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Liquid Crystals Today

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Discotic Liquid Crystals

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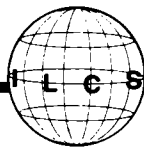
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Liquid Crystals

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**TODAY**

Discotic Liquid Crystals Self-Organizing Molecular Wires

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Bijan Movaghar*Centre for Self-Organising Molecular Systems,
The University of Leeds, Leeds LS2 9JT, UK*

When considering the possibility of commercially viable applications for discotic liquid crystals it is worth noting that in the case of calamitic liquid crystals some 80 to 90 years elapsed between their discovery in 1888 and their first application in displays. Since discotic mesophases were only discovered in 1977 [1], it is not surprising that the first applications are yet to be realized.

Recent research has established that the individual molecular columns in discotic liquid crystals can act as molecular wires for the transport of charge [2,3] or excitons [4,5]. This unique property is set to give rise to commercial applications in fast, high-resolution light scanning and Xerography, and in environmental gas sensors in the immediate future, and, in the longer term, to hybrid computer chips which will enable us to communicate electronically with molecules.

The reasoning behind this optimistic vision of the prospects for discotics is discussed in the context of recent and current research.

Discotics as arrays of molecular wires

The high mobility of charge carriers along the individual molecular columns (wires) in discotic liquid crystals stems from their unique architecture. They are comprised of disordered stacks of disc-shaped molecules, such as the hexaalkoxytriphenylenes, arranged on a two-dimen-

sional lattice, figure 1. The separation between the aromatic cores is of the order of 3.5 Å, so that considerable overlap of π^* orbitals of adjacent aromatic rings occurs. This produces a quantum band structure along the columns with a band gap of 2–4 eV and a band width of approximately 0.1 eV. Charge carrier mobilities are in the range 10^{-2} to 10^{-5} $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ and typically at least 10^3 greater than the corresponding mobilities in the perpendicular direction. The perpendicular transport is fluctuation controlled or impurity assisted.

Long-range one-dimensional transport is generally not realistic in molecular solids due to the presence of structural defects, or deep traps. However, in discotic mesophases the liquid-like fluctuations in columnar order, which take place on a time scale of less than 10^{-5} s, provide a 'self-repairing' mechanism.

This combination of properties is quite unique and opens up new opportunities for applications of liquid crystals.

Applications

Fast, high-resolution Xerography

Recently it has been demonstrated that mobilities for photoinduced charge carriers in the columnar phases of pure, triphenylene-based discotic liquid crystals are of the order of 10^{-4} to 10^{-3} $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ [3,6] and are as high as 0.1 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ in the highly-ordered helical phase of hexahexylthiotriphenylene [7]. This makes them suitable for use as the active charge transport layer in fast and high resolution xerographic and laser printing applications.

PEOPLE in the NEWS

Professor Neville Boden, one of our contributors to this edition of *Liquid Crystals Today*, is founding Director of a new multi-disciplinary research centre devoted to self-organizing molecular assemblies. The Centre for Self-Organising Molecular Systems (SOMS), of the University of Leeds, UK, was formed to bring chemists, physicists and biochemists together to explore possibilities using biological-type responses for applications in sensors and advanced materials. The Centre was opened in June 1995 by Professor Sir Mark Richmond, former Vice-Chancellor of Manchester University, a distinguished scientist and champion of the course of multi-disciplinary research. Funding for the SOMS Centre was provided by the University of Leeds and the Wolfson Foundation.

Further information from:

**Professor Neville Boden,
SOMS Centre, University of Leeds,
Leeds LS2 9JT, UK.**

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Assistant Professor in Organic Chemistry (Liquid Crystal Synthesis)

To begin August 1996. Applications are invited to fill a tenure-track position in Department of Chemistry. The successful candidate will be expected to establish a vigorous and well-funded research programme involving the design and synthesis of novel small molecule organic liquid crystalline materials. He/she will have excellent collaborative opportunities through Kent's Liquid Crystal Institute and will be eligible to participate in the NSF Science Technology Center for Advanced Liquid Crystalline Optical Materials (ALCOM) based at Kent. A PhD degree in organic chemistry and postdoctoral experience are preferred. Curriculum vitae,

undergraduate and graduate transcripts, a detailed description of research plans, and three letters of recommendation should be sent to:

