three-dimensional confinement of electrons and holes in a small volume.

In the present contribution, the phase separation kinetics, morphology, thermophysical and electro-optical properties of dispersions of diamond nanoparticles in polymer/liquid crystal (LC) systems were investigated. These materials were prepared from the nematic LC mixture E7 and pre-polymeric composition NOA65, which represents a commercial UV curable prepolymer mixture containing trifunctional thiol and a tetrafunctional urethane allyl ether (the ene).

The phase separation process was photoinduced by UV light and monitored by measuring transmittance kinetics of the polymer/LC films in the presence and absence of diamond nanoparticles, while the sample morphology was observed by polarizing optical and scanning electron microscopies. Increase of curing light intensity dramatically influenced phase separation kinetics and the final structure of these polymer/LC samples. Electro-optical characteristics were strongly influenced by the presence of small amounts of diamond nanoparticles. In particular, diamond doped polymer/LC systems present higher switching voltages as well as a lower transmission plateau in the ON state, compared to the system without diamond nanoparticles.

Calorimetric measurements performed with polymer/LC/diamond samples revealed that the presence of diamond nanoparticles leads to a reduction of both polymer glass transition and nematic-isotropic transition temperatures.

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LYOTROPIC QUASICRYSTALS WITH 12- AND 18-FOLD SYMMETRY

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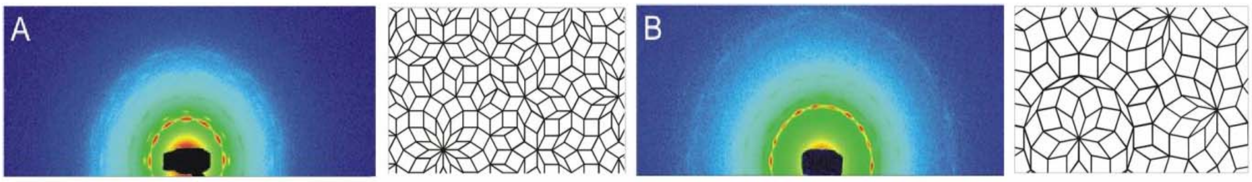
We present for the first time lyotropic quasicrystals, which are formed by spontaneous self-assembly of micelles in water. Amphiphilic block copolymers are macromolecules consisting of a lyophobic and a lyophilic block. Depending on the proportions of each block, they self-assemble into two- or three-dimensional structures such as micelles. These can self-assemble into different mesophases. Spherical micelles normally arrange to cubic packages such as body centered cubic (bcc) or face centered cubic (fcc). We have now discovered quasicrystals with 12-fold and 18-fold diffraction symmetry near the ordered/disordered phase transition, which has earlier been theoretically predicted. Quasicrystals with 18-fold diffraction symmetry have never been observed before. Phase transitions between the fcc-phase and the two quasicrystalline phases were traced by *in situ* time-resolved diffraction experiments. For our study, we used microfocus synchrotron small-angle X-ray scattering (DESY, Hamburg), and small-angle neutron scattering at the D11-instrument (ILL, Grenoble). Our discovery contributes to the theoretical understanding of quasicrystals and is of particular importance for the use of quasicrystals in advanced materials, as it opens the route to quasicrystalline photonic band gap materials via established water-based colloidal self-assembly techniques.



Diffraction image of a lyotropic quasicrystal with 12-fold symmetry (A) and 18-fold symmetry (B) with the corresponding tiling aside.

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STRUCTURES AT LIQUID-CRYSTAL/LIQUID INTERFACES: VARIATION OF THE LIQUID PHASE

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The surfactant-laden interface to water can exert pronounced ordering effects on liquid-crystal materials: even at temperatures above the liquid-crystal - isotropic transition, a thin nematic or smectic film may exist at the interface, provided that the surfactant induces a homeotropic anchoring of the director. The magnitude of the surfactant coverage determines how the liquid-crystal film behaves when the temperature is decreased towards the liquid-crystal - isotropic bulk transition, i.e., by tuning the surfactant coverage, one can induce partial or complete wetting of the interface by the liquid-crystal phase [1,2], layering transitions [3], and prewetting transitions [4].

In the previous studies, the tuning of the surfactant coverage of the interface was achieved by varying the volume concentration of the surfactant (which was dissolved in either the liquid-crystal or the water phase). In the present study, we consider a different approach: the water phase is replaced by different water-glycerol mixtures, i.e., we vary systematically the polarity of the non liquid-crystal fluid phase, while the volume concentration of the surfactant (dissolved in the liquid-crystal phase) is held constant. By studying the layering transitions of 12CB and the prewetting transitions of 9CB, we show that the variation of the polarity of the non liquid-crystal fluid phase has qualitatively the same effect as the variation of the volume concentration of the surfactant. Our results indicate that the magnitude of the surfactant coverage of the interface is in both cases the key quantity which determines the ordering behaviour at the interface.

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LIQUID-CRYSTALLINE POLYMORPHISM OF SYMMETRICAL AZOBANANAS: BIS(4-(4-ALKYLOXYPHENYL)AZOPHENYL) 2-NITROISOPHTALATES

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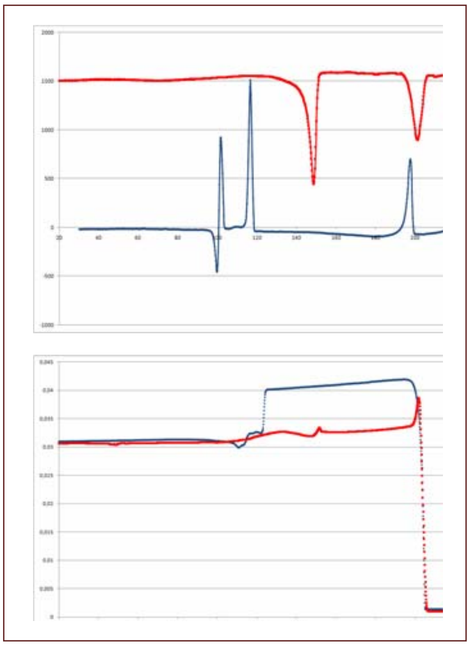
Today the most important problem in the bent-core systems is their liquid-crystalline polymorphism [1,2]. Even the small change of the structure seriously influences on the mesophase topology. Recently we have described properties of bis[(4-alkyloxyphenyl)azophenyl] nitroisophtalates [3], with symmetrical alkyl chains. Nematic and banana mesophases, have been recognized, but only one derivative has two banana mesophases. Among them especially interesting were non-nematic mesphases with the shortest alkyl chains because their columnar type of orientation.

In this presentation similar series of bend-core molecules are described with the same main structure as in [3] and as chains were introduced alkyloxy groups.

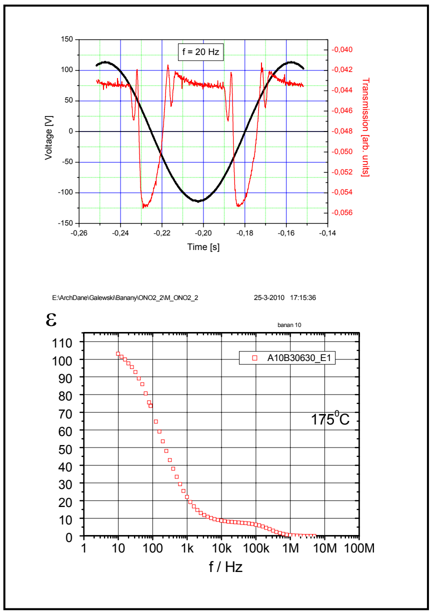


Fig,1. Thermooptic (TOA) and calorimetric (DSC) characteristics of decyl derivative.

This series has stable nematic phase from methyl up to nonyl derivative. Very unusual is the presence of second calamitic phases (probably SmC) in derivatives from methyl to butyl.

Typical POM and DSC measurements for decyl derivative is shown in Figure 1. Very interesting are dielectric properties of these compounds. They are very sensitive into light and even in the dark they often degraded when electric field is applied. Figure 2a shows switching properties in the smectic C. One peak is connected with the ferroelectric properties.

The second figure (2b) described dispersion relation in the decyl derivative. The first plateau is connected probably with the ferroelectric mode, but conductivity effect is significant. The second dispersion is typical for the rotation according to the short axis of molecules.



Fig,2. a),Switching properties of 4'-(4-decyloxyphenyloazo)phenylo 2-nitroisophtalate b) dispersion relation of dielectric permittivity of decyl derivative.

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DESIGN OF NEMATOGENIC BENT-CORE MESOGENS

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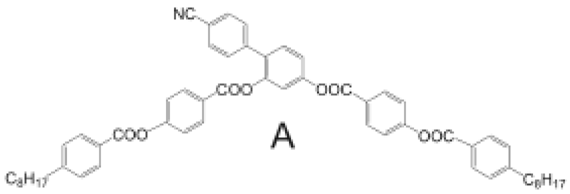
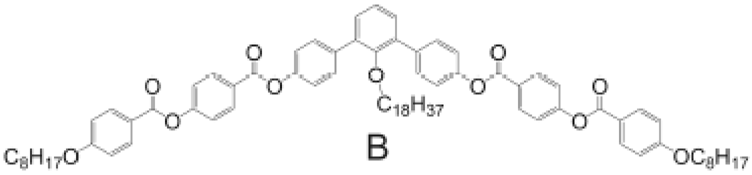


A



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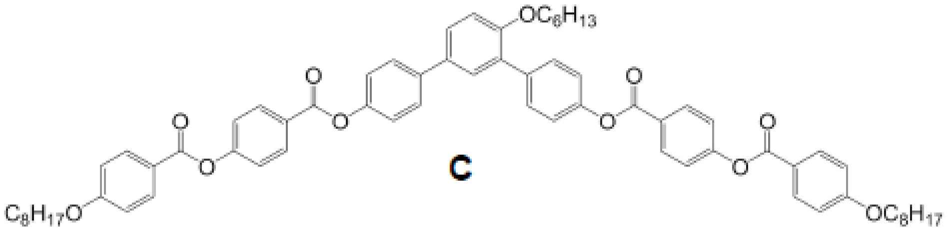
Due to the typical shape of bent-core molecules there is a favored packing of these molecules in polar smectic phases. One target of our work is to design bent-core molecules which avoid smectic phase formation and form nematic phases instead, eventually also the biaxial nematic phase. There are several concepts to design such bent-core molecules. So called lambda-shaped molecules **A** [1], bent-core molecules with a lateral alkyl chain in the bay position of the bent aromatic unit – the umbrella-shaped molecules **B** [1] and bell-shaped molecules with alkyl chains at the apex of the bent unit were reported [2]. Here we report another type of new bent-core molecules with a lateral alkyl chain outside of the bay position for which a first example was recently reported by Vaupotič et al. [3]. Alkyl substituents on the 4-position of the central 1,3-disubstitutet benzene ring should have a disturbing effect on layer formation. The steric effect of longer chains in this position should separate the aromatic core of the molecules and could inhibit the formation of smectic phases and may lead to nematic phases. Herein, several bent-core molecules, such as **C**, with a bent m-terphenyl unit as central core, an alkoxy chain at the 4-position of the central 1,3-disubstitutet benzene ring and rod-like phenyl benzoate wings, were synthesised and investigated.



