Final Report of Organic Materials for Electronics Consortium (OMEC)

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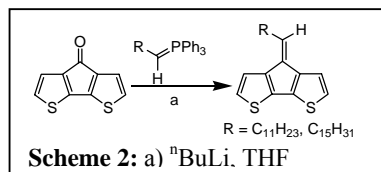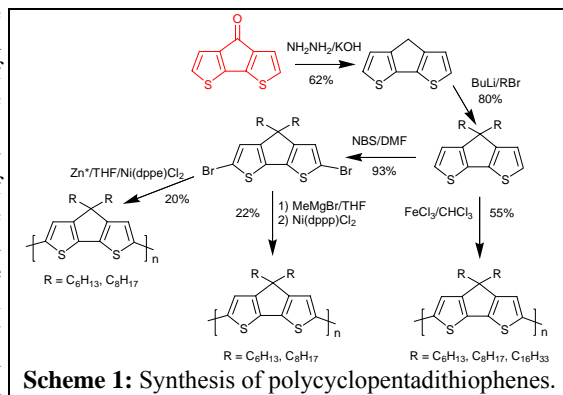
1. Introduction

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 the programme and this report presents a record of achievement for the full three years of the programme. It builds on two previous reports (for years 1 and 2) which are available on www.omec.org.uk. The EPSRC funding for OMEC has resulted in a tremendous output over three years including 31 refereed journal papers, 3 patents and a large number of conference papers. In addition the consortium members presented the work at numerous international conferences and organised a very successful one-day OMEC Showcase meeting in June 2005 with around 80 participants. Speakers from the consortium presented their latest results and Professor Peter Bauerle (University of Ulm) and Dr Walter Reiss (IBM, Zurich) gave invited lectures about recent progress in organic electronics.

OMEC has secured funding for additional OMEC projects from EPSRC (Accelerated Discovery, GR/S96685/01) and the UK Home Office (Low cost sensors, CBRN 10-57)and has expanded the original consortium to include physical chemists (Dr Patrick Fairclough, Sheffield), electrical engineers (Dr Aimin Song, Manchester) and informatics experts (Professor Douglas Kell, Manchester). It has started to develop an international profile and has held discussions with a number of companies about exploitation of intellectual property and collaborative opportunities (*e.g.* ICI, Corning and Toppan printing).
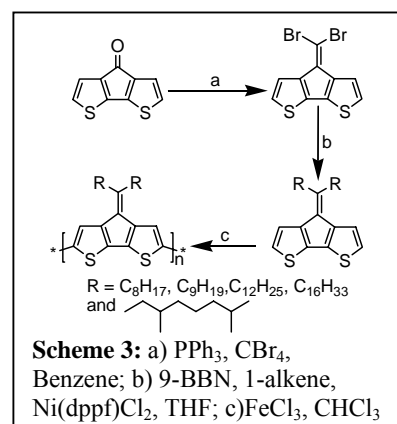
2. Conjugated Polymer Synthesis

2.1 Preparation of polycyclopentadithiophenes and solid phase synthesis of oligothiophenes

Three protocols for the preparation of poly(4,4-dialkylcyclopentadithiophenes) have been investigated (see **Scheme 1**). [1,2,3] The three methods afford soluble materials, free of mislinkages and showing extended conjugation in solution. Polymers obtained by an oxidative protocol show a higher molecular weight ($M_n > 10^4$) than those prepared by transition metal catalyzed polymerization. NMR spectroscopy and MALDI-TOF mass spectrometry showed that the moderate degree of polymerization (15-20 units) achieved by Kumada and Negishi type polymerization is probably due to incomplete formation of the organometallic intermediate. For these polymers the main chain conjugation can be directly correlated to the length of the polymer backbone. UV-visible spectra of polymer fractions show absorption maxima that increase with the average degree of polymerization as determined by GPC up a limiting value of around 20.[3] These materials are not liquid crystalline as expected by analogy with the polyfluorenes and their mobilities are disappointing (10^{-4}-10^{-5} cm^2/Vs) when compared to those of the analogous regioregular polythiophenes.[4] The low mobilities are presumably due to the amorphous nature of the films obtained by spin coating from a range of solvents and after annealing at elevated temperatures.

Scheme 1: Synthesis of polycyclopentadithiophenes.