**Dr Paul Sampson, Chair, Search Committee,
Department of Chemistry, Kent State
University, PO Box 5190, Kent, OH 44242-
0001, USA, fax: (216) 672 3816.**

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Preparation of material

- Contributions should be submitted on disk (1 ASCII file and 1 word processing file as used by author) (we regret we cannot handle TEX), along with 1 paper hard copy using double-line spacing, single sided on A4 paper, with margins top and bottom, and left-hand side of at least 4 cm.
- Articles must contain suitable headings and sub-headings.
- References should be numbered serially in the text by means of superscript Arabic numerals.
- Bibliographic references (not footnotes) should follow the main text and should have the format:
REDMOND, M., COLES, H., WISCHERHOFF, E., and ZENTEL, R., 1993, *Ferroelectrics*, **148**, 323.
BAUR, G., DELAVIER, P., ETZBACH, K.H. MEYER, F., KIEFER, R. SIEMENSMEYER, K., and WAGENBLAST, G., 1994, *Abstracts of 15th International Liquid Crystals Conference*, Budapest, Hungary, p.780.
- Journal titles should be abbreviated according to the Chemical Abstracts Service Source Index (CASSI).
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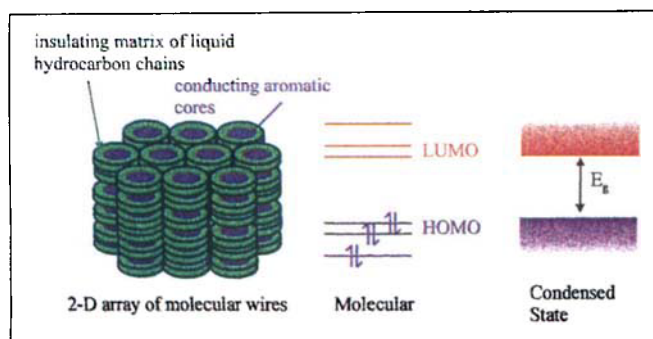


Figure 1. A schematic view of both the D_h phase in discotic liquid crystals and a simplified electronic structure of an isolated molecule and the condensed state showing the band gap E_g .

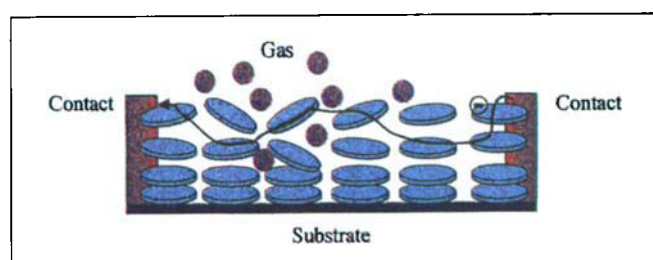


Figure 2. A schematic illustration of a gas sensor exploiting the surface conductivity of the discotic liquid crystalline film.

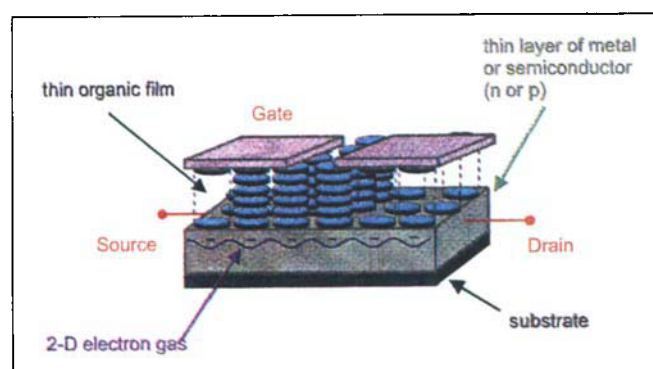


Figure 3. A schematic view of a hybrid discotic liquid crystal/silicon field effect transistor. The molecular wires generate a 2-D band structure in the silicon inversion layer. The source-drain current is therefore sensitive to signals along the columns produced by sensing molecules absorbed in the film.

