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Strategies towards functionalised electronically conducting organic copolymers†

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Here we describe the synthesis and electrochemical polymerisation of 2,5-di(2-thienyl)-3-(3-cyanopropyl)pyrrole, 2,5-di(2-thienyl)-3-(3-cyanopropyl)furan, and 3′-(3-cyanopropyl)-2,2′:5′,2″-terthiophene. We report a synthetic methodology to these important conducting polymer precursor compounds that is facile, convenient and flexible. The key precursor to this study is the functionalised diketone 1,4-bis(2-thienyl)-2-(3-cyanopropyl)butane-1,4-dione. This molecule undergoes convenient ring closure to the terthiophene and dithienylpyrrole and dithienylfuran derivatives, all of which are, to our knowledge, new compounds. Importantly, this approach provides a flexible route to a range of heterocyclic polymer precursors because the cyanoalkyl functionality is grafted to the diketone before ring closure. Subsequently the nitrile group provides synthetic utility either by reduction to the amine, or hydrolysis to the carboxylic acid. The new compounds described here undergo electrochemical polymerisation leading to fixed ratio copolymers of functionalised pyrrole, thiophene and furan with thiophene itself. We describe the characterisation of these polymers using FT-IR and X-ray photoelectron spectroscopies.

1 Introduction

Interest in chemically functionalised conducting polymer materials continues to expand and currently encompasses *e.g.* electronic and electro-optic devices,[1,2] energy storage systems,[3] bioelectrochemical sensors,[4–6] artificial olfaction and others.[7] Consequently there is a keen interest in the methodology of chemical synthesis for the precursor monomer and oligomer units particularly in respect of thiophene and pyrrole. Well developed methods for synthesis of substituted pyrrole and especially thiophene monomers have been reported and substituents are numerous, including crown ethers,[8] metallocenes,[9,10] amino acids and peptides,[11] proteins and enzyme derived species.[12] However, introduction of substituent groups onto the pyrrole and thiophene monomers has a detrimental influence and often results in materials with poor electronic conductivity. This is attributed to the effect of neighbouring group steric interactions that reduce the conjugation length of the polymer strands and is most noticeably the case for *N*-substituted pyrroles. In addition to this effect, a high density of functional groups inhibits inter-chain electron transfer that also lowers conductivity.[13] Consequently many research efforts have concentrated on copolymer materials synthesised from a solution mixture of functionalised and non-functionalised monomers. This approach leads to materials with a lower proportion of functional groups and higher conductivities are observed.[14] Despite the convenience of this approach there are key problems, for example, the resultant materials are usually intractable and so hard to characterise, control of copolymer composition is difficult because of the disparate nature of the monomer reactivities, and, it is difficult to prove that the resultant materials are indeed copolymers rather than blends of homogeneous strands.

In response to these difficulties many research groups are focusing on functionalised oligomeric species such as sexithiophene,[15] terthiophene, and dithienylpyrrole[16] derivatives for which the ratio of functional groups to heterocyclic repeat units is less than one. On polymerisation these small oligomer units yield copolymer materials that have a well defined, prescribed structure in which the functional group substituents are spaced out to minimise steric interactions and spatial conflict. Consequently this reduces the steric interactions between adjacent functional groups of a polymer chain resulting in improved conjugation length and high conductivity.[17] An additional motivation for studies involving functionalised oligomers also arises from reports that soluble polymers can be produced from these precursors thereby offering enhanced processibility for practical applications.[1–7] The drawback to this approach, however, lies with the arduous nature of the chemical synthesis of the oligomeric precursors.

In the present study we are concerned with the synthesis and electrochemical polymerisation of a number of substituted three-unit pyrrole, thiophene and furan based species (Scheme 1). The functional group substituent for these species is carried on the central ring so that steric interactions between substituent groups on adjacent component blocks are minimised.‡ We have sought to develop a versatile synthetic route to functionalised conducting polymers that have both useful functional group properties and high electrical conductivity. In addition, our studies of electron-transfer reaction kinetics between organic polymers and small redox proteins have determined that a low anodic bias potential is required so that the onset of electrical conductivity in the polymer lies within an accessible potential window for redox activity of the protein system under investigation.[18,19] Since polythiophenes commonly have quite positive anodic bias potentials we have focused our efforts on trimeric species in which the electronic properties of the thiophene units are modulated by the presence

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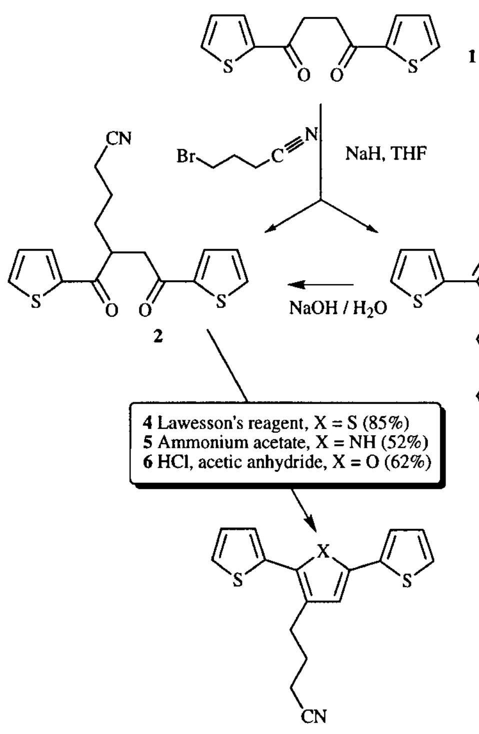
‡The copolymer is presumed to be regio-randomly constructed.



Scheme 1

of a pyrrole or furan unit. Consequently our strategy, described here, encompasses not only functionalised terthiophene and dithienylpyrroles but also dithienylfuran derivatives, a group of polymer precursors of which, to our knowledge, there are only a very few reported examples.

The established synthetic methods leading to functionalised terthiophenes and dithienylpyrrole derivatives are relatively few and commonly feature coupling reactions of functionalised and non-functionalised monomer units. Such coupling reactions are often facilitated by transition metal catalysts using α-dibromo and α-alkylstannylated monomer derivatives.[20] Consequently these methods are usually rigorous and involve air sensitive intermediates.[20–23] As an alternative to this approach we have adopted a strategy in which a functional group is grafted onto a dithienyl diketone precursor. This precursor can then undergo a ring closure reaction to yield either the thiophene, pyrrole or furan derivatives by choice of the appropriate reagent.

Here we describe for the first time the synthesis and characterisation of this novel precursor together with that of the terthiophene, dithienylpyrrole and dithienylfuran derivatives. In addition we report the electrochemical polymerisation of these new molecules and the subsequent characterisation of the polymers using FT-IR and X-ray photoelectron spectroscopies.

