

Novel Substituted Poly(benzo[*c*]thiophenes); Controlling the n- and p-Doping Potentials

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Methyl-, chloro- and fluoro-substitution in the C₆ ring has little effect on the oxidation of polybenzo[*c*]thiophene films to the p-doped conducting form, but has a marked effect on reduction to the n-doped form: poly(5,6-dichlorobenzo[*c*]thiophene) is n-doped at $E < -0.35$ V (SCE).

The electrochemical cycling of polyheterocycle-modified electrodes between the neutral, insulating, and cationic (p-doped), conducting forms has been the subject of innumerable studies in the last fifteen years.¹ In contrast, few examples of the reduction of polyheterocycles to the anionic (n-doped) conducting form have been studied.^{2,3} Conducting polymers switchable between anionic, neutral and cationic forms have potential as materials for novel types of molecular electronic devices. However, attempts to characterise n-doped polyheterocycle materials have been restricted to date by the very negative potential usually required, which makes the n-doped polymer highly reactive. There is a direct correlation between the band gap of a conducting polymer and the difference between onset potentials for p-doping and n-doping. Most n-doping studies have featured polythiophenes, which generally become p-doped at $E > +0.5$ V.† Since their band gaps are generally *ca.* 2 eV, these materials are not significantly n-doped until $E < -1.5$ V.

MO calculations⁴ (tested experimentally⁵) indicated that grafting butadiene fragments to the thiophene rings in polythiophene would lead to a reduction in the band gap to *ca.* 1 eV for polybenzo[*c*]thiophene (**1a**, Scheme 1). Consequently, polybenzo[*c*]thiophene films are p-doped at $E > ca.$ -0.2 V and n-doped at $E < ca.$ -1.1 V.⁶ However, the n-doped form, like that of polythiophene,² is still very sensitive to traces of water or oxygen in electrolyte solutions.⁶ Polybenzo[*c*]thiophenes are also of interest because of their unusual optical properties; the intense oscillator strength associated with the interband transition in the reduced form (blue) decreases and moves into the IR on oxidation, giving a colour change to transparent.

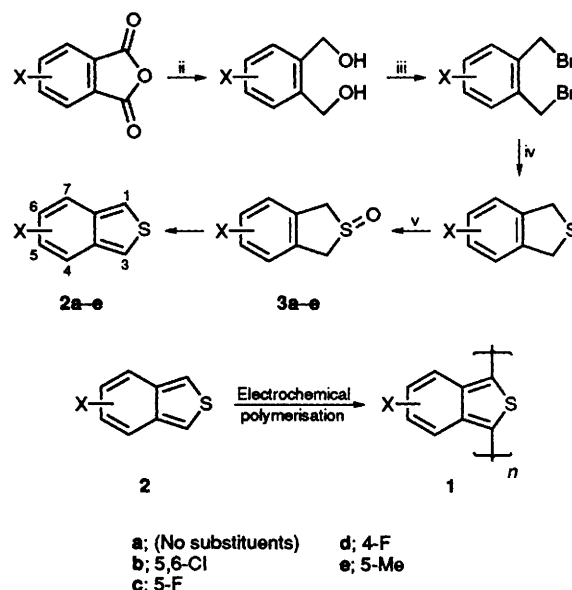
We were intrigued by the possibility of tuning the redox potentials for polybenzo[*c*]thiophene n- and p-doping by appropriate substitution in the C₆ ring. Few examples of substituted polybenzo[*c*]thiophenes have been claimed to date;⁷⁻⁹ the syntheses of potential monomers **2** are lengthy¹⁰ and the molecules themselves are usually unstable. n-Doping has only been examined for **1a** itself.⁶

Sulfoxides **3b-e** were obtained as shown in Scheme 1, using routes similar to that described in the literature for **3a**.¹¹ Benzo[*c*]thiophenes **2b-e** sublimed on a cold (-20 °C) finger as white, crystalline solids on heating sulfoxides **3b-e**, intimately mixed with twice the mass of activated alumina, at 125 °C under vacuum (*ca.* 0.1 mm Hg; **2b**) or reduced pressure (25 mm Hg nitrogen; **2c-e**). Benzo[*c*]thiophenes are usually unstable unless substituted in the 1- and 3-positions,¹⁰ but **2b** is stable in air at room temp. for >24 h, and decomposes only slowly in solution (CDCl₃; $t_{1/2}$ *ca.* 12 h), greatly facilitating studies of its electropolymerisation (the stabilising influence of electron-withdrawing C₆ ring substituents on benzo[*c*]thiophenes has been noted before¹²). Also helpful was the fact that sulfoxide **2b** was particularly readily obtained, since all the intermediates were crystalline, air-stable solids. The novel benzo[*c*]thiophenes **2b-e** were characterised, as appropriate, by ¹H NMR, IR spectroscopy and mass spectrometry.‡

We found that electrodes modified with **1b-e** were best prepared using a variation of the protocol established earlier for films of **1a**,¹³ namely by repeated potential cycling in a solution of **2b-e** in dry, deoxygenated 0.2 mol dm⁻³ Et₄NBF₄-MeCN. Interