

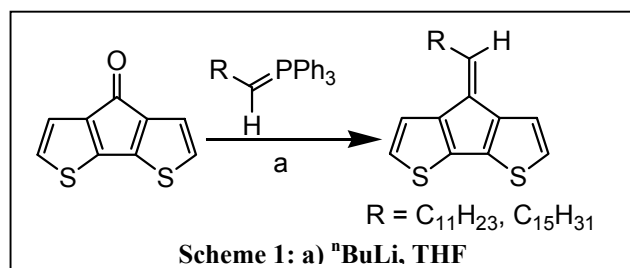
1. Introduction

The aims of OMEC are to synthesise, characterise, process and evaluate the device performance of novel, self-organising molecular materials of high purity which exhibit high carrier mobilities and which are suitable for the simple-in-principle manufacture of organic electronic devices on substrates useful for practical applications. These aims have remained valid throughout the course of this year and this report presents a record of achievement in the second year.

2. Conjugated Polymer Synthesis

2.1 Preparation of Polycyclopentadithiophenes¹

Following on from the previous years research,² polycyclopentadithiophenes in which the alkyl substituents are held in the plane of the polymer backbone have been investigated. When compared to the sp³ hybridised dialkyl analogue³ it was expected that this arrangement would allow for much closer packing of the aromatic units. In the first instance monomers were prepared with a single alkyl chain attached via a sp² hybridised carbon. These were



Scheme 1: a) ^tBuLi, THF

readily synthesised in a single step from the previously reported ketone via the Wittig reaction with primary alkyl Wittig salts (Scheme 1). X-ray crystallography showed that these molecules packed closely together in the solid state with an interfacial distance of 3.5 Å. The monomers were oxidatively polymerised using iron (III) chloride in chloroform. Whilst the polymers were initially soluble, upon storage for any length of time the materials became insoluble. This was thought to be due to the formation of

aggregates or cross-linking of the polymer chains.

The use of the Wittig reaction to prepare dialkyl derivatives of these molecules was limited by the availability of secondary alkyl halides. Furthermore, those that were available were found to isomerise during the preparation of the Wittig salt. Therefore a new route was sought.

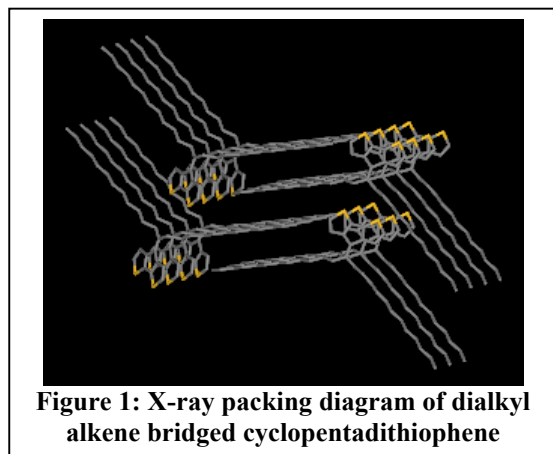
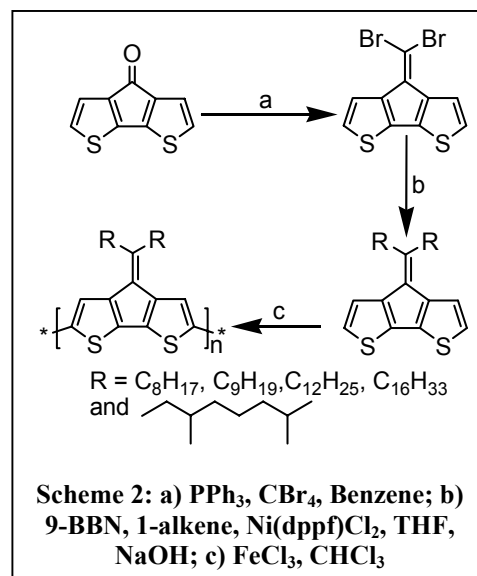


Figure 1: X-ray packing diagram of dialkyl alkene bridged cyclopentadithiophene

Geminal dibromo alkenes were reported to undergo efficient Suzuki type cross-coupling when reacted with alkyl derivatives of 9-borabicyclononane, in the presence of palladium complexes as catalysts and a base as a proton scavenger. The alkyl derivatives of 9-borabicyclononane



Scheme 2: a) PPh₃, CBr₄, Benzene; b) 9-BBN, 1-alkene, Ni(dppf)Cl₂, THF, NaOH; c) FeCl₃, CHCl₃

are readily prepared in situ by reaction between 9-BBN and a primary alkene, in anhydrous tetrahydrofuran. This reaction was found to yield the desired dialkyl product (Scheme 2). An X-ray crystal structure was obtained of the didodecyl substituted monomer and the packing diagram showed that whilst the chains are twisted slightly out of plane the thiophene units are well ordered, stacking with an interfacial distance of 3.6 Å (Figure 1). These monomers were oxidatively polymerised using iron chloride in chloroform. It was found that this yielded insoluble polymers with short and medium length alkyl chains. However, the dihexadecyl substituted derivative was fully soluble in organic solvents and the characterisation data are given below (Table 1).

M _n	M _w /M _n	λ _{max} solution (nm)	λ _{max} solid (nm)	ε(L mol ⁻¹ cm ⁻¹)
6119	1.4	646	696	142,303

Table 1: Characterisation data for soluble dialkyl alkene bridged polycyclopentadithiophene

The solution absorption spectra shows that the polymer has a λ_{\max} at 646 nm, corresponding to the $\pi - \pi^*$ transition. This is red shifted by 50 nm compared to the previously reported sp^3 bridged polycyclopentadithiophenes, due to the conjugation being extended over the alkene bridge. The absorption maximum was shown to be independent of the concentration of the solution (**Figure 2**) indicating that the polymers are not aggregated in solution. On transferring to the solid state (**Figure 3**) the absorption maximum red-shifts to 696 nm, showing significant ordering in the solid state.

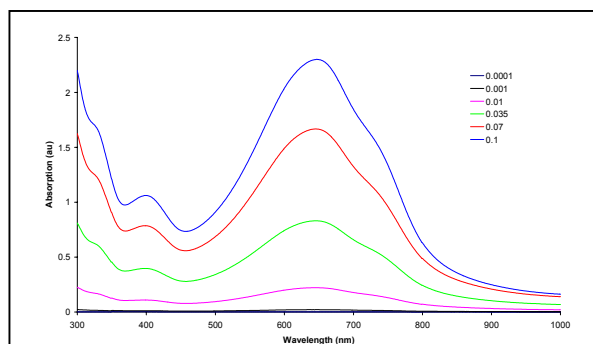


Figure 2: Absorption of polymer in $CHCl_3$ solution. Concentrations shown in $g L^{-1}$

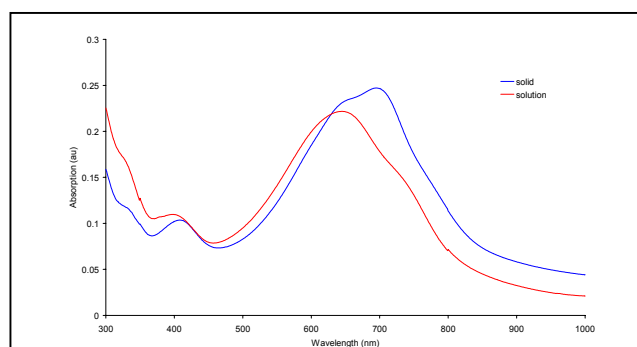


Figure 3: Comparison of solution and solid state absorption spectra.

The measurement of the FET mobilities of a range of fused-ring thiophene polymers and co-polymers featuring sp^2 hybridisation at the bridging position is currently on-going at Avecia. Whilst initial results have been disappointing, several improvements in film formation may be envisioned in order to achieve high mobilities, including the development of better formulations (solvents, solids % etc), in controlling the temperature of deposition and in choice of substrate. The measurement of FET mobilities of calamitic liquid crystalline organic semiconductor materials supplied under this work package task (not shown) is also on-going at Avecia.

2.2 Synthesis of Anthraquinone/n-Type Polymers

Work on the synthesis of quinone-containing polymers continues. The polymers containing 1,4-linked anthraquinone moieties, such as **1**, reported last year showed little evidence of conjugation as judged by UV spectroscopy and cyclic voltammetry (CV). As judged from the X-ray crystal structures of model compounds the torsion angles between the aromatic units were close to 90° except when thiophene was one of the units. In these materials the torsion angle was 38° but the quinone unit was significantly twisted.

