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# Polyterthiophenes incorporating 3,4-difluorothiophene units and their application in organic field effect transistors

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Two terthiophenes bearing core fluorinated thienyl units have been synthesised as potential semiconductor materials for organic field-effect transistors (OFETs). Polymerisation of these compounds has been achieved using conventional iron(III) chloride oxidative coupling methods and by electrochemical oxidation. Characterisation of the fluorinated materials has been achieved by absorption spectroscopy and cyclic voltammetry. A soluble hexyl-functionalised polymer (poly**8b**) was used in an OFET device; hole mobilities were measured up to $3 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$, and the device had an on/off ratio of $10^5$ and a turn-on voltage of +4 V.

## Introduction

Recently oligo- and polythiophene derivatives have been extensively studied owing to their attractive electronic and optical properties.[1] Architectural modification of the thiophene framework through chemical synthesis has shown them to be excellent candidates in a variety of applications, ranging from the active semi-conducting layer in organic field effect transistors[2] (OFETs) to electroluminescence[3] and photovoltaic devices.[4] In terms of OFET behaviour, regioregular head-to-tail poly(3-hexylthiophene) and some analogous alkyl substituted polythiophenes with fused repeat units[5] have shown some of the highest charge carrier mobilities reported for any soluble polymeric system. Such solution processability, coupled with excellent stability, means large area, low cost, flexible devices can be readily exploited.[6] A primary reason for this is the crystalline nature of the thin films obtained from solution, where the polymer chains self-organise into a well ordered lamella with co-facially stacked polymer backbones.[7] The resulting short co-facial distances($\sim$3.8 Å) give rise to efficient charge-carrier hopping. However, one drawback of a fully conjugated thiophene polymer is that in some transistor morphologies, the electrical performance can be degraded as a result of unintentional p-type doping of the semiconductor layer with atmospheric oxygen.[6-7] Doping of the material has typically been shown to alter the threshold voltage and reduce the on/off ratio within such devices. Such interactions are disadvantageous when considering device applications such as TFTs in display backplanes,[8] which require higher on/off ratios. In order to improve the device performance and limit such problems, many structural modifications have been carried out on thiophene-based oligomers.[9] The electron affinity and ionisation potential in oligothiophenes can be increased, with respect to vacuum, by the introduction of strongly electronegative groups, such as nitriles[10] and fluorine[11] or by the incorporation of electron-deficient nitrogen containing moieties, including oxadiazole,[12] triazole,[13] thiadiazoles,[14] benzobisthiazoles[15] and thiazolothiazole[16] heterocycles.

There are several good reasons for studying fluorine-containing materials. Fluorine is the most electronegative element, but its negative inductive ($\sigma I = 0.51$) and positive mesomeric effects ($\sigma R = 0.51$)[17] strongly influence the intra- and intermolecular interactions of organofluorine compounds and such interactions play a pivotal role in materials chemistry.[6] For example, Facchetti *et al*[11d] have demonstrated that end-capping α-quaterthiophenes with pentafluorophenylene groups results in an inversion from a p-type compound to the less common n-type material. Various fluorine-containing materials have been reported, including aromatic perfluorocarbons such as perfluoro-p-sexiphenyl (**1**), which is an efficient n-type semiconductor and functions as an electron-transport layer in organic light-emitting diodes.[18] Conjugated thiophene and selenophene copolymers with di- and tetrafluorophenylenes (**2**) have been synthesised for OFETs[11a-c] and poly(bithienylene-diflurovinylene) polymers (**3**) have been studied as a liquid crystalline materials.[19]

((Insert Chart 1 here))

By varying the chemical composition of conjugated materials, one can manipulate the HOMO and LUMO energy levels of the material and this can have positive effects on the stability towards oxidation and, in the case of semiconductor devices, unwanted reactions with wet oxygen. In furthering our work on fluorinated conjugated materials, we have synthesised compounds **8a** and **8b**. Herein, we report on the electrochemical and chemical polymerization of these monomers and report the OFET characteristics of a device based on poly**8b**.