2 Experimental

2.1 General methods

Commercial reagents were used without further purification. Solvents were purified and degassed according to standard procedures. ^{1}H and ^{13}C NMR data were obtained on Varian *Unity Inova* 400 MHz and Bruker AC-F 250 MHz spectrometers. Chemical shifts are given in ppm. FT-IR spectra were recorded using a Nicolet 205 FT-IR spectrometer, polymer film spectra were recorded *ex situ* using a specular reflectance accessory at an incident angle of 45°. In order to prevent spectral baseline distortion cased by conduction band effects the polymer samples were prepared in their fully reduced form. Mass spectra were recorded on a Finnigan MassLab Navigator. UV–Visible absorption spectra were recorded using a Perkin Elmer Lambda 9 spectrometer. The composition of the polymer films was examined using the Scienta ESCA 300 X-ray photoelectron spectrometer (typical slit width = 0.8 mm, take off angle = 90°) at the CCLRC RUSTI facility at Daresbury.

2.2 Synthesis

1,4-Bis(2-thienyl)butane-1,4-dione, 1. To a suspension of $AlCl_3$ (16 g, 0.12 mol) in CH_2Cl_2 (15 ml) a solution of thiophene (9.61 ml, 0.12 mol) and succinyl chloride (5.51 ml, 0.05 mol) in CH_2Cl_2 was added dropwise. The red mixture was stirred at r.t. for 18 h. This was then quenched with ice and conc. HCl (5 ml). After intensive stirring for 2 h the dark green organic phase was separated, washed with 2 M HCl, H_2O $NaHCO_3$ solution and dried over $MgSO_4$. After evaporation of the solvent a blue–green solid remained, which was suspended in ethanol. Filtration and washing with ethanol and diethyl ether provided a green solid. Column chromatography (SiO_2, CH_2Cl_2–hexane (1 : 1)) and recrystallisation from ethanol gave **1** as a white solid 9.98 g (39.81 mmol; 80%). Mp 126–127 °C; IR(KBr): $\nu = 3101$–3083, 2918, 1651 cm^{-1}; ^{1}H-NMR: (250 MHz; $CDCl_3$) $\delta = 3.38$ (s, 4H, C*H*$_2$–C*H*$_2$–); 7.13 (dd, 2H, *H*-4,4′); 7.63 (dd, 2H, *H*-3,3′); 7.80 (dd, 2H, *H*-5,5′); ^{13}C-NMR: (250 MHz; $CDCl_3$) $\delta = 33.20$ (–*C*H$_2$–*C*H$_2$–); 128.18 (*C*-4,4′); 132.15 (*C*-5′,5″); 133.69 (*C*-3,3′); 143.78 (*C*-2,2′); 191.42 (*C*=O).

1,4-Di(2-thienyl)-2-(3-cyanopropyl)butane-1,4-dione, 2, and 1,4-di(2-thienyl)-1-(3-cyanopropoxy)but-1-en-4-one, 3. To an ice cooled suspension of NaH (0.144 g, 6.00 mmol) in 10 ml of THF a solution of **1** (1 g, 4.01 mmol) in 20 ml of THF was added dropwise. This mixture was stirred at r.t. for 90 min after which 3-bromobutyronitrile was added dropwise (0.8 ml, 8.02 mmol). The deep red reaction mixture was stirred at 65 °C for 72 h. This was subsequently allowed to cool to r.t. and poured into 30 ml of H_2O. Extraction with Et_2O (3 × 15 ml), washing with H_2O, drying over $MgSO_4$ and concentration under reduced pressure provided a brown oil. Column chromatography (SiO_2, petroleum ether (40/60)–Et_2O (3 : 1)) gave a mixture of **2** and **3** as an orange oil. Subsequent column chromatography of this mixture resolved both pure compounds and their spectroscopic data are listed below.

1,4-Di(2-thienyl)-2-(3-cyanopropyl)butane-1,4-dione, 2. 0.799 g (2.52 mmol; 63%); Elemental analysis for $C_{16}H_{15}NO_2S_2$: %Calc. C 60.05, H 4.76, N 4.41, S 20.20; %Found C 59.89, H 4.76, N 4.46, S 19.58; IR: $\nu = 3103$, 2938, 2869, 2246, 1655 cm^{-1}; ^{1}H-NMR: (250 MHz; $CDCl_3$) $\delta = 1.63$–1.84 (m, 2H, –C*H*$_2$–CH$_2$–CH$_2$–CN); 1.89–2.01 (m, 2H, –C*H*$_2$–CH$_2$–CN); 2.34 (t, $J = 6.71$ Hz, 2H, CH$_2$–C*H*$_2$–CN); 3.10 (dd, $J = 5.2$ Hz, 17.4 Hz, 1H, –C*H*$_2$–C=O); 3.56 (dd, $J = 7.4$ Hz, 17.4 Hz, 1H, –C*H*$_2$–C=O–), 3.93–4.03 (m, 1H, CH$_2$–C*H*–C=O), 7.12 (dd, $J_{4',5'} = 5.2$ Hz, $J_{4',3'} = 4.0$ Hz, 1H, *H*-4′), 7.16 (dd, $J_{4'',3'} = 5.2$ Hz, $J_{4'',5'} = 4.0$ Hz, 1H, *H*-4″); 7.63 (dd, $J_{5',3'} = 1.2$ Hz, $J_{5',4'} = 5.2$ Hz, 1H, *H*-5′); 7.67 (dd, $J_{5'',3''} = 1.2$ Hz, $J_{5'',4''} = 5.2$ Hz, 1H, *H*-5″); 7.73 (dd, $J_{3',5'} = 1.2$ Hz, $J_{3',4'} = 4.0$ Hz, 1H, *H*-3′); 7.85 (dd, $J_{3'',5''} = 1.2$ Hz, $J_{3'',4''} = 4.0$ Hz, 1H, *H*-3″); ^{13}C-NMR: (250 MHz; $CDCl_3$) $\delta = 17.27$ (–*C*H$_2$–CN); 23.28 (CH$_2$–*C*H$_2$–CH$_2$–CN); 31.72 (*C*H$_2$–CH$_2$–CH$_2$–CN); 41.57 (–*C*H$_2$–C=O); 42.39 (–*C*H–C=O), 119.11 (CN), 128.27, 128.50 (*C*-4′, *C*-4″); 132.38 (*C*-3′); 132.62 (*C*-3″); 134.15 (*C*-5′); 134.56 (*C*-5″); 143.45, 143.81 (*C*-2′, *C*-2″); 190.55, 194.85 (2 × C=O); MS (ESI$^+$, eV): *m*/*z* = 340 ([M + Na]$^+$, 100), 318 ([M + H]$^+$, 84); 356 ([M + K]$^+$, 18), 657 ([2M + Na]$^+$), 496, 109.

1,4-Di(2-thienyl)-1-(3-cyanopropoxy)but-1-en-4-one, 3. 0.330 g (1.04 mmol; 26%); Elemental analysis for $C_{16}H_{15}NO_2S_2$: %Calc. C 60.05, H 4.76, N 4.41, S 20.20;

%Found C 60.17, H 4.81, N 4.22, S 19.84; IR: $\nu = 3103$, 2927, 2853, 2248, 1734, 1652 cm^{-1}; ^{1}H-NMR: (250 MHz; CDCl$_3$) $\delta = 2.03$ (dt, $J = 13.4$ Hz, $J = 6.1$ Hz, 2H, $–CH_2–CH_2–CH_2–$); 2.44 (t, $J = 7.3$ Hz, 2H, $–CH_2–CN$); 3.28 (d, $J = 7.3$ Hz, 2H, $CH–CH_2–C{=}O$); 4.22 (t, $J = 6.1$ Hz, 2H, $–O–CH_2–CH_2–CH_2–CN$); 6.32 (t, $J = 7.3$ Hz, 1H, $–CH_2–CH{=}C–O–$), 6.87 (dd, $J_{3',5'} = 1.2$ Hz, $J_{3',4'} = 3.7$ Hz, 1H, *H*-3′), 6.93 (dd, $J_{4',3'} = 3.7$ Hz, $J_{4',5'} = 5.2$ Hz, 1H, *H*-4′); 7.03 (dd, $J_{3'',5''} = 1.2$ Hz, $J_{3'',4''} = 3.7$ Hz, 1H, *H*-3″); 7.08 (dd, $J_{4'',3''} = 3.7$ Hz, $J_{4'',5''} = 5.2$ Hz, 1H, *H*-4″); 7.19 (dd, $J_{5',3'} = 1.2$ Hz, $J_{5',4'} = 5.2$ Hz, 1H, *H*-5′); 7.39 (dd, $J_{5'',3''} = 1.2$ Hz, $J_{5'',4''} = 5.2$ Hz, 1 H, H-5″); ^{13}C-NMR: (250 MHz; CDCl$_3$) $\delta = 14.30$ ($–CH_2–CN$); 24.85 ($CH_2–CH_2–CH_2–CN$); 35.16 ($=CH–CH_2–C{=}O$); 62.54 ($–O–CH_2–CH_2–CH_2–CN$); 118.81 ($–CN$), 121.38 ($–CH{=}C–O–$); 125.02 (*C*-5′); 126.1 (*C*-3′); 126.39 (*C*-5″); 126.98 (*C*-4″); 127.31 (*C*-4′); 128.25 (*C*-3″); 131.90 (*C*-2′); 138.70 (*C*-2″); 145.64 (*C*-1), 171.01 (*C*-4); MS (ESI$^+$, eV): *m*/*z* = 319 ([M + H]$^+$, 15); 205, 195, 110.

Conversion of 1,4-di(2-thienyl)-1-(3-cyanopropoxy)but-1-en-4-one, 3, to 1,4-di(2-thienyl)-2-(3-cyanopropyl)butane-1,4-dione, 2. Compound **3** (1.300 g; 4.10 mmol) was dissolved in 10 ml of MeOH to which was added dropwise an aqueous solution of NaOH (0.656 g; 16.4 mmol) in 10 ml of dist. H$_2$O. This mixture was stirred at 65 °C for 3 h, after which time the mixture was allowed to cool to r.t. The reaction mixture was subsequently placed in an icebath and the solution neutralised with 50% aqueous H$_2$SO$_4$ (5 ml). The product was extracted with CH$_2$Cl$_2$ (3 × 20 ml) and the combined organic fractions were dried over MgSO$_4$. Column chromatography (SiO$_2$, CH$_2$Cl$_2$) gave pure **2** as an orange oil, 1.12 g (3.53 mmol; 86%).

3′-(3-Cyanopropyl)-2,2′:5′,2″-terthiophene, 4. A mixture consisting of compound **2** (0.350 g, 1.10 mmol), Lawesson's reagent (0.539 g, 1.32 mmol) and dry toluene (15 ml) was slowly heated and maintained at reflux for 6 h. The orange solution was allowed to cool down to r.t. and poured into 10 ml of H$_2$O. Extraction with Et$_2$O (3 × 15 ml), washing with H$_2$O, drying over MgSO$_4$ and concentration under reduced pressure provided a brown oil. Column chromatography (SiO$_2$, hexane–ethyl acetate (6 : 1)) gave **4** as a yellow solid, 0.284 g (0.9 mmol; 82%); mp 36 °C. Elemental analysis for C$_{16}$H$_{13}$NS$_3$: %Calc. C 60.92, H 4.15, N 4.44, S 30.49; %Found C 60.35, H 4.26, N 4.38, S 29.46; IR(KBr): $\nu = 3106–3070$, 2936, 2868, 2246 cm^{-1}; ^{1}H-NMR: (400 MHz; CDCl$_3$) $\delta = 2.03$ (tt, $J = 7.3$, 7.6 Hz, 2H, $–CH_2–CH_2–CH_2–$); 2.38 (t, $J = 7.3$ Hz, 2H, $–CH_2–CN$); 2.92 (t, $J = 7.6$ Hz, 2H, $CH_2–CH_2–CH_2–CN$); 6.99 (s, 1H, *H*-4); 7.02 (dd, $J_{4',3'} = 3.7$ Hz, $J_{4',5'} = 5.2$ Hz, 1H, *H*-4′); 7.08 (dd, $J_{4'',3''} = 3.7$ Hz, $J_{4'',5''} = 5.2$ Hz, 1H, *H*-4″); 7.13 (dd, $J_{3'',5''} = 1.2$ Hz, $J_{3'',4''} = 3.7$ Hz, 1H, *H*-3″); 7.16 (dd, $J_{3',5'} = 1.2$ Hz, $J_{3',4'} = 3.7$ Hz, 1H, *H*-3′); 7.28 (dd, $J_{5',3'} = 1.2$ Hz, $J_{5',4'} = 5.2$ Hz, 1H, *H*-5′); 7.33 (dd, $J_{5'',3''} = 1.2$ Hz, $J_{5'',4''} = 5.2$ Hz, 1H, H-5″); ^{13}C-NMR: (400 MHz; CDCl$_3$) $\delta = 16.79$ ($–CH_2–CN$); 26.13 ($CH_2–CH_2–CH_2–CN$); 27.98 ($–CH_2–CH_2–CH_2–CN$); 119.33 ($CH_2–CN$), 123.94 (*C*-3′); 124.76 (*C*-5′); 125.88 (*C*-4); 125.92 (*C*-5″); 126.47 (*C*-3″); 127.69 (*C*-4′); 127.97 (*C*-4″);130.72 (*C*-3); 135.0; 136.11; 136.73, 137.09 (*C*-2′, *C*-2″, *C*-2, *C*-5); MS (ESI$^+$, eV): *m*/*z* = 316 ([M + H]$^+$, 49), 222, 204, 163, 133; UV–VIS (CH$_3$CN): $\lambda_{\max}$/nm (ε): 367 (17768); 275 (16035).

2,5-Di(2-thienyl)-3-(3-cyanopropyl)pyrrole, 5. To a solution of **2** (0.335 g; 1.06 mmol) in acetic acid (5 ml), NH$_4$OAc (0.82 g, 10.6 mmol) and acetic anhydride (0.26 ml; 2.77 mmol) were added dropwise at r.t. The bright orange solution was held at reflux with stirring for 48 h. It was then allowed to cool and poured into 100 ml of an aqueous Na$_2$CO$_3$ solution. Extraction with CH$_2$Cl$_2$ (3 × 15 ml), washing with H$_2$O, drying over MgSO$_4$ and concentration under reduced pressure provided a brown oil. Column chromatography (SiO$_2$, hexane–ethyl acetate (5 : 1)) gave **5** as a yellow crystalline powder 0.164 g (0.55 mmol; 52%); mp 113–114 °C. Elemental analysis for C$_{16}$H$_{14}$N$_2$S$_2$: %Calc. C 64.40, H 4.73, N 9.39, S 21.49; %Found C 64.40, H 4.76, N 9.21, S 21.17; IR(KBr): $\nu = 3332$, 3104–3071, 2933–2853, 2247 cm^{-1}; ^{1}H-NMR: (400 MHz; CDCl$_3$) $\delta = 1.97–2.04$ (tt, $J = 7.02$ Hz, $J = 7.32$ Hz, 2H, $–CH_2–CH_2–CH_2–$); 2.39 (t, $J = 7.32$ Hz, 2H, $–CH_2–CN$); 2.82 (t, $J = 7.02$ Hz, 2H, $CH_2–CH_2–CH_2–CN$); 6.31 (d, $J = 2.7$ Hz, 1H, H-4); 6.99 (dd, $J_{4',3'} = 3.7$ Hz, $J_{4',5'} = 5.2$ Hz, 1H, *H*-4′); 7.02–7.06 (3dd, 3H, *H*-4″, *H*-3′, *H*-3″); 7.13 (dd, $J_{5',3'} = 1.2$ Hz, $J_{5',4'} = 5.2$ Hz, 1H, *H*-5′); 7.22 (dd, $J_{5'',3''} = 1.2$ Hz, $J_{5',4'} = 5.2$ Hz, 1H, *H*-5″) 8.27 (s, broad, 1H, N- *H*); ^{13}C-NMR: (400 MHz; CDCl$_3$) $\delta = 17.66$ ($–CH_2–CN$); 26.49 ($CH_2–CH_2–CH_2–CN$); 27.38 ($–CH_2–CH_2–CH_2–CN$); 109.82 (*C*-4); 120.92 (*C*N); 122.24, 122.32, 124.14, 124.32 (*C*-3, *C*-3′, *C*-5′, *C*-3″); 124.71 (*C*-2′); 125.04 (*C*-5″); 127.84 (*C*-2″); 128.70; 128.86 (*C*-4′, *C*-4″); 135.46; 136.42 (*C*-2, *C*-5); MS (ESI$^+$, eV): *m*/*z* = 321 ([M + Na]$^+$, 100), 300 ([M + H]$^+$, 40), 275, 106; UV–VIS (CH$_3$CN): $\lambda_{\max}$/nm (ε): 370 (12315); 257 (9548).

2,5-Di(2-thienyl)-3-(3-cyanopropyl)furan, 6. Compound **2** (0.573 g; 1.81 mmol) was dissolved in 20 ml of dry acetic anhydride and cooled to 0 °C. Concentrated HCl (1 ml, 36%) was then added dropwise. The yellow solution was stirred at r.t. for 24 h. This mixture was poured onto ice and neutralised with an aqueous Na$_2$CO$_3$-solution. Extraction with CH$_2$Cl$_2$ (3 × 15 ml), washing with H$_2$O, drying over MgSO$_4$ and concentration under reduced pressure provided a brown oil. Column chromatography (SiO$_2$, hexane–ethyl acetate (5 : 1)) gave **6** as a brown oil 0.331 g (1.12 mmol; 62%). Elemental analysis for C$_{16}$H$_{13}$NOS$_2$: %Calc. C 64.18, H 4.38, N 4.68, S 21.42; %Found C 62.75, H 4.50, N 4.52, S 20.45; IR(KBr): $\nu = 3107–3075$, 2937, 2870, 2246 cm^{-1}; ^{1}H-NMR: (400 MHz; CDCl$_3$) $\delta = 2.02$ (tt, $J = 7.6$, 7.3 Hz, 2H, $–CH_2–CH_2–CH_2–$); 2.42 (t, $J = 7.3$ Hz, 2H, $–CH_2–CN$); 2.83 (t, $J = 60$ Hz, 2H, $CH_2–CH_2–CH_2–CN$); 6.46 (s, 1H, *H*-4); 7.05 (dd, $J_{4',3'} = 3.7$ Hz, $J_{4',5'} = 5.2$ Hz, 1H, *H*-4′); 7.09 (dd, $J_{4'',3''} = 3.7$ Hz, $J_{4'',5''} = 5.2$ Hz, 1H, *H*-4″); 7.24 (dd, $J_{5',3'} = 1.2$ Hz, $J_{5',4'} = 5.2$ Hz, 1H, *H*-5′); 7.28–7.30 (3dd, $J_{5',3'}$, 3H, *H*-3″, *H*-3′, *H*-5″); ^{13}C-NMR: (400 MHz; CDCl$_3$) $\delta = 16.71$ ($–CH_2–CN$); 24.58 ($CH_2–CH_2–CH_2–CN$); 25.41 ($–CH_2–CH_2–CH_2–CN$); 109.37 (*C*-4): 119.37 ($CH_2–CN$): 120.52 (*C*-3); 122.94, 123.52, 124.53, 124.56 (*C*-3′, *C*-3″, *C*-5′, *C*-5″); 127.63, 127.80 (*C*-4′, *C*-4″); 132.68, 133.13 (*C*-2′, *C*-2″), 144.42, 148.01 (*C*-2, *C*-5); MS (ESI$^+$, eV): *m*/*z* = 300 ([M + H]$^+$, 100); 194, 204, 223, 235, 158, 251; UV–VIS (CH$_3$CN): $\lambda_{\max}$/nm (ε): 367 (12045); 283 (12143).

3′-(4-Aminobutyl)-2,2′:5′,2″-terthiophene, 7. To a cooled, stirred suspension of lithium aluminium hydride (0.175 g; 4.6 mmol) in THF (25 ml), a solution of **4** (1.45 g; 4.6 mmol) in THF was added dropwise. The mixture was then stirred at r.t. for 6 h after which it was heated to reflux for a further 10 h and allowed to cool. Dist. H$_2$O (1 ml), 20% NaOH (1 ml) and again dist. H$_2$O (1 ml) were added successively. The brown mixture was filtered and the solution was dried over MgSO$_4$. The solvent was evaporated and orange oil remained. Kugelrohr distillation provided **7** as a yellow oil 1.19 g (3.72 mmol; 81%). Elemental analysis for C$_{16}$H$_{17}$NS$_3$: %Calc. C 60.15, H 5.36, N 4.38, S 30.11; %Found C 58.72, H 5.95, N 4.44, S 26.30; IR: $\nu = 3436–3289$, 3110–3068, 2929–2857 cm^{-1}; ^{1}H-NMR: (250 MHz; CDCl$_3$) $\delta = 1.37$ (s, broad, 2H, $–CH_2–NH_2$); 1.46–1.75 (2 tt, 4H, $–CH_2–CH_2–CH_2–CH_2–NH_2$); 2.71–2.78 (2t, 4H, $–CH_2–CH_2–CH_2–CH_2–NH_2$); 7.0 (dd, $J_{4',3'} = 3.7$ Hz, $J_{4',5'} = 5.2$ Hz, 1H, *H*-4′); 7.01 (s, 1H, *H*-4); 7.06 (dd, $J_{4'',3''} = 3.7$ Hz, $J_{4'',5''} = 5.2$ Hz, 1H, *H*-4″); 7.12 (dd, $J_{3'',5''} = 1.2$ Hz, $J_{3'',4''} = 3.7$ Hz, 1H, *H*-3″); 7.15 (dd, $J_{3',5'} = 1.2$ Hz, $J_{3',4'} = 3.7$ Hz, 1H, *H*-3′); 7.20 (dd, $J_{5',3'} = 1.2$ Hz, $J_{5',4'} = 5.2$ Hz, 1H, *H*-5′); 7.30 (dd, $J_{5'',3''} = 1.2$ Hz, $J_{5'',4''} = 5.2$ Hz, 1H, *H*-5″); ^{13}C-NMR: (400 MHz; CDCl$_3$) $\delta = 28.90$ ($CH_2–CH_2–CH_2–NH_2$); 30.13 ($–CH_2–CH_2–CH_2–CH_2–NH_2$); 34.61 ($–CH_2–CH_2–NH_2$); 43.05 ($–CH_2–NH_2$); 124.66 (*C*-3′);

125.43 (*C*-5′); 126.47 (*C*-4); 127.01 (*C*-5″); 127.44 (*C*-3″); 128.51 (*C*-4′); 128.90 (*C*-4″); 130.74 (*C*-3); 136.33; 136.79; 138.18, 140.89 (*C*-2′, *C*-2″, *C*-2, *C*-5); MS (ESI^+, eV): $m/z = 320$ ($[M+H]^+$, 100); 362, 348, 334, 304; UV–VIS (CH_3CN): λ_{max}/nm (ε): 379 (17992), 275 (shoulder).

2.3 Electrochemical polymerisation

Electrochemical polymerisation of acetonitrile solutions containing **4**, **5**, or **6** with 0.1 M $[NBu_4][BF_4]$ was performed both under galvanostatic control, at a constant current of *ca.* 0.1 mA cm^{-2}, and by potentiostatic control, at $E \approx +0.8$ V *versus* the ferrocenium|ferrocene ($Fc^+|Fc$) couple referenced internally. Gold foil (1.5 cm^2), Pt (0.03 cm^2), and glassy carbon (0.07 cm^2) disks were used as electrode substrates and the solutions were thoroughly degassed with Ar prior to polymerisation. During galvanostatic polymerisations particular care was taken to ensure the applied potential did not rise sufficiently high so as to cause over oxidation of the polymer film (typically the potential was not allowed to rise above +1.0 V *versus* $Fc^+|Fc$). All electrochemical procedures were carried out on an E.G.&G. M263A potentiostat/galvanostat driven by the M270 software package.

3 Results and discussion

Compounds **4**, **5**, and **6** were synthesised using the strategy presented in Scheme 1. The cyanopropyl moiety was chosen as a substituent because the terminal nitrile group is versatile, being readily transformed to an amine by reduction or facilitating carbonyl chemistry by hydrolysis. In addition 3-bromobutyronitrile, and other bromoalkyl nitriles, are commercially available and the bromine atom of this molecule is easily substituted by the nucleophilic attack from the lone pair of the carbanion generated by reaction of 1,4-bis(2-thienyl)butane-1,4-dione, **1**, with a strong base. Consequently our strategy is based on the synthesis of 1,4-bis(2-thienyl)-2-(3-cyanopropyl)butane-1,4-dione, **2**, Scheme 1. This molecule is then converted *via* ring closure reactions to the terthiophene **4** and dithienyl derivatives **5** and **6**, all of which are, to our knowledge, new compounds. Importantly, this approach provides a flexible route to a range of heterocyclic polymer precursors because the cyanoalkyl functionality is grafted to the diketone before ring closure. A similar route has been exemplified in the alkylation reactions of **1** in a previous report,[17] however, incorporation of another functionality *e.g.*, at the end of a flexible alkyl chain, can result in unwanted cyclisation reactions associated with the relative acidity of the methylene protons adjacent to the functional group. In other examples the nitrile group has been grafted directly onto a terthiophene system,[24] this has been achieved by substitution of the corresponding bromoterthiophene and so is less attractive as a general strategy. Consequently our results, described here, represent a useful and significant advance in the convenient synthesis of functionalised copolymer precursors.

3.1 Synthesis and characterisation of oligomers

The precursor 1,4-bis(2-thienyl)butane-1,4-dione, **1**, Scheme 1, was prepared in high yield by the literature method.[25,26] Treatment of **1** with NaH and 4-bromobutyronitrile in THF gave a mixture of compounds **2** and **3**, rather than a cyclic adduct such as those formed during a Thorpe-type reaction. Although the ratio of **2** and **3** in the reaction mixture was variable and sensitive to solvent and other conditions, the compounds were isolated by column chromatography and characterised individually (63% **2**, 26% **3**, experimental yields in a typical example). These structures were assigned on the basis of ^1H NMR (400 MHz), ^{13}C NMR, mass spectrometry and FT-IR data. For example ^1H NMR spectra of compounds **2**, **3**, **6** are shown in Fig. 1. In addition to the protons of the thiophene ring systems the ^1H NMR spectrum of molecule **3** (Fig. 1a) showed a symmetrical A–X spin system featuring a triplet at 6.30 ppm (1H) and the corresponding doublet at