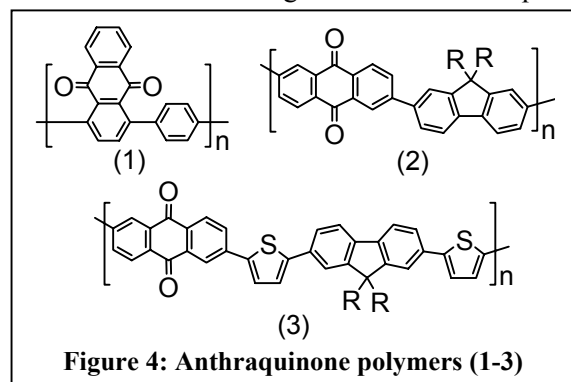


Figure 4: Anthraquinone polymers (1-3)

from X-ray crystal structures of model compounds the torsion angles between the aromatic units was $ca.31^\circ$ when a phenylene residue was involved but only $ca.7^\circ$ when a thiophene unit was involved. This prompted the synthesis of polymer **3**. By cyclic voltammetry the polymers had excellent redox properties, but whilst the π -conjugation was better than with the 1,4-linked anthraquinones, it was not considered to be large enough. It was concluded that the main backbone of the polymer needs to be made up of traditional aromatic units that produce a near-planar backbone, whilst the quinone moiety is present as a fully integrated side chain. This prompted the synthesis of phenanthraquinone-type polymer **4** and the dibenzophenazine polymer **5**. Polymer **4** shows evidence of conjugation but these materials are still being evaluated.

Attention was turned to other linkage patterns. Poly(2,6-diylanthraquinone), prepared by the Yamamoto coupling of the bistriflate of 2,6-dihydroxyanthraquinone, was too insoluble to obtain significant degrees of polymerization (DPs) and the product had only a DP of about $ca.13$. The polymer was exceedingly insoluble in all except very acidic solvents (e.g. methanesulfonic acid). However, copolymerization of the bistriflate with various bis-boronic acids or esters gave in several cases polymers with molecular weights (M_n) of $>16,000$, for example **2**. As judged

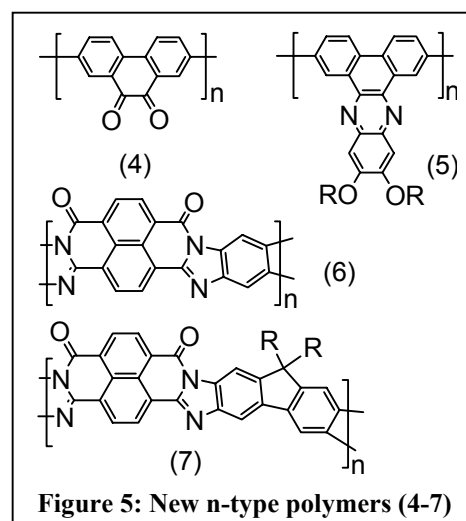


Figure 5: New n-type polymers (4-7)

BBL (6) is reported to be a polymer that exhibits substantial electron mobilities. It is, however, very intractable. A sample of BBL was prepared successfully using the literature method, but the previous mobility result could not be reproduced. BBL moieties obviously have the potential to exist in various isomeric forms. A range of soluble model compounds were synthesized and studied by ^1H NMR spectroscopy. It is clear that in general several of the possible BBL isomers are present in significant amounts. A series of polymers with solubilizing aromatic units, such as polymer 7 were prepared and the electronic properties are under investigation.

As reported previously, when considering n-type materials the mobility of the material is probably not the most important factor, as the stability of the material to ambient conditions and the threshold voltage are also key. Materials which meet these requirements have not yet been realised, however we remain interested in copolymers of anthraquinones and are actively seeking to measure their performance in FET devices. The polymers based on imide chemistry (7) are being investigated at Avecia. Current problems with these materials are associated with formulation issues, principally solubility in useful solvent systems. Once these problems are overcome, we hope to be able to report results on these materials.