**Results and discussion**

Synthesis

Terthiophenes **8a** (R = H) and **8b** (R = $C_6H_{13}$) were prepared according to **Scheme 1** from 2,5-dibromo-3,4-difluorothiophene (**7**)[11e] using palladium catalysed aryl-aryl coupling. The

synthesis of **8a** was achieved by reacting commercially available 2-(tributylstannyl)thiophene (**6**) with 2,5-dibromo-3,4-difluorothiophene (**7**) in the presence of tetrakis(triphenylphosphine) palladium (0).[20] The product was obtained as a fine orange powder in an overall yield of 40%. 2-(Trimethylstannyl)-3-hexylthiophene (**5**) was prepared *via* lithiation of 2-bromo-3-hexylthiophene (**4**),[21] using *n*-butyllithium at -80°C, and reacting this *in situ* with trimethyltin chloride. Compound **5** was obtained in 90% yield.[11c] Reaction of **5** with the dibromo reagent **7**, resulted in the isolation of terthiophene **8b** in 44% yield. Improved reaction conditions can be achieved utilising microwave-assisted synthesis. For example, a ten minute irradiation of **5** and **7** in the presence of tris(dibenzylideneacetone)-dipalladium (0) / tri-o-tolylphosphine at 140°C yields **8b** in a much improved yield of 62%. The microwave-assisted synthesis also results in fewer impurities, making the purification of **8b** an easier task.

Compounds **8a** and **8b** were polymerised by slow addition of a solution of monomer in chloroform to a ferric chloride solution in chloroform. After prolonged stirring, the reaction mixture was poured into methanol and the crude product isolated by filtration. The crude product was stirred in aqueous ammonia to dedope the polymer, and was further purified by Soxhlet extraction using methanol, acetone, dichloromethane then chloroform. The chloroform extract was concentrated and reprecipitated into methanol. After chloroform extraction, some insoluble material remained which could not be dissolved in any organic solvents. Poly**8a** was found to be insoluble in all common solvents. Poly**8b**, on the other hand, was found to be readily soluble in solvents such as chloroform, toluene and THF. Gel permeation chromatography (GPC) experiments for poly**8b** indicated that the isolated materials were short-to-medium chain polymers with approximately 12 repeat units in the longest chains (from Mn). Similar MW material was afforded in repeat polymerisations.

((Insert Scheme 1 here))

Absorption Studies

The absorption spectra of **8a** ($\lambda_{max}$ = 254, 353 nm, hexane) and **8b** ($\lambda_{max}$ = 254, 316 nm, hexane) are shown in Figure 1. If we compare **8a** to its unfluorinated analogue, 2,2':5',2"-terthiophene ($\lambda_{max}$ = 354 nm, dioxane, or 254 and 350 nm in methanol,[22] it is apparent that fluorination of the central thiophene has little influence on the HOMO-LUMO gap of the terthiophene. For **8b**, the absorption spectra of the identical unfluorinated analogue has not been reported, but we can make a reasonable comparison with 3,3"-dimethyl-2,2':5',2"-terthiophene, in which methyl chains have replaced the hexyl of **8b** ($\lambda_{max}$ = 254, 348 nm, methanol)[22b] or 3,4,3",4"-tetrabutyl-2,2':5',2"-terthiophene ($\lambda_{max}$ = 342 nm, dichloromethane).[23] In this case it is apparent that fluorination of the central thiophene in **8b** causes a significant hypsochromic shift. Since inductive effects can be ruled out due to the similar spectra for **8a** and 2,2':5',2"-terthiophene, it is likely that steric effects are dominating, causing the thiophenes to twist out of plane of the conjugated chain in compound **8b**. To corroborate this assumption, DFT calculations were performed on compounds **8a**, **8b** and 3,3"-dihexyl-2,2':5',2"-terthiophene at the B3LYP/6-31G* level (SPARTAN08), in which the structures in each case were allowed to relax to an equilibrium geometry from an all-anti conformation. Compound **8a** was found to be essentially planar, whilst the dihedral angles between the peripheral thiophene rings and the central ring were found to be 42.6-45.0° for **8b** and 34.2-40.3° for 3,3"-dimethyl-2,2':5',2"-terthiophene. These results clearly show that there is a loss of co-planarity within the terthiophene units on addition of the alkyl groups and that the fluorine atoms in **8b** increase the dihedral angles even further.


((Insert Figure 1 here))


In order to study the solid-state absorption characteristics and HOMO-LUMO energy levels of poly**8a** and poly**8b**, the monomers were electropolymerised onto ITO glass using repetitive

cyclic voltammetry (Figure 2). Dichloromethane solutions of each monomer (*ca.* $10^{-4}$ M), containing *n*-tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte, were used to grow the polymer films. The cycles covered the range of the oxidation peaks of the monomers (up to +1.5 V *vs* Ag/AgCl). The deposition of poly**8b** was impeded due to the solubility of the polymer in dichloromethane, but a stable film was isolated nevertheless at 0°C.

