Hexyl-substituted oligothiophenes with a central tetrafluorophenylene unit: crystal engineering of planar structures for p-type organic semiconductors†

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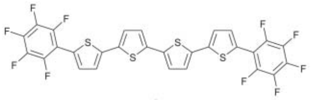
Rigidification has been achieved in thiophene–tetrafluorophenylene architectures through strong $S\cdots F$ and $H\cdots F$ intramolecular interactions; the resulting materials are promising candidates for p-type organic field effect transistors.

Organic conjugated oligomers and polymers are an important class of semiconductor, attracting great interest in applications such as light emitting diodes,[1] photovoltaics[2] and thin film transistors (TFTs).[3] Achieving efficient device performance (approaching that of amorphous silicon) is the major challenge for organic semiconductors. For TFTs, the drive is to design and synthesise materials that possess a low threshold voltage, a high on/off ratio, high mobility and stability under ambient and operating conditions. Several strategies have been investigated to promote the self-assembly of conjugated systems in order to increase non-covalent interactions between chains and maximise the efficiency of charge transport in the bulk material. Exploiting liquid crystal properties[4] or using inherently 'flat' molecules, such as pentacene, are good examples in which co-facial packing is achieved. In the latter case, ribbon or ladder type structures can suffer from poor solubility and processability. Materials that give a planar conformation through intrachain non-bonding interactions can provide a high degree of co-planarity in the solid state.[5] At the same time, the materials possess good solubility due to the rotational freedom of the main chain in solution.

With respect to the above, fluorinated conjugated oligomers are of recent topical interest.[6–8] Katz and co-workers have found that structures such as **1**–**3**[9] are essentially p-type. Incorporating the fluorinated units serves to lower both the LUMO and HOMO energies of the materials and also facilitates the planarization of **2**. Lowering of the HOMO energy level is a prerequisite in obtaining oxidative stability in thiophene containing polymers. Within this theme, we present a series of compounds (**4**–**6**) bearing a central tetrafluorophenylene unit. The non-covalent interactions of the fluorine atoms with components on adjacent thiophene rings result in highly planar structures in the solid state, together with excellent solubility of the oligomers and corresponding polymers in common organic solvents.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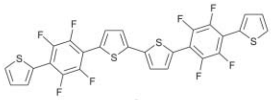
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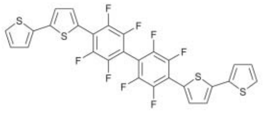
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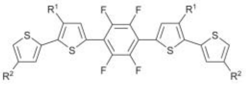
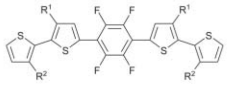
4a R = H
4b R = hexyl

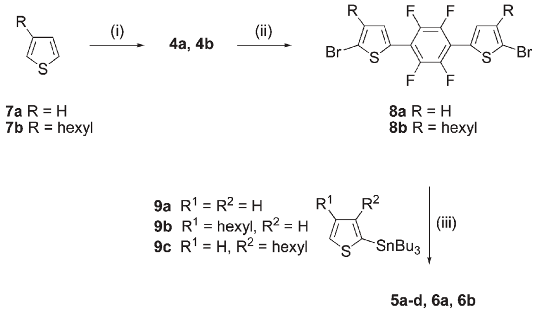


5a $R^1 = R^2 = H$
5b R^1 = hexyl, R^2 = H
5c R^1 = H, R^2 = hexyl
5d $R^1 = R^2$ = hexyl



6a R^1 = H, R^2 = hexyl
6b $R^1 = R^2$ = hexyl

Compounds **4**–**6** were prepared according to Scheme 1. The reaction of 2-thienyllithium and 4-hexyl-2-thienyllithium with hexafluorobenzene gave the triaryl derivatives (**4a**[10] and **4b**) in 65 and 66% yield, respectively. The procedure is noteworthy for two reasons: (i) ease of synthesis compared to the Stille route used for compounds **2** and **4a**; (ii) the lithiation of 3-hexylthiophene is regiospecific and results in the isolation of **4b** as a single isomer. Bromination of **4a** and **4b** was achieved in *ca.* 90% yield using *N*-bromosuccinimide, whilst the pentaaryl derivatives, **5a**–**d**, **6a** and **6b**, were obtained by palladium catalysed coupling with the corresponding stannylated thiophenes **9a**–**c** (45–70% yield).



Scheme 1 *Reagents and conditions*: (i) *n*-BuLi, THF, −78 °C, then hexafluorobenzene, reflux; (ii) NBS, $CHCl_3$, AcOH; (iii) $Pd(PPh_3)_4$, toluene.