For the last 30 years polymer organic photoconductors have been widely used as photoconductive media in the field of xerography and laser printing. The efficiency of photocopiers and laser printers is primarily due to the mobility of charge carriers in the photoconductive layer. Polyvinylcarbazole (PVK), for instance, exhibits a mobility in the range of $10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. However, this is too slow for application in fast laser printing and photocopying, and toxic inorganic compounds of selenium and tellurium are therefore used.

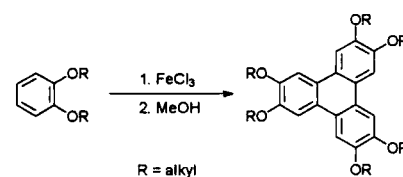
The surface field effect gas-sensor

The present generation of 'electronic noses' are based on an array of 16–32 individual gas sensors, each made from a conducting organic polymer which displays reversible changes in conductivity when exposed to polar volatile odours. Although the response is non-specific to individual odour molecules, a characteristic odour 'fingerprint' is obtained from the response of an array of sensors. However, a serious limitation of conducting polymers is the lack of response to non-polar molecules.

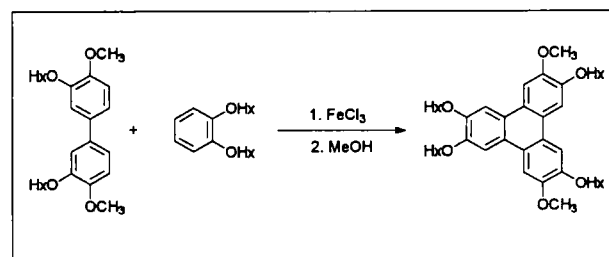
The surface of a discotic liquid crystal has a unique topology, figure 2. Fluctuations in the lengths of the columns results in a 'conductive' surface layer. The carrier mobility along the surface is fluctuation assisted and the tunnelling rates are exponentially dependent on the molecular core spacings. The core-core separation fluctuates with the surface and changes as soon as the surface is disturbed: i.e. locally melts, freezes, reorientates, etc. The electrical conductivity of this surface layer is, therefore, very sensitive to the absorption of molecules. Discotic liquid crystals can therefore be used as very sensitive gas sensors for both polar and non-polar molecules. The response has a physical origin and does not rely necessarily on charge transfer between the adsorbed molecule and the discotic aromatic core.

Communicating with molecules

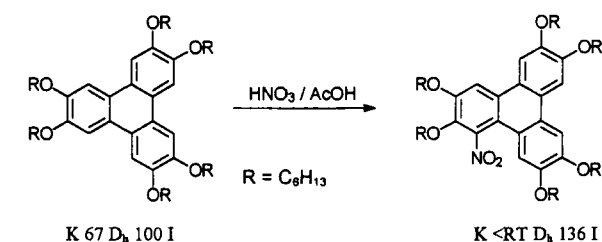
The narrow electronic band structure, and the slow speed of response in discotic liquid crystals rule out many traditional semiconductor applications. We can, however, envisage applications for hybrid systems which combine the unique electronic properties of discotic liquid crystals with current silicon technology, figure 3. Discotic liquid crystals form high-quality insulating films and could, therefore, replace the traditional oxide insulating gate in a field effect transistor. The novel feature now is that self-assembled molecular wires in the liquid crystal can address the 2-D



Scheme 1. Synthesis of 2,3,6,7,10,11-hexaalkoxytriphenylenes.



Scheme 2. Synthesis of unsymmetrical triphenylene polymer precursor.