New derivatives were prepared in which the alkyl chains are held in the plane of the polymer backbone (**Schemes 2** and **3**) and it was hoped that these materials pack more effectively in the solid state, leading to higher mobilities. Single crystal X-ray diffraction studies of the monomers (e.g. see **Figure 1**) suggests that this may indeed be the case.[5] In the first instance monomers were prepared with a single alkyl chain attached via a sp^2 hybridised carbon. These were readily synthesised in a single step from the previously reported ketone via the Wittig reaction with primary alkyl Wittig salts (**Scheme 2**). X-ray crystallography

Scheme 2: a) ^{n}BuLi, THF

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.
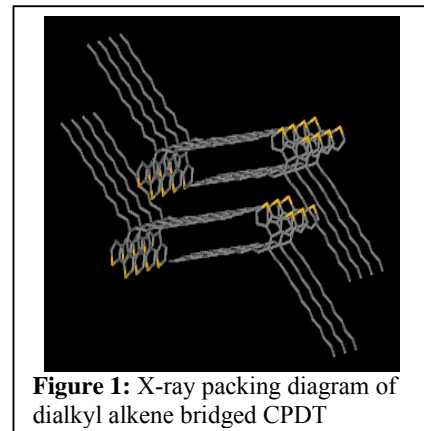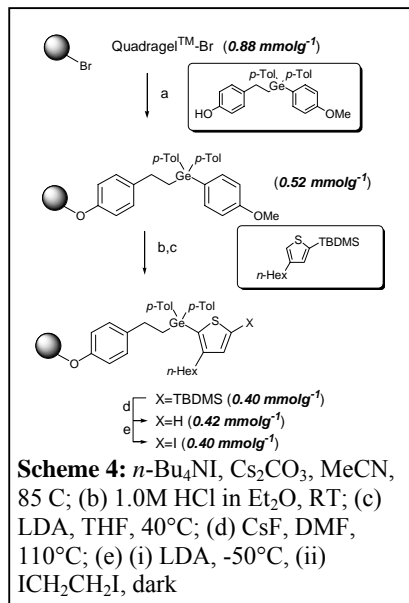

Scheme 3: a) PPh$_3$, CBr$_4$, Benzene; b) 9-BBN, 1-alkene, Ni(dppf)Cl$_2$, THF; c)FeCl$_3$, CHCl$_3$

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. 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 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 3**). An X-ray crystal structure was

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

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.

The solution absorption spectra shows that the polymer has a λ_{max} at 646 nm, corresponding to the π-π* transition. This is red shifted by 50 nm compared to the previously reported sp³ 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 indicating that the polymers are not aggregated in solution. On transferring to the solid state the absorption maximum red-shifts to 696 nm, showing significant ordering in the solid state. The charge mobility in this material is now being investigated and they are also being studied for application as the light harvesting layer of photovoltaic cells.

Scheme 4: *n*-Bu$_4$NI, Cs$_2$CO$_3$, MeCN, 85 C; (b) 1.0M HCl in Et$_2$O, RT; (c) LDA, THF, 40°C; (d) CsF, DMF, 110°C; (e) (i) LDA, -50°C, (ii) ICH$_2$CH$_2$I, dark