3. New Insulators for Field Effect Transistors and New Device Architectures.

We have continued the development of high capacitance gate insulators based on thin, anodised metal oxide films. We have pushed the state-of-the-art to flexible transistors with solution-processed, pinhole-free Al_2O_3 insulators of only 6.5 nm thickness, which display capacitance of more than 600 nF/cm^2 .⁴ (Fig. 6). While 'bare' anodic oxides lead to reduced carrier mobility, we could show that surface modification with octadecyltrichlorosilane (OTS) or poly(α -methyl-styrene) (PAMS) alleviates that problem.⁵ We have extended the concept of anodisation to titanium, as bulk TiO_2 can have a dielectric constant, k , of up to 200. Unfortunately, TiO_2 is a wide bandgap semiconductor, not an insulator. Nevertheless, we manufactured OFETs with TiO_2 gate insulators that operate below 1 Volt, with outstanding inverse subthreshold slope of 130 mV/dec ,⁶ Fig. 7. At such low voltages, gate leakage due to the semiconducting character of TiO_2 is not excessive. Also, an organic transistor with an ultra-thin silicon dioxide gate was shown to be feasible.⁷

We have improved the "FerroFET" organic memory device, which we had filed for patent in 2003.⁸ The FerroFET uses the unique ferroelectric-like remanent polarisation that the nylon polymer, MXD6, displays in the amorphous phase. This allows us to prepare films with memory function from solution without high temperature annealing steps. Through optimisation of deposition, we have achieved 'memory ratios' of $2\text{-}3 \times 10^4$, which is comparable to the best inorganic memory transistors, and memory retention for at least 12 hours, Fig. 8. The publication of these results in *Adv. Mater.*⁹ has already attracted industrial interest in our intellectual property.

Another key aspect of OFET architectures is the quality of the metal/organic semiconductor contact, which in practise is often non-ohmic. For the highly relevant example of the gold-pentacene contact, we have shown improved injection by selective contact-doping beneath the source and drain electrodes with iron(III) chloride. The result are OFETs with higher saturation drain current, while on/off ratio remained large.¹⁰ We have also improved contacts by electroplating of a noble metal (Pt, work function 5.65 eV) on to a less noble 'base' metal (Ti). Electroplating is a highly economical, solution-based process to selectively deposit high quality films of noble metals without waste. We have demonstrated OFETs with plated Pt source / Pt drain contacts, as well as OFETs with asymmetric contacts (plated Pt source / Ti drain), simply by plating only one of the contacts.¹¹ These OFETs display strong in-built bias. This is a viable approach to asymmetric contacts, which will play an important role for ambipolar and light emitting OFETs.

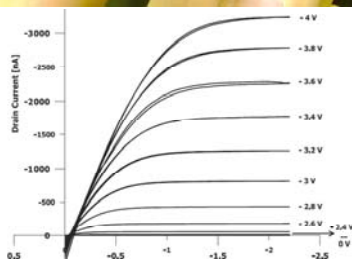
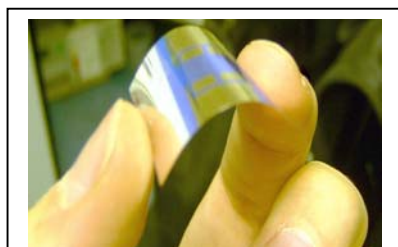


Figure 6: Top: Flexible OFET with 6.5 nm gate insulator. Bottom: Output characteristic of flexible OFET with ultrathin Al_2O_3 gate insulator and pentacene

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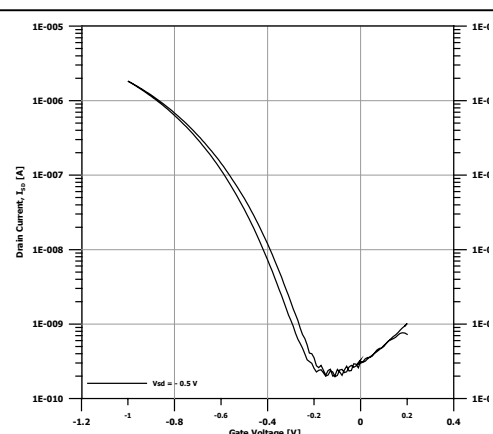
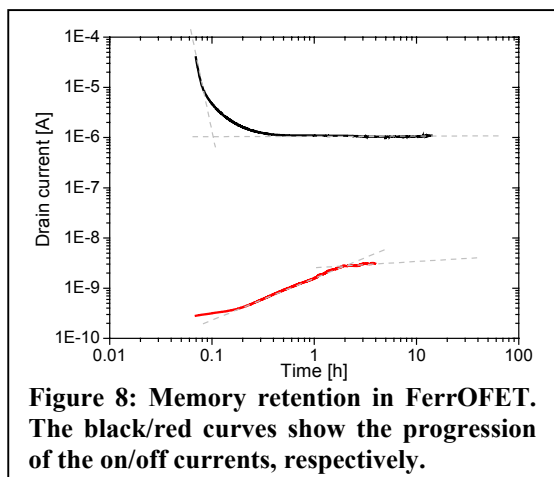