((Insert Figure 2 here))

The thin film absorption spectra of poly**8a** and poly**8b** show broad featureless transitions centred around 465 and 421 nm, respectively (Figure 1). The optical band gaps for the monomers and polymers, measured from the onset of the longest wavelength absorption band are 1.9 eV for poly**8a** and 2.2 eV for poly**8b**. Comparing poly**8a** to unfluorinated poly(terthiophene) prepared by electrochemical polymerisation,[24] we can observe very similar broad and featureless spectra with a similar optical band gap and maximum absorption (poly(terthiophene) is reported as 480 nm, although the broad peaks make it difficult to identify a precise maximum for both this polymer and poly**8a**). In contrast, the absorption maximum of poly**8b** is significantly blue-shifted compared to high molecular weight (Mn 13,000 g/mol) poly(3,3"-dioctylterthiophene), which exhibits an absorption maximum at 550 nm, and a pronounced vibronic shoulder at 590 nm.[25] Lower molecular weight poly(3,3"-dioctylterthiophene) exhibits a blue-shifted absorbance maximum and loses the vibronic structure indicative of ordering in the polymer film.[26] However poly(3,3"-dioctylterthiophene) of similar molecular weight to poly**8b** (Mn 5,500 g/mol) has a thin film absorbance at 516 nm, and even very low weight fractions (Mn 1,500 g/mol) have absorption maxima at 463 nm. This suggests that electronic interactions between the fluorine substituents and the adjacent 3-hexylthiophene rings in poly**8b** are preventing the polymer from forming a

planar, delocalised backbone in the solid state. Indeed, the absorption maxima of poly**8b** is similar to that of poly(4,4"-dioctylterthiophene) in which adjacent head-to-head octyl side-chains also cause significant torsion of the polymer backbone and prevent planarisation in the solid state.[25] This polymer has an absorption maxima around 438 nm, even for high molecular weight material.

Redox properties and thermal analysis

Cyclic voltammograms for both polymers were conducted in monomer-free acetonitrile solutions containing *n*-tetrabutylammonium hexafluorophosphate (0.1 M). In this discussion we focus more on the electrochemical properties of the hexyl substituted polymer, since this material was used as a solution processable polymer for OFETs. Poly**8b** gave an irreversible oxidation wave with a peak at +1.22 V (*vs* Ag/AgCl) and an irreversible wave at -1.38 V (the peak at -0.93 V is due to dissolved oxygen in the electrolyte solution, see Figure 3). The difference between the onsets of these peaks (estimated at +1.1 V and -1.1 V), gives the HOMO-LUMO band gap and this was determined to be 2.2 V, in excellent agreement with the optical data. The redox potential of ferrocene under these conditions was *ca.* +0.45 V, giving a HOMO of -5.45 eV and a LUMO of -3.25 eV. In comparison, the corresponding data for poly**8a** (see Figure 4) give an electrochemical band gap of 1.95 eV and HOMO and LUMO energies of -5.25 and -3.30 eV, respectively.

((Insert Figures 3 and 4 here))

Thermal analyses were performed on poly**8b**. Thermogravimetric analysis showed a first onset of degradation at 133°C with a loss of 20% weight. A second onset was observed at 425°C with a loss of 43% weight. Differential scanning calorimetry was carried out using a standard heat-cool-reheat procedure; this allows the removal of thermal history on the first

heating cycle, allowing examination of any thermal processes on cooling and the second heating step. The temperature range for the first heat was from -90°C to 120°C at 10°C/min. Cooling was performed at a slower rate of 5°C/min to -90°C and the second heat cycle was performed at 10°C/min to 250°C.

It was clear from the initial heat that the material contained small amounts of residual chloroform (from which the material was precipitated). A heat capacity shift was evident on both the cooling and second heat suggesting a wide thermo-reversible transition at around -22°C to 0°C, indicating a relaxation of the material. To confirm the nature of the relaxation and if it is a glass transition, further work would be required to understand and confirm the molecular dynamics of the relaxation (e.g. dielectric spectroscopy, temperature dependent NMR), which is beyond the scope of the current work.

