EUROPEAN **S**YNCHROTRON **R**ADIATION **F**ACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** COMPLEX SOFT HONEYCOMB NANOSTRUCTURES	**Experiment number**: SC-2198
Beamline: ID02	**Date of experiment**: from: May 2007 to: May 2007	**Date of report**: 31/08/07
Shifts: 6	**Local contact(s)**: Dr. Peter Boesecke	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Prof. G. Ungar, Dr. X. B. Zeng and Dr. M. Shcherbina
Department of Engineering Materials
Sheffield University
Sheffield S1 3JD
UK

Report:

Recently it was shown that complex superstructures can be formed by T-shaped molecules with three incompatible segments. These molecules have a rod-like biphenyl or terphenyl core, to which a polar group is attached at each end and a long aliphatic chain in a lateral position ("bolaamphiphiles") [1]. Alternatively, an aliphatic chain is attached at each end and a polar (oligo-oxyethylene) chain with or without an ionic terminal group is attached laterally ("facial amphiphiles") [2,3]. The experiments carried out at ID02 were designed to determine these structures, and to further our understanding of the principle of self-assembly in thermotropic amphiphiles.

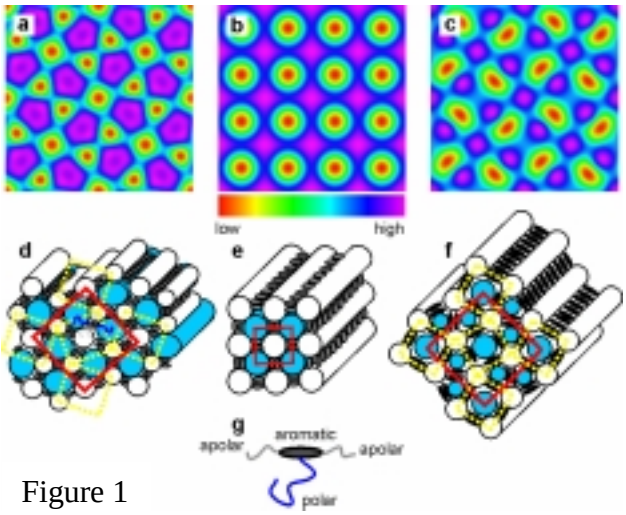

Figure 1

Previous experiments performed on these T-shaped molecules have revealed a number of 2-d and 3-d liquid crystal phases with novel geometries [2-5]. Figure 1 shows electron density maps of three related phases, reconstructed from synchrotron X-ray data [5]. Corresponding schematic molecular models are shown underneath. Rigid aromatic rod-like groups provide the walls of these novel honeycomb structures containing polar channels of different polygonal cross-sections. In addition to hexagonal honeycombs, structures with triangular, square and pentagonal channels were established, depending primarily on the geometry of the molecules, and the presence of ions or water. As shown in Figure 1, with decreasing volume of the polar group, the shape of the cross-section of the polar channels changes from pentagon (a), through square (b), to

mixed triangular and square (c). More complex modes of self-assembly have been found, by changing the relative size of the three incompatible segments. Some of these have 3-d order on the mesoscale, while still remaining liquid-like on the atomic scale.

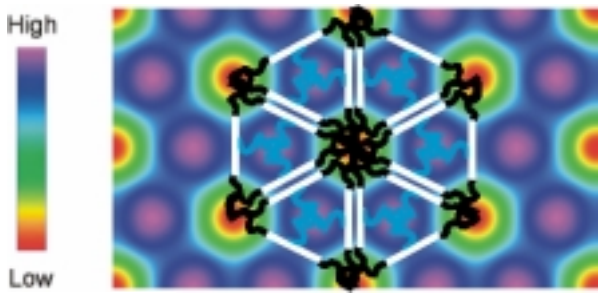

Figure 2

In the first group of experiments we investigated facial amphiphiles with the relative length of polar chains reduced below those displaying the square-triangle lattice (Figure 1c). A new liquid crystal phase, which is made up exclusively of triangular channels, has been found. A typical example of the reconstructed electron density map of this phase, with schematic drawings of molecular arrangement in the structure, is shown in Figure 2. The observation of this new phase further validates our models for these honeycomb structures made up of columns of polygonal cross-sections. When the volume ratio of polar chains in the system decreases, the ratio between the cross-section area of the columns to their circumferences should also decrease. This is achieved by reducing the number of sides of the polygons, hence the observed phase sequence: hexagonal → pentagonal → square → mixed square and triangular → triangular on decreasing length of polar chains.

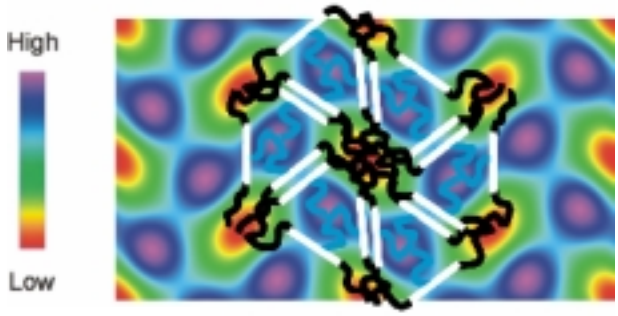

Figure 3

An even more intriguing novel 2-d liquid crystal phase is found close to the triangular phase in a number of T-shaped amphiphiles. Preliminary X-ray experiments carried out on an oriented sample using an in-house instrument suggest a hexagonal lattice, with a large unit-cell parameter. However, with the help of high resolution available at the synchrotron, it was found that what was considered as the first diffraction peak consists in fact of two closely spaced peaks. The plane group of the phase is thus determined to be p2gg. The reconstructed electron density map of this phase (Figure 3) reveals that the phase is also made up exclusively of triangular channels. However, the triangles are no longer equilateral but distorted. As shown by the schematic drawing of molecular arrangement on top of the electron density map (Figure 3), the molecular ends are further apart at one corner of each triangle than at the other two. By doing this the structure is able to support a slightly larger ratio of polar parts in the system, without changing the number of sides of the polygonal channels. This is in line with the fact that this phase is observed in between the triangular phase (Figure 2) and the mixed square and triangle phase (Figure 1c). The high resolution availabe at the synchrotron radiation source was crucial for the determination of this structure, which otherwise would not have been possible.

In addition to the two phases mentioned above, several other complex honeycomb structure have also been identified, and work is in progress on determination of their structures.

References:

1. X.H. Cheng, *et al.*, *J. Am. Chem. Soc.* 2003, **125**, 10977.
2. Chen, XB Zeng, U Baumeister, S Diele, G Ungar and C Tschierske, *Angew. Chem.* 2004, **43,** 4540.
3. B Chen, U Baumeister, G Pelzl, M Kumar Das, XB Zeng, G Ungar, C Tschierske, *J. Am. Chem. Soc.*, 2005, **127,** 16578.
4. B Chen, U Baumeister, S Diele, MK Das, XB Zeng, G Ungar, C Tschierske, *J. Am. Chem. Soc.* 2004, **126**, 8608.
5. B Chen, XB Zeng, U Baumeister, G Ungar, C Tschierske, *Science*, 2005, **307**, 96.