

Synthesis, solid state structure and polymerisation of a fully planar cyclopentadithiophene[†]

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The new fully planar cyclopentadithiophene, 4-*n*-dodecylidene-4*H*-cyclopenta(2,1-*b*;3,4-*b'*)dithiophene, shows extensive π -stacking in the solid state with short intermolecular distances (ca. 3.5 Å) between adjacent molecules. Polymerisation of this monomer by two different protocols gave solution processable alkenyl-bridged cyclopentadithiophene polymers with extended π -conjugation in the main chain.

Solution processable organic semiconductors have received tremendous recent interest for use as charge transport materials in electronic devices.¹ The rate limiting step for charge transport is inter-chain hopping² and this process is maximised by close π - π stacking between adjacent molecules. For example bis(dithienothiophene) shows one of the smallest reported π - π stacking distances and a high field effect mobility.³ In conjugated polymers that show efficient charge transport, such as poly-3-alkylthiophenes, a highly regioregular structure is essential to ensure a close stacking between adjacent chains.⁴

Solution processable poly(dialkylcyclopentadithiophenes) have been recently reported.⁵ These fused ring thiophene polymers are highly conjugated but they show poor charge transport when fabricated in field effect transistors.⁶ This has been attributed to the presence of alkyl chains normal to the polymer backbone which prevent close approach of the thiophene rings of adjacent chains. It is clear that a fully planar and conjugated structure is necessary to achieve a close π - π stacking and recent reports by Zotti *et al.* clearly indicate how conductivity in the doped state in poly(cyclopentadithiophenes), obtained by anodic coupling, is enhanced for structures where the substituents are in the plane of the conjugated backbone.⁷

To date no simple alkene-bridged cyclopentadithiophene polymers have been reported that are processable from solution.⁸ In this contribution we report the preparation of fully conjugated alkene-bridged cyclopentadithiophene monomers and their polymerisation to give solution processable poly(4-dodecylidene-cyclopentadithiophene-2,6-diyl).

The synthesis of 4-*n*-dodecylidene-4*H*-cyclopenta(2,1-*b*;3,4-*b'*)dithiophene (**3a**) and 2,6-dibromo-4-*n*-dodecylidene-4*H*-cyclopenta(2,1-*b*;3,4-*b'*)dithiophene (**3b**) were achieved by Wittig condensation between dodecylidene-triphenylphosphine ylide (**2**) and cyclopenta(2,1-*b*;3,4-*b'*)dithiophen-4-one (**1a**)⁹ or its 2,6-dibromo derivative (**1b**). Compounds **3a,b** were isolated in 65–75% yield as yellow and orange crystals respectively.

Recrystallisation of **3a** from ethanol afforded X-ray quality crystals and the solid state structure (Fig. 1) reveals a planar structure for monomer **3a**.[†] The packing diagram (Fig. 2) shows a face to face stacked configuration, as expected for an oligothiophene carrying alkyl chains.¹⁰ The intermolecular distance along the X-axis is 3.5 Å, while the sulfur atoms are displaced by 1.8 and 3.4 Å along the Z and Y axis, respectively.

Oxidative polymerisation of **3a** using FeCl₃ was performed using procedures described for the synthesis of poly(3-

alkylthiophenes).¹¹ A blue polymer was obtained after dedoping treatment with hydrazine. This material was purified by Soxhlet extraction with acetone and hexane and was soluble in chloroform. GPC against polystyrene standards showed polymer **4a** to be of high molecular weight (Table 1) with values similar to analogous polycyclopentadithiophenes obtained by oxidative polymerisation using FeCl₃.^{5d} The polymer structure was confirmed by ¹H NMR spectroscopy (see ESI),[†] and the UV-visible absorption of polymer **4a** in solution (Table 1) is highly red shifted, when compared to poly-3-alkylthiophenes, and is similar to the absorptions of polycyclopentadithiophenes. Polymer **4a** became less soluble on extended storage in the solid state, possibly due to the formation of strongly bound aggregates.