Figure 7: Transfer characteristic of 1 Volt OFET with TiO_2 gate insulator. Subthreshold slope 130 mV/dec , threshold -0.4 V

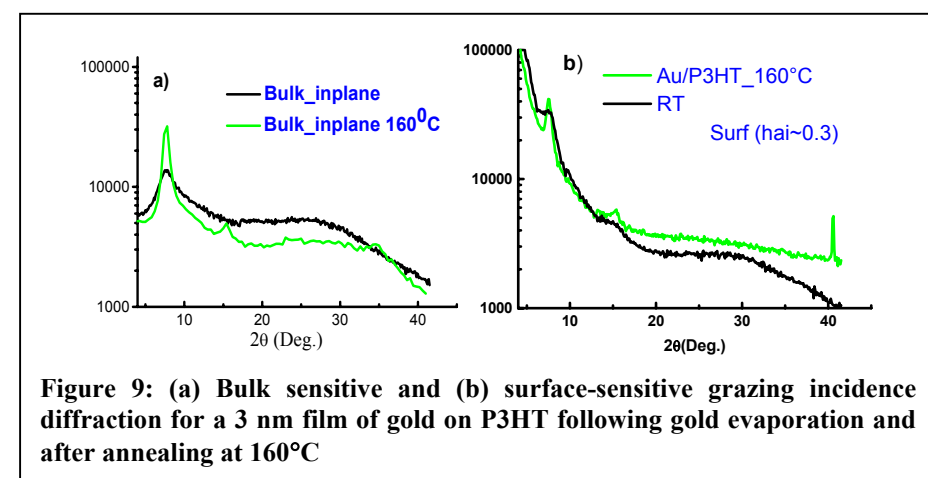
A test-bed for novel p-type and n-type semiconducting materials has been established at the University of Sheffield. We use highly doped silicon substrates with 100 nm and 300 nm thermally grown SiO₂ gate insulators, which we modify with OTS, and Au top contacts for p-type materials, Ag or Al top contacts for n-type materials. Optionally, we can use a vacuum measurement stage down to 10⁻⁵ Torr. We confirmed our test-bed with well-established materials as the benchmark, i.e. P3HT, pentacene (p-type) and fluorocarbon capped NTCDI (n-type), we confirmed our test-bed against literature values. Materials studied so far include poly(4,4-



diocylcyclopentadithiophene), phenylene-thiophene-thiophene-phenylene (PTTP) derived molecules as p-type semiconductors, and anthraquinones as n-type semiconductors, amongst other materials. For PTTP, we were able to confirm the mobility values reported in the literature, but all n-type materials (**1-3**) failed to show mobility values above our resolution threshold of 10⁻⁷ cm²/Vs. A formulation of Avecia poly(triarylamine) was supplied to Sheffield Physics with optimum processing conditions and target charge mobility and layer thickness data. It is hoped that progress on characterising FET devices featuring anodised aluminium oxide gate dielectrics will be facilitated by testing this robust, amorphous, air stable semiconductor material. Variable temperature experiments on these novel devices developed within the consortium are under development in collaboration with Avecia.

