Persistent thiophene cation radicals

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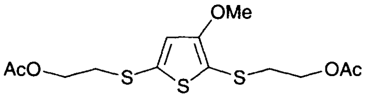
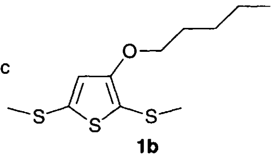
Persistent 3-alkoxy-2,5-bis(alkylthio)thiophene cation radicals are identified by CV, UV–VIS, and EPR spectroscopy in hexafluoropropan-2-ol.

α-Oligothiophenes (oligo-2,5-thienylenes) are receiving considerable attention as models for conducting polythiophenes[1–8] and as materials for electronics and electrooptics.[9] A particular aspect of central interest has been the stability, spectra, aggregation and solid state conductivity of cation radicals and dications of oligothiophenes. Several sets of oxidized oligomers (up to a 16-mer) have been characterized.[1–8] Until now, however, terthiophenes are the smallest oligothiophenes to have spectroscopically characterized cation radicals. For example, we found that the methyl end-capped, methoxy-substituted terthiophene **3a** formed a cation radical sufficiently stable in methylene chloride to record spectra at room temperature, but that the corresponding bithiophene **2a** was only stable for about a minute.[1c] The isomeric terthiophene **3b** was completely unstable due to reaction on the terminal methyl group.[1e] In the present study alkylthio groups replace the terminal methyl groups. This substitution led to substantially increased cation radical stability and enabled the observation of not only bithiophene, but 'monothiophene' cation radicals.

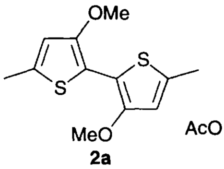
The present study began with the synthesis of several oligomers terminated with hydroxyethylthio or acetoxyethylthio groups that were of use in the preparation of conducting polyesters containing oligothiophene units as isolated conducting entities.[10] Electrochemical studies eventually led us to investigate the bis(acetoxyethylthio)bithiophene **2b** and then the analogous thiophenes **1a** and **1b**. The synthesis of **1a**, **1b** and **2b** was accomplished as shown below following procedures that have been previously reported for similar compounds.[10–11] A full report on the synthesis and characterization will follow.[12] Cyclic voltammetry (CV) at a glassy carbon electrode in methylene chloride or 1,1,1,3,3,3-hexafluoropropan-2-ol[13] containing 0.1 mol dm^{-3} Bu_4NPF_6 gave one reversible (60 mV peak separation and E_p independent of sweep rate) couple for **1a**, **1b** and two reversible couples for **2b** as shown in Table 1.



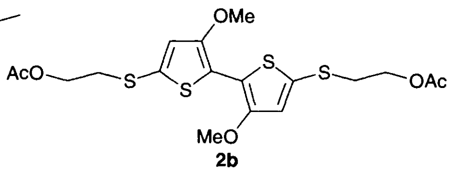
1a



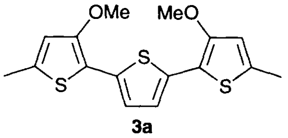
1b



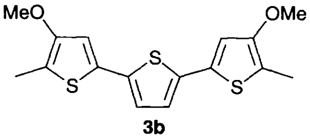
2a



2b



3a



3b

These voltammograms suggested that the cation radicals **1a**$^+$, **1b**$^+$ and **2b**$^+$ were stable on the CV time scale of 10 mV s^{-1}.

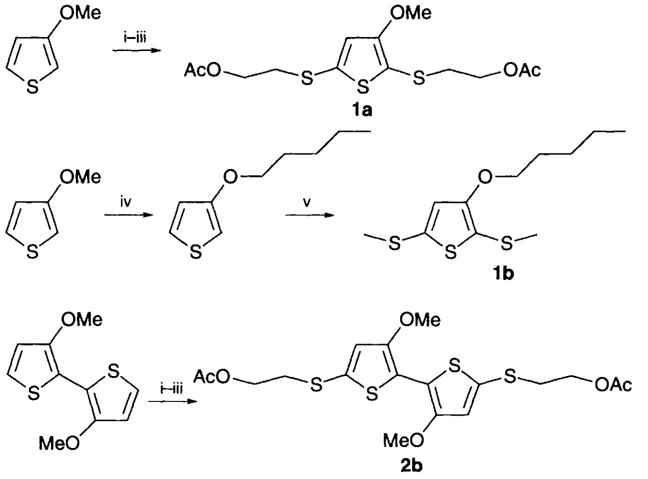
Spectroscopic attempts to confirm this stability were only marginally successful when methylene chloride was employed as solvent. Following a suggestion from Professor Lennart Eberson we turned to 1,1,1,3,3,3-hexafluoropropan-2-ol.[13] When this solvent (unpurified, but degassed with argon) was employed with the oxidant $NOPF_6$ it was possible to measure the EPR and optical spectra of the three cation radicals. The decay of spectral intensity with time showed that **1a**$^+$ and **1b**$^+$ have half lives of several hours and 30 min, respectively. The spectra of **2b**$^+$ were unchanged after 24 h.