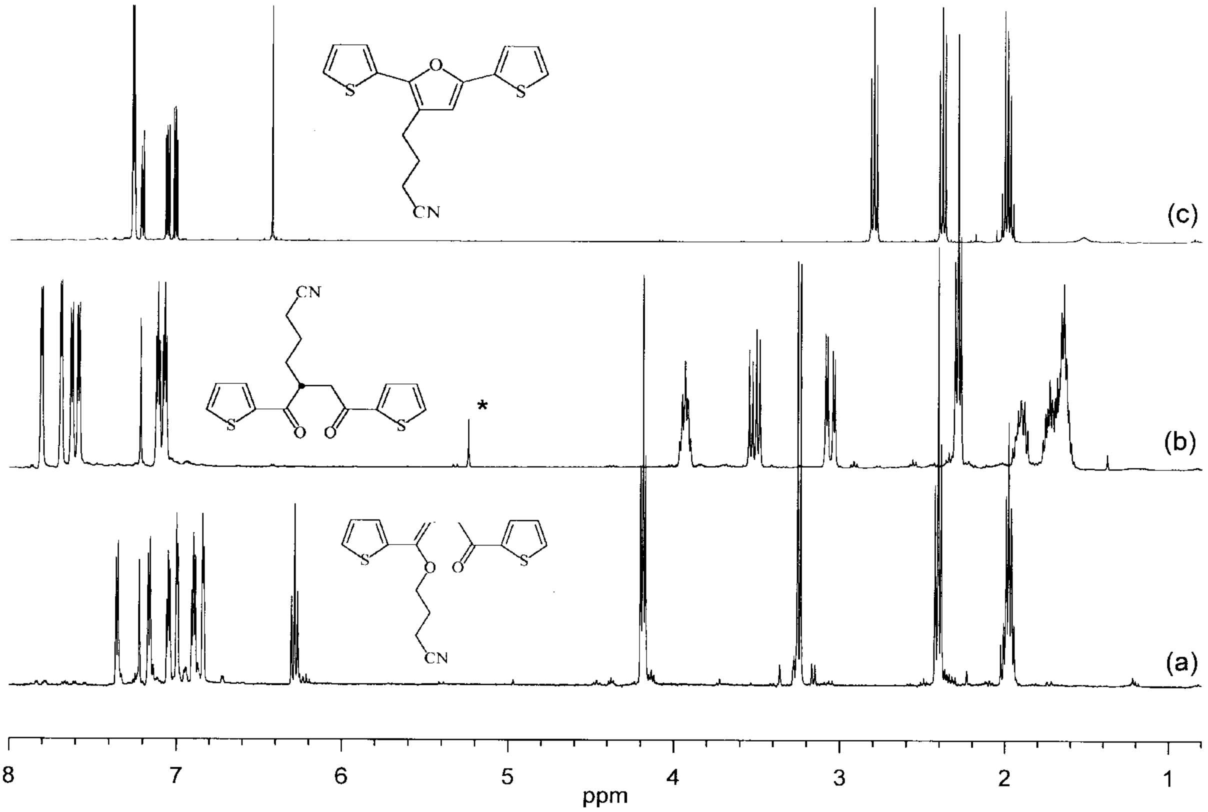


Fig. 1 ^1H NMR spectra of molecules; (a) **3**, (b) **2**, and (c) **6**, recorded at 400 MHz in $CDCl_3$ and referenced using TMS. The asterix indicates solvent impurities.

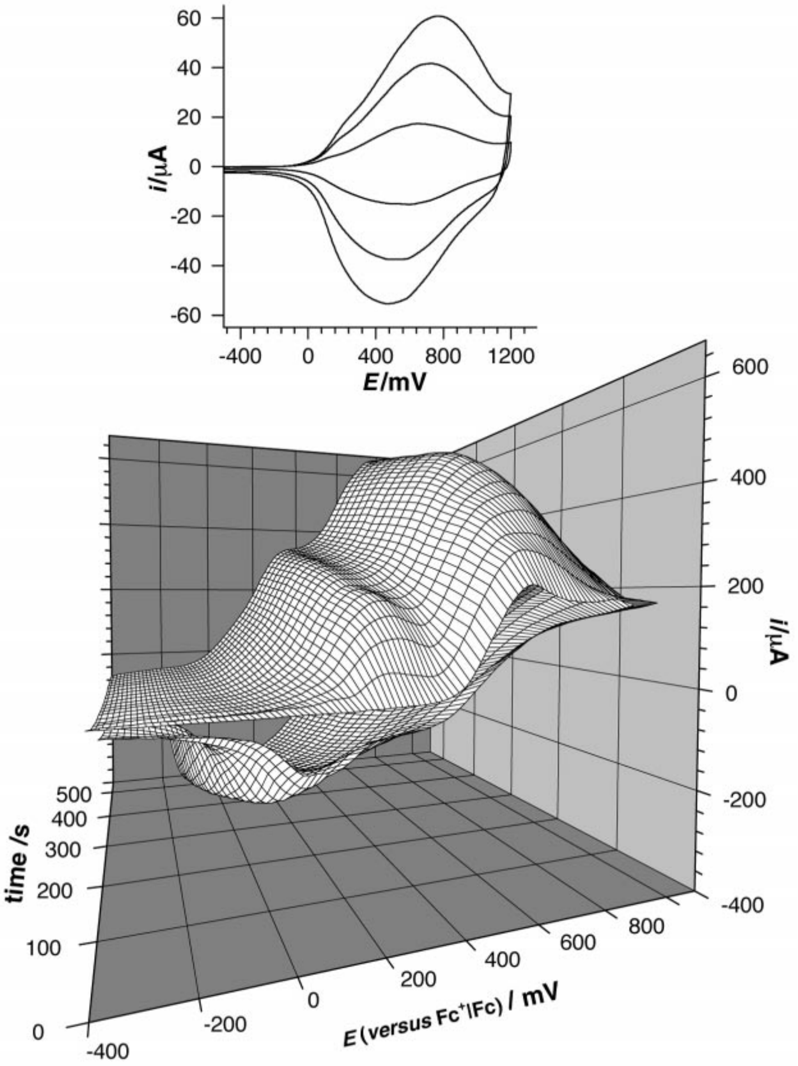


Fig. 2 Cyclic voltammogram of molecule **5** in 0.1 M $[NBu_4][BF_4]$/MeCN at a 2 mm Pt disk electrode and referenced internally using ferrocenium/ferrocene ($Fc^+|Fc$) couple. CV shows polymerisation over 20 voltammetric cycles at a potential scan rate, $v = 100$ mV s^{-1}. The polymer coated electrode was subsequently removed from the solution, rinsed and the voltammogram was recorded in fresh electrolyte solution ($v = 20$, 50, and 75 mV s^{-1}), as shown in the insert.

3.25 ppm (2H) which we assign to the three protons of the allyl moiety. The appropriate features of the alkyl nitrile substituent were also clearly visible with the protons on the C atom attached to the O of the enol ether showing a triplet resonance at 4.20 ppm (2H). Spectral data from ^{13}C, and 2D shift correlation experiments were also consistent with these assignments. On the other hand the ^1H NMR spectrum of **2** (Fig. 1b) revealed a non-symmetrical structure showing an A–B–X spin system with a multiplet resonance at 3.9 ppm (1H) which we assign to the single proton attached to the stereogenic carbon. The corresponding signals for the two protons of the methylene group adjacent to the other carbonyl group appeared as two separate resonances, each a doublet of doublets, at 3.06 and 3.56 ppm (2H). The latter is consistent with the presence of a stereogenic centre in the cyanopropyl substituted thienyl diketone. Molecules **2** and **3** exhibited *m*/*z* peaks at 318 and 340 derived from the parent ion $[M + H^+]$ and $[M + Na^+]$, respectively, in the electrospray ionisation mass spectrum.