OFET measurements

Thin film transistors of poly**8b** were prepared by drop-casting onto bottom gate, bottom contact substrates. The $SiO_2$ dielectric interface was treated with a hydrophobic SAM monolayer (OTS) before deposition in order to promote ordering of the polymer in the transistor channel. The transfer and output plots are shown in Figure 5. The devices show typical p-type behaviour with no n-type characertistics observed under these conditions. The devices turned on around +4V with a current modulation of $10^5$. The devices showed low hysteresis on the forward and return scans. The output characteristics showed little evidence of contact resistance. The highest observed saturated mobility was $3 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$, however device-to-device reproducibility was low. This is most likely due to the rather low molecular weight of the polymer which resulted in inhomogeneous thin films. The charge carrier mobility was approximately one order of magnitude lower than the analogous non-fluorinated poly(3,3"-dioctylterthiophene) measured under similar device conditions,[25] but was remarkably high considering the apparent lack of order in the film. For comparative

purposes, regioregular P3HTmeasured under the same device conditions had an average saturated mobility of $5 \times 10^{-2}$ cm$^2$/V s.

((Insert Figure 5 here))

## Conclusion

A new fluorinated, soluble polythiophene has been investigated as a p-type material in OFETs. The strategy for the incorporation of the fluorine substituents was to manipulate the HOMO in order to provide a more stable material under ambient device operating conditions. Thus, the HOMO of poly**8b** (-5.45 eV) is much lower than the value required to avoid electrochemical reactions with wet oxygen (-4.9 eV).[27] In comparison to poly(3,3"-dihexyl-2,2':5',2"-terthiophene) ($E_g \approx 1.9$ eV)[28] and poly(3,3"-dioctyl-2,2':5',2"-terthiophene) ($E_g \approx$ 2.05 eV),[26] close non-fluorinated analogues of poly**8b**, the introduction of the halogen substituents serves to widen the band gap of the polymer (2.2 eV for poly**8b**) and hence stabilise the HOMO. It has been shown that hole mobilities for poly(3,3"-dioctyl-2,2':5',2"-terthiophene) depend on the molecular weight of the polymer.[26] The values range from $4 \times 10^{-5}$ to $2 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ for polymers with a DP (number of thiophene units) of 12 to 38. In the case of poly**8b**, the DP was 37 and the hole mobility of this polymer was found to be $3 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$, highly comparable with that of the non-fluorinated analogue.

## Experimental Part

### General

Unless, otherwise stated all reactions were performed under an inert atmosphere of dry nitrogen using standard Schlenk techniques. All glassware was flame-dried under vacuum prior to use. All solvents and reagents were purchased from Sigma-Aldrich chemical company and used as received. UV/Vis spectra were recorded using a Unicam UV-300 Spectrophotometer in the range 210-1100 nm, using a 1 cm path length quartz cell. Mass spectra were recorded on a Kratos concept 1S instrument. Infrared spectra were recorded on a Specac single reflectance ATR instrument (4000-400 $cm^{-1}$, resolution 4 $cm^{-1}$). Polymer molecular weight determinations were carried out in chlorobenzene solution at 60°C on an Agilent 1100 Series HPLC using two Polymer Laboratories Mixed B columns in series, and the system was calibrated against narrow-weight PL polystyrene calibration standards. Thermogravimetric analysis was performed on poly**8b** in a standard platinum pan with a Perkin Elmer TGA7 under a constant flow of helium (20 $cm^3$/min). The temperature was raised to 50°C followed by an isothermal period of 5 minutes. The temperature was raised again at a rate of 10°C/min until 500°C when the polymer sample was left for an isothermal period of 30 min. The percentage weight loss over time was recorded at this temperature and the data was processed using the Pyris Series Software. Differential scanning calorimetry was conducted on a TA Instruments Q1000 with a RC-90 refrigerated cooling unit attached. The calibration was conducted using indium (melt temperature 156.42°C, $\Delta H_f$ 28.42 J/g). Elemental analysis was performed by the University of Manchester micro-analytical laboratory. Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected. 2,5-Dibromo-3,4-difluorothiophene,[11e] 2-bromo-3-hexylthiophene[19] and

tetrakis(triphenylphosphine) palladium (0)[20] were prepared according to standard literature procedures.

Thin-film organic field-effect transistors (OFETs) were fabricated in a dry nitrogen glove box environment on highly doped silicon substrates with a thermally grown silicon oxide (SiO2) insulating layer (thickness 230 nm), where the substrate served as a common gate electrode. Transistor source-drain gold contacts were photolithographically defined on the SiO2 layer. FET substrates were solvent cleaned and then ozone treated for 10 min in a custom built low-pressure mercury lamp setup. Devices were then treated with octyltrichlorosilane by immersing substrates in 10mM solutions in heated toluene (60°C) for 15 min, followed by a thorough washing with hexane, acetone and isopropanol. Samples were prepared by drop-casting from warm (80°C) solutions (10 mg/ml) in 1,2-dichlorobenzene .The samples were then dried and annealed at 100°C for 10 min and measured in the absence of light.