C

Further modifications of the structure were done by elongation of the lateral chain, introduction of additional F-substituent in the o-position of the outer benzene rings and reversion of the direction of the outer ester groups.

Acknowledgment: This work was supported by the EU within the FP7 funded Collaborative Project BIND (Grand No. 216025).

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SELF-ASSEMBLY PROPERTIES OF β-GLYCOLIPIDS WITH DIFFERENT TYPES OF ALKYL CHAINS

P - 16

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Abstract

We have synthesized a series of spacered and non spacered -glycolipids with chain lengths ranging from C8 to C12. The effect of the chain length on micelle formation in aqueous solution was investigated by small angle neutron scattering (SANS-1) [1]. The Surface tension was determined by tensiometric measurements. Also the thermotropic and lyotropic phase behaviour was examined.

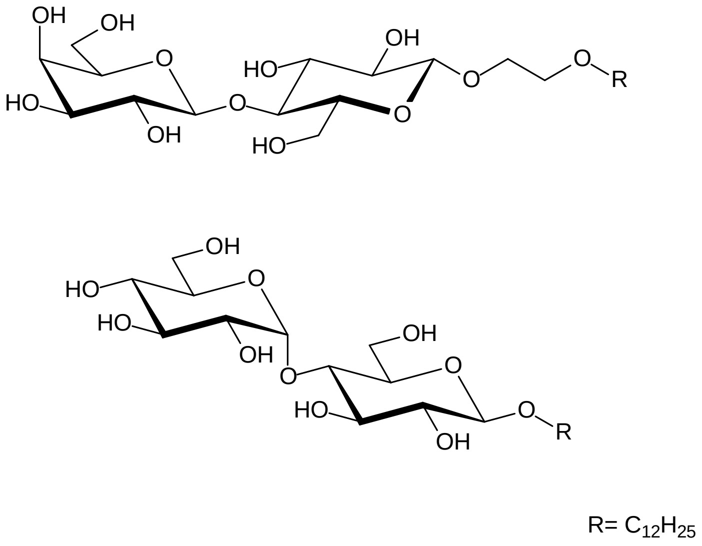

Fig.1: Examples of Structures

SYNTHESIS AND STRUCTURE-PROPERTY-RELATIONSHIPS OF DONOR-ACCEPTOR SUBSTITUTED STAR-SHAPED MESOGENS – A NEW DESIGN CONCEPT FOR PHOTOVOLTAIC MATERIALS?

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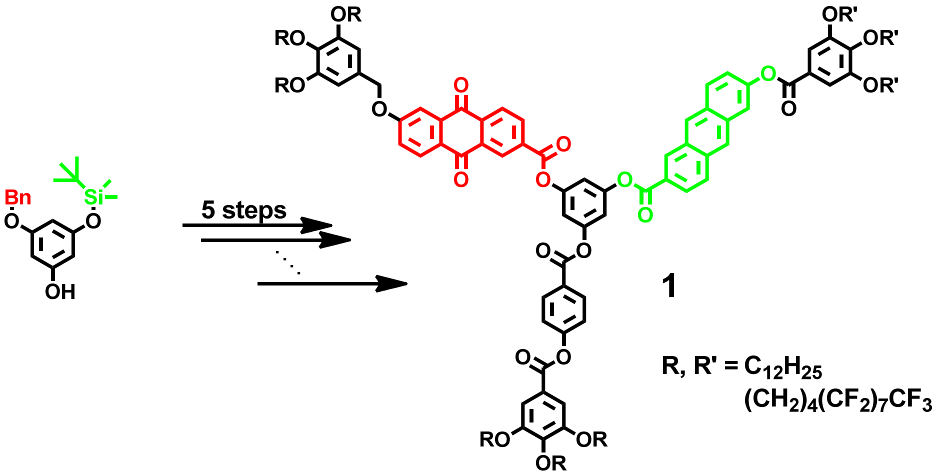
The conversion of light to chemical or electrical energy is not only a long existing and fascinating process used successfully by plants and bacteria for energy production, but will be of increasing relevance for power generation in the modern society.[1] Besides silicon based solar cells, organic photovoltaic materials will provide photovoltaic devices with cheaper production costs and high flexibility. Therefore, they will become progressively the focus of scientific interest, although currently the efficiency η is low, comprising cells with η = 5–8%.



1

R, R' = $C_{12}H_{25}$
$(CH_2)_4(CF_2)_7CF_3$

Figure: Synthesis of donor-acceptor substituted mesogens **1**.

Star-shaped Mesogens (Hekates) fold and pack into hexagonal columnar and helical, orthorhombic columnar structures.[2] Incorporation of donor and acceptor chromophores, e. g. anthracene and anthraquinone, may result in new organic photovoltaic active materials, when the arms can be nano-segregated by incompatible peripheral flexible chains, such as alkyl or semiperfluorinated chains. The synthesis of the chromophores is of crucial importance, since they must be substituted with carboxy and hydroxy groups at defined positions. In this contribution, we present the five step synthesis towards Hekates with three different arms with incompatible peripheral chains, different chromophores and discuss their mesomorphic behaviour. The photophysical and thermotropic properties are investigated by UV-Vis, fluorescence spectroscopy, optical microscopy, differential scanning calorimetry and X-ray scattering.

<u>Acknowledgement</u>: This work was supported by DFG and BMBF.

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SYNTHESIS OF CALAMITIC LIQUID CRYSTALS WITH LATERALLY SUBSTITUTED CORE AND THEIR MESOMORPHIC PROPERTIES

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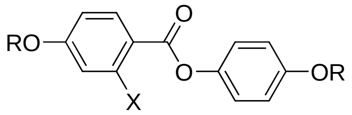
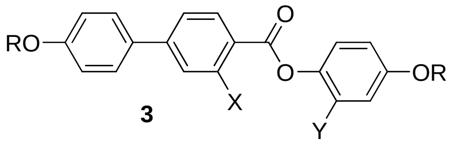
Recently, Takezoe with co-workers have reported symmetry breaking in SmC phase of achiral mesogen **1** [1,2]. The authors assumed restricted rotation around the C-O bond in the ester function resulting in formation of chiral domains consisting of *P* or *M* conformers in SmC phase. However, their conclusions were criticized by Walba [3]. The nature of the observed symmetry breaking has still been unclear.

This interesting phenomenon gripped our attention. We supposed that lateral substitution of the core by halogens in *ortho* position(s) to ester function should increase the rotational barrier and increase the probability of the separation of *P* and *M* conformers in SmC phase. Since lateral substitution of mesogens influences their mesomorphic behaviour [4], at first we were looking for substances exhibiting stable SmC phases. As expected, 2-halogenbenzoates **2** are not prone to form mesophases. Stable SmC phases existing within broad temperature intervals were observed in the case of biphenylcarboxylates **3** and benzoates **4** where the additional phenyl ring stabilizes the liquid crystalline state. Since the biphenyl moiety gives the possibility of restricted rotation around 1,1' σ bond in the mesophase, we have also prepared biphenylcarboxylates **5**. Until now, symmetry breaking was found for **3** (X = F, Y = H and X = H, Y = F, R = $C_{10}H_{21}$) [5]. Further investigation of this phenomenon is in progress.



1 X = H
2 X = F, Cl



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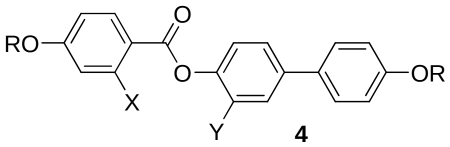

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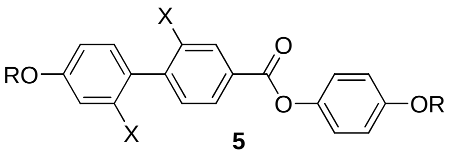

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In **3** - **5**: X, Y: H or F or Cl; R: C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$

Acknowledgement

The research was funded by the Czech Science Foundation (project No. 202/09/0047 and 204/11/0723) and Ministry of Education, Youth and Sports of the Czech Republic (project No. MSM 6046137301).

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MODIFIED ELECTROLUMINESCENCE OF AN ORGANIC LIGHT EMITTING DIODE INCORPORATING A COLUMNAR PERYLENE DERIVATIVE AND A SI_3N_4/SIO_2 BRAGG REFLECTOR

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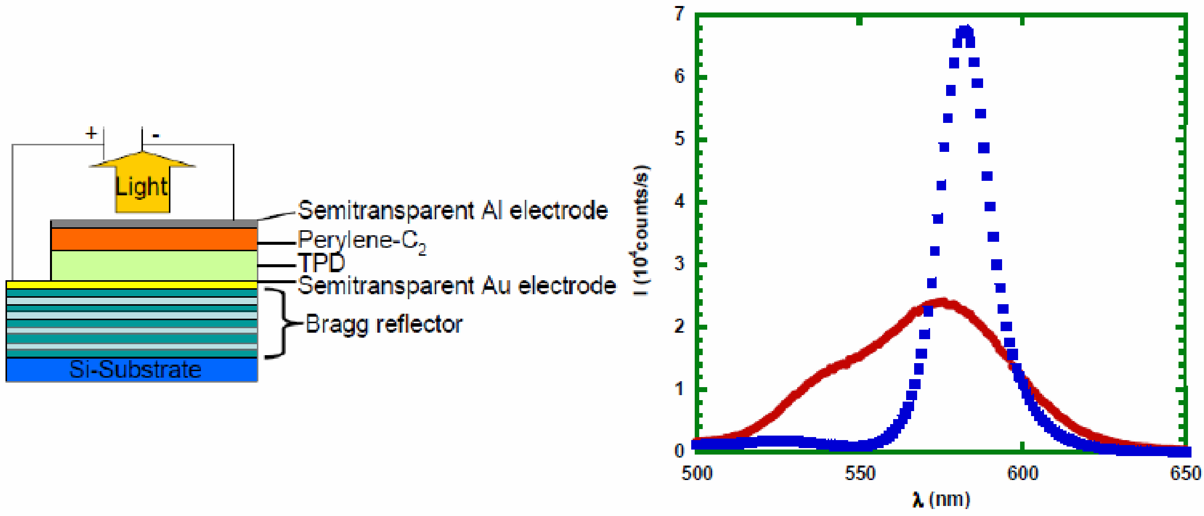
Organic light emitting diodes (OLEDs) have a large potential for novel displays. Easy fabrication, fast switching times, active light emission and wide viewing angle of OLEDs are ideal preconditions for developing large, flexible, lightweight, flat-panel displays. Only gradually, it becomes recognized that discotic and calamitic liquid crystals can contribute to OLED developments owing to their unique semiconducting and anisotropic properties, respectively.