Although the yield of **2** from the first step of the synthetic Scheme 1 is apparently low, treatment of the other major product of this reaction, enol ether **3**, with aqueous sodium hydroxide resulted in essentially quantitative conversion to the desired compound **2**. This improved the isolated yield of the functionalised diketone, **2**, to 85%. The mechanism of this isomerisation, a formal analogue of the Chapman rearrangement of aromatic imino ethers, is uncertain. An intramolecular nucleophilic attack by the enolate carbon derived from the remaining carbonyl in **3** at the oxygen bearing carbon of the cyanopropyl group is precluded since in this endocyclic process the three relevant atoms can not become collinear.[27,28] An intermolecular counterpart is however in order.

Ring closure of the functionalised diketone to the terthiophene, **4**, dithienyl pyrrole, **5**, or dithienylfuran, **6**, was achieved by treatment of **2** with Lawesson's reagent, ammonium acetate, or HCl–acetic anhydride, respectively, in a manner consistent with earlier reports, Scheme 1.[17,25,26,29] In all cases experimental yields were generally good. Spectral data from NMR, FT-IR, and mass spectrometry were consistent with the assigned structures, for example carbonyl stretches in the infrared spectrum associated with the ketone groups of **1** and **2** were absent in the FT-IR spectra of **4**, **5**, and **6**. The nitrile stretching band was also clearly visible in the FT-IR spectrum of molecules **2–6** at 2246–2248 cm^{-1}. The ^1H NMR spectrum of **6** is shown in Fig. 1c, and is again consistent with formulation. In addition, peaks at $m/z = 316$, 321, and 300 derived from the molecular ions of **4** $[M + H^+]$, **5** $[M + Na^+]$, and **6** $[M + H^+]$, respectively, were located in the electrospray ionisation mass spectra. To our knowledge there are no previous reports of the synthesis of compounds **2–6**. Further-

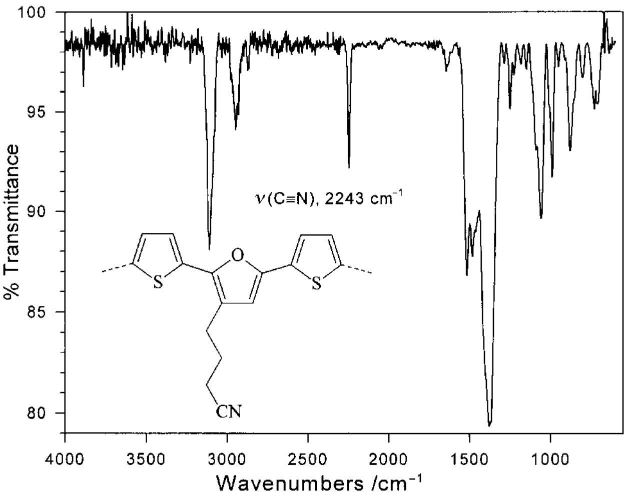


Fig. 3 FT-IR spectrum of poly(**6**) (thin film, *ca.* 0.5 μm) supported on a Au coated SiO$_2$ electrode. The spectrum was recorded in air using a 45° reflectance accessory at a resolution of 4 cm^{-1}.

more, to emphasise the synthetic utility of this scheme the amino derivative, **7**, was also prepared as a pale yellow oil (after distillation) in high yield (81%) by reduction of **4** using LiAlH$_4$ in THF.

3.2 Electrochemical polymerisation

Compounds **4**, **5**, and **6** all underwent facile electrochemical polymerisation from degassed solutions of 0.1 M MeCN–[NBu$_4$][BF$_4$] on Pt, Au, and glassy carbon substrates at relatively low anodic potentials in excess of +0.8 V *versus* ferrocenium|ferrocene. Under galvanostatic conditions the compounds also gave thin films of insoluble polymer material. These films were brown–black in colour for the pyrrole and furan derivatives and pinkish red for the terthiophene. For example the potentiodynamic polymerisation of **5** by repetitive scan cyclic voltammetry is shown as a time resolved series in Fig. 2. The initial voltammetric scans of this series clearly show the irreversible anodic wave corresponding to oxidation of the three-unit system. The polymer coated electrode was removed from the polymerisation solution and rinsed with freshly distilled MeCN. Subsequent examination, by cyclic voltammetry, in fresh electrolyte solution showed typical anodic cathodic waves associated with doping and de-doping processes of the conducting polymer electrode, Fig. 2 (insert). The peak current of the anodic wave showed a linear dependence on potential scan rate, at moderate potential scan rates ($\nu < 150$ mV s^{-1}), consistent with the redox process of a surface confined species. In separate chronoamperometric potentiostatic experiments the polymerisation yields for compounds **4**, **5**, and **6** were estimated at 50–60% based on coulometric