4. GIXRD Studies of the Effect of Annealing of Au Films on Regioregular Poly(3-alkylthiophenes)

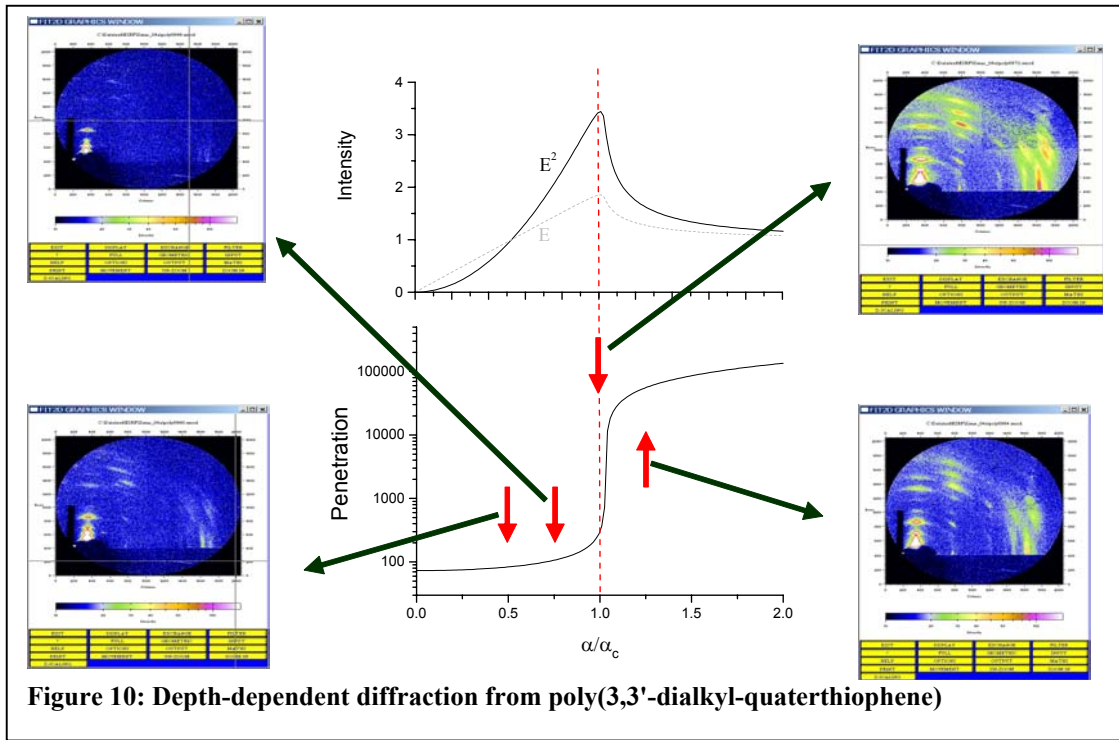
GIXRD is well known to provide useful information from surface and bulk diffraction based on the depth of penetration around the critical angle of the film.^{12,13} Figure 9a,b shows the application of GIXRD for investigating in-plane bulk structural properties of a P3HT thin film (~ 50 nm) and 3 nm Au on 50 nm P3HT film, respectively. Annealing at a temperature of 160⁰C (Fig. 9a) clearly indicates highly crystalline domain structures when compared to an as-spun film.



Similar crystalline features are also observed for Au/P3HT system at the same annealing temperature. However, simple curve fitting analysis of the peak (at ~8⁰) indicates a broader feature for Au deposited system while compared with annealed P3HT film. It appears from EFM and GIXRD studies that Au induces structural changes in the films, and given the importance of gold contacts in electronic devices this behaviour needs further study to develop a better understanding.

Beam damage is a serious problem for organic materials exposed to an X-ray beam for an extended period during data acquisition. In addition to avoiding beam damage, the study of crystallisation kinetics demands fast time resolution. Therefore, there is a need to acquire data rapidly and hence we have investigated the use of an area detector for the GIXRD experiment. This is probably the first such polymer surface scattering recorded with an area detector. One of the key issues is that the GIXRD signal is of the order of 10⁻⁹ of the incident beam flux and therefore excellent background suppression is required.