3',4'-Difluoro-[2,2';5',2"]terthiophene (**8a**)

A mixture of 2,5-dibromo-3,4-difluorothiophene **7** (200 mg, 0.72 mmol), 2-(tributylstannyl)-thiophene **6** (280 mg, 0.72 mmol) and tetrakis(triphenylphosphine)palladium(0) (21 mg, $1.8 \times 10^{-5}$ mol) in anhydrous toluene (20 cm$^3$) was stirred at reflux for 24 h. After cooling to room temperature the bright yellow extract was washed with 2 M hydrochloric acid (20 cm$^3$), water (20 cm$^3$) and brine (20 cm$^3$) before drying over magnesium sulphate. Concentration under reduced pressure yielded a crude yellow oil. Trituration from methanol and subsequent recrystallisation from ethanol afforded 40mg of an orange powder (40%, Mpt 145-147°C) UV/Vis (hexane) = 254,353 nm; FT-IR (KBr): 2911-2857 (C-H str), 1502 (Ar C=C str), 1228 (C-F str) cm$^{-1}$; $^1$H NMR (CDCl$_3$): δ = 7.11 (m, 2H, Ar-H), 7.32 (d, 2H, Ar-H), 7.40 (d, 2H, Ar-H) ppm ; $^{19}$F-{$^1$H} NMR (CDCl$_3$): δ = -128.487 (d, 2F, Ar-F) ppm; MS (APCI): m/z =

284/281 (100%, M+H); (Found: C 50.47 H 2.41 F 13.31 S 33.49 %. $C_{12}H_6F_2S_3$ requires C 50.68 H 2.13 F 13.36 S 33.83 %.)


3',4'-Difluoro-3,3''-dihexyl-[2,2';5',2'']terthiophene (**8b**)

A mixture of 2,5-dibromo-3,4-difluorothiophene **7** (200 mg, 0.72 mmol), 2-(trimethylstannyl)-3-hexylthiophene **5** (480 mg, 1.44 mmol) and tetrakis(triphenylphosphine)palladium(0) (41 mg, $3.6 \times 10^{-5}$ mol) in N,N-dimethylformamide (20 cm$^3$) was stirred at 80°C for 24 h. After cooling to room temperature, 10% potassium fluoride solution (20 cm$^3$) was added and the yellow extract stirred overnight. The resulting yellow solution was diluted with diethyl ether (100 cm$^3$) and the layers separated. The organic extract was washed with brine (100 cm$^3$) before drying over magnesium sulphate. Concentration under reduced pressure yielded a crude orange oil. Purification by preparative HPLC chromatography [100% hexane, Rf = 0.54 (silica)] yielded 174 mg of yellow oil (53%) UV/Vis (hexane) = 254, 316 nm; FT-IR (KBr): 2904-2861 (C-H str), 1494 (Ar C=C str), 1226 (C-F str) cm$^{-1}$; $^1$H NMR (CDCl$_3$): δ = 0.95 (t, 6H, 2CH$_3$-R), 1.41 [m, 12H, 2CH$_3$-(CH$_2$)$_3$], 1.68 (m, 4H, 2Ar-CH$_2$-CH$_2$), 2.78 (t, 4H, 2Ar-CH2-CH2) 7.04 (d, 2H, 2Ar-H), 7.40 (d, 2H, 2Ar-H) ppm ; $^{19}$F-{$^1$H} NMR (CDCl$_3$): δ = -128.487 (d, 2F, Ar-F) ppm; MS (APCI): m/z = 452 (40%, M+H) 433(61% M-F);


Microwave assisted synthesis of **8b**

A mixture of 2,5-dibromo-3,4-difluorothiophene **7** (200 mg, 0.72 mmol), 2-(trimethylstannyl)-3-hexylthiophene **6** (480 mg, 1.44 mmol) and tetrakis(triphenylphosphine)palladium(0) (41mg, $3.6 \times 10^{-5}$ mol) in N,N-dimethylformamide (20 cm$^3$) was irradiated at 140°C for 10 min. The resulting yellow solution was diluted with diethyl ether (100 cm$^3$) and the organic extract was washed with brine (100 cm$^3$) before drying over magnesium sulphate. Concentration under reduced pressure yielded a crude

orange oil. Purification by preparative HPLC chromatography [100% hexane, Rf = 0.51 (silica)] yielded 210 mg of a yellow oil (65%).