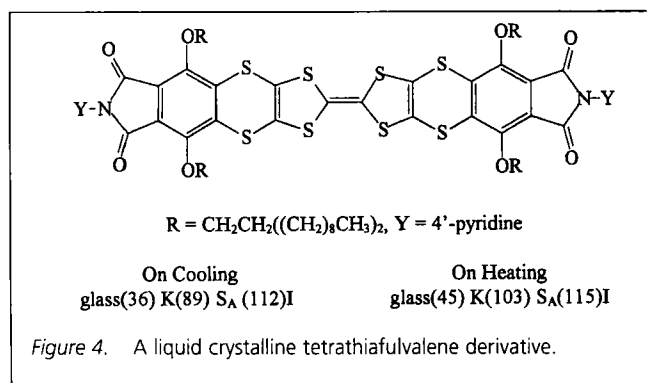


Scheme 3. Nitration of 2,3,6,7,10,11-hexahydroxytriphenylene

electron gas in the inversion layer of the silicon. This coupling is strong enough to give rise to a hybrid band structure in the inversion layer with the effect of amplifying perturbations in the molecular wires via restrictions imposed on quantum pathways. In this way we can transform molecular signals arriving in the molecular wires into electronic signals in silicon chips. Once in the chip, molecular signals, in the form of local current changes, or channel switching events ('on - off'), can be processed in the usual way.

Developments in design and synthesis

In our work we have used mainly hexaalkoxytriphenylenes. They are stable to heat, light and redox processes and their chemistry is fairly accessible. We are now able to produce large quantities of these materials of high purity and at an economic price. Routes for synthesizing low molar mass discotics [8], (Scheme 1), polymeric discotics [9], (Scheme 2), and for introducing substituents into the triphenylene ring [10], (Scheme 3), are now available. The latter enables the electrical properties and phase behaviour to be fine-tuned. Device applications of discotic liquid crystals require the development of materials which are liquid crystalline at room temperature and can be easily processed as polymers.



Smaller band gaps can be achieved by using porphyrin, phthalocyanine or larger delocalized aromatic cores. Significantly, we have recently made smectic A phases from calamitic molecules with tetrathiafulvalene (TTF) cores having band gaps of order 2.5 eV, figure 4. The in-layer conductivity ($1.99 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ at 110°C) is 10^4 greater than that along the normal to the smectic layer. This behaviour stems from local $\pi - \pi$ stacking of TTF cores. By intelligent design it should be possible to build charge transport into all of the calamitic phases with the tantalizing prospect of new applications for liquid crystals.

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Conference on Dynamics and Defects in Liquid Crystals

Honouring Alfred Saupe

Report by O. D. Lavrentovich, Kent State University, Kent, Ohio, USA

At ALCOM's international symposium on 12 - 13 October, 1995, over 100 participants gathered in beautiful Cuyahoga Falls, Ohio, to discuss current developments in dynamics and defects in liquid crystals and to honour Professor Alfred Saupe on the occasion of his 70th birthday. ALCOM, the US National Science Foundation and Technology Center on Advanced Liquid Crystalline Optical Materials, is a consortium of Kent State, Case Western Reserve and Akron Universities.

During the conference, it became evident that the areas of defects and dynamics in liquid crystalline materials, topics which have played an important role in many of Alfred Saupe's contributions, were opening doors onto new challenges in the development of liquid crystal physics as well as onto new strategies to advance our understanding of non-linear non-equilibrium systems. Contributions made during the conference also clearly demonstrated that during his scientific career, Alfred Saupe laid the groundwork in the physics of liquid

crystals on which much of the current knowledge and research is based.

The first of these was the clear recognition that H. Pleiner (Mainz, Germany) gave the Symposium's Keynote Address: 'Alfred Saupe - 40 Years of Research'. This lecture was an efficient (one year per minute) and thorough overview of Alfred Saupe's classic pioneering contributions to the science. These include the Maier-Saupe model of the nematic phase; predictions of a cubic defect structure for blue phases; prediction of helix structures in chiral smectics; discovery of biaxial nematics in lyotropic systems; first hydrodynamic theory of biaxial nematics and smectic C liquid crystals; modern presentation of the divergence terms in the elastic free energy, the first calculations of the elastic constants based on model intermolecular potentials. The talk was divided into four parts, covering contributions in the areas of

- structure and order
- defects, dynamics and instabilities
- new phases and phase transitions, and
- applied research.