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Ionic Liquid Crystals: Charged Ordered Soft Matter with Fascinating Properties

The transformation of the economy to sustainable green technologies and products is an urgent challenge of our society today in order to reduce the effects of the climate change [1]. At the beginning of this process stands the basic interdisciplinary research for the development of optimized new materials. One promising family of materials of broad interest e.g. for energy applications or waste water purification are ionic liquid crystals (ILCs), which came only in the last two decades in the focus of research [2-4]. Although the field is still in its infancy, the liquid crystal (LC) properties of this substance class were studied already by the LC pioneers, O. Lehmann and G. Friedel, more than 100 years ago [5]. They investigated fatty acid salts and lecithin, which are omnipresent in nature. ILCs merge liquid crystals with ionic liquids, in which intermolecular forces lead to structures of 2D sheets (Lam phase), 3D channels (Cub_v), 1D cables (Col) or micelles (Cub₁) of anions and cations (Figure 1A). The liquid crystalline phases are either induced by temperature changes (thermotropic ILC) or by the addition of a solvent (lyotropic ILC). ILCs are amphiphiles consisting of hydrophobic tails and ionic heads. In the typical ILCs, one ion is covalently attached to the organic building block containing aliphatic chains and often also aromatic units prone to the generation of LC properties. Thus, ILCs can be considered as single ion electrolytes, since only the relative smaller counter ions are mobile. The precise structure can be tailored and fine-tuned by the relative size (volume fraction) of the hydrophobic and the ionic units. Similar to ionic liquids, ILCs are liquid salts self-assembled in anisotropic structures. Their liquid nature makes ILCs

stimuli responsive and thus their alignment can be controlled by external fields (magnetic, electric), mechanical forces or by the nature of surfaces. This can be employed to correctly align the material in a device in order to optimize the performance, which represents a major advantage over conventional materials. Further advantages of the ILC materials are their non-toxicity and the possibility to functionalize the organic scaffold. If the flexible chains are equipped with polymerizable groups, the liquid crystal phase can be immobilized and thus the leakage of such a solidified electrolyte is impeded. Thus, ILCs are highly attractive for applications for which new electrolytes are needed among others, such as supercaps, batteries, dye sensitized solar cells and electrochromic devices [2-4]. In a conventional ILC design the cations are linked with the organic units and the counter ions are inorganic anions [2-4].

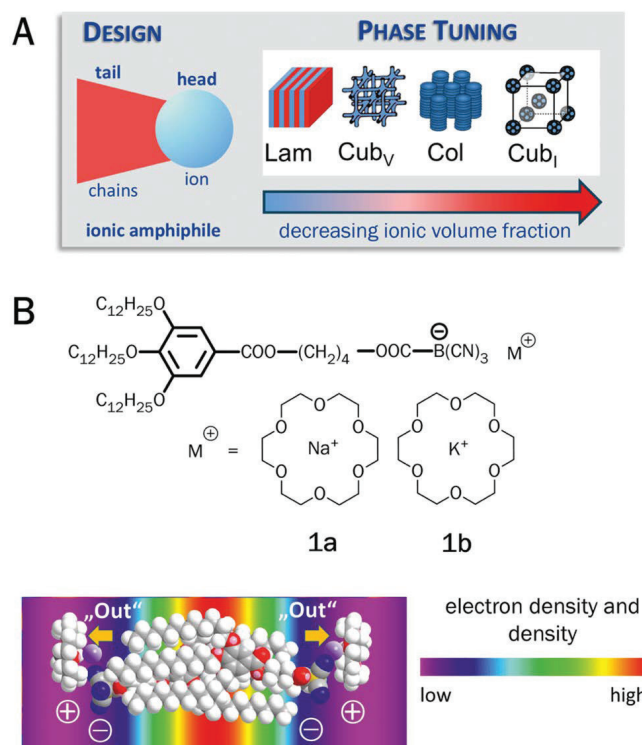


Fig. 1: A: General molecular design of ICLs and structure formation. B: New borate ILC electrolytes with structural model of the bilayer phase. The figure was modified from ref. [5].

