ESRF	**Experiment title:** Surface structure determination of self-assembled semi-conducting oligomers using GIWAXS	**Experiment number**: SC-2704
Beamline: BM28	**Date of experiment**: from: 16th Dec 2009 to: 21st Dec 2009	**Date of report**: 17th Feb 2010
Shifts: 15	**Local contact(s)**: Oier Bikondoa	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Dr Wuge Briscoe* - University of Bristol, School of Chemistry

Dr Charl Faul - University of Bristol, School of Chemistry

Thomas Dane* - University of Bristol, School of Chemistry

Georgia Pilkington* - University of Bristol, School of Chemistry

Phillip Cresswell* - University of Bristol, School of Chemistry

Zhecheng Shao* - University of Bristol, School of Chemistry

Report:

Synchrotron radiation was utilized to perform grazing-incidence wide-angle x-ray scattering (GIWAXS) on nanofilms prepared from aniline-based oligomer-surfactant complexes of varying molecular architecture. Each system was observed in both the undoped and the surfactant-doped states so as to demonstrate the power of ionic self-assembly to generate well-ordered, functional systems. The structures of materials used in this experiment are shown in Figure 1.

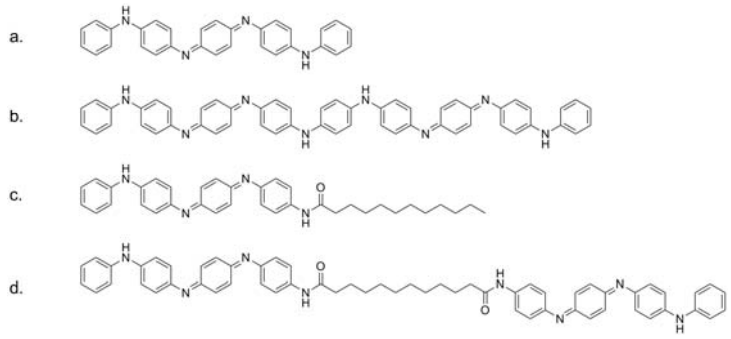

Figure 1. Structures of oligoaniline derivatives studied. Each is shown in the emeraldine base (EB) oxidation state. (a) tetraaniline (TANI); (b) octaaniline (OANI); (c) diblock structure with alkyl tail (TANI-AMD-C12); (d) triblock structure with alkyl linker (TC12T).

When the aniline oligomers are introduced to an acid surfactant the oligomer is doped forming a dication radical as which is stabilised by the oppositely charged surfactant counterion. This radical species acts as the charge carrier unit and permits the conductivity of electronic charge (see Figure 2). The action of the surfactant has an additional function in providing another chemical building block to contribute to the structural ordering of the system.

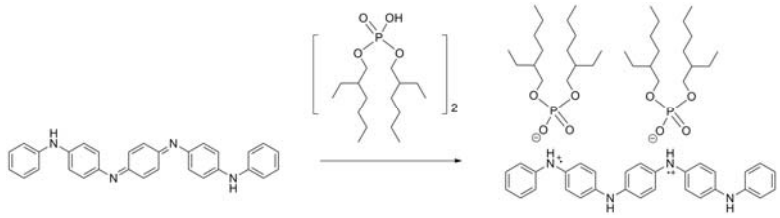

Figure 2. The doping process of TANI using the acid surfactant BEHP. The reaction requires two equivalents of BEHP to form the dication radical – the unit of electrical conductivity – by means of protonation at the two nitrogen atoms on the quinoid ring.

This process has been well-studied in the bulk phase but little is known of the structure at surfaces, an understanding which is paramount to the development and improvement of devices. For this reason synchrotron radiation at a grazing incident angle was used to study the structure of the nanofilms.

Sample preparation involved deposition of the molecules on an Si (100, boron-doped) substrate by a solvent anneal process from THF. In addition to varying the molecular architecture of the oligomers, the films were also observed as a function of layer thickness and scanned over a range of range of temperatures to detect any thermally-induced structural changes. Varying layer thickness was achieved through a calculation of the area of the molecular system and varying the solution concentration for deposition. In terms of experimental setup, we used a home-made chamber that had been carefully designed and built by Dr John Emyr MacDonald (University of Cardiff, Physics). The sample was mounted on a resistive heating element monitored by two thermocouples and controlled by a Lakeshore temperature controller (already presesnt at BM28). This allowed us to carefully scan each sample over a selected temperature range. The chamber was sealed and flushed with helium gas so as to reduce the background scattering from air. The scattering geometry involved a very small incident angle of radiation so as to give a large footprint and generate long-range in-plane structural information. In picking an angle close to the critical angle of the substrate it can be assumed that all scattering arises from the deposited materials. Data was recoreded on a Mar CCD detector which was placed close to the chamber and an angle of $2\theta = 10°$ in order to a) reduce the background scattering from air and b) complete the wide-angle geometry for observation of the small legnth scales involved with the molecular system.

Our initial results suggest that through the addition of the surfactant to the system, the level of order and in-plane structure is increased dramatically. The nanofilm structure also depends sensitively on the film thickness and temperature with clear order-disorder transitions observed. It was found that the majority of systems generated largely powder-like scattering profiles indicating that there was little long range, in-plane structure present. However, it was observed that under certain conditions detailed scattering patterns were generated with many off-specular reflections indicating well-ordered films. This was most clearly observed for the doped TANI molecular system. This provides conclusive evidence that through the technique of ionic self-assembly the structure of these materials at surfaces can be controlled demonstrating a clear improvement in order upon the addition of the dopant to the system.

We are currently in the process of performing analysis on the data we have obtained to elucidate detailed in-plane structural information. This will be combined with AFM and STM studies for morphological information and X-ray reflectometry data (for out of plane structure). We intend to submit one manuscript for publication on the TANI system by September 2010.

In terms of user experience, we found the experiment highly enjoyable. The local contact (Dr Oier Bikondoa) was both knowledgable and helpful and the experiment would not have been possible without him. Equipment, facilities and other supporting staff have made this experiment an overal success. We did experience a slight problem with the MarCCD detector which would give somewhat different background scattered intensities in each of the four quadrants. Overall we were very pleased with how efficiently we were able to work and managed to obtain large quantity of data.