In previous studies, we have characterized the electroluminescence of OLEDs made from columnar perylene derivatives, which have promising charge conducting properties and very high luminescence quantum efficiencies [1]. The present work describes organic light emitting diodes based on perylene-tetracarboxylic ethylester that are designed according to the resonant cavity-enhanced LED approach. For this purpose, the organic light emitting layers are embedded between a Si_3N_4/SiO_2 Bragg reflector and a highly reflecting metal electrode (Fig. 1). Au was used as transparent bottom electrode and Al as top electrode. Two organic layers were deposited by thermal evaporation in high vacuum ($5x10^{-7}$ mbar), namely TPD as hole transport layer and the perylene derivative as electron transport and emitting layer. The optical design is based on the Fabry-Perot cavity theory. The resonant cavity embedded sample shows considerable spectral narrowing in comparison with a reference sample that contains no Bragg reflector (Fig. 1b).



(a) **(b)**

Figure 1: (a) Schematic structure of the OLEDs. (b) Electroluminescence spectrum of a reference sample on ITO-coated glass without Bragg reflector (red) and a cavity enhanced sample (blue).

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INTERACTION MECHANISMS BETWEEN MYCOBACTERIA AND ANTIMICROBIAL PEPTIDES

P - 20

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Tuberculosis kills 2 million people per year worldwide. Mycobacterium tuberculosis is resistant against a large number of host defence peptides, which are active against other Gram-negative or positive bacteria. One reason for this resistance is the unique structure of the mycobacterial cell wall, which contains trehalose dimycolate (TDM) as an important component.

In this ongoing work we focus on the membrane forming properties of TDM as well as on the interaction of bacterial model membranes with small cationic peptides, called antimicrobial peptides (AMPs). Besides the cathelicidin LL32 we used the defensin hBD-3 in its natural folded form as well as in a synthetic linear form.

To investigate membrane-lipid interactions, we used permeability experiments using planar lipid bilayers, atomic force microscopy (AFM) on solid supported membranes and fluorescence microscopy using giant unilamellar vesicles (GUVs) prepared by means of electroformation.

AFM showed that TDM alone formed very stable monolayers and, when embedded into a phospholipid matrix self-aggregated into stable domains. Using force spectroscopy we observed that TDM layers had a higher mechanical stability as compared to pure phospholipid membranes. Furthermore, reconstituted TDM-containing membranes could not be permeabilized by the antimicrobial peptide LL32, which is the highly active fragment of human cathelicidin. In contrast, a derivative of the defensin hBD-3 can permeabilize the membrane and kill mycobacteria. These results are in good agreement with killing experiments, in which we could show that LL32 is not active against mycobacteria. We propose that TDM contributes to the stability of the mycobacterial cell wall and strongly impairs the membrane permeabilization by host defence peptides.

NEW CLASS OF SYNTHETIC PEPTIDES (SALPs) SHOW PROTECTION AGAINST SEPTIC SHOCK

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Thomas Gutsmann[1], Klaus Brandenburg[1]

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The increasing number of antibiotic resistant bacterial strains is a severe problem in treating SEPSIS. Therefore, it is necessary to find new defense strategies and treatment options to reduce the high number of deaths worldwide. In this context the work is dedicated to the analysis of several newly synthesized anti-LPS peptides (SALPs). These peptides are synthetic compounds designed to effectively neutralize lipopolysaccharide (LPS), and hence, act as new potential drugs. Preliminary biophysical studies using isothermal titration calorimetry (ITC) showed that all SALPs are able to bind LPS at low concentrations with high affinity. Following *in vitro* studies on LPS-stimulated macrophages clearly showed an inhibition of TNFalpha and Il-6, which are cytokines known as key players during the immune reaction causing sepsis. Furthermore, we could support these results in *in vivo* studies. Mice with LPS-induced sepsis symptoms could be cured with subsequent administration of SALPs. To ensure the medical applicability, cytotoxicity analyses have been performed using LDH and MTT as well as hemolysis and Alamar blue® assays. All investigated peptides showed no cytotoxicity at concentrations, at which complete neutralization of LPS could be observed. Therefore, we propose that these peptides lead to the neutralization of the endotoxin and can be used in clinical trials for the therapy of sepsis patients.

CUBOSOMES AND PHASE BEHAVIOR OF THE PHYTANTRIOL/WATER/ETHANOL SYSTEM

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Cubosomes [1] (Fig.a) are submicrometric crystals of cubic lyotropic phases dispersed in L1 phase. Their production requires the perfect knowledge of the phase behavior of, for example, phytantriol/water/ethanol ternary system.

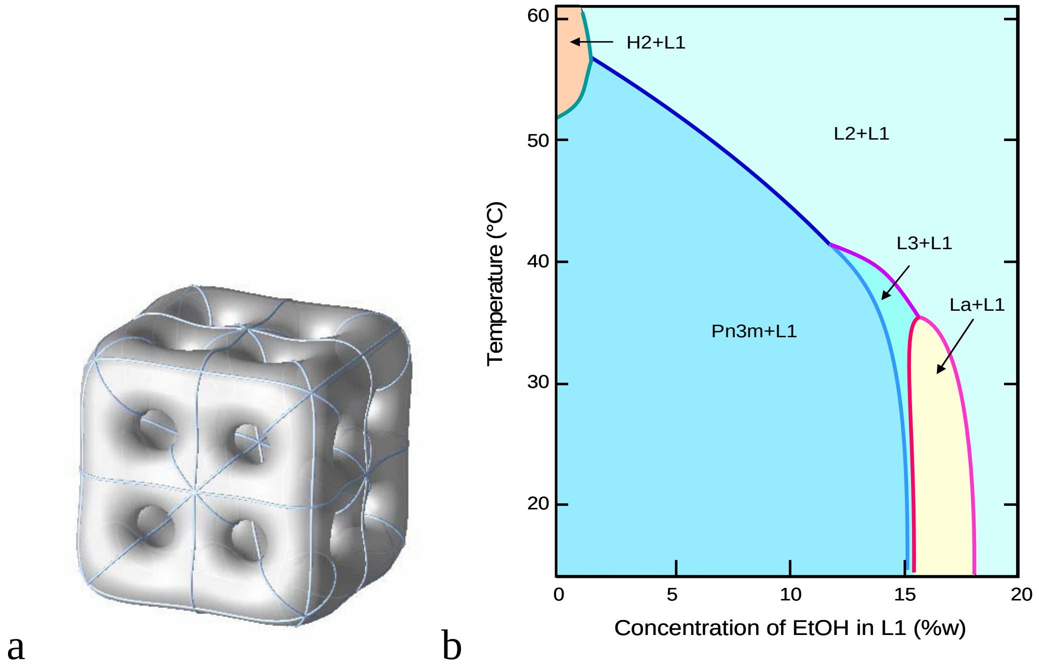

Figure: a) Simulation of a cubosome by means of a Landau-Ginzburg model , b) Phase diagram of the phytantriol/water/ethanol ternary system

We will report on experiments that allowed us to establish the phase diagram shown in Fig.b. Its structure involves equilibria of two, three and four phases. We will discuss consequences of such a complex phase behavior as well as out-of-equilibrium phenomena occurring in this system.

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POLAR ORDER IN ORTHOGONAL PHASES FORMED BY 4-CYANORESORCINOL DERIVED BENT-CORE MESOGENS

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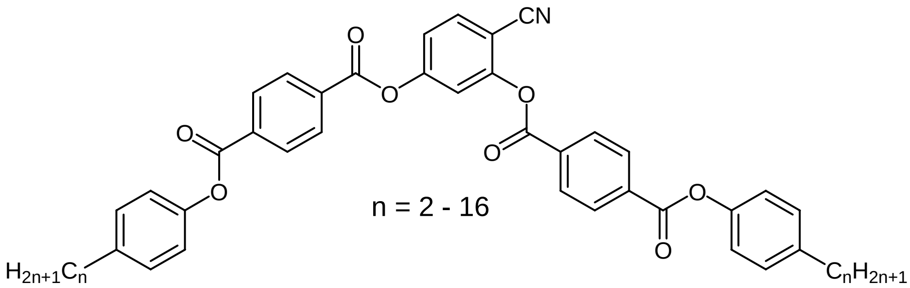
Most smectic phases of bent-core mesogens represent tilted smectic phases (B2 phases) and modulated variants of them. More recently nematic [1] and also nontilted smectic phases formed by bent core mesogens have attracted significant interest, among them the polar biaxial SmA$_b$P$_A$ phase [2] and the SmAP$_R$ phase with randomization of the polar direction.[3] Recently we have reported a series of three orthogonal smectic phases SmA–SmAP$_R$–SmAP$_A$ formed by alkyl substituted 4–cyanoresorcinol 1,3–bisbenzoates with terephthalate based rod–like wings [4].



A homologue series of these bent-core mesogens with even-numbered terminal alkyl chains (n = 2–16) has been synthesized and investigated by means of polarizing microscopy, differential scanning calorimetry and X-ray (XRD) of surface aligned samples as well as electrooptical experiments.
While compounds with short alkyl chain length (n = 2–4) show only monotropic N$_{cybA}$ and non-switchable SmA phases, mesogens with longer chains form switchable SmA phases. Herein the unique phase series SmA–SmAP$_R$–SmAP$_A$ was discovered for all long chain compounds (n = 10–16). The development of polarity in this specific phase sequence is described with two distinct models.

Acknowledgements

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V-SHAPED BENZODITHIOPHENES AND THEIR NEMATIC MESOMORPHISM

P - 24

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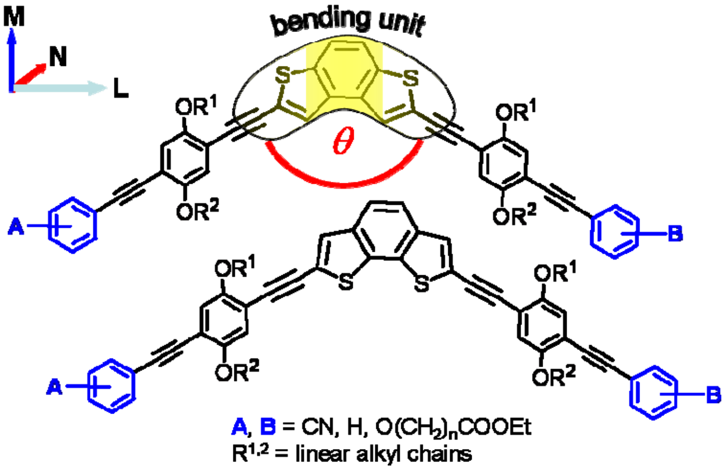
The formation of thermotropic, biaxial nematic phases from low molar mass compounds is recently controversy debated. The formation of such mesophases in the series of banana molecules seems to depend on certain molecular conformations and the self organisation in cybotactic or *meta*-cybotactic clusters.[1] Shape-persistent nematogens avoid the influence of conformers of different shape and reveal no tendency to self-organise in layered structures.[2] Only nematic phases were observed. Recently, we presented benzodithiophene derivatives **1** and **2** with a moderate dipole along the bisector of the molecule, realising a 109° and 134° bend of the molecule.[3] The tetrahedral angle was proposed to be ideal in order to find a direct transition from the isotropic to the biaxial nematic phase.[4] The investigation of these two similar compounds, which distinguish only by their apex angle, were expected to help to reveal the influence of the bending angle on the possible biaxial nematic mesomorphism.



