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Synthesis of extended α,α′-oligo(silylthiophenes) by cerium(IV) oxidative coupling reactions

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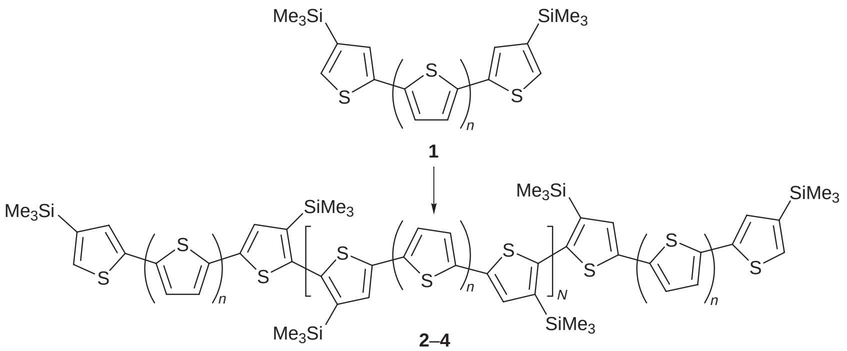
Cerium(IV) oxidative dimerisations of 4,4′-bis(trimethylsilyl)-2,2′:5′,2″-terthiophene and the quaterthienyl analogue 1c gave the corresponding sexi- and octi-thiophenes; the latter have been used to prepare α-linked hexadecithiophene and tetracosithiophene derivatives.

The extreme insolubility of extended oligothiophenes renders purification and spectral analysis increasingly difficult for unsubstituted systems containing more than six α-linked thiophene units. Only two literature citations can be found for oligomers beyond octithiophene, namely decithiophene, obtained by electrochemical oxidation of quinquithiophene and characterised by absorption spectra in the solid state,[1] and dodecithiophene, identified as an impurity in crude samples of octithiophene by mass spectroscopy.[2] Oligo(alkylthiophenes) bearing long-chain β-substituents are much more soluble, and derivatives containing up to sixteen rings have been characterised.[3–5] The longest of these, an octadodecylhexadecithiophene, was obtained in 19% yield after coupling of the corresponding lithiooctithiophene with $CuCl_2$.[5] We reasoned that silylated oligomers should be soluble enough to aid purification and, *via* electrophilic displacement of silicon, subsequently afford straightforward access to the unsubstituted analogues and other derivatives required for physical studies. We describe here our results to date, culminating in the isolation of the twentyfour-ring dodecakis(trimethylsilyl)tetracosithiophene **4d**, the longest oligomer yet reported.

We obtained β,β-disilylated thiophenes **1b–e**† by the $NiCl_2$(dppp)-catalysed couplings[6] of 2 equiv. of the Grignard reagent prepared from 2-bromo-4-trimethylsilylthiophene‡ with 2,5-dibromothiophene, 5,5′-dibromo-2,2′-bithiophene, 5,5′-dibromo-2,2′:5′,2″-terthiophene and 5,5‴-dibromo-2,2′:5′,2″:5″,2‴-quaterthiophene,‡ respectively. The yields increase on moving from **1b** to the quinquithienyl **1d**, but the very low solubility of both the sexithienyl **1e** and the dibromoquaterthienyl precursor rendered this route impractical for the preparation of oligomers containing more than five rings.

To circumvent this problem we turned our attention to coupling the readily-soluble quaterthienyl **1c**. We were encouraged by the observation that aged thin-layer chromatograms of **1c** showed progressive formation of a lower R_f component on re-elution. This was attributed (and subsequently confirmed by comparison with pure samples) to photooxidation of **1c** to the dimer **4a** on the silica surface. A reaction of **1c** with ceric ammonium nitrate gave moderate yields (*ca.* 15%) of **4a**, the major product being 3,4‴-bis(trimethylsilyl)-5-nitro-2,2′:5′,2″:5″,2‴-quaterthiophene (43%). When using ceric ammonium sulfate as the oxidising agent the octithiophene **4a** was isolated in up to 66% yield,§ with varying amounts of the dodecithiophene **4b** (4–7%) and hexadecithiophene **4c** (0.5–2%) as byproducts (Scheme 1). The high yield of dimer obtained under these conditions is surprising, bearing in mind that oxidation potentials for these systems should be inversely related to the size of the oligomer.[6,7] Cerium(IV) sulfate oxidations were more rapid, but the relative proportions of **4b**,**c** and other higher molecular weight products increased with respect to **4a**. The oligomers **4a–c** are bright yellow crystalline solids which exhibit intense greenish fluorescence in dilute solution. The UV–VIS absorption spectra show only a small bathochromic shift on moving from **1c** (λ_{max} 389 nm) to **4c** (λ_{max} 419 nm), in contrast to the n-dodecyl derivatives,[5] which move from yellow (λ_{max} 379 nm) to violet (λ_{max} 464 nm) along the same sequence. In our series, the closer proximity of the bulky silyl substituents to the point of coupling presumably leads to a higher degree of twisting about every fourth α,α′-linkage, reducing through-conjugation. This may be fortuitous—levelling the oxidation potentials of these systems and hence suppressing their tendency to polymerise.