The use of supported reagents combines the advantages of polymer-supported reactions (e.g. excess of reagents and reaction by-product can be removed by simple filtration instead of standard workup techniques) with the benefits of solution phase chemistry (e.g. the desired cleaved products need no further purification and can be monitored by mass spectrometry, and ¹H NMR). Preliminary work, prior to the start of the grant established proof-of-concept for a novel method for the synthesis of oligothiophenes using a germanium-based linker model system *in solution* [A.C. Spivey et al, *Org. Lett.* 2002, **4**, 1899-1902]. The method consisted of an iterative synthesis in which cross-coupling yields for each iteration (i.e. addition of a thiophene monomer) could be driven to completion by 'double-coupling'. The ability to perform double-coupling was contingent upon the use of a silyl 'blocking' group at the α-position of each newly introduced thiophene monomer which needed to be stable to the cross-coupling conditions and able to be selectively removed without affecting the germanium-based linker. The model studies had established that a trimethylsilyl (TMS) blocking group in combination with a dimethylgermyl linker displayed these properties but had also alerted us to the fact that the TMS group becomes increasingly labile towards adventitious acid as the length of the oligomer increases. Consequently, before proceeding to the solid phase it was decided to re-engineer the system so as to define a more robust blocking group/linker combination that retained the possibility to perform double-coupling but that was significantly more robust towards acid. This first required the development of a completely new route to germanium-based linkers that would allow for variation of the 'spectator' ligands on the germanium centre. This was achieved in a manner that also circumvented the need to employ tin (IV) chloride, the achilles heel of the previous route.
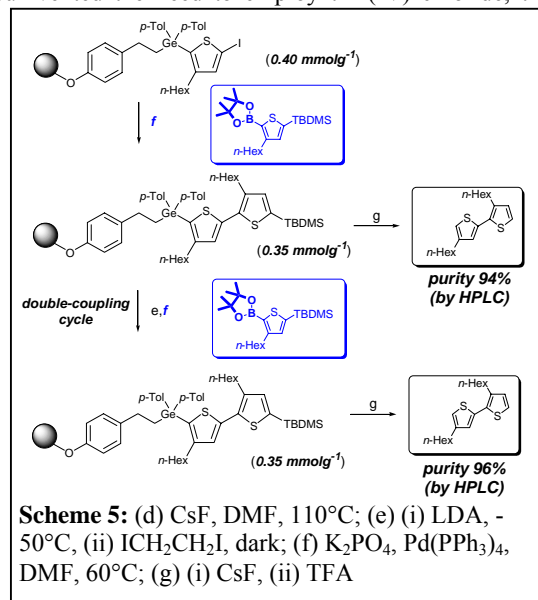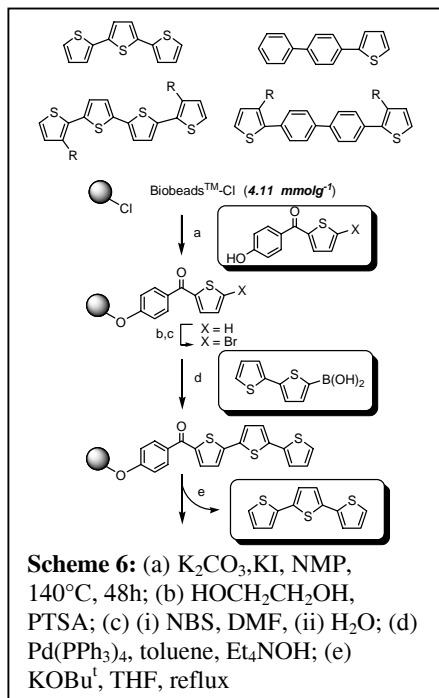
With this new route established a series of optimisation studies were performed using soluble linker model systems in combination with thiophene monomers having different silyl blocking groups (i.e. TES, TBDMS, and TIPS). As the result of these experiments it was decided that the best combination of blocking group and linker would be: TBDMS blocking group with di-*p*-tolylgermyl linker. Preliminary studies in solution clearly established that this combination showed good stability towards acid whilst retaining the orthogonal stability of the two groups towards fluoride that forms the basis of the selective de-blocking procedure. Moreover, the greater stability of the TBDMS group towards bases as compared to the TMS group allowed for the development of a more robust Suzuki-type cross-coupling protocol than had been possible in the previous work. Using this combination of groups preliminary work on the solid phase has been performed. Three solid supports have been evaluated: Merrifield resin, Hypogel® (a grafted PS resin with a distribution of 3-6 oxyethyl repeats) and Quadragel® (a grafted PS resin with 4 oxyethyl repeats). The Quadragel® was found to be the optimal from both a chemistry point of view and also from the perspective of giving the highest quality MAS-NMR spectra. To date, synthesis has been carried out to the dimer stage;[6] work that has unambiguously established the utility of the double-coupling tactic for enhancing iteration efficiency as measured by HPLC of cleaved samples of the bithiophene (**Schemes 4** and **5**).

Scheme 5: (d) CsF, DMF, 110°C; (e) (i) LDA, -50°C, (ii) ICH$_2$CH$_2$I, dark; (f) K$_2$PO$_4$, Pd(PPh$_3$)$_4$, DMF, 60°C; (g) (i) CsF, (ii) TFA

A preliminary communication detailing much of the above work has appeared.[7] A UK patent application has also been filed in conjunction with Avecia Ltd.[8] and research workers at Avecia have also applied this methodology to the synthesis of oligoarylamines. Additionally, and in parallel with the above work, efforts have focussed on developing new methods for the cleavage of oligothiophenes from the germanium-based linker so as to concomitantly install useful functionality at the point of attachment. Specifically, new protocols have been developed by which cleavage can be achieved concomitant with: (i) boronic ester formation using BCl$_3$/pinacol; (ii) Friedel-Crafts type acylation using the appropriate acid chloride and AlCl$_3$ and (iii) germyl-Stille type cross-coupling to introduce an aryl group using Pd(0) catalysis, KF, and the appropriate aryl halide. Work is ongoing to delineate the scope of these new methods and to make them as reliable as possible for generating end-group functionality that is useful either for block co-oligomer synthesis or as terminating groups for the oligomers.