Poly **8b**

To a solution of anhydrous FeCl$_3$ (0.13 g, 0.81 mmol) in dry chloroform (10 cm$^3$) under an inert nitrogen atmosphere was added a solution of monomer **8b** (0.083 g, 0.18 mmol) in chloroform (5 cm$^3$) over 15 min. The resulting blue solution was stirred at room temperature for 48 h. The reaction mixture was precipitated in methanol. The resulting solid was isolated, and then stirred in concentrated aqueous ammonia solution for 1 h. After filtration, the polymer was purified *via* soxhlet extractions using acetone, methanol, dichloromethane and finally chloroform to obtain the polymer (18 mg). Mn 5,600, Mw 8,600. $^1$H NMR (CDCl$_3$): δ = 0.88 (m, 6H), 1.32 (m, 12H), 1.67 (m, 4H), 2.77-2.63 (m, 4H), 7.07 (m, 0.5 H) and 7.52-7.34 (m, 2H). The sample contained low molecular weight fractions.

Keywords: ((conjugated polymers; electrochemistry; fluorine; organic field effect transistors; polythiophene))

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**Figure Captions**

*Scheme 1.* Reactions & Conditions: (i) *n*-BuLi / THF, -80°C 45 min; (ii) $(CH_3)_3SnCl$, -80°C to RT, 12 h; (iii) DMF / $Pd(PPh_3)_4$, 80°C or PhF / $Pd_2(dba)_3$ / TTP, 10 min ( μw).

*Figure 1.* Top - absorption spectra for **8a** (hexane solution) and poly**8a** (thin film). Bottom - absorption spectra for **8b** (hexane solution) and poly**8b** (thin film).

*Figure 2.* Electrochemical growth of poly**8a** (top) and poly**8b** (bottom).

*Figure 3.* Cyclic voltammograms of monomer **8b** (*ca.* $10^{-4}$ M in dichloromethane solution, Au working electrode) and poly**8b** (as a thin film on ITO glass in acetonitrile). Electrolyte solutions contained *n*-tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte. The data are referenced *vs* Ag/AgCl.

*Figure 4.* Cyclic voltammograms of monomer **8a** (*ca.* $10^{-4}$ M in dichloromethane solution, Au working electrode) and poly**8a** (as a thin film on ITO glass in acetonitrile). Electrolyte solutions contained *n*-tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte. The data are referenced *vs* Ag/AgCl.

*Figure 5.* Operating characteristics of an OFET incorporating poly**8b**. Top – output characteristics at varying gate voltages. Bottom – Transfer characteristics and field-effect hole mobility *vs* gate voltage.

# Figures
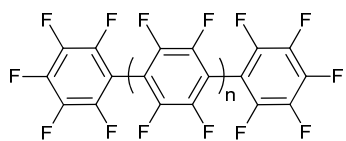


**1**
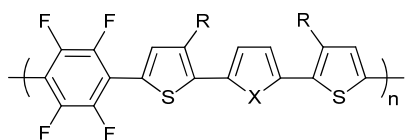


**2**

Where X = S or Se and R = H or $C_6H_{13}$
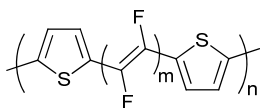


**3**
m = 1 or 2

Chart 1
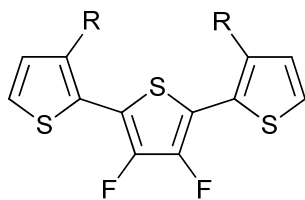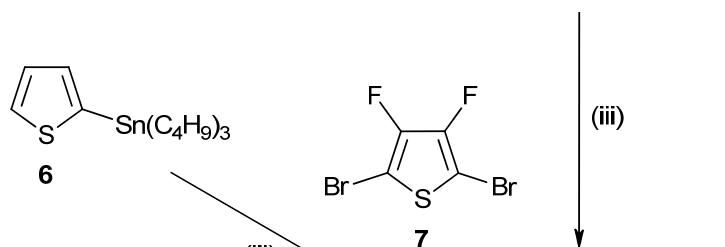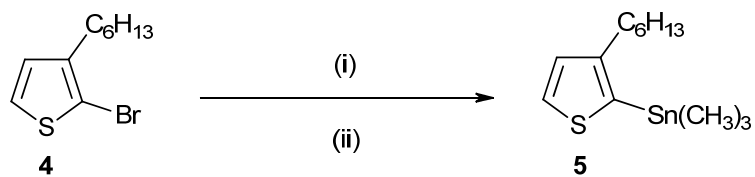