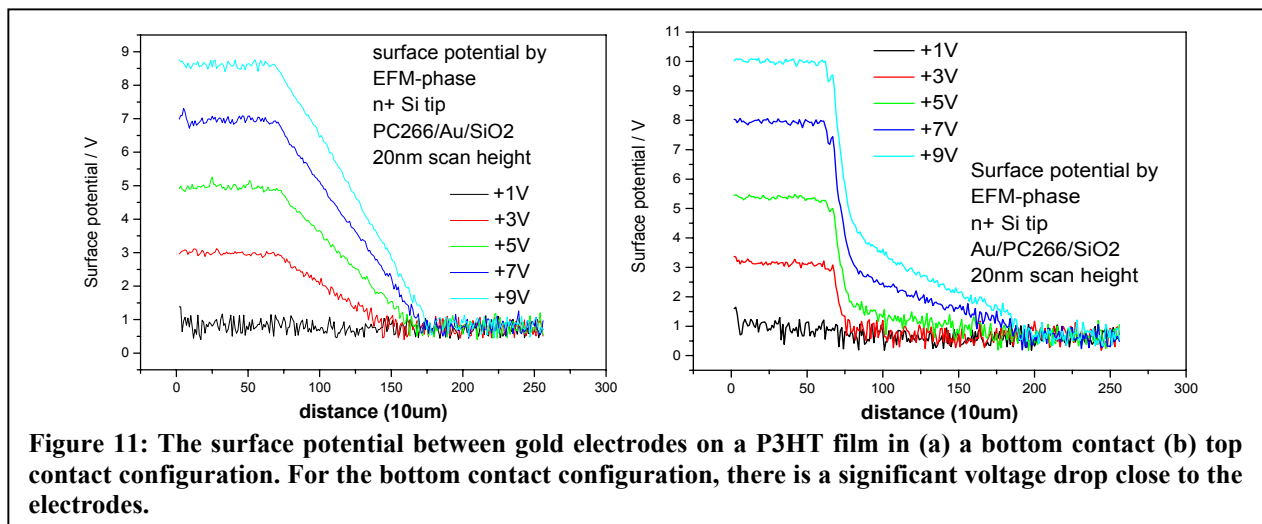
By varying the incident angle close to the critical angle, it is possible to probe surface and bulk properties of thin films. Figure 10, depicts images from a solution-processable regioregular polythiophene, poly(3,3'-dialkyl-quaterthiophene), film with a variation of incident angle. At well below the critical angle of the semiconducting polymer, little in-plane structure is observed. However, at incident angles close to the critical angle or above, highly ordered in-plane peaks are clearly seen from Figure 10. The detailed structure and the depth-dependence of these observations is currently being analysed.



5. Application of EFM-Phase Mode for Imaging of Conjugated Polymer-Metal Contacts

Understanding and control of the relation between the electronic transport properties and the structure and morphology of semiconducting polymers is a crucial issue for carbon based electronics. Moreover, carrier mobility within the interfacial layer in contact with the gate insulator and contact resistance arising from metal-organic contacts are of significant importance in limiting the performance of practical devices. Earlier we have developed EFM-phase techniques for parallel surface morphology and high-resolution surface potential measurements.^{14,15} These EFM-phase measurements have been applied to semiconducting polymer systems to investigate electronic structure at interfaces, particularly at metal-polymer contacts region.

The application of EFM-phase mode to elucidate the underlying electronic behaviour at the interface between Au and poly(3-hexylthiophene-2,5-diyl) (P3HT) is shown in Figure 11. P3HT is spin coated on a SiO₂ surface between two Au electrodes with a separation of 4 μm. The potential distribution within the Au/P3HT/Au structure under various biases are presented with an emphasis on top or bottom Au contacts. A calibration method has been developed to convert phase data quantitatively to potential values.¹⁶ The contact resistance is analysed based on the EFM-phase measurements. The potential drops across the Au/P3HT contacts are totally different at the top and the bottom contacts (deposited by thermal evaporation). The EFM-phase data show clearly a high resistance area close to the gold electrode for the top-contact (Fig 11b). It appears that high energy Au atoms play an important role in changing the Au/P3HT interface properties and I-V measurement supports the data analysis of EFM-phase measurements. This study clearly demonstrates the potential of EFM-phase mode in understanding electronic properties at metal-semiconductor interfaces as well as transport in the bulk of the polymer film.



6. Research Output from November 2003 to November 2004

6.1 Oral Presentations.

- (1) 3rd November 2004, F.Hoffman LaRoche, Basel, Switzerland, "Solid phase synthesis using organogermanium linkers."
- (2) 10th December 2004, UMIST, "Solid phase synthesis using organogermanium linkers."
- (3) 9th January 2004: University of Linz, Austria, "Solution Processible Cyclopentadithiophenes"
- (4) 18th March 2004, University of East Anglia, "Solid phase synthesis using organogermanium linkers".
- (5) 7th April 2004, University of Sheffield, Macro Group Young Researchers Meeting, "Synthesis and Characterisation of Novel High Electron Affinity Conjugated Polymers for Application in Electronic Devices".
- (6) 27th May 2004: Chemical Elements, The Heath, Runcorn: "Organic Materials for Electronics Consortium"
- (7) 11th June 2004: CBE Workshop, Kings College, "Organic Materials for Electronics Consortium"
- (8) 16th June 2004: FPI6, Cornell University, USA, "Synthesis and Properties of Cyclopentadithiophene Polymers and Copolymers with Fluorenes and Thiophenes"
- (9) 18th June 2004: FPI6, Cornell University, USA, "All-Organic Single Transistor Permanent Memory Device"
- (10) 25th June 2004: OMIC Showcase, "Organic Materials for Electronics Consortium"