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A recent comprehensive study of new ILCs by Weinberger et al. uses robust and non-nucleophilic cyanoborates, which are attached to an organic hydrophobic building block via a short spacer (Figure 1B) [5]. The alkali metal cations are complexed

by a crown ether and can be varied by ion exchange stirring over the desired alkali metal salt solution. In this first study sodium **1a** and potassium **1b** salts were explored. Compared to previous crown ether ILCs the cation conductivity could be increased by three orders of magnitude in the ionic double layer. The comprehensive structural study by solid-state NMR and X-ray methods revealed that the crown ether cation complexes are expelled from the anion layer in an extra sheet and the organic parts are completely interdigitated. Thus, the calculated density in the ionic layer area is extremely low ($< 0.7 \text{ g mL}^{-1}$) which rationalizes the relatively large single ion conductivity of the crown ether complexes of $10^{-4} \text{ Sm cm}^{-1}$ at $80 \text{ }^\circ\text{C}$ and $10^{-5} \text{ Sm cm}^{-1}$ at $40 \text{ }^\circ\text{C}$. The design of the molecules allows in the future a number of synthetic and structural optimizations in order to approach the conductivity of $> 10^{-3} \text{ Sm cm}^{-1}$ at room temperature needed for electrolyte applications.

Characteristic properties of LC phases can also be merged with other physical properties such as luminescence, which is highly relevant for electro-optical devices and sensors. To achieve this Ebert et. al. synthesized a hybrid system of organic guanidinium chloride ILC and inorganic molybdenum clusters (Figure 2A) [6], which revealed that the LC self-assembly is strongly dependent on the counterion. Organic ILCs **2a** form

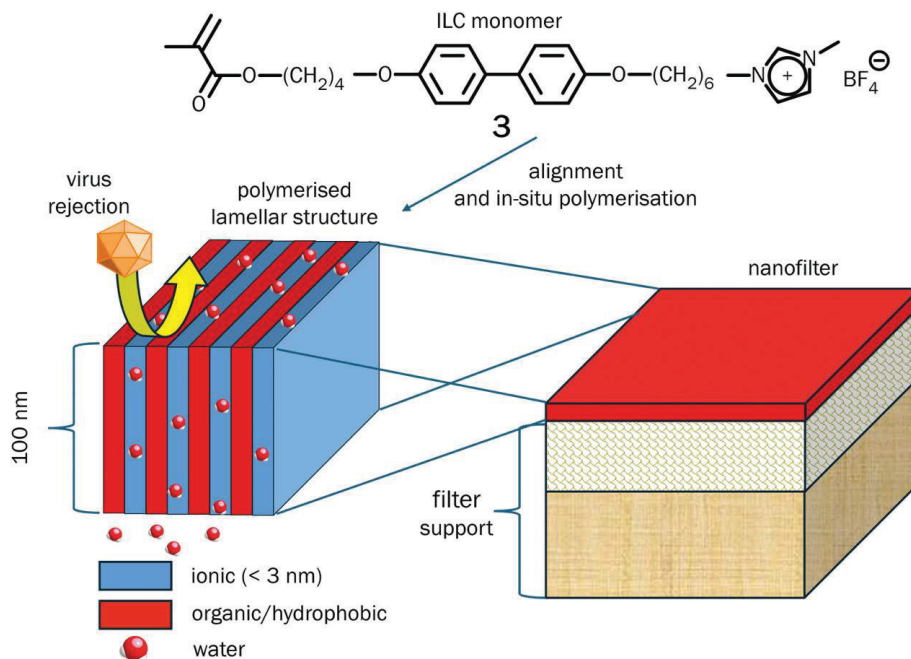


Fig. 3: ILC-based nanofilter for water purification.

a columnar mesophase, whereas the corresponding clustomesogens with $[\text{Mo}_6\text{I}_8(\text{OCOC}_2\text{F}_5)_6]$ anion **2b** form an undulated lamellar (SmA) phase. These clustomesogens display a strong red emission, which depends on the type of cluster anion and is little affected by the side chains. Clustomesogens containing $[\text{Mo}_6\text{Cl}_8\text{Cl}_6]$ anion emit around 740 nm , whereas those with $[\text{Mo}_6\text{I}_8(\text{OCOC}_2\text{F}_5)_6]$ anion emit at 667 nm with quantum yields up to 26 %. Emission intensity of the clustomesogens is strongly sensitive to O_2 enabling O_2 sensor applications.

A fascinating field of ILC research is the engineering of nanofiltration membranes [7]. For this purpose either bi-continuous 3D, layer 2D and columnar 1D structures are suitable. The ionic nanophases are water permeable and either inorganic anions or viruses can be rejected as a function of the pore size. The flux is highest for the 2D layer phase. Kato et al. have demonstrated that monomers **3** (Figure 3) can be correctly aligned and polymerized and that such almost defect-free layers can be transferred to the filter support. These nanofilters are rejecting subsequently $> 99.9999 \%$ of viruses as small as 25 nm and thus can be employed as a new generation of materials for water purification.

These selected examples demonstrate both the challenges and need for fundamental research as well as the broad impact of ILCs for applications.