An alternative approach to the solid phase synthesis of aryl-thiophene oligomers was investigated. This approach, outlined in **Scheme 6**, is based on a traceless linker derived from benzophenone. Hodge *et al* (*J. Chem. Soc (C)*, 1971, p 455) first showed that benzophenone derivatives can undergo cleavage reactions cleanly on treatment with a mixture of potassium tert-butoxide and water (mole ratio 10:3) in an aprotic solvent. In this project we have shown that α-thienyl phenyl ketones can be cleaved easily to release

Scheme 6: (a) K_2CO_3, KI, NMP, 140°C, 48h; (b) $HOCH_2CH_2OH$, PTSA; (c) (i) NBS, DMF, (ii) H_2O; (d) $Pd(PPh_3)_4$, toluene, Et_4NOH; (e) $KOBu^t$, THF, reflux

the thiophene in high yield. Such ketones can therefore be used as traceless linkers for the synthesis of well-defined aryl-thiophene oligomers. The chosen traceless linker was bound via a covalent linkage to a Merrifield resin. The supported thiophene was then functionalised (by bromination) and coupled to a new aryl unit (*e.g.* via Suzuki coupling) dissolved in a suspension of the polymer-supported material. The process has been repeated until the desired oligomer (see examples shown in **Scheme 6**) is assembled. The required products were successfully cleaved from the polymer support in yields ranging from 60 to 70% at high purities.

2.2 Synthesis of anthraquinone polymers

Quinones are involved in various natural electron transfer processes such as photosynthesis and oxidative phosphorylation. Anthraquinone is a well-studied member of this family. It has excellent chemical and thermal stability and its electron accepting properties have been extensively studied. The project therefore evaluated the design, synthesis and characterisation of novel conjugated polymers based on anthraquinones.

The few publications that report polymers with anthraquinones in a conjugated backbone show that the materials have very low solubilities unless a 1,4-linkage is chosen. In order to allow the synthesis of copolymers, using Suzuki coupling, a range of dibromo-substituted anthraquinone monomers were prepared (see **Figure 3**). The synthesis of several 4-bisarylanthraquinones was also carried out in order to prepare model compounds and new monomers for polymerisations. An X-ray structure of bis-(4-bromophenyl)anthraquinone showed that the phenyl rings and anthraquinone groups are rotated out of

Figure 3: Anthraquinone monomers and polymers and copolymers (Ar = Ph, dioctylfluorene) plus packing diagram of X-ray structure of bis-(bromophenyl)anthraquinone.

the plane with respect to each and hence are not conjugated but the packing diagram does show extensive π-stacking of the anthraquinone groups. The monomers have been polymerised by Yamamoto and Suzuki couplings to prepare homopolymers and copolymers with fluorene units. The structure of the materials was characterised by NMR, IR, GPC, TGA and DSC. The UV-vis absorption, the fluorescence and the electrochemical behaviour of the different compounds were analysed. Air-stable, solution processible polymer/oligomeric n-type materials having high mobility ($>10^{-3}$cm^{2}V^{-1}s^{-1}) are very scarce and it was hoped that poly- and oligo-anthraquinones could address this deficiency. To date poly(1,4-anthraquinones) prepared in this project were found not to have a measurable FET mobility up to a gate voltage of +80V under ambient atmosphere or moderate vacuum. It is clear that 1,4-linked anthraquinone moieties, such as **1**, show little evidence for conjugation as judged by UV spectroscopy and cyclic voltammetry (CV).