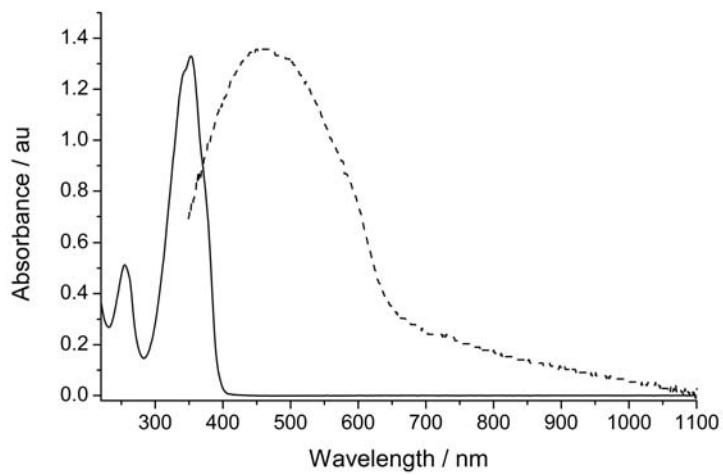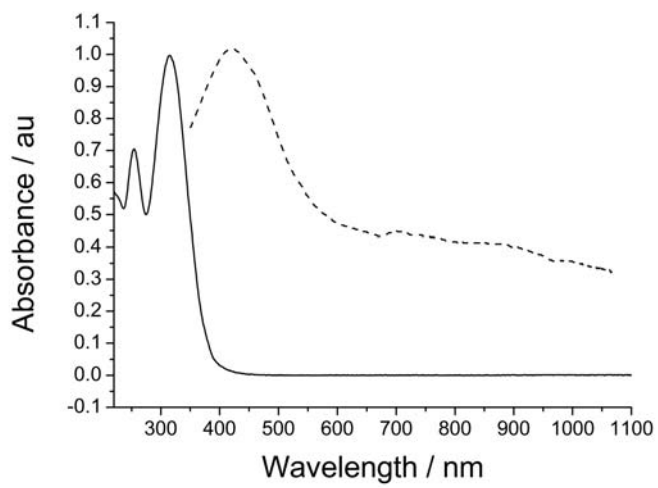**8a** R = H
**8b** R = $C_6H_{13}$

Scheme 1

Figure 1 (top)