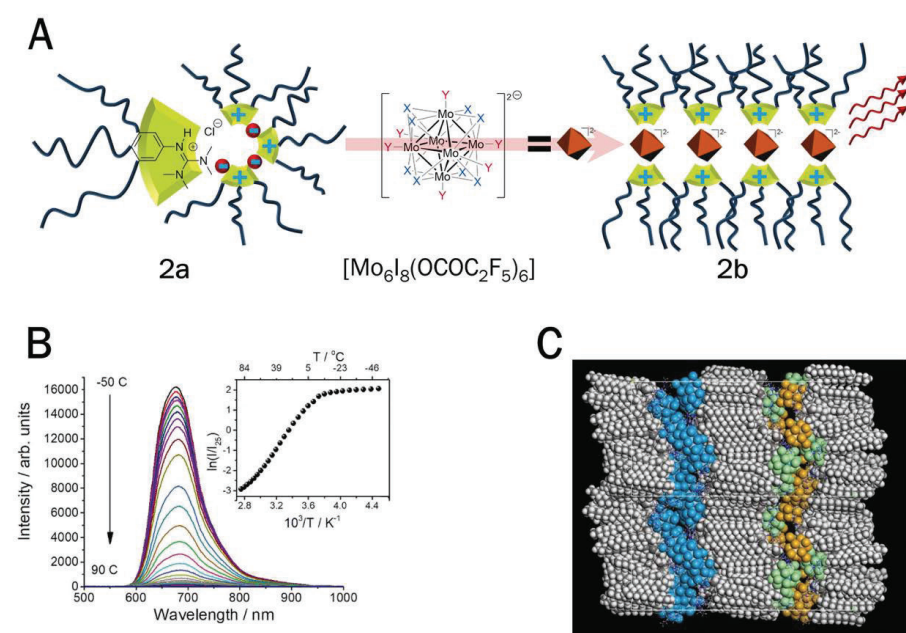


Fig. 2: A: Guanidinium chloride ILCs self-assemble into a columnar mesophase. The reaction with molybdenum cluster salts results in new clustomesogens. This leads to a red-NIR emitting lamellar (SmA) phase. B: Temperature-dependent emission of clustomesogen. C: Structural model of the undulated lamellar phase of the clustomesogen (Y = OCOC_2F_5 ; X = I; colored) and (tetradecyloxy)phenylguanidinium cations (grey). The figure was modified from ref. [6].

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Dr. Sabine Laschat

Sabine Laschat studied Chemistry at the University of Würzburg (1987) and earned a PhD at the University of Mainz under the supervision of Horst Kunz (1990). After postdoctoral studies with Larry E. Overman at the University of California, Irvine (1991), and habilitation at the University of Münster, she was appointed as Associate Professor at the TU Braunschweig (1997–2002). Since 2002 she is Full Professor of Organic Chemistry at the University of Stuttgart. She served as Vice Rector of Research and is currently speaker of the Carl-Zeiss-Foundation project *ChitinFluid*. Her research interests include liquid crystals, bio-inspired materials, natural product synthesis and (bio)catalysis under confinement.

Prof. Dr. Matthias Lehmann

Matthias Lehmann is a Professor in Organic Materials – Soft Materials and Liquid Crystals – since 2011 at the University of Würzburg and held before the prestigious Heisenberg fellowship of the German Science Foundation. He studied Chemistry at the University of Mainz, and began his independent career as a Juniorprofessor at the Chemnitz University of Technology after Postdoc positions at the University of Zaragoza and the Free University of Brussels. His research interest focus on the synthesis, self-assembly and application of complex soft matter with liquid-crystalline properties as new emerging materials. Special emphasis lays in the structural control, which is studied by comprehensive X-ray scattering methods, modelling and simulation.

Nikolai Scheuring, MSc

Nikolai Scheuring received his M. Sc. in Chemistry at the Julius-Maximilians-Universität Würzburg in 2018. Subsequently, he started his PhD studies in the field of organic chemistry under the supervision of Prof. Matthias Lehmann, focusing on thermotropic liquid crystals. His research involved the successful synthesis, characterization and analysis of low molecular weight biaxial molecules which should be able to form enantiotropic biaxial phases. He then continued his scientific career in the research group of Prof. Frank Giesselmann at the University of Stuttgart. At the Institute of Physical Chemistry, he extended his research area to different types of liquid crystals and increased his repertoire of characterization and analysis methods. There his work is focused on new ionic liquid crystals.

News and further information about liquid crystal research can be found on the website of the German Liquid Crystal Society: <http://www.liquidcr.ovgu.de/>