Attention was therefore 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

Figure 4: Anthraquinone polymers (1-3)
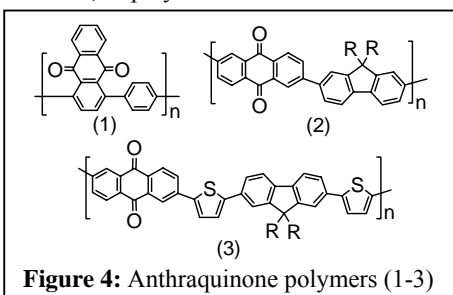
gave in several cases polymers with molecular weights (M_n) of >16,000, for example **2**. As judged from X-ray crystal structures of model compounds the torsion angles between the aromatic units was *ca.*31° when a phenylene residue was involved but only *ca.*7° with a thiophene unit. This prompted the synthesis of polymer **3**. By CV 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 aromatic units that produce a near-planar backbone, whilst the quinone moiety is present as a fully integrated side chain. This pro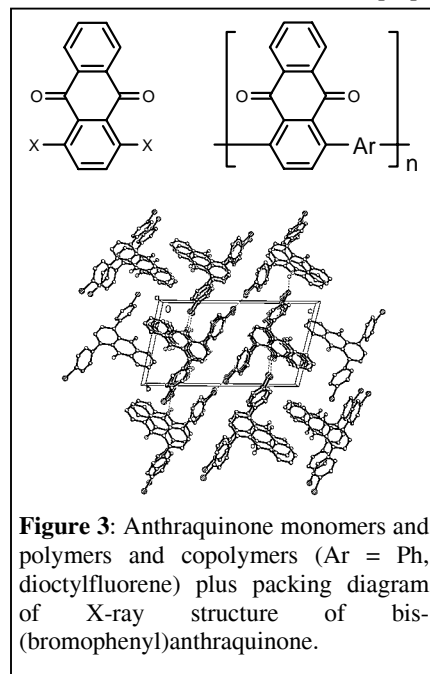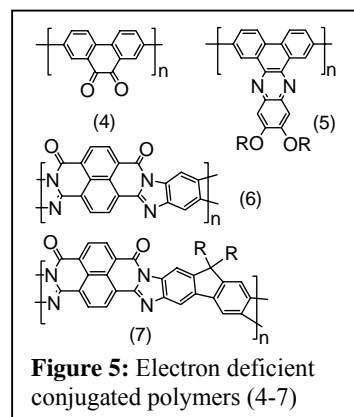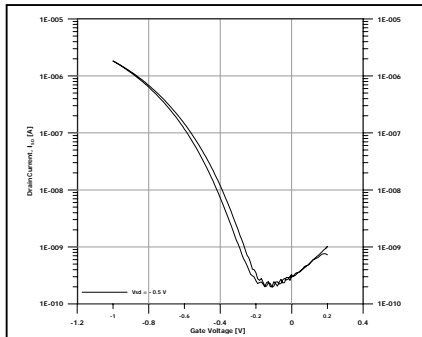mpted the synthesis of phenanthraquinone-type polymer **4** and the dibenzophenazine polymer **5**. Polymer **4** shows evidence of conjugation but these materials are still being evaluated.

BBL (**6**) is reported to be a polymer that exhibits substantial electron mobilities. It is, however, very intractable. A range of soluble model compounds were synthesized and studied by ^{1}H NMR spectroscopy. It is clear that in general several of the possible BBL isomers are present in significant amounts, initial OFET devices fabricated from these materials show electron mobilities of 10^{-3} cm^2/Vs. A series of polymers with solubilising aromatic units, such as polymer **7** were prepared and the electronic properties are under investigation. The polymers based on imide chemistry (**7**) are currently being investigated. 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.

**Figure 5:** Electron deficient conjugated polymers (4-7)

3

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

Some of the envisaged applications of organic electronics are in cheap, disposable integrated circuits, RF-ID tags, and active matrix backplanes for novel displays. Given the recent advances in organic semiconductor performance, the limiting factor of OFET performance has shifted from the semiconductor to the insulator [L L Chua et al., *Nature* 2005, **434**, 194], and the metal/semiconductor contacts [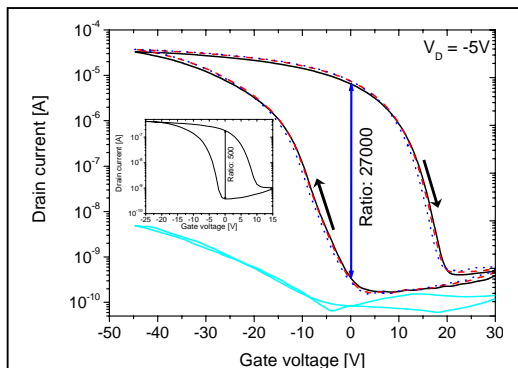L Bürgi *et al, J. Appl. Phys*. 2003, **94**, 6129]. The key figures-of-merit that quantify the quality of a gate insulator are its capacitance, and its leakage, with a desire to prepare high capacitance (several 100 nF/cm^2) insulators with very low leakage. Also, the interface between insulator and semiconductor is of particular importance [J. Veres et al., *Chem. Mater.,* 2004, **16**, 4543]. High capacitance is achieved by insulators with both high dielectric constant, k, and low thickness. However, preparing low thickness insulators for OFETs has proven to be difficult. Conventional deposition methods of both organic and inorganic insulators at low thickness lead to films containing pinholes, which defeat the insulators' prime objective, insulation of the gate contact from the transistor channel. Within this project, we have shown that **anodisation**, that is electrochemical oxidation of metals, can lead to very thin insulators that are free of pinholes.[9,10,11,12,13,14,15,16] 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 (**Figure 6**).[10,14] 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,[14] (**Figure 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[17] and high-k fillers were used to increase the capacitance.[18]