1 ($\theta = 109°$)

2 ($\theta = 134°$)

In this contribution, we present the design and synthesis of the benzodithiophene nematogens. Their mesomorphism is comprehensively investigated by Orthoscopy and Conoscopy in LC cells with planar alignment layers and cell gaps of 23 and 50 µm. The nature of the nematic phases is additionally studied by means of X-Ray scattering.

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STEP-INDEX SILICA FIBER WITH PARALLEL LIQUID-CRYSTAL-FILLED MICRO-CHANNEL

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The optical properties of fused silica step-index fibers with Ge-doped cores and parallel liquid-crystal-filled channels, running along the entire fiber length, are reported (Fig. 1a). Several fibers with channel diameters of 0.6 to 1.8 µm were filled with E7. Due to these relatively small channel diameters, the liquid crystal (LC) was heated to the isotropic phase and forced into the channel using a small pressure gradient. Fibers with lengths of several cm were completely filled. In a polarizing optical microscope the LC strand appeared bright if the polarizers were crossed and the fiber axis was adjusted to 45° (Fig. 1b), which indicates a parallel LC alignment [1].

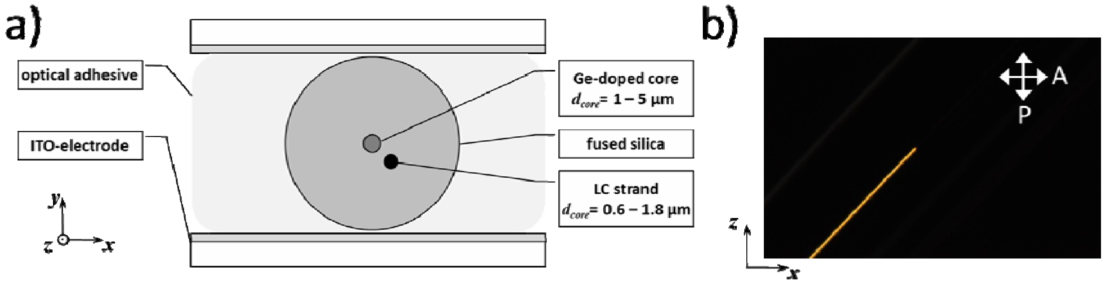

Fig.1. Scheme of a step-index fiber with an air hole liquid-crystal-filled channel, glued between two planar ITO-electrodes (≈ 200 nm electrode gap). b) Transmitted light polarized optical micrograph (crossed polarizers) of a fiber with one single hollow channel (1.8 µm diameter). A 7 cm length is filled with E7. The end of the LC-strand is shown in order to distinguish the LC-filled section from the silica glass background.

Waveguiding was investigated in fibers with completely LC-filled channels by coupling white light into the Ge-doped core. High transmission was observed at the free-end of a fiber in that core only. In contrast, the LC strand showed no transmission, due to the high scattering losses caused by thermal fluctuations of the director. However, the presence of the LC core had a strong influence on the light guided in the glass core: Strong modulation of the transmitted light was observed when a transverse electric field (Fig. 1a, field provided by two ITO-plates) was applied reorienting the LC director (sample length: 4 cm). A polarization-dependent transmission-modulation was observed when changing the electric field, with time constants ($t_{on}+t_{off}$) < 8 ms, which is more than two times smaller than in fibers with periodic arrays of LC strands having a parallel director field [1].

The modulation of the glass core mode can be explained by the sensitivity of the modal coupling process on the properties of the modes involved. Both Ge-doped core and LC strand have refractive indices higher than that of the surrounding fused silica, leading to the formation of guided modes. These modes couple at those wavelengths their dispersions match. In our experiment, the properties of the LC-mode are changed externally by the electric field, and the transmission of the glass core mode is modified.

Our structure does not require any anchoring agents for the LC, and the small diameter of the LC strands leads to a relatively fast switching speed.

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TRIPHENYLENE-SILANES FOR DIRECT SURFACE ANCHORING IN BINARY MIXED SELF-ASSEMBLED MONOLAYERS

P - 26

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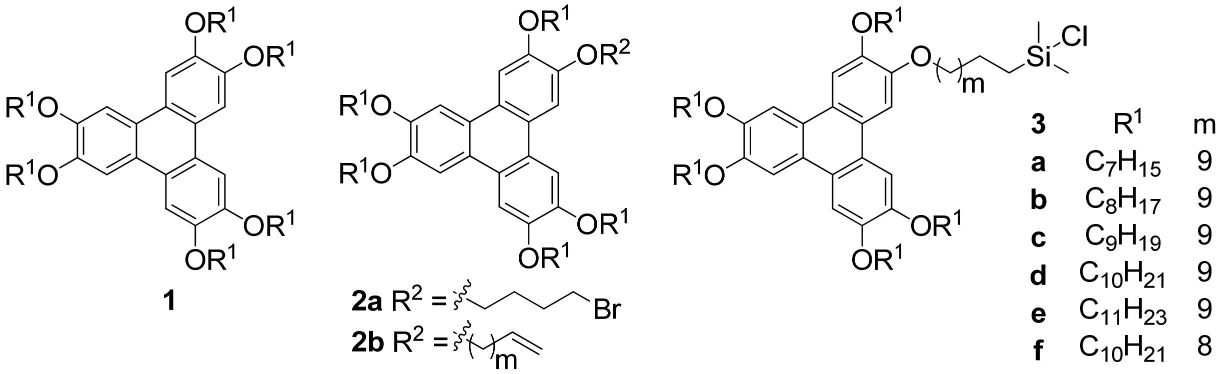
Recently we investigated the dealkylation of hexaalkyloxytriphenylenes **1**. Subsequent etherification gave the corresponding non-symmetrical substituted triphenylenes **2** [1]. Here we report the synthesis of novel triphenylene-based silane derivatives **3** (Scheme 1) and their self-assembly behaviour at oxide surfaces [2]. The silanes **3** were synthesized by hydrosililation from the corresponding alkene-substituted triphenylenes **2b**. Triphenylenes **3c**, **f** showed discotic lamellar mesophases as derived from POM, DSC and WAXS/SAXS.



1

2a R^2 =

2b R^2 =

3	R^1	m
a	C_7H_{15}	9
b	C_8H_{17}	9
c	C_9H_{19}	9
d	$C_{10}H_{21}$	9
e	$C_{11}H_{23}$	9
f	$C_{10}H_{21}$	8

Scheme 1

Compound **3d** was co-assembled with chlorodecyldimethylsilane or chlorodimethyloctadecylsilane in different mole fractions to obtain binary mixed self-assembled monolayers (SAMs).

All films were formed from solution and investigated by water contact angle measurements, null-ellipsometry and X-ray reflectivity in combination with theoretical modeling by a multi-dimensional Parratt-algorithm.

The monolayers film thickness showed a strong dependence of the triphenylene-silane content even at low mole fractions.

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SELF ASSEMBLY OF NANOPARTICLES IN LINEAR ARRANGEMENTS USING OPTICAL STORAGE MEDIA FOR NANOIMPRINT LITHOGRAPHY

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For the construction of functional nanodevices, it is important to control the dimensions and orientations of nanopatterns. One routine is the controlled arrangement of nanoparticles by using optical storage medias for nanoimprint soft lithography.

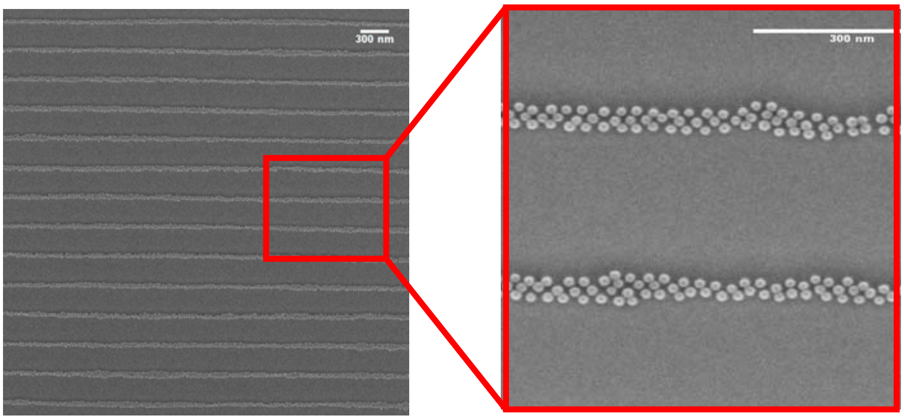

Figure 1: SEM image of embedded linear FeO_x-nanoparticles in a prestructured glass surface of BD-R lattice [1]

We were able to combine the self-assembly with the printing process using pre-structured silicone stamps in such a way, that one-dimensional arrays of nanoparticles appear. We produce these PDMS (poly-dimethylsilan) stamps, which are manufactured by molding a master-lattice of DVD-R (Digital Video Disc-Recordable) and BD–R (Blu Ray Disc-Recordable) to cover these pattern. First, a FeO_x-nanoparticle solution is coated on a flat substrate, and then the PDMS stamp is pressed into the solution. The particle solution is displaced into the remaining spaces. The solvent evaporates and after releasing the stamp, we obtain a linear arrangement of the nanoparticles. Another routine uses the same imprint technology to first form a structured glass substrate and then embed nanoparticles into the superstructure (Figure 1). We investigate these nanostructured patterns by using synchrotron radition in a GISAXS experiment at BW4 (HASYLAB (DESY) / Hamburg, Germany). The sample was rotated around its normal axis under incident angles of the synchrotron beam onto the surface. The observed GISAXS patterns show strong vertical (q_z) reflexions of the 1-dimensional lattice and horizontal (q_y) reflections of the 2D-lattice.The distances between the reflections change by the rotation. The vertical distance of the reflections depend on the repeating units of the linear pattern along the beam axis. Out of plane cuts along q_y at the critical angle of the substrate give information about the interparticle distance and domain size inside the linear arrangements. It can be shown that the nanoparticles from single domains in each groove with a very high degree of order.