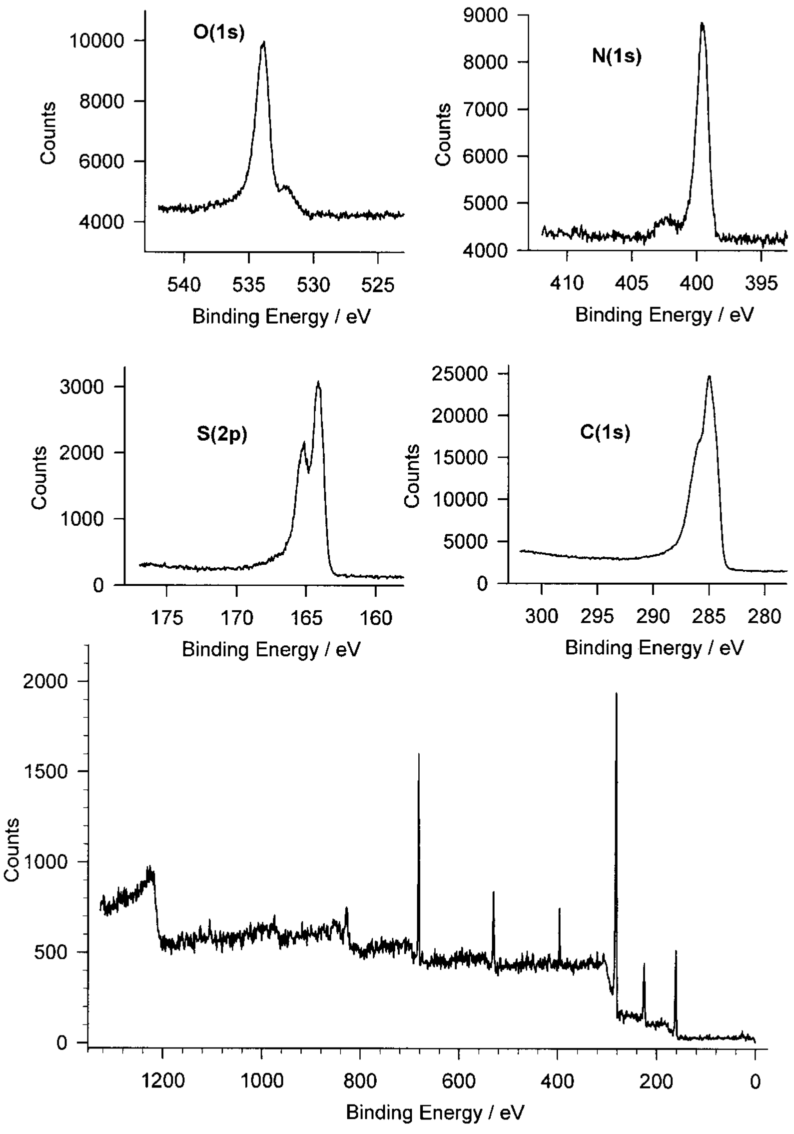


Fig. 4 X-ray photoelectron spectra of poly(**6**) (thin film, *ca.* 0.5 μm) supported on a Au coated SiO$_2$ electrode recorded using a slit width of 0.8 mm and a take off angle of 90°.

measurements.§ This is a relatively poor polymer yield and suggests the formation of low molecular weight polymer fragments. Alternatively the low yield of polymer material at the electrode surface may be indicative of high solubility in the cyanopropyl substituted copolymers. This hypothesis, whilst not substantiated by any physical measurements reported here, is consistent with observations reported recently for similar oligomers substituted with alkyl chains.[17] Electrochemical polymerisation of the aminobutyl terthiophene derivative, **7**, was also successful, however in accordance with observations on amino derivatised pyrroles,[30] a proton source (*e.g.* $Et_2O{\cdot}HBF_4$) was necessary in order to prevent inhibition of the polymerisation reaction by the nitrogen lone pair of the amino group.

3.3 Polymer characterisation

Analysis of polymer samples derived from compounds **4**, **5**, and **6** by reflectance FT-IR spectroscopy clearly showed the nitrile stretch at *ca.* 2243 cm^{-1} confirming the presence of the substituent functional group in the polymer material. A sample FT-IR spectrum for the polymer film derived from compound **6** is presented in Fig. 3. FT-IR spectra of poly(**7**) yielded no sign of the nitrile stretch but instead showed a characteristic band at 3500 cm^{-1} assigned to the N–H stretch. The polymer materials were also examined using X-ray photoelectron spectroscopy. The survey spectrum for poly(**6**) together with inserts for the S(2p), N(1s), and O(1s) spectral regions are presented in Fig. 4. These spectra clearly show the presence of the component elements in the polymer samples. Subsequently quantitative elemental analysis of the polymer samples was achieved by integration of the peak intensities of the S(2p), N(1s) and O(1s) regions of the spectrum. These data are summarised in Table 1. Examination of the data in Table 1 shows, for example, an S : N : O elemental ratio of 2 : 1.07 : 0.96 for poly(**6**), and an S : N ratio of 1 : 1.02 for poly(**5**). These data and the similar comparisons for poly(**4**) and poly(**7**) are consistent with the structural assignment based on their parent oligomers. Elemental ratios determined by integration of the C(1s) spectral region did not give reliable quantitative data. This was presumably due to sample contamination by surface adsorption of airborne species during sample transfer.

The C(1s) regions of the X-ray photoelectron spectra of poly(**4**) and poly(**7**) samples are presented in Fig. 5. The spectrum of poly(**4**), Fig. 5a, clearly shows a high energy shoulder at 286.3 eV in addition to the intense signal at 285 eV. This feature is consistent with the presence of the nitrile C atom of the polymer substituent. However, in the spectrum of the polymer derived from the reduced amino species, poly(**7**), Fig. 5b, this high energy shoulder is absent. These observations are consistent with the absence of the nitrile functionality in the polymer derived from **7**.

Table 1 Relative integrated signal intensity for the S(2p), N(1s), and O(1s) regions of the X-ray photoelectron spectrum. The relative signal intensity is expressed as a weighted percentage of the total signal intensity collected for each sample

Polymer sample	Relative %S	Relative %N	Relative %O
4 Thiophene nitrile	13.4	4.3	—
5 Pyrrole nitrile	8.6	8.8	—
6 Furan nitrile	8.8	4.7	4.2
7 Thiophene amine	12.5	4.5	—

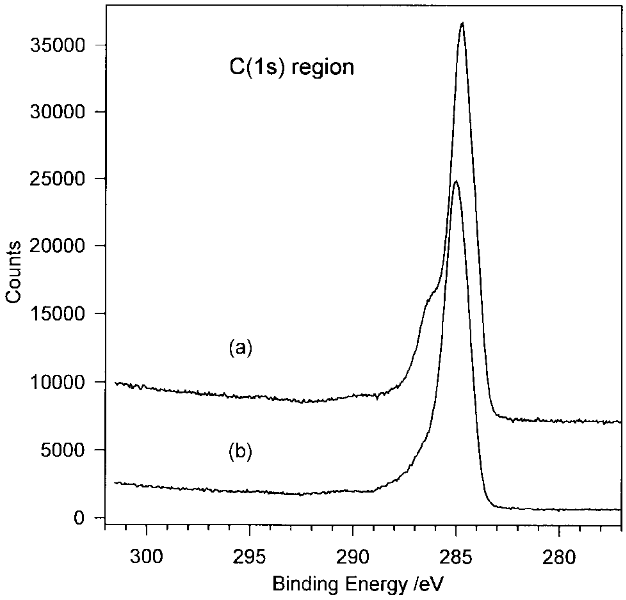


Fig. 5 X-Ray photoelectron spectra of the C(1s) region of: (a) poly(**4**) with nitrile functionality, and (b) poly(**7**) with amine functionality. The spectra were recorded for thin films (*ca.* 0.5 μm) supported on a Au coated SiO_2 electrode using a slit width of 0.8 mm and a take off angle of 90°.

4 Conclusions

In conclusion we have developed a facile methodology for the convenient synthesis of functionalised thienyl pyrrole, furan and terthiophene derivatives as precursors to fixed-ratio polymeric organic conductors. In addition, all new molecules underwent rapid anodic electropolymerisation. Our results are significant because synthesis of mixed heterocyclic species is often the rate limiting step in the development of specific materials for practical applications. Currently no such methodology exists beyond those that involve coupling reactions of substituted and unsubstituted monomeric species. These methods require specialised facilities, anaerobic conditions, often involve unstable intermediates and generally offer poor yields. To our knowledge all the species described here are new (apart from compound **1**) and in particular we know of no previous reports describing the synthesis and characterisation and polymerisation of functionalised thienyl furans.

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§The polymerisation efficiency was estimated by taking the ratio of charge required to fully dope the polymer coated electrode to the integrated current–time curve recorded during polymerisation. This is weighted for a maximum polymer doping level of 1 positive charge to 3–4 ring units.

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