Figure 7: Transfer characteristic of 1 Volt OFET with TiO_2 gate insulator. Subthreshold slope 130 mV/dec, threshold -0.4 V
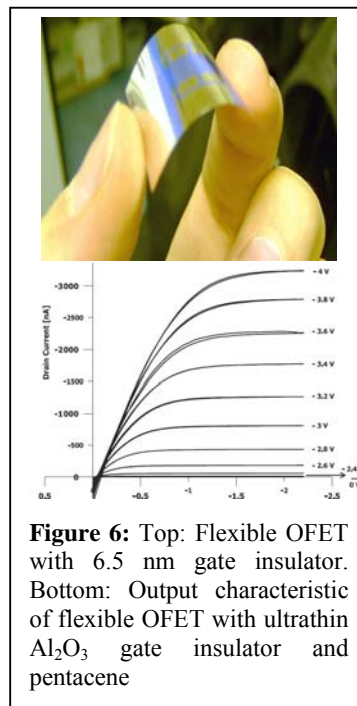
Figure 6: Top: Flexible OFET with 6.5 nm gate insulator. Bottom: Output characteristic of flexible OFET with ultrathin Al_2O_3 gate insulator and pentacene

We have developed the "FerrOFET" organic memory device and filed a patent for this device in 2003.[19] The FerrOFET uses the unique ferroelectric-like remanent polarisation that the nylon polymer, MXD6, displays in the amorphous phase. We have demonstrated OFETs with MXD6 gate insulator that display memory function, see **Figure 8**.[20,21] The transfer characteristic has two branches ('up' and 'down') which are shifted by $\Delta V_T \approx 20$ V, the so-called 'memory window', and can be cycled repeatedly and reversibly. At zero gate voltage, the OFET's drain current can be either 'on' or 'off', with an on/off or 'memory' ratio of 27000. The light blue curve shows gate leakage current, which is orders-of-magnitude smaller than drain current, and memory is retained for at least one day. The key to good memory devices is the control of spin conditions (concentration, temperature, rpm) for the gate insulator, to achieve smooth and amorphous films. However, for practical applications, we need to reduce the memory window and increase the 'on' current; currently, pentacene on MXD6 has mobility in the order of 10^{-3} cm^2/Vs only. Simply reducing MXD6 thickness leads to lower memory window, but also significantly reduced memory ratio, see inset to **Figure 8**.

Figure 8: Transfer characteristic of a pentacene / MXD6 OFET with memory effect. Inset is OFET with reduced MXD6 thickness.

Another key aspect of OFET architectures is the quality of the metal/organic semiconductor contact, which in practise is often non-ohmic.[22] 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 results are OFETs with higher saturation drain current, while on/off ratio remained large.[23] 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 one of the contacts.[24] We also used another electrodeposition technique, **electropolymerisation**, to prepare a film of the synthetic metal PEDOT/PSS onto Au bottom contacts. We used an electrochemical cell filled with 0.1M EDOT/Na-PSS in acetonitrile/water as the working fluid. Electropolymerisation was facilitated using Au contacts as working electrode (anode) for oxidative polymerisation of EDOT in the presence of the dopant PSS. Pentacene and polytriarylamine OFETs that used contacts electropolymerised with PEDOT/PSS were fabricated. Again, we used asymmetric contact designs to provide an 'internal standard' for comparison of PEDOT/PSS-on-Au contacts with uncoated Au contacts. We find that pentacene OFETs display 2.5 times higher drain saturation currents when the PEDOT/PSS-coated contact is used as source, rather than the uncoated Au contact. For PTAA OFETs, the enhancement is six-fold.[25] These results are surprising, because our OFETs had rather long channels (40-60 μm), and PTAA has moderate mobility (order 10^{-3} cm^2/Vs). From theory, contact-limited OFET operation is expected for short channel transistors (roughly, 2μm or less) in conjunction with high mobility organic semiconductors (0.1 cm^2/Vs or more) [C]. Further, output characteristics do not display curvature in the supposedly linear regime, the standard diagnostic for contact-limited OFET operation. On the other hand, we clearly see a six-fold higher drain current within the same device when the PEDOT/PSS-coated contact is used as source, rather than the untreated Au contact. This observation is a

challenge to current OFET theory, which has no explanation for it. Practically, our finding means that OFET output may be improved almost by an order of magnitude by improving the contact, even when the OFET is apparently *not* contact-limited.