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GENERATION OF MEMBRANE CURVATURE AND MULTIBUDDED TUBULES MEDIATED BY THE COAT PROTEIN COMPLEX II ON ARTIFICIAL LIPOSOMES

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ZIK HALOmem, MLU Halle-Wittenberg, Kurt-Mothes-Str. 3, 06120 Halle, D

COPII-coated vesicles form at the Endoplasmic Reticulum and transport cargo molecules to the Golgi apparatus. The COPII coat is recruited to the membrane by the small GTPase Sar1p. Upon GDP-GTP exchange, which is promoted by Sec12p, Sar1p undergoes a conformational change, which leads to the exposure of an N-terminal amphipathic helix and binding of Sar1p to the lipid bilayer. Formation of the coat continues with the recruitment of the Sec23p/Sec24p complex and of the outer coat protein complex, Sec13p/Sec31p.

We have used purified yeast COPII proteins in conjunction with Giant Unilamellar Vesicles as an artificial lipid bilayer system to examine the roles of the small GTPase and the COPII scaffold in membrane curvature generation and vesicle fission *in situ*, without any biochemical separation steps. Sar1p in the presence of Sec12p and GTP lead to the formation of some rigid lipid tubules, which retract on illumination. Adding also the other COPII components, Sec23p/Sec24p and Sec13p/Sec31p under conditions of reduced GTP hydrolysis produces long rigid strings of buds, i.e. tubules carrying constrictions at regular intervals, which do not fission. We interpret these observations in the mechanistic context of how COPII vesicles form and how budding proceeds through fission.

We applied the film balance technique to study the interaction of Sar1p with lipid monolayers, a commonly used model membrane system for peripheral proteins. In the presence and absence of GDP and GTP and at different starting pressures of the lipid monolayer Sar1p shows a strong insertion tendency. In contrast, ΔNSar did not insert into lipid monolayers because of the missing N-terminal helix.

FABRICATION OF MAGNETIC NANODOT ARRAYS USING DIBLOCK COPOLYMER MICELLES AS TEMPLATES

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Controlling the structure of matter at the nanometer scale and assemble nanoparticles into arrays and networks in a controlled manner is the key to new technologies. Nanosphere lithography is one of the most simple and effective methods for the preparation of large-area, two-dimensional nanostructure arrays. We present the size-controlled formation of nanoparticles inside micelle cores. Inorganic precursors of the desired nanoparticles were introduced into micelles. By means of dip- and spin-coating we are able to form lateral hexagonal long-range ordered micellar coatings. The nanoparticles have tuneable diameters and distances between 10 and 100 nm, controlled by the block lengths of the initial polymer. AFM and SEM-investigations show highly ordered particles in large domains. Corresponding GISAXS patterns show strong hexagonal diffraction peaks. By analyzing the scattered intensity, we were able to determine the lateral scales of the structure. Furthermore, simulations of the diffraction patterns were successful generated and models with precise length scale parameters were calculated.[1]

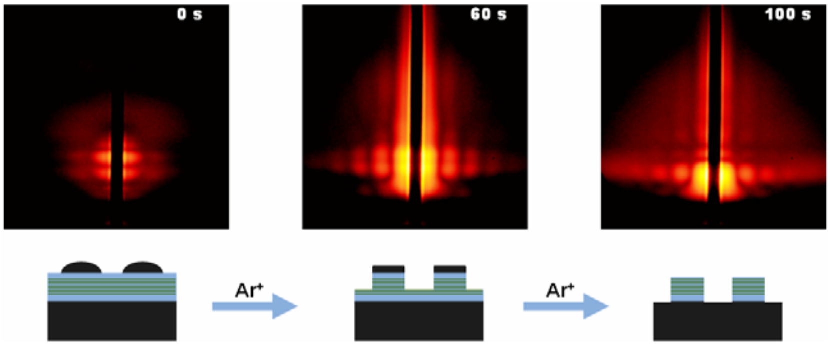

Figure: In-situ GISAXS during formation of magnetic dots by argon ion milling

Magnetic nanostructure arrays are created using diblock copolymer micelles with metal oxide (vanadium oxide, titanium oxide, iron oxide and silica) loaded cores. The number of preparation steps is kept as low as possible to simplify the formation of the nanostructure array. The structure of the cores is transferred into the film via ion milling under normal incidence. The generated dots were made of $(Co/Pt)_2$-multilayers. They show different magnetic behaviour, depending on their size, interparticle distance and milling time.[2] Therefore, high resolution in-situ GISAXS investigations while Ar^+-ion milling were perfomed at ID01 / ESRF, to get the precise height and length scales of the nanostructures during their formation (Figure). The magnetic properties were investigated by means of MOKE (magnetooptical Kerr effect). After ion bombardment, the remains of the Co/Pt multilayer stay ferromagnetic on sputtering.

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MEASUREMENT OF THE TENSION OF FREELY-SUSPENDED LIQUID CRYSTAL FILAMENTS

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[1] *Otto-von-Guericke-Universität Magdeburg, Institut für Experimentelle Physik*

Newtonian fluid rods are not stable and collaps into drops because of the Rayleigh-Plateau-Instability [1]. The surface tension causes a fluid cylinder with a slenderness ratio (length to diameter) greater than π to become unstable. In contrast some liquid crystal phases are able to form so called free-standing filaments (liquid fibers) with slenderness-ratios of over 1000. This is due to their inner anisotropic structure but until now it is not clear which features of the phase in detail suppress the instability.

This work deals with filaments of bent-core mesogens in the B7-phase. Filaments made of the material studied are exceptionally stable among those made of other phases of bent-core mesogens, making them a good candidate for determination of the origin of the suppression of the Rayleigh-Plateau-Instability [2]. We study the tension of filaments by attaching weights to them and deflecting them perpendicular to their long axis (figure 1).

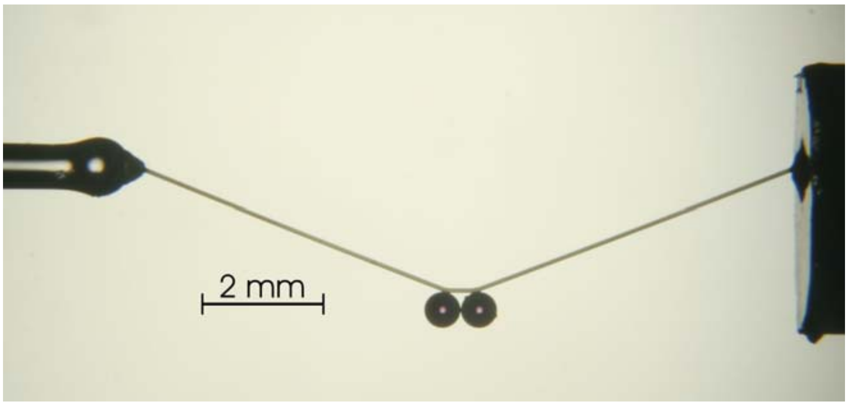

Figure 1: B7-filament deflected under load of two ruby beads

The parameters temperature, circumference, and cross section are changed, providing a detailed analysis of the different dependencies. At low temperature, we find extremely high filament tensions which cannot be explained by surface tension contributions alone. This work expands our previous investigations of the mechanical properties of the filaments [3] and confirms the presence of an additional "bulk"-term to the tension of the filaments.

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INVESTIGATION OF ENVIRONNEMENTAL HAZARDS: CHARACTERIZATION OF COMMERCIAL LCD BLENDS

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Technologies involving liquid crystals (LCs) have enjoyed considerable success during the 70s, in the field of panels, and since the 90s in the field of LC displays (LCD). However, LC materials are often considered as potentially hazardous substances that would have significant adverse impact on the eco-environnement. This reveals the need to provide more data on the influence of the constituents of LC mixtures on the environment.

Hence, the interest of this study is focused on the characterization of different commercial LC mixtures in order to know their composition and to determine the possible components that can be classified as dangerous for the environment. Combined microscopical and thermal analysis were carried out on a large number of LC blends allowing to characterize their optical properties as a function of temperature. LCs blends have been studied through chemical analysis methods such as infrared spectroscopy, nuclear resonance spectroscopie (^{1}H NMR, ^{19}F NMR) and gas chromatography coupled with mass spectroscopy (GC/MS) to obtain qualitative and quantitative data.

It appeared that all mixtures revealed interesting thermo-optical properties. The nematic-isotropc transition temperatures were found between 70 and 80°C, depending on the mixture, and well defined clearing temperatures were observed for all blends. A particular attention has been given to the presence of halogen-containing molecules because most of these mixtures contain one or more fluorinated LCs. Indeed, the combination of polar and steric effects and the great strength of the C-F bond confers more stability on LC molecules. The stability of C-F bond probably prevents the release of fluorine in the environnement since fluorinated LCs are recognized to be highly resistant to light and heat.

Some conclusions were drawn concerning the environnemental issues of the analyzed LC blends.

THERMOTROPIC AND LYOTROPIC PHASE BEHAVIOUR OF SPACERED ALKOXY DISACCHARIDE GLYCOLIPIDS

P - 32

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Abstract

A number of spacered alkoxy glycolipids consisting of branched and unbranched saturated C2 and C3 spacers and saturated C12 alkyl chains linked with the disaccharide head groups lactose and melibiose were synthesized[1-3]. Alongside the general synthetic procedures and the NMR-spectroscopic examination, the phase behaviour was characterized by polarisation microscopy.

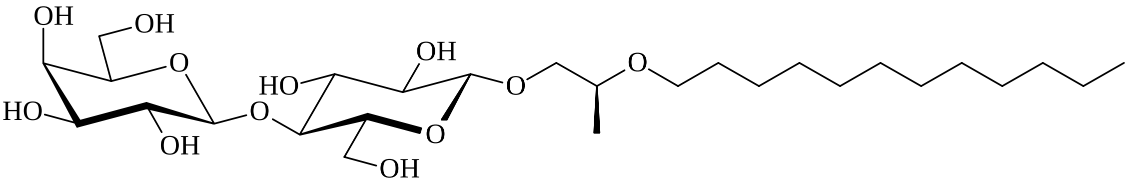

Fig. 1: A branched spacered alkoxy glycolipid

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PREPARATION OF DEFINED MICRO- AND NANOMETER-SIZED STRUCTURES FROM LIQUID CRYSTALLINE ELASTOMERS

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Liquid crystalline elastomers (LCEs) are interesting materials. They combine the elastomers. If the mesogenic molecules are aligned in a uniform direction, yielding liquid crystalline monodomains, the samples show a reversible shape change during the transition from the liquid crystalline to the isotropic phase. Thereby they can yield displacements of up to 400% in length, thus being suitable materials for the production of mechanical actuators.