Coupling of the terthiophene **1b** under conditions as described above gave the sexithiophene **3a** (48% yield) and the nonithiophene **3b** (11%) as major products,¶ along with higher oligomers. This reaction proved more sluggish than that above, probably as a consequence of the higher energy of the terthienyl cation radical intermediate. A reaction of 4-trimethylsilyl-2,2′:5′,2″-terthiophene resulted in coupling in even lower yield



1a $n = 0$
b $n = 1$ (42%)
c $n = 2$ (83%)
d $n = 3$ (94%)
e $n = 4$ (8%)

2 $n = 0, N = 0$

3a $n = 1, N = 0$
b $n = 1, N = 1$

4a $n = 2, N = 0$
b $n = 2, N = 1$
c $n = 2, N = 2$
d $n = 2, N = 4$
e $n = 2, N = 6$

Scheme 1

(8%), between the two α-positions adjacent to the β-silyl group; the sexithiophene **1e** and its 4,3′′′-disilyl isomer were not detected. These observations are in line with a recent study on the stabilising effect of progressive β-methylation on cation radicals derived from 5,5′-dimethyl-2,2′-bithiophene.[8] Attempts to dimerise 4,4′-bis(trimethylsilyl)-2,2′-bithiophene **1a** to **2** in like manner resulted in quantitative recovery of the starting material.

The octithiophene **4a** oligomerised on reaction with cerium(IV) sulfate in 1,2-dichloroethane at room temperature to give the sexadecithiophene **4c** (35% yield), the tetracosithiophene **4d** (11%), and a mixture of higher oligomers (*ca*. 20%) after column chromatography on silica. The dotriacontithiophene **4e** appears to be the major constituent of the residue, corroborated by TLC studies of dimerisation attempts using **4c**, but we have not yet been able to isolate pure samples. The relative insolubility of the higher oligomers of **4** has prevented preparative separation by chromatography, while the more soluble analogues **3** are not satisfactorily resolved beyond **3b**. We anticipate that replacement of either or both trimethylsilyl substituents in **1c** by more lipophilic alkylsilyl groups should circumvent this problem and ultimately, *via* protodesilylation, enable preparation of the parent systems. Preliminary studies indicate that compounds **3a** and **4a** give quantitative yields of analytically pure sexithiophene and octithiophene respectively, on treatment with TFA in CH_2Cl_2.

Notes and references

† New compounds have been characterised by spectroscopic and microanalytical data.

‡ Prepared by bromination of the appropriate disilyl derivative: NBS, aq. THF, 0 °C.

§ Preparation of **4a**: Finely ground cerium ammonium sulfate (10.5 g) was added in portions over *ca*. 6 h to a stirred solution of **1c** (3.0 g) in C_6H_6 (40 cm^3). The resulting suspension was stirred at room temperature for *ca*. 30 h, the solvent removed under reduced pressure, and the solid residue extracted with pentane (100 cm^3). The extract was chromatographed directly on silica (the column should be shielded from light) eluting with pentane to give unreacted **1c** (0.72 g). Further eulution with 4% CH_2Cl_2 in pentane gave **4a** (1.87 g, 62%, 82% based on consumed **1c**), bright yellow crystals, mp 147–149 °C (Found: C, 55.9; H, 5.3. $C_{44}H_{50}S_8Si_4$ requires C, 55.8; H, 5.3%); δ_H(250 MHz, $CDCl_3$) 7.29 (2 H, d, α-H, A,H-rings), 7.20 (2 H, d, β-H, A,H-rings), 7.13 (2 H, s, D,E-rings), 7.08 (8 H, m, B,C,F,G-rings), 0.29 (18 H, s, $SiMe_3$, A,H-rings), 0.17 (18 H, s, $SiMe_3$, D,E-rings); δ_C 130.8, 129.3, 128.3, 124.7, 124.6, 124.3, 124.2 (C-H), 143.7, 143.2, 140.6, 137.9, 137.8, 136.4, 136.1, 135.8, 135.6 (quaternary carbons), 0.6, −0.7 (CH_3); *m/z* (LSI) 947 $(M + 1)^+$ (100%). Further gradient elution up to 25% CH_2Cl_2 in pentane gave **4b** (125 mg, 4%), followed by **4c** (14 mg, 0.5%) and a mixture of higher oligomers (15 mg).

¶ The yields for coupling reactions of **1b** and **4a** have not been optimised, and do not take into account recovery of the precursors.

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