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† Electronic supplementary information (ESI) available: X-ray structure of **5b**, UV-vis absorption data and experimental conditions for X-ray crystallography, cyclic voltammetry and device fabrication. See http://www.rsc.org/suppdata/cc/b4/b417642a/

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The structures of compounds **5b** and **5d** have been determined by X-ray crystallography.‡ In both cases, the common central unit of the conjugated oligomers is held in good planarity by strong H···F and S···F non-covalent intramolecular contacts. For **5d** the contact distances are 2.210 Å (H···F) and 2.704 Å (S···F) and the maximum torsion angle between the thiophene and benzene ring is 1.99° (sum of the van der Waals radii: H + F = 2.67 Å, S + F = 3.27 Å).[11] Compound **5d** is more co-planar throughout the chain than **5b**, with maximum torsion angles between adjacent thiophene rings at 4.08° for the former and 7.05° for **5b**. Oligomer **5d** forms chains of molecules (Fig. 1) through intermolecular S···S contacts (3.408 Å, van der Waals radii for S + S = 3.60 Å). The molecules are arranged in sheets in which parallel chains are insulated by the alkyl groups. In the third dimension, the pseudo-chains form slipped stacks (ESI†); the mean co-facial distance between the chains is 3.557 Å. The interactions described above give the material a unique two-dimensional assembly of strong intermolecular contacts.

Compounds **5a–d** and **6a** display absorption maxima in the range 378–394 nm (hexane), significantly higher than the values for **4a** and **4b** (310 and 332 nm, respectively, in CH_2Cl_2), due to an increase in conjugation length. As expected, the absorption maximum for **6b** is at a shorter wavelength compared to those of its direct analogues (353 nm, hexane), due to the steric effect of the head–head hexyl thiophene units. In the solid state (evaporated from hexane as a film), the absorption maximum of **5d** is shifted bathochromically by only 11 nm to 396 nm, indicating that the planarity of the material is retained in solution state. Compound **5d** was extended by two thiophene units *via* the reaction of **5d** with NBS to give **7** (60%), followed by Stille coupling with 4-hexyl-2-tributylstannylthiophene to afford **8** (25%) (Scheme 2). The absorption maximum of **8** is red-shifted to 405 nm (hexane) and 433 nm (film), indicative of an increase in conjugation length. In order to assess the degree of self-assembly in polymeric analogues, we prepared polymer **9** *via* Pd catalysed coupling of the dibromo derivative **7** and 2,5-bis(tributylstannyl)thiophene. The resulting polymer was extracted using Soxhlet procedures with a range of solvents (firstly acetone, methanol, then dichloromethane and chloroform). The chloroform fraction contained the highest molecular weight, $M_n = 10.5 \times 10^3$; $M_w = 21.5 \times 10^3$, equating to about 70 aryl units in the polymer chain. The absorption maximum for this material was found to be 420 nm (chloroform), only slightly higher than that of oligomer **8**. However, a drop cast chloroform solution of **9** gave absorption maxima at 508 and 566 nm. These large bathochromic shifts, together with the detailed structure of the absorption band (ESI†), is indicative of high ordering in the solid state. In addition to the above, we have also prepared poly(**5d**) by electrochemical polymerisation (ESI†). Absorption maxima appear at 492, 526 and 569 nm and the absorption characteristics are very similar to those of polymer **9**. This is quite surprising, since one would expect that the head–head coupling inherent in poly(**5d**) would be detrimental to the planarity and effective conjugation length of the polymer.