The EPR spectrum of **1a**$^+$ [Fig. 1(*a*)] showed ten lines and was analysed as resulting from coupling with one hydrogen (attached to the 4-position) with a_H = 4 G and seven hydrogens (three methoxy and four thiomethylene) with a_H approximately 2 G. The accidental equivalence (the lines are rather broad consistent with approximate equivalence) of the a_H values for the three different types of hydrogens is reasonable since a Huckel calculation shows similar coefficients on the three ring positions. Consistent with this assignment was the twelve line (with broadening) spectrum of **1b**$^+$ [Fig. 1(*b*)]. This radical has one ring hydrogen, again assigned a 4 G a_H, and eight (two methyleneoxy and six thiomethyl) almost equivalent hydrogens with a_H = 2 G.

Table 1 Cyclic voltammetry in hexafluoropropan-2-ol, 0.1 mol dm^{-3} Bu_4NPF_6[a]

Compounds	$E_1{}^0$/V	$E_2{}^p$/V
1a	0.79	1.51 (irrev)
1b	0.53	1.33 (irrev)
2b	0.36	0.79[b] (rev)

[a] Glassy carbon electrode, V = 20 mV s^{-1}, SCE ref. (E^0 for ferrocene–ferricenium = 0.12 V). [b] E^0 = 0.76 V.



Scheme 1 *Reagents and conditions*: i, butyllithium, sulfur powder; ii, 2-bromoethanol; iii, DMAP, AcCl; iv, pentanol, $KHSO_4$, toluene; v, butyllithium, MeSSMe

The optical spectrum of **1a**$^+$ in either methylene chloride or hexafluoropropan-2-ol had bands at 410 and 550 nm. The bithiophene cation radical **2b**$^+$ showed bands at 505 and 730 nm. The terthiophene **3a**$^+$ had bands at 580 and 890 nm. Thus, the new cation radicals show two π–π^* bands as previously observed for larger oligomers,[1–8] one corresponding to HOMO–SOMO and the other to SOMO–LUMO, but shifted to shorter wavelengths as expected. These new data allow a further correlation of the reciprocal of oligomer size with π–π^* transition energies as illustrated in Fig. 2. The figure correlates data taken for 31 different oligomers, ignoring the fact that they are substituted with different alkyl and alkoxy groups. There is a reasonable linear correlation (r > 0.97), with the exception of the new, small, thio-substituted oligomers. The transition energies for these compounds are smaller than expected from the correlation. The donor, alkylthio substituents extend the conjugation of these small oligomers significantly, stablizing the excited states.

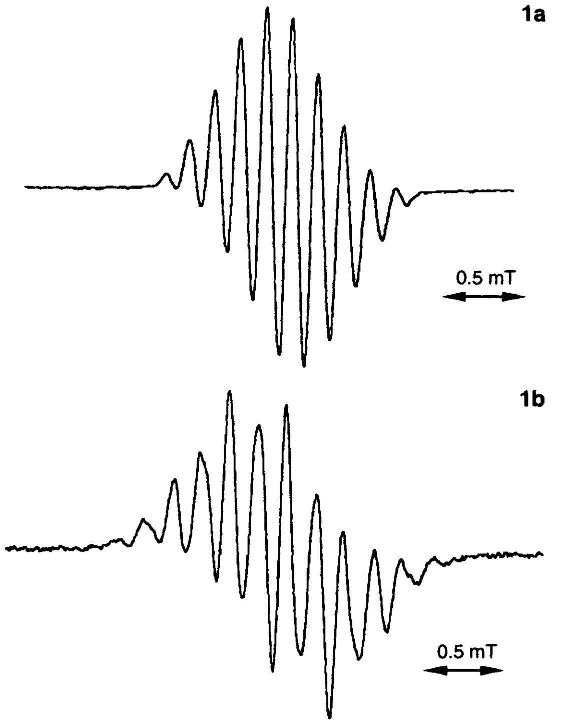


Fig. 1 EPR spectra for **1a**$^+$ and **1b**$^+$, approximately 2 mmol dm^{-3} in hexafluoropropan-2-ol

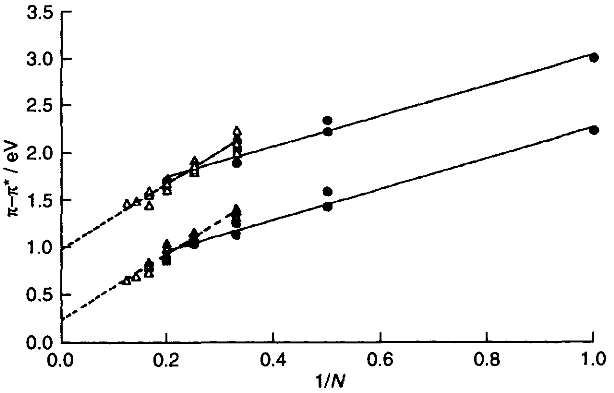


Fig. 2 Correlation of π–π^* transition energies of cation radicals with oligomer size, where N is the number of thiophene rings in oligothiophenes. Filled circles are those from alkylthio substituted oligomers and unfilled triangles are those from the rest. r > 0.97 for all four lines. Data from refs. 1–8.

The utility of hexafluoropropan-2-ol in these studies led us to briefly reexamine the oxidation of **3b** using NOPF$_6$ in this solvent. The oxidant reacted immediately, but generated decomposition products, not a stable cation radical.

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