6.2 Poster Presentations

- (1) 16th June 2004: FPI6, Cornell University, USA, J. Maunoury, R. Schroeder, M. Grell and M.L Turner, "Conjugated Reactive Mesogens for Organic Field Effect Transistors"
- (2) 25th June 2004: OMIC Showcase, P. Coppo, D. C. Cupertino, S. G. Yeates, M. L. Turner, "An investigation of the optical and electronic properties of solution processed polycyclopentadithiophene thin films."
- (3) 9th July 2004, World Polymer Congress, J. Gautrot, Dr A. Ben Haida and P.Hodge, "Synthesis and Characterisation of Novel High Electron Affinity Conjugated Polymers for Application in Electronic Devices"
- (4) 30th September.-1st October, workshop on *Surface And Interface Science*, ESRF, Grenoble, France, A.Das, D.Trolley, H.E.Thomas, J. E. Macdonald, M.Geoghegan, R.A.L. Jones, 'Molecular alignment in semiconducting polythiophene films: towards high mobility'
- (5) 4-7th April, 2004, *CMMP-04*, University of Warwick, UK. A. Das, C.H. Lei, H. Thomas, J.E. Macdonald and M. Elliott, 'Interface of Au-P3HT Contacts studied by EFM-Phase Measurements'
- (6) 28th June-2nd July, IVC-16 and Nano-8 Conference, Venice, Italy. A. Das, C. H. Lei, H. E. Thomas, M. Elliott and J. E. Macdonald, "Semiconducting Polymer-Metal Contacts and Networks at the Nanometer Scale."

6.3 Papers/Patents Published and Submitted

- (1) P. Coppo and M.L. Turner, *J. Mat. Chem.*, feature article accepted for publication.
- (2) A.C. Spivey, D.J. Turner, M.L. Turner, and S.G. Yeates, *Synlett* 2004,111.
- (3) P. Coppo, R. Schroeder, M. Grell and M.L. Turner, *Synth. Met.*, 2004, **143**, 203.
- (4) L. A. Majewski, R. Schroeder, and M. Grell, *J. Phys. D: Appl. Phys.*, 2004, **37**, 21.
- (5) L. A. Majewski, R. Schroeder, M. Grell, P.A. Glarvey and M.L. Turner, *J. Appl. Phys.*, in print.
- (6) L. A. Majewski, R. Schroeder, and M. Grell, *Adv. Mater.*, in print.
- (7) L. A. Majewski, R. Schroeder, and M. Grell, *Synth. Met.*, 2004, **144**, 97-100.
- (8) M. Grell, *UK patent application*, 0318522.0.
- (9) R. Schroeder, L. A. Majewski, and M. Grell, *Adv. Mater.*, 2004, **16**, 633-636.
- (10) R. Schroeder, L. A. Majewski, M. Grell, *Appl. Phys. Lett.*, 2004, **84**, 1004-1006.
- (11) L.A. Majewski, R. Schroeder, and M. Grell, *Appl. Phys. Lett.*, in print.
- (12) A. Bolognesi, C. Botta, C. Mercogliano, W. Porzio, P.C. Jukes, M. Geoghegan, M. Grell, M. Durell, D. Trolley, A. Das, J.E. Macdonald, *Polymer*, 2004, **45**, 4133-4138.
- (13) J. E. Macdonald, M. Durell, D. Trolley, C. Lei, A. Das, P.C. Jukes, M. Geoghegan, A. M. Higgins and R.A.L. Jones *Radiation Physics and Chemistry*, 2004, **71**, 811-815.
- (14) C. H. Lei, A. Das, M. Elliott, and J. E. Macdonald, *Appl. Phys. Lett.*, 2003, **83**, 482-484.
- (15) C.H. Lei, A. Das, M. Elliott, J.E. Macdonald and M.L. Turner, *Synthetic Metals*, 2004, **145**, 217.
- (16) C H Lei, A Das, M Elliott and J E Macdonald, *Nanotechnology*, (2004) **15**, 627-634