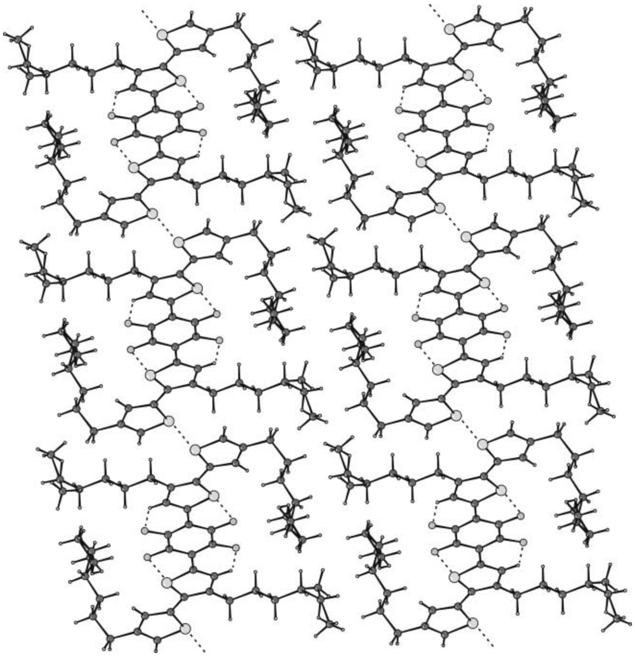
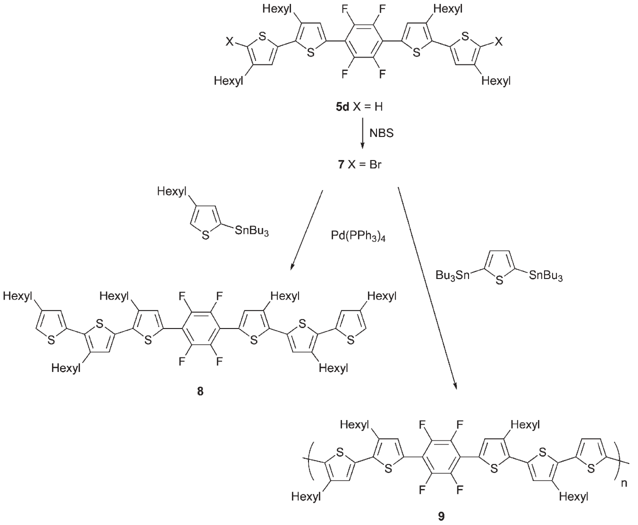


Fig. 1 Packing diagram of compound **5d**, viewed along the *a* axis, showing intra- and inter-molecular contacts.



Scheme 2

In conclusion, we have prepared a series of oligothiophenes bearing a central tetrafluorophenylene unit and shown the effect of planarisation through H···F and S···F contacts by X-ray crystallographic and absorption studies. Polymeric materials have been obtained by chemical and electrochemical methods and show good evidence for high order in the solid state. The introduction of hexyl chains provides excellent solubility: all materials are soluble in common organic solvents. Moreover, the out-of-plane extension of the hexyl chains observed in **5d** encourages interplane interdigitisation of the alkyl groups and hence stabilises the crystal phase. Compounds **5b** and **5d** show a tendency to form highly ordered, two-dimensional materials in the crystalline state with several non-covalent intermolecular contacts. The deposition of active films by cheap, solution processing techniques is highly desirable. Preliminary results on hole mobility measurements for spin coated polymer **9** give values *ca.* 2×10^{-3} cm^2 V^{-1} s^{-1} (ESI†). These results were obtained without any transistor fabrication optimisation, which would be expected to significantly improve charge carrier mobility,[12] and are encouraging for materials incorporating the dithienyl tetrafluorophenylene core. Further work is under way to optimise the mobilities of these materials.

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Notes and references

‡ *Crystal data*: Data were collected at 120 K on a Nonius KappaCCD area detector situated at the window of a rotating anode (λ(Mo-Kα) = 0.71073 Å). The structures were solved by direct methods, SHELXS-97, and refined using SHELXL-97. Hydrogen atoms were included in the refinement, but thermal parameters and geometry were constrained to ride on the atom to which they are bonded. The data were corrected for absorption effects using SORTAV. **5b**: $C_{34}H_{34}F_4S_4$, tetragonal, $P4_12_12$, a = 20.5113(12), c = 14.2496(11) Å, V = 5995(7) Å^3, Z = 8, D_c = 1.433 Mg m^{-3}, μ = 0.366 mm^{-1}, θ_{max} = 27.98°, 59088 measured, 6585 unique (R_{int} = 0.2283) and 4093 ($I > 2\sigma(I)$) reflections, $R1$ (obs.) = 0.1388 and $wR2$ (all data) = 0.3407, ρ_{max}/ρ_{min} = 0.734/−0.828 e Å^{-3}. **5d**: $C_{46}H_{58}F_4S_4$, triclinic, $P\bar{1}$, a = 6.1497(2), b = 11.3722(8), c = 15.4457(10) Å, α = 91.678(3), β = 11.3722(8), γ = 102.556(4)°, V = 1043.26(11) Å^3, Z = 1, D_c = 1.297 Mg m^{-3}, μ = 0.278 mm^{-1}, θ_{max} = 27.50°, 13381 measured, 4477 unique (R_{int} = 0.1914) and 3138 ($I > 2\sigma(I)$) reflections, $R1$ (obs.) = 0.0839 and $wR2$ (all data) = 0.2350, ρ_{max}/ρ_{min} = 0.919/−1.500 e Å^{-3}. CCDC 245178 (**5b**) and 245177 (**5d**). See http://www.rsc.org/suppdata/cc/b4/b417642a/ for crystallographic data in .cif or other electronic format.

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