

**Proposal:** 9-11-1649                      **Council:** 10/2012

**Title:**                      STUDY OF MACROMOLECULAR CONFIGURATION OF POLYFLUORENES IN SOLUTION

**This proposal is a new proposal**

**Research Area:** Soft condensed matter

**Main proposer:** URBINA Antonio

**Experimental Team:** URBINA Antonio  
ABAD Jose

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**Samples:** polyfluorene PFO (F8) in solution (solvent: deuterated toluene)  
polyfluorene OG841 (F8:F6) in solution (solvent: deuterated toluene)  
polyfluorene OG848 (F8:F5) in solution (solvent: deuterated toluene)  
polyfluorene OG852 (F8:F5) in solution (solvent: deuterated toluene)

<b>Instrument</b>	<b>Req. Days</b>	<b>All. Days</b>	<b>From</b>	<b>To</b>
D11	2	1	07/03/2013	08/03/2013

**Abstract:**

We propose to study by small angle neutron scattering a family of polyfluorenes, which are based on poly(9,9-dioctylfluorene). The materials have been designed to provide insight into the effect on charge transport of a number of key factors influencing molecular packing, in particular the structure and number of side-chains and the polymer molecular weight. During the experiments, the temperature dependence of the structural transitions will be carefully studied for solutions at low volume fraction. The SANS scans on the solutions will be performed at several temperatures, ranging between 300K and 450K, in order to study the radius of gyration of the macromolecule, the conformational changes in solution and the possible onset of a coil-globular transition and the aggregation/nucleation points of crystallization during processing in solution as a function of temperature.

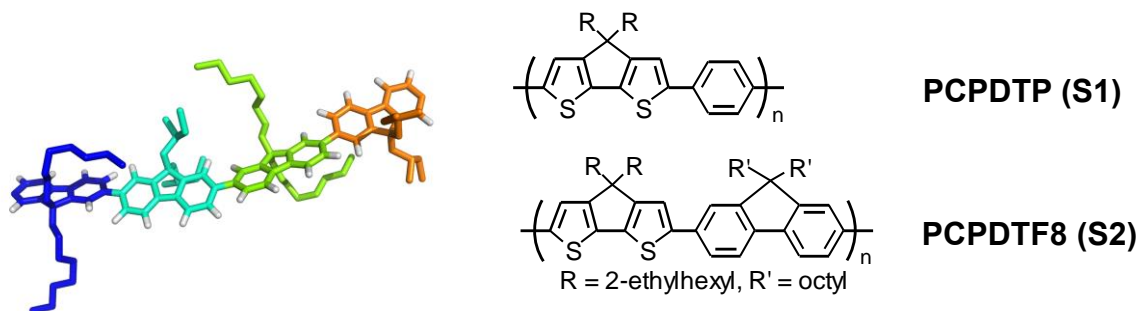
# EXPERIMENTAL REPORT FOR PROPOSAL 9-11-1649

Instrument D11, March 2013

## STUDY OF MACROMOLECULAR CONFIGURATION OF POLYFLUORENES IN SOLUTION

### 1. Introduction:

Conjugated polymers have been developed since the past 30 years, but only recently, applications to optoelectronic devices such as thin film transistors, light emitting diodes, organic lasers and organic solar cells have become close to commercial applications [1]. Whilst the desirable properties of polymers for these various applications are many and distinct, each of them requires materials with optimised charge carrier mobility. Important breakthroughs have been made in increasing charge carrier mobility, with mobilities of  $>1 \text{ cm}^2/\text{Vs}$  achieved in thin film transistors [2], but high mobility comes at a cost to other material properties, and charge transport remains a major limiting factor in the performance and efficiency of many organic electronic devices. Higher efficiencies will therefore require the design of new materials or materials combinations and new processing routes. An understanding of the relationship between macroscopic charge transport and the chemical structure and nano-morphology of the material will be crucial in guiding material design.



**Figure 1.** F8-F5-F8-F5 fluorene tetramer showing the alternation of different side-chains (left). The measured polymers are composed of hundreds of these alternating units. Molecular dynamic simulations have been performed to model the 3D structure and charge transfer characteristics of the bulk polymers. The molecular structure of two of the measured samples are shown on the right hand side.

### 2. Understanding the self-organization process of the polyfluorenes:

It is well-established that the details of the molecular packing are critical in determining the bulk transport properties of the material. The family of polyfluorenes, which are based on poly(9,9-dioctylfluorene) (PFO, or F8), have been designed to provide insight into the effect on charge transport of a number of key factors influencing molecular packing, in particular the structure and number of side-chains and the polymer molecular weight. The polyfluorenes are a well-studied family of conjugated polymers, but recent work at Imperial College London has shown that the system offers much greater potential for understanding the mechanisms involved in enhancing charge transport. In [3], simple chemical modification of PFO was shown to lead to a much-enhanced carrier mobility, whilst simultaneously optimising the photoluminescence quantum efficiency of thin-film devices. This finding provides a route towards the development of efficient organic laser devices. Recently, we have extended this study by considering further modified polyfluorenes, controlling the polymer molecular weights, and exploring alternative processing conditions and methods.