Transition metal catalysed polymerisations have been reported to give high purity, regioregular poly-3-alkylthiophenes suitable for use in electronic devices.^{4a} The Negishi protocol using a nickel catalyst and Rieke zinc is reported to be tolerant

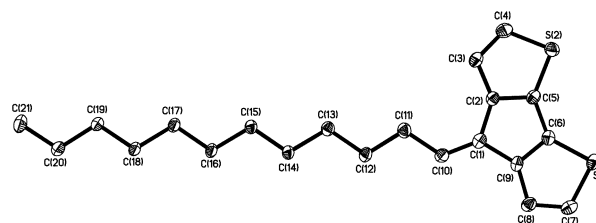


Fig. 1 Solid state structure of compound **3a**.

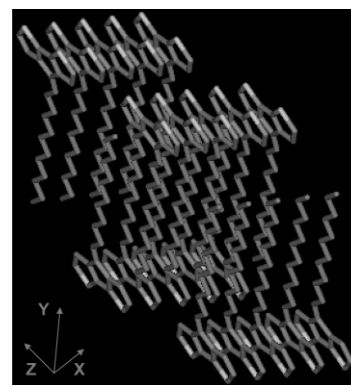


Fig. 2 Packing diagram of compound **3a** showing the X, Y and Z axes.

Table 1 Physical characterisation data for polymers **4a** and **4b**; molecular weight determined by GPC and λ_{max} from chloroform solution, drop cast thick film and spin coated thin film UV-vis absorption spectra

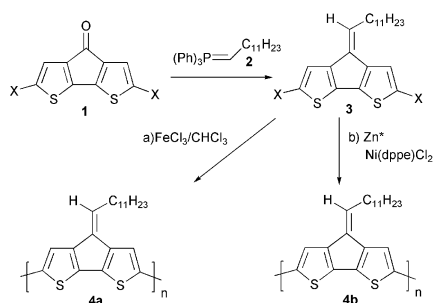
	M_w/M_n	$\lambda_{\text{max}}/\text{nm}$ (solution)	$\lambda_{\text{max}}/\text{nm}$ (thick film)	$\lambda_{\text{max}}/\text{nm}$ (thin film)
4a	320000/14600 ^a	599	614	628
4b	3600/2300	576	588	616

^a The high polydispersity is possibly due to the formation of aggregates in filtered chloroform solutions.

[†] Electronic supplementary information (ESI) available: Supplementary characterisation data for compounds **3a/b**, **4a/b**; tables of bond lengths and angles for compound **3a**. See <http://www.rsc.org/suppdata/cc/b3/b306171j/>

of reactive functional groups and it was therefore employed for the polymerisation of **3b**, as shown in Scheme 1.¹² Polymer **4b** was purified by precipitation in methanol and Soxhlet extraction in methanol. The polymer structure was confirmed by ¹H NMR spectroscopy (see ESI)[†] and the molecular weight of **4b** was determined by GPC against polystyrene standards (Table 1). The molecular weight was significantly lower than that of **4a** and MALDI-TOF mass spectrometry (Fig. 3) revealed that most of the chains are terminated by H atoms, as has been previously reported for poly(4,4-dialkylcyclopentadithiophenes) prepared by the Negishi protocol.^{5d} It is likely that reduction of thienyl-zincio groups resulted in chain capping to give a H-terminated low molecular weight polymer. The presence of a single alkyl substituent on the bridging alkene results in the potential for H–H, H–T and T–T regioisomers in the polymer backbone. All three regioisomers are presumably present as aqueous quenching of the reaction between one molar equivalent of Rieke zinc and monomer **3b** showed no selectivity for insertion at the 2- or 6-position (ratio of 4 : 6 observed, see ESI).[†]

The solution UV-vis spectrum of **4b** shows an intense absorption at 576 nm indicating that the conjugation length of this polymer is significantly shorter than that of the higher molecular weight polymer **4a**. A similar dependence of the conjugation length on molecular weight has been reported for poly(4,4-dialkylcyclopentadithiophenes).^{5d} Thin films of **4a** spin coated from chloroform solutions showed a bathochromic shift of 30 nm from the λ_{max} recorded in solution, while in thick films, drop cast from a concentrated chloroform solution, the red shift is limited to 15 nm. For polymer **4b** spin coated films show a greater bathochromic shift of 40 nm, together with an increased resolution of the vibronic structure. This significant red shift was not observed for poly(4,4-dialkylcyclopentadithiophenes) and may be associated with a similar solid state self assembly to that observed for monomer **3a**. Cyclic voltammetry