4. High resolution electrical measurements of conjugated polymer structures

Spatially-resolved potential measurements are key to understanding and modelling the transport behaviour of operating devices. In conjugated polymers, there are no dangling bonds to distort electrical measurements made by scanning probe techniques, whose potential has been demonstrated by Sirringhaus and co-workers [L. Burgi *et al, Appl. Phys. Lett.,* 2002, **80**, 2913]. We have adapted the EFM-phase measurement, which has been used several times as a qualitative high resolution electrostatic imaging e.g. [Bachtold *et al, Phys. Rev. Lett.*, 2000, **84**, 6082] and developed a calibration approach that transforms it into a quantitative measure of electrical potential.[26] Our approach has been demonstrated to have electrical spatial resolution of 15 nm as a result of minimising interactions with the cantilever and the upper portion of the tip.[26,27] The high spatial resolution has particular potential for understanding metal-molecule contacts. The cause of contrasting I-V measurements of top and bottom contact Au-P3HT structures was clearly determined by 2-D electrostatic images and 1-D potential profiles. These demonstrated excellent Ohmic behaviour for bottom contact P3HT-on-Au contacts, contrasting with the existence of a narrow high-resistance region in the P3HT at the Au top contact (**Figure 9**). This behaviour is consistent with localised damage to the P3HT by the thermal energy of the incoming Au atoms during vacuum deposition.[28] Similar measurements on F8-Au electrodes showed the existence of barriers at both interfaces with a sharper potential drop for top contacts than bottom contacts. The EFM-phase measurements showed the existence of trapped charge at the F8-SiO$_2$ interface that depended on the surface treatment prior to spin-coating.[29] A systematic investigation of contact behaviour is in progress.

The work funded by this grant has led to a SRIF-funded AFM-STM system coupled with UPS and XPS. The in-vacuum variable temperature SPM has all-digital feedback enabling a new hybrid EFM-STM electrostatic microscopy mode which we are developing to attain ~1 nm resolution. A proposal has been submitted with H L Anderson (Oxford) and R Nichols (Liverpool) on single molecule conductance in porphyrins. The new system will also enable ultra-high resolution studies on metal-molecule and molecule-molecule contacts.
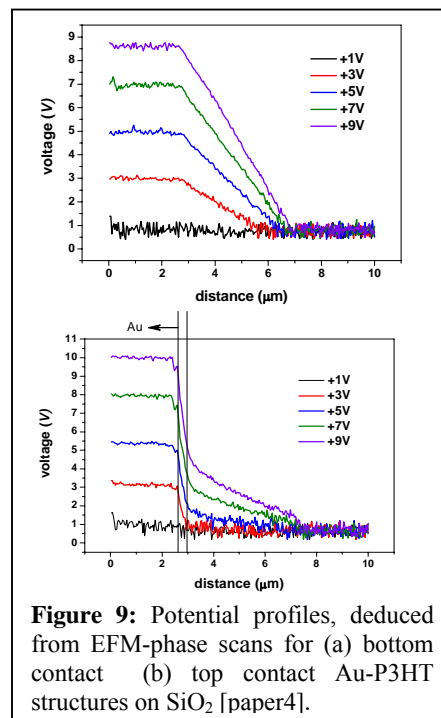
Figure 9: Potential profiles, deduced from EFM-phase scans for (a) bottom contact (b) top contact Au-P3HT structures on SiO$_2$ [paper4].

5. Grazing incidence x-ray diffraction studies of conjugated polymer films[30]

Grazing incidence diffraction provides a unique probe of the surface and bulk structure of polymer thin films by performing wide-angle scattering over a range of incident angles α [Durrell *et al, Europhys. Lett.,* 2002, **58**, 844 and Jukes *et al, Macromolecules*, 2005, **38**, 2315]. The technique has been used to identify the mechanism of molecular alignment by brushing the conjugated polymer surface (rather than a polyimide pre-layer) in poly[3-(hexylmethoxy)thiophene] (P6OMe). A dichroic ratio of 3.3 is obtained by rubbing the P6OMe surface, which increases to 5.2 on annealing at 120°C. Bulk powder diffraction had shown that the anneal produces a single phase from as-prepared polymorphic material. However, GIXRD data demonstrated that the unannealed as-spun films comprised a single phase with a second phase being introduced anisotropically by rubbing.[31] Grazing incidence diffraction studies of conjugated polymers F8, F8T2, P3HT and polycyclopentadithiophenes showed no significant difference in structure at the film surface compared with the bulk of the film. Towards the end of the second year of the grant, the XMaS beamline at ESRF, where most of the measurements were performed, acquired a MAR area detector. Following careful optimisation of background scattering ($<10^9$ because of the weak surface signal), data throughout reciprocal space was collected rapidly as a function of incident angle (**Figure 10**) and, in the most recent experiment, in real time during in-situ annealing, enabling structural
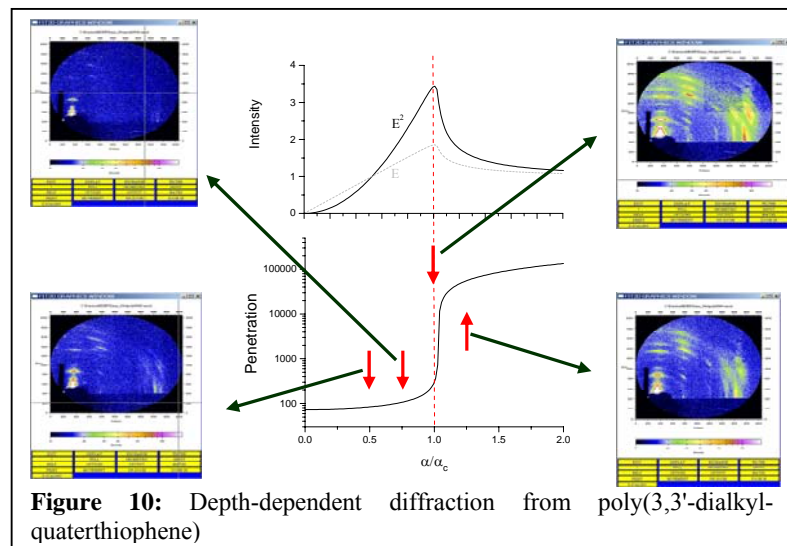