Since self-assembly processes are driven from nucleation points when the polymers are in solution, the morphology of the polyfluorene films is strongly dependent on processing variables such as the solvent used in the preparation of the layers, the deposition method (whether spin-coating, solvent annealing, doctor-blading etc) and the temperature during processing, as well as any thermal annealing cycles in the post-preparation stage. Whilst confirming and extending the findings in [3], we have recently found an order of

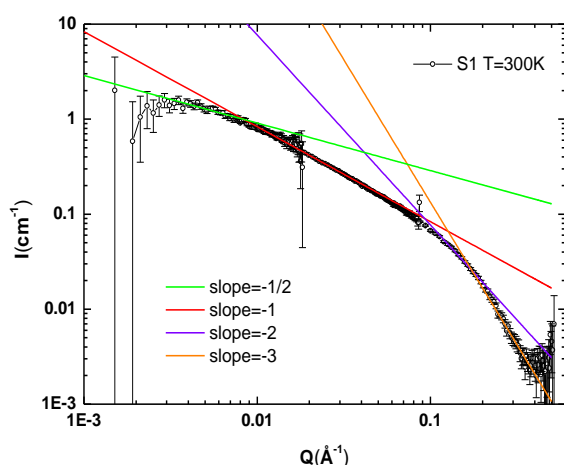
magnitude effect on the carrier mobility of the processing temperature and method. We also observe significant changes in the energetic disorder within the polymer film, which could be related to conformational changes which depend on the solution phase and the temperature of process, as well as the polymer structure [4].

### 3. Preliminary results of Small Angle Neutron Scattering experiments:

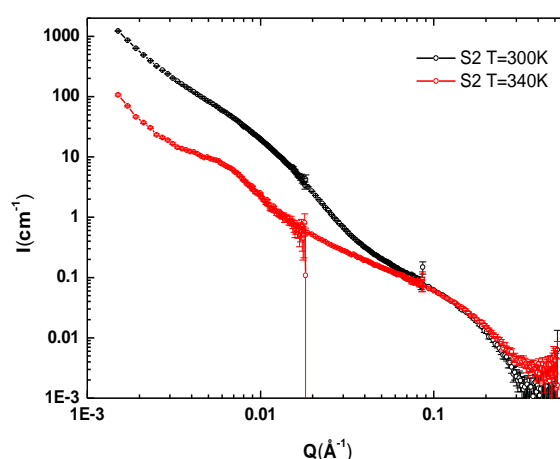
We have measured small angle neutron scattering using the **D11** instrument on five different variations of polyfluorenes and other conjugated polymers: PCPDTP, PCPDTF8 (both shown in Figure 1-right and named S1 and S2 in following figures), PCPDTBT, PCPDTT2 and PC3B2. All samples are solutions at 1%wt in deuterated toluene.

The instrumental configuration was: incident wavelength  $\lambda=6\text{\AA}$  and detector bank in positions 1.2m, 8m and 39m, providing a good range of Q transfer from  $10^{-3}\text{\AA}^{-1}$  to  $0.4\text{\AA}^{-1}$ . Calibration runs were performed on Teflon and water. Measurements at room temperature (300K) for all samples and at high temperature (340K) for three samples were performed.

Examples of measurements and initial fit using linear slopes are shown in Figures 2 and 3. S1 shows a clear section with a rigid rod behaviour (slope -1) typical of conjugated polymers, while S2 presents onset of aggregation at two length scales and with a clear influence of temperature, which upon a slight heating clearly reinforces the aggregation effect. A more detailed analysis and modelling of results are under way.



**Figure 2:** SANS measurement on S1 at room temperature. Lines at fixed slopes have been superimposed on the experimental data.



**Figure 3:** SANS measurement on S2 at two temperatures. Note the increment of scattering intensity ( $\text{cm}^{-1}$ ) when compared with S1.

The preliminary analysis of the results of the SANS experiment confirms the onset of aggregation or nucleation points while the polymer is still in solution. Although the range of explored temperatures has been reduced to two due to the lack of beamtime, this effect has been clearly demonstrated. By considering the charge carrier transport properties in combination with these structural measurements and molecular dynamic simulations, we hope to elucidate the important mechanisms responsible for the enhanced carrier mobility linked to structural changes in the macromolecule, and to develop design rules for high mobility polymers.

#### References:

- [1] J. Burroughes et al. *Nature*, **347**, 539 (1990); C.J. Brabec, et al., *Advanced Functional Materials*, **11**, 15 (2001); H. Sirringhaus et al., *Advanced Materials*, **17**, 2411 (2005); I. D. W. Samuel et al., *Chemical Review*, **107**, 1272 (2007).
- [2] H. N. Tsao et al., *Advanced Materials*, **21**, 209 (2009).
- [3] B. K. Yap et al., *Nature Materials*, **7**, 376 (2008).
- [4] T. Kreouzis et al., *Physical Review B* **73**, 235201 (2006).