Figure 1 (bottom)
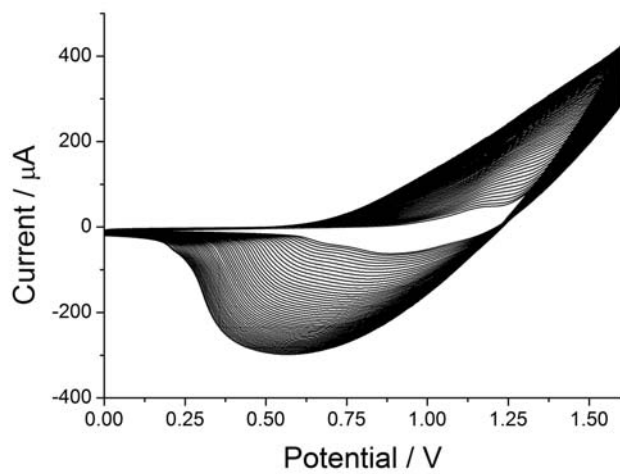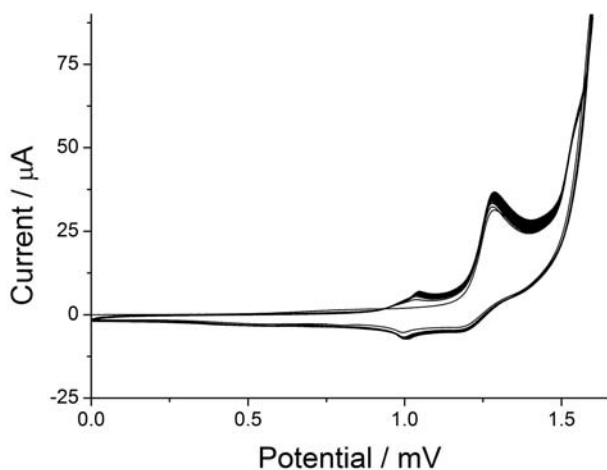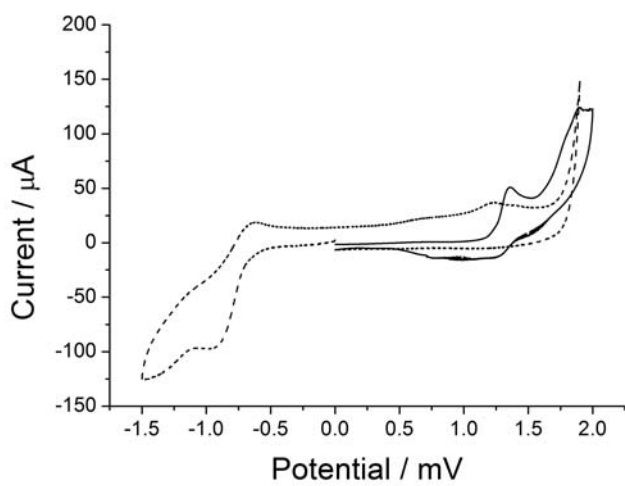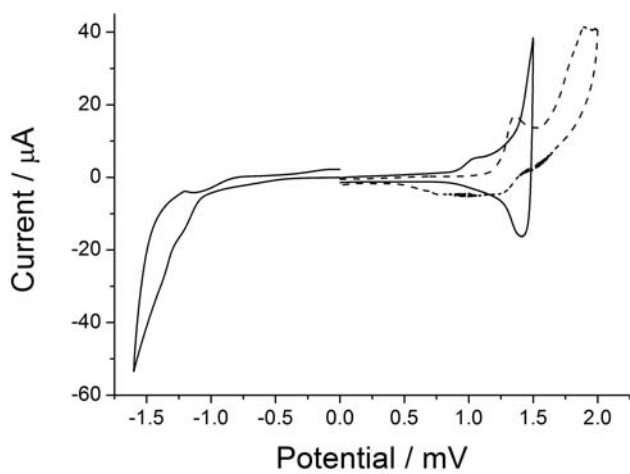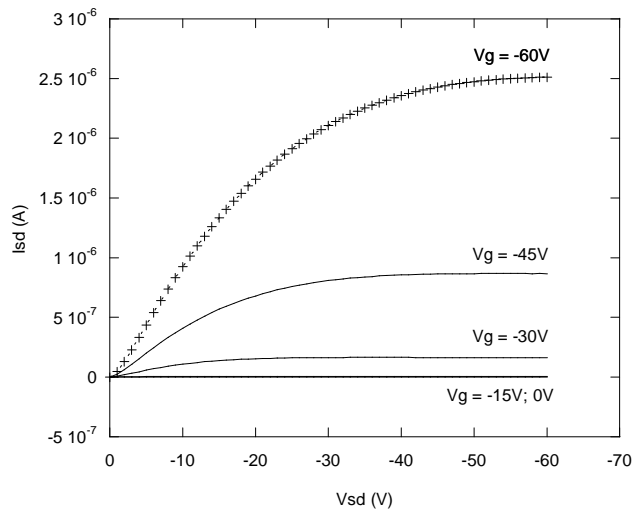


Figure 2 (top)

Figure 2 (bottom)



Figure 3



Figure 4

Figure 5 (top)
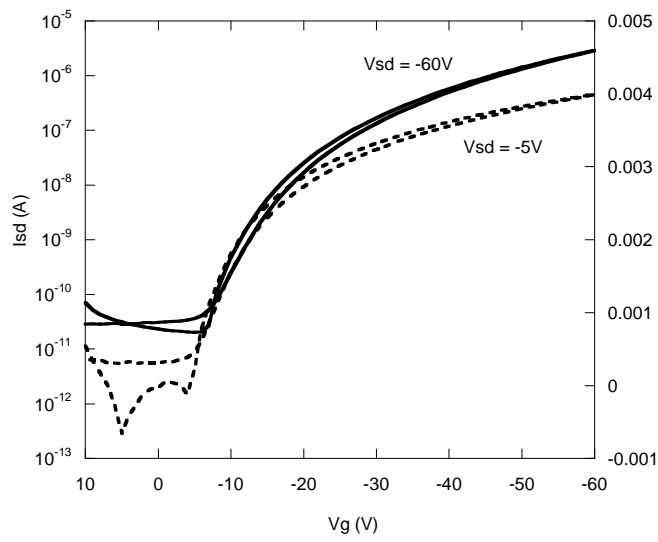


Figure 5 (bottom)

**3,4-Difluoroterthiophenes have been polymerised and their electronic and redox properties discussed.** OFET devices have been fabricated from poly**8b** using a bottom-gate, bottom-contact configuration. The material gives a maximum hole mobility of $3 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$, and the device has an on/off ratio of $10^5$.

David J. Crouch, David Sparrowe, Martin Heeney, Iain McCulloch and Peter J. Skabara *

Polyterthiophenes incorporating 3,4-difluorothiophene units and their application in organic field effect transistors