Figure 10: Depth-dependent diffraction from poly(3,3'-dialkyl-quaterthiophene)

changes during crystallisation to be followed. The detailed molecular packing of most conjugated polymers is unknown: structural analysis of crystalline diffraction patterns are required. Their large unit cells of low symmetry make a direct structural determination difficult. We are currently working on an integrated approach involving Patterson function analysis of diffraction data coupled iteratively with molecular modelling. This is at an early stage, but if successful, could be widely applicable, leading to a new grant proposal.

6. Electrochemical growth of nanowires

During the early stages of the EFM study above, we found that networks of conducting conjugated polymer wires could be formed between electrodes by spin-coating of dilute solutions.[27] The network density could be controlled by spin-coating conditions. Conducting wires of 100 nm length and about 15 nm thickness formed spontaneously at the surface in a narrow composition range.
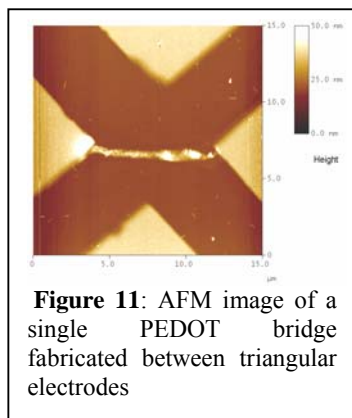
Figure 11: AFM image of a single PEDOT bridge fabricated between triangular electrodes

Attempts to nucleate or trap these wires between electrodes failed, the likely cause being the slow diffusion of the conjugated polymer aggregates. However, monomers diffuse easily in electric fields but cannot be easily fixed between electrodes once a nanowire is formed. We successfully combined *electromigration* of EDOT monomers in acetonitrile solution, where the spatial variation of the electric field is used to direct the monomer flow between the electrodes, together with instantaneous *electropolymerisation* of the monomers at the growing wire front.[32] The resulting PEDOT wire is insoluble and a good conductor with Ohmic contacts to gold electrodes (**Figure 11**). Electropolymerisation, confirmed by micro-Raman spectroscopy, is thus achieved without additives such as PSS. This combined approach of electromigration and electropolymerisation to form nanowires is the subject of a patent application.[33]

7. Summary

OMEC held quarterly meetings throughout the course of the grant to update all members about progress across the consortium. The minutes from these meetings, including all presentations were circulated as CDs to all members quarterly and with the two annual reports (2002-2003, 2003-4). The success of OMEC can be judged by the number of papers with co-authors from more than institution that have appeared. This work would not have been achieved without the award of the ESPRC grant. Further support for the consortium has been received from EPSRC, Home Office and SRIF. There are a number of further applications for funding to be submitted in the immediate future and at least one company seriously considering support postdoctoral support for OMEC.

8. Budget

The financial reports of the individual grants (GR/S02303/01, GR/S02280/01, GR/S02297/01) have been submitted separately. The expenditure was within the overall sum requested. There was some transfer of funds between consumables, equipment and travel, mainly due to the re-location of the principal investigator during the course of the grant and the resulting additional travel/consumables costs. The under-use of the allocated beam-time was due to the limitation to point detectors and weak signals at Daresbury (station 9.4), superseded by the acquisition of an area detector at station BM28 (ESRF) leading to a 200-fold increase in data collection rate (from Autumn 2004) and eliminating beam damage effects. The PDRA time at Cardiff was spent increasingly on investigating the use of quantitative EFM in understanding metal-polymer contacts, following initial success by a student after the original proposal was submitted. The importance of this interface was highlighted by the observation in Sheffield that mobility can be limited by the metal-contact even in apparently channel-limited OFETs.[24,25]

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