Scheme 1 Synthesis of polymers **4a** (**3a**: X = H) and **4b** (**3b**: X = Br)

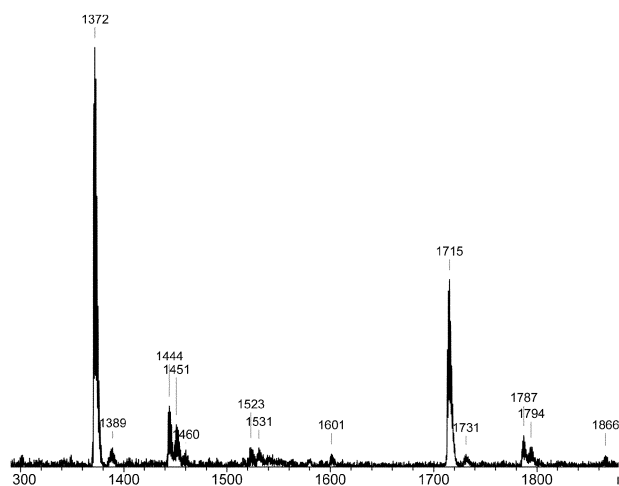


Fig. 3 MALDI-TOF mass spectrum of polymer **4b** before purification, showing peaks associated with the tetramer and the pentamer.

of polymer **4b** showed two reversible oxidations waves at 0.65 and 1.05 V, the first oxidation is similar to that previously obtained for analogous polycyclopentadithiophenes.^{7,8}

In summary, a new fully planar cyclopentadithiophene has been synthesised and the solid state structure determined by single crystal X-ray diffraction. This study shows extensive π -stacking of adjacent molecules with short intermolecular distances (*ca.* 3.5 Å). These alkenyl-bridged cyclopentadithiophenes can be polymerised to give highly conjugated polymers that show an estimated HOMO–LUMO gap of 1.6 eV (band edge at 750 nm) in solution processed thin films. The electronic properties of these materials are currently under investigation.

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Notes and references

† Crystal data for **3a**: C₂₁H₂₈S₂, *M* = 344.55, monoclinic, space group *P*2₁/*c*, *a* = 9.056(6) Å, *b* = 5.486(3) Å, *c* = 38.19(2) Å, α = 90°, β = 93.995(15)°, γ = 90°, *U* = 1893(2) Å³, *Z* = 4, *D*_c = 1.209 g cm⁻³, μ = 0.280 mm⁻¹, crystal size = 0.43 × 0.24 × 0.08 mm³, reflections collected 10949, 4480 were unique (*R*_{int} = 0.0697). The final *wR*2 = 0.1719 (all data), *R*1 = 0.0657 [*F*² > 2 σ (*F*²)], Goodness-of-fit on *F*² *S* = 0.890.

¹³C NMR in CDCl₃ of **3a**: 146.34 (C), 142.62 (C), 139.11 (C), 135.86 (C), 132.85 (CH), 130.99 (C), 124.46 (CH), 124.09 (CH), 122.62 (CH), 119.52 (CH), 31.90 (CH₂), 30.14 (CH₂), 29.64 (CH₂), 29.64 (CH₂), 29.61 (CH₂), 29.55 (CH₂), 29.50 (CH₂), 29.41 (CH₂), 29.33 (CH₂), 22.68 (CH₂), 14.13 (CH₃). Elemental analysis % (calc.) found: C (73.20) 73.37; H (8.19) 8.31; S (18.61) 18.63.

¹³C NMR in CDCl₃ of **3b**: 143.76 (C), 140.02 (C), 138.75 (C), 135.46 (C), 135.19 (CH), 130.36 (C), 125.45 (CH), 122.60 (CH), 110.87 (C), 110.38 (C), 31.90 (CH₂), 30.18 (CH₂), 29.62 (CH₂), 29.61 (CH₂), 29.52 (CH₂), 29.45 (CH₂), 29.42 (CH₂), 29.33 (CH₂), 29.27 (CH₂), 22.68 (CH₂), 14.13 (CH₃). Elemental analysis % (calc.) found: C (50.21) 50.08; H (5.22) 5.30; Br (31.81) 31.69; S (12.77) 12.85. CCDC 212050. See <http://www.rsc.org/suppdata/cc/b3/b306171j/> for crystallographic data in .cif or other electronic format.

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