We have developed synthetic strategies to produce aligned LCE samples with a size in the macro-, micro- and in the nanometer region. The main technique applied for this purpose was microfluidics. Thereby, micrometer sized droplets from a nematic liquid crystalline monomer were made and polymerized in a continuous process. When heated to the isotropic phase or exposed to a solvent, the resulting particles showed a reversible shape change. Thereby they transferred from a spherical to a rod-like shape. By processing chiral liquid crystalline materials, cholesteric particles with interesting optical properties were obtained. Using a slightly different microfluidic approach we succeeded in the fabrication of highly aligned fibers from a crosslinked, smectic main-chain polymer. These samples had an infinite length and a diameter between 20 and 50 micrometers. During the phase transition they showed a contraction along the fiber axis, thereby creating strong forces. A second patterning technique applied on liquid crystalline materials was anodized aluminum oxide templating. This allowed the preparation of nanometer-sized wires from polymerized and crosslinked nematic mesogens. The obtained structures showed reversible actuation on a nanometer size scale.

FREELY SUSPENDED SMECTIC FILMS IN AQUEOUS ENVIRONMENT

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Smectic liquid crystals easily form thin films which are freely suspended on a solid frame in air. These systems have been thoroughly studied for various purposes such as structural studies of smectic phases, investigating phase transitions in two-dimensional systems, and studying various physical properties of liquid crystals [1].

In the present study, we explore the preparation of freely suspended smectic films in water [2]. A prerequisite is the presence of a surfactant which accumulates at the liquid-crystal/water interface and induces a homeotropic anchoring of the director, so that the smectic layers align parallel to the two film surfaces. The presence of the surfactant might also serve as a handle to tune properties such as the surface tension of the films (which is hardly possible for freely suspended films in air). We study the formation of films in water using different frames and different surfactants, and we focus especially on the thinning behaviour which occurs when the temperature is increased towards the smectic - nematic or smectic - isotropic transition.

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REACTION-DIFFUSION MODEL FOR HOLOGRAPHIC POLYMER-DISPERSED LIQUID CRYSTALS UTILIZING NMR DATA OF THE DIFFUSION COEFFICIENTS

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Polymer-dispersed liquid crystals (PDLC) fabricated in a holographic setup are promising materials for switchable holograms, optical data storage, tunable beam deflectors and various diffractive optical elements, which can be addressed by electric fields. The present paper describes investigations on the grating formation in a simple model system based on mixtures containing 49 wt. % of the monomer trimethylolpropane triacrylate (TMPTA), 50 wt. % of the liquid crystal E7 and 1 % of the photoinitiator Irgacure 784. One dimensional phase gratings were fabricated by exposing the samples to the interference pattern of two coherent laser beams from a frequency doubled Nd:YAG laser (532 nm), thereby creating a polymer grating due to photopolymerization. During the grating formation, the diffraction of a HeNe laser beam (633 nm) was studied and the diffraction efficiency versus time was recorded. The materials were characterized by measuring the refractive indices of the single components (Leitz-Jelley-refractometer), the reaction rate of the monomer (photo-DSC), and the diffusion constants (NMR).

The measurement of the diffusion constants D is based on the pulsed field gradient technique and leads to a value of $D = 2.28 \times 10^{-10}$ m^2/s for the diffusion of the monomer in a mixture containing 50 wt. % monomer.

Using the experimental values of the reaction rate and the diffusion coefficients, a reaction-diffusion model can be applied in order to simulate the development of the diffraction efficiency during the grating formation. The result is in good agreement with experimental values of the diffraction efficiency.

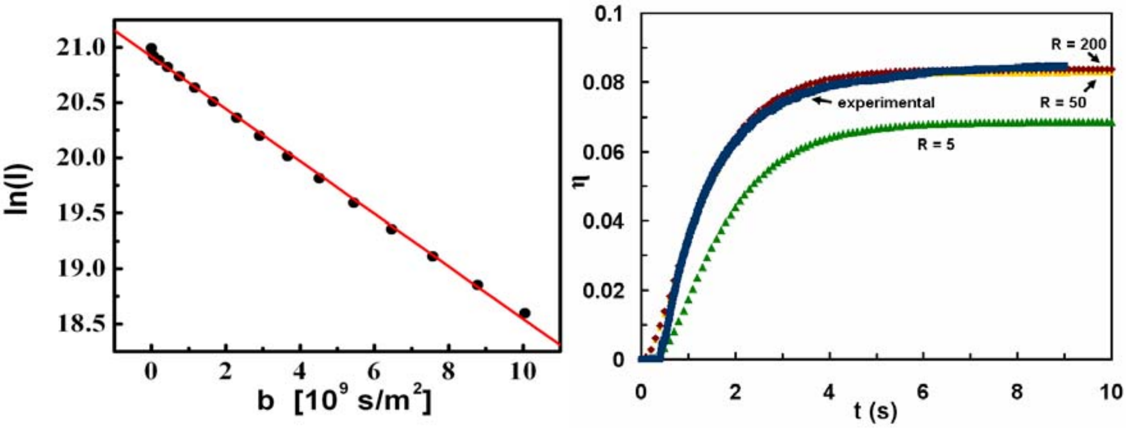

Fig. 1 *Left:* NMR echo intensity I versus $b = (\gamma G \delta)^2 t_d$, where γ is the gyromagnetic ratio of ^1H, G the variable gradient strength, δ the gradient width, and t_d the effective diffusion time. *Right:* Diffraction efficiency versus time (o) Experimental values for the sample containing 49% TMPTA, 50% E7 and 1% Irgacure 784. (◊, Δ) Theoretical values expected for different ratios R between the reaction rate und the diffusion rate. The experimental values correspond to R > 100.

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TRISTRIAZOLOTRIAZINES WITH π-CONJUGATED BRANCHES – FLUORESCENT DISCOTIC LIQUID CRYSTALS

P - 36

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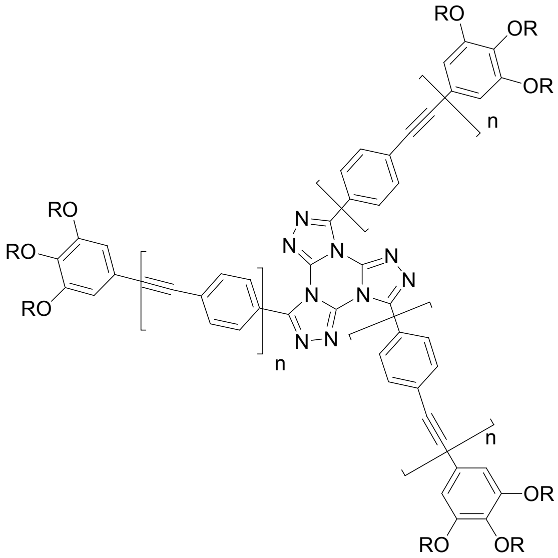
Planar polycyclic hydrocarbons with high symmetry have become important materials in organic electronics and as mesogenes for discotic liquid crystals with a variety of possible applications [1,2]. Similarly, aza-analogous aromatic polycycles like hexaazatriphenylene and triazatruxene have gained considerable attention as core for liquid crystals and star-shaped π-systems [3]. The annulation of three triazoles to a central 1,3,5-triazine can result in three C_3-symmetrical tristriazolotriazines. Recently, Gallardo [4] and we [5] discovered the ability of the tristriazolotriazine (TTT) to be a new core for the formation of discotic liquid crystals. A convergent synthesis, following the procedure reported by Huisgen [6], connects three arylsubstituted tetrazoles to cyanuric chloride. A threefold ring transformation generates the tristriazolotriazine. We report the synthesis, optical and thermal properties of tristriazolotriazines with three 3,4,5-trialkoxyphenyl groups and higher conjugated homologues with one or two phenylene ethynylene moieties between the core and the lateral groups. Whereas the triphenyl-TTTs can form broad hexagonal columnar mesophases, the higher homologues are not mesomorphic or form LC phases with a different structure.



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CHIRALITY-INDUCED CHANGES OF MICELLAR SHAPES

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So far, the mechanism of chiral induction in lyotropic liquid crystalline systems remains unclear. Mainly, there are two models being discussed, one based on sterical interactions within the micelles, the other on dispersive interaction between neighboring micelles. In researching these mechanisms of chirality transfer, we looked at the changes of micellar shapes that occurred by adding a chiral dopand to an achiral host phase. While the binary mixture of cetyl dimethyl ethyl ammonium bromide (CDEAB) and water consists of rod-like micelles, the addition of decanol as a co-tenside resulted in the formation of disc-like micelles. The latter system was used in our research, with (R)-mandelic acid being the chiral dopant added to it.

Micellar shapes and dimensions were investigated by x-ray-scattering on well-aligned samples. In the induced cholesteric phase, the director precesses along a helix. The helical axis needs to have a homogeneous direction throughout the whole scattering volume, which could be achieved using a strong magnetic field. The well-aligned samples with different dopant concentrations gave us very nice 2D-scattering diagrams, from which the height and diameter of the micelles could be obtained by a new model based on an older suggestion by Dörfler [1].

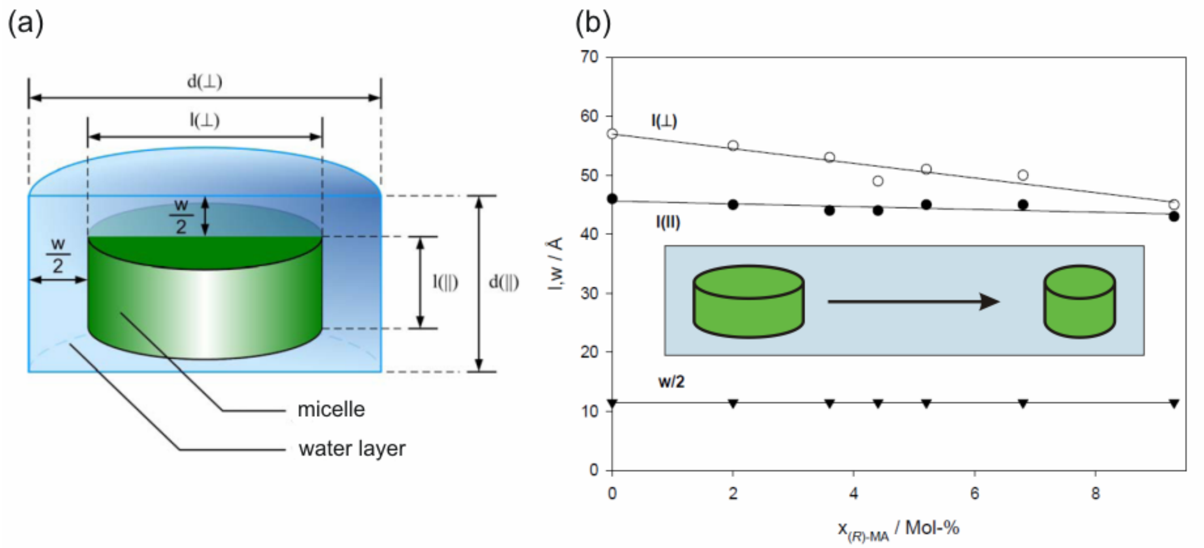

Figure 1: Schematical illustration of the dimensions of a discotic micelle and its surrounding water layer (a). Dependency of micellar dimensions and the intermicellar water layer from the concentration of a chiral dopant (b). While the diameter l(⊥) of the micelle decreases with an increasing content of dopant, its height l(||) and the thickness of the intermicellar water layer w remain nearly constant.

The anisotropy of the micellar dimensions is surprisingly small in the non-chiral host phase. With the addition of chiral dopant, the micellar anisotropy as well as the micellar volume decrease even further. While the height of micelles remains more or less the same, it is the diameter that gets smaller until its size is nearly identical to the height. Considering possible mechanisms of chiral induction, the constant height of the micelles indicates a dispersive mechanism rather than a sterical one.

Financial support by the *Deutsche Forschungsgemeinschaft* is gratefully acknowledged.

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INFLUENCE OF A FACIAL AMPHIPHILE ON LIPID MODEL SYSTEMS

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Lyotropic, amphotropic and thermotropic liquid crystals are indispensable for biological, medical or materials sciences. We are surrounded by various liquid crystalline systems in our daily life. Amphiphilic molecules such as phospholipids function as membrane builders in our organisms and synthetic liposomes are investigated for possible future medical applications.

In this work the membrane disturbing properties of the nearly T-shaped amphiphilic molecule A6/6 [1] on DPPC and DMPC model membranes were investigated. We used tensiometric methods to investigate the properties of the pure substances and mixed systems with an excess amount of lipid at the air / water interface. Differential Scanning Calorimetry (DSC) was used to study the interactions of A6/6 with lipid vesicles in aqueous suspensions. Finally, Transmission Electron Microscopy (TEM) and cryo-TEM were employed to visualize the aggregation behaviour of the liquid crystal A6/6 mixed with phospholipids. We found that in the mixtures with A6/6 bicelles were formed having a relatively narrow size distribution. This finding was supported by Atomic Force Microscopy (AFM) and Dynamic Light Scattering (DLS) investigations. Solid state NMR measurements gave information about the ratio of mixed associates to phase separated pure aggregates which again are in accordance to the findings of Differential Scanning Calorimetry [2]. A model for the aggregation of A6/6 with phospholipids into bicelles is presented.

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EFFECTS OF COUNTERIONS ON PHOTOCONDUCTIVITY IN COLUMNAR MESOPHASES

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P - 39

Thermotropic discotic liquid crystals including conjugated π–systems form columnar mesophases that exhibit photoinduced quasi one-dimensional charge carrier transport along the self-healing stacks. The most important aspect is the structure of the discotic mesogen, small changes can cause huge variations in the phase behaviour and electronic properties.

The main task of this work is to explore the effects of counterions on structure and charge carrier transport in columnar mesophases formed by new crown ether based mesogens [1] (Figure 1).

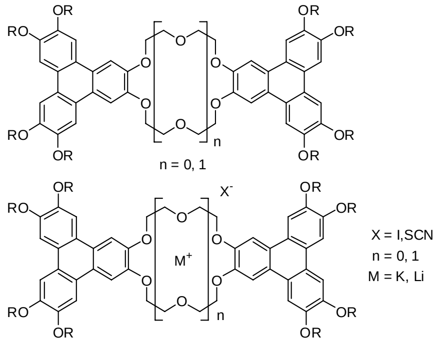

Figure 1: New crown ether based mesogens composed by two triphenylene units linked either by neat or ion complexing crown ether.

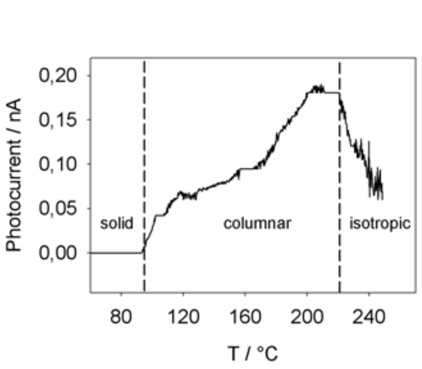

Figure 2: Phase dependent photo response of the crown-6 derivative (R = $C_{12}H_{25}$) plus KSCN in a 3.5 µm cell.

Important parameters that impact on the charge carrier transport are the nature of the columnar phase, the stacking distance of the mesogens in the columns and the macroscopic alignment on the surface of the device. All these elements are determined by SAXS/WAXS measurements and polarizing microscopy. Due to the introduction of counterions the thermal stability and even the X-ray diffraction pattern of the mesophase changes dramatically depending on the counterion species.

The photo response of the compounds is investigated by a homemade setup, charge carriers are excited by mechanical chopped monochrome light of a Xe-lamp and a lock-in amplifier measures the total photocurrent. This setup allows the variation of different important parameters like temperature (Figure 2), wavelength of the incident light, chopping frequency or DC field. Supporting methods to obtain more information about the transport and excitation procedure are UV-Vis and impedance spectroscopy.

Columnar liquid crystals are promising materials on the field of organic electronics. By the introduction of different counterions in our new systems columnar structure and thermal stability are highly affected. In this study we will show how counterions can influence charge carrier transport due to structural changes in columnar mesophases formed by new crown ether based mesogens.

Financial support of the IMPRS-AM is gratefully acknowledged.

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IONIC LIQUID CRYSTALS WITH 5-PHENYLPYRIMIDINE BUILDING BLOCK

P - 40

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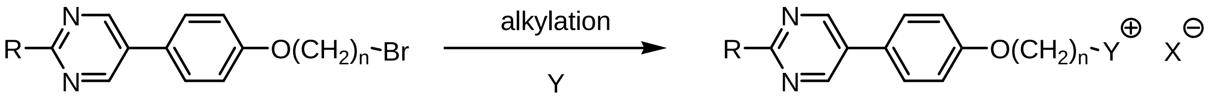
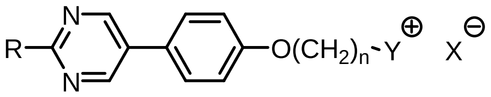
Ionic liquid crystals as materials combining properties of liquid crystals and ionic liquids, became very interesting in the last years and much research activity has been done in this field and is still going on [1]. A simple modification by alkylation of 5-phenylpyrimidine derivatives with liquid crystalline properties [2, 3] lead to ionic liquid crystals with broad mesophase ranges (Scheme 1).



R = alkyl chain
Y = head group

Scheme 1

We investigated the mesophase range depending on the cationic head group and the spacer chain length and further made several anion exchanges to analyse the influence of the anion on the liquid crystalline properties (Scheme 2). The mesomorphic behaviour of these compounds was investigated by DSC, POM and X-ray diffraction.



R = alkyl chain

variation of:

- head group: Y
- anion: X
- spacer chain length: n

Scheme 2

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THE ROLE OF ESTER GROUP ORIENTATION ON MESOMORPHIC PROPERTIES OF BENT-CORE LIQUID CRYSTALS: FROM LAMELLAR TO NEMATIC PHASES

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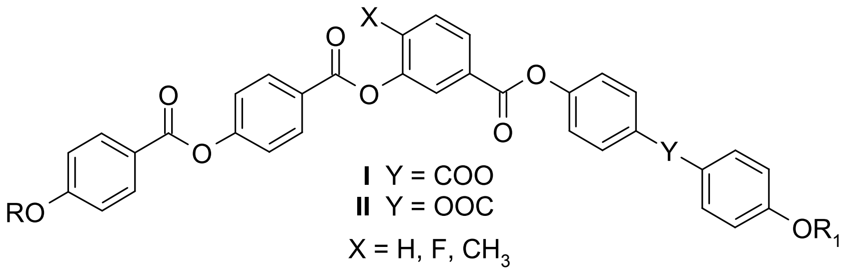
In our previous research we investigated symmetrical and non-symmetrical bent-shaped liquid crystals with laterally substituted naphthalene-2,7-diol central unit [1-3]. Herein, we report the synthesis and physical study of novel materials based on 4-substituted 3-hydroxybenzoic acid core, molecular structure of whose was modified by lateral substitution (X = H, F, CH_3), length of terminal alkyl chains and orientation of the outer ester group. Physical properties have been investigated by texture observation and differential scanning calorimetry, for some compounds the x-ray analysis of the structure has been performed.



I Y = COO
II Y = OOC
X = H, F, CH_3
R = C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{11}H_{21}$
R_1 = C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{11}H_{23}$

Mesomorphic behaviour of materials of series **I** depended on the length of the terminal chain. Materials with the longer terminal chain exhibited formation of lamellar phases, on the other hand, compounds **II** were nematogenic only regardless the type of lateral substitution.

Acknowledgement

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PLATEAU BORDERS OF SMECTIC LIQUID CRYSTALLINE FILMS

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#School of Physics, University of Exeter

The Belgian physicist Joseph Antoine Ferdinand Plateau in 1873 laid the foundations for the description of equilibrium states of thin liquid films and foams. One of his basic findings is that three films in an equilibrated dry foam meet at an angle of 120°. This “Plateau rule” has been extended by Weaire et al. for foams that contain liquid in the Plateau borders [1].

We check Weaire’s “decoration theorem” for liquid crystal foams. For that purpose we use SmA LC-films. The geometry is chosen such that a circular Plateau border surrounds a planar smectic film and connects it with two smectic catenoids, see Figure 1.

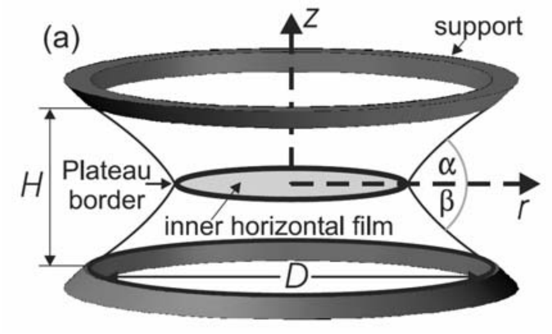

Figure 1: Sketch of the three film geometry

To evaluate our measurements we use digital image analysis of 2D images of the catenoids, see Figure 2. We measure deviations from Plateau’s rule in smectic freestanding films. Such deviations arise from the decoration of the dry foam skeleton with liquid crystal. We compare them to theoretical predictions [1,2] and measurements on soap films [2].

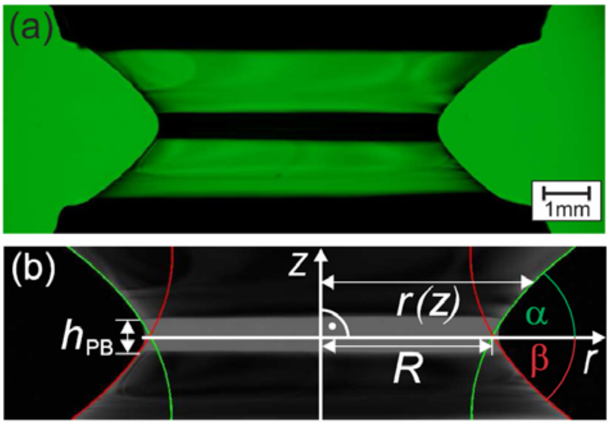

Figure 2: a) original sideview image of the experimental situation b) digital processed image that clarifies the evaluated data

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MICROSCOPIC STUDY OF THE FRÉEDERICKSZ TRANSITION IN A LIQUID CRYSTAL EMBEDDING A MICRODISK RESONATOR

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The dielectric anisotropy of nematic liquid crystals can be used to achieve electrical tunability of optical whispering gallery modes in microdisk resonators [1,2]. However, the relation between the orientation of the liquid crystal and the shift in resonator mode frequencies is not well understood, owing to two reasons: First, it is not obvious to which extent the dielectric permittivity in the vicinity of the microresonator influences the whispering gallery modes. The second reason is that the precise director field around the microdisk resonators is still unknown. Thus, the director field configuration is investigated in this study by polarising optical microscopy (POM) and confocal fluorescence polarising microscopy (FCPM). The expectations originating from numerical simulations are compared with the experimental results.

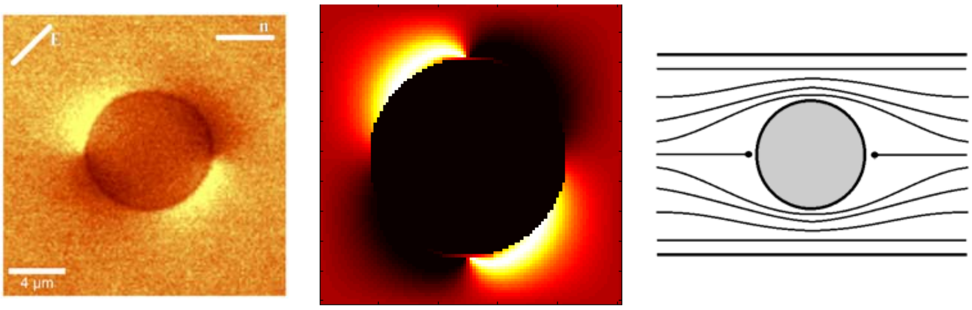

Figure 1: Summary of the investigations of the director field around a microdisk resonator. *left:* experimental FCPM image of a microdisk resonator embedded in a nematic liquid crystal using linearly polarised light, *center:* Corresponding FCPM-image by numerical simulations, *right:* schematic drawing of the director field in the (x,y)-plane.

The results show a parallel director orientation along the easy direction of the cell, featuring two diametrical boojums at the disk body. As shown by experiments and numerical simulations, the energy minimised director configuration exhibits almost no z-components. The director configuration under an electric field is characterised by a typical S-type Fréedericksz transition. The lateral director configuration with two boojums along the easy direction of the cell remains the same, except of higher z-components in the director field. Thus, the change of the dielectric environment in the vicinity of the disk is marked by a tangential rotation of the liquid crystal molecules. This knowledge allows further detailed studies on the mechanism of mode shifting in tuneable photonic resonator devices.

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NANOCOMPOSITE MATERIALS FOR OPTICAL AND SENSOR DEVICES

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During the last years a stronger accent has been made on the organic electronics development taking into consideration the new sensibilizator application. Thin film organic materials on the basis of liquid crystals (LCs) structured by carbon sensibilizators may become competitive and can replace a number of three-dimensional electrooptical and photorefractive structures used for the purposes of micro- and nanoelectronics, optics and non-linear optics [1]. High orienting possibility of LC under the influence of electric and magnetic fields allows to use them as easy-to-operate matrices. Implementation of multiwall carbon nanotubes (MCNTs) into liquid crystals is of certain interest.

It induced us to research the representatives of the cholesterol esters as LC matrices. The data concerning the influence of dispersed MCNTs on physical properties of cholesterol matrices, particularly, those depending on hydrocarbon periphery of the mesogens forming the matrix are presented in the report. Such important for optical and sensor devices characteristics as phase transition temperature, optical and rheological properties (Fig.1) were analyzed. Besides, interesting results relating to the composites in the crystal phase were obtained (Fig. 2).

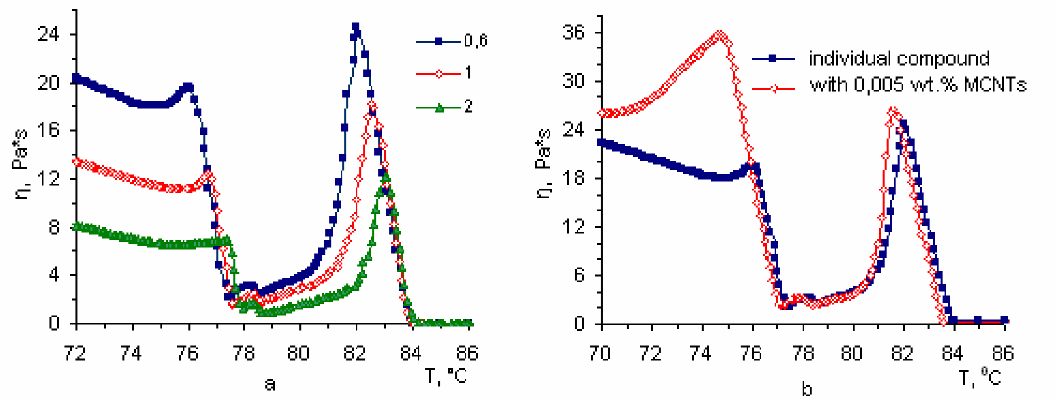

Fig. 1. Temperature dependences of dynamic viscosity of cholesterol myristate on cooling:
a) an individual compound at various shear rates, b) in system with MCNTs at shear rate 0.6 sec^{-1}.

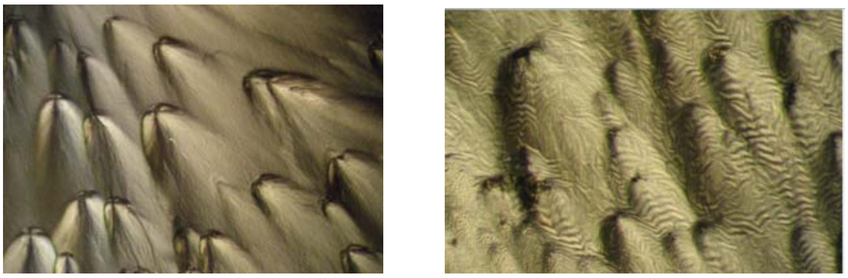
a b

Fig. 2. Polygonal textures of the crystal phase of cholesterol myristate:
a) an individual compound, b) in system with 0,005 wt. % MCNTs.

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INCORPORATION OF INORGANIC NANORODS INTO CHOLESTERIC LIQUID CRYSTALS

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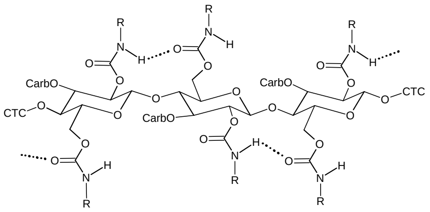
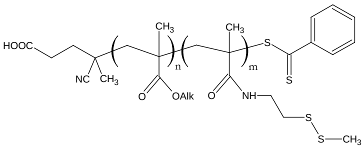
Cholesteric Liquid Crystals (CLC) consist of „nematic layers“ whose directors rotate along an axis parallel to the layer normal. The distance needed for one 360° rotation is called the cholesteric pitch, which is very sensitive to various stimuli like temperature, mechanical stress, concentration and dimensions of the mesogens. In this work we want to use this helical superstructure to orient inorganic nanorods made of CdSe@CdS *[1]* and finally to prepare a mirrorless lasing device with improved performance than known systems. Thereby we face several challenges. First of all the inorganic nanorods are about 50 - 100 nm in length and around 5-10 nm in diameter. Monomeric mesogens like cholesterol derivatives are not suitable based on being too small in comparison to the inorganic nanorods. So we chose derivatives of cellulose having a comparable size and are able of forming CLC in solution *[2]*.



Chemical structure of the used polymeric mesogens

The second challenge is aggregation and phase separation of these nanorods in organic solvents. To prevent this they need to be surface-modified with polymers containing an anchor block to bind on the surface and a block for increased solubility in the solvent used.



Chemical structure of the polymer for CdSe@CdS surface modification

Finally we use polymerizable acrylic solvents to stabilize the cholesteric structure after tuning to fix all adjustments permanently.

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ω-NITROGENFUNCTIONALIZED GLYCOLIPIDS
-THERMOTROPIC AND LYOTROPIC PHASE BEHAVIOR-

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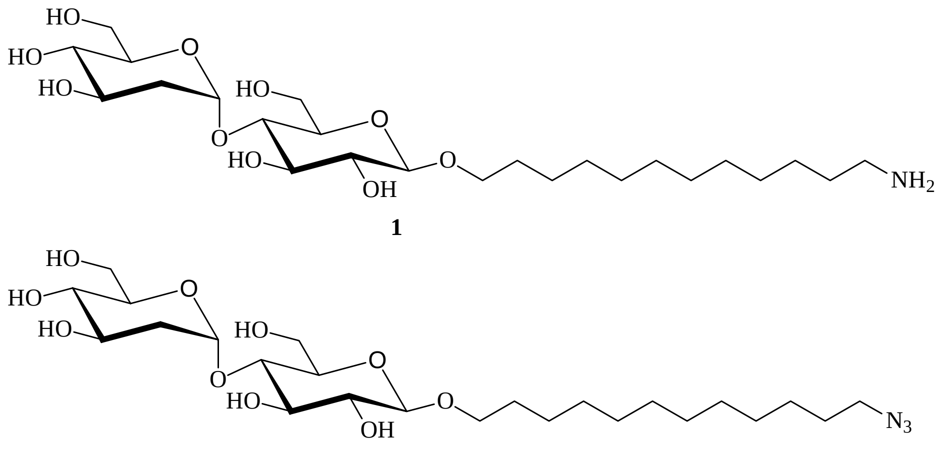
Abstract

A series of monoalkylated glycolipids with ω-nitrogenfunctionalized alkyl chain lengths ranging from saturated C12 to C16 with disaccharide head groups (e.g. maltose, melibiose, lactose and gentiobiose) were synthesized. Beside the general synthetic procedures and the NMR-spectroscopic examination, the structural polymorphism of the glycolipids was investigated by using Fourier-transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC) and small-angle X-ray scattering (SAXS). Dynamic light scattering (DLS) was used for the investigation of micellar behaviour.



1

2

Fig. 1: Examples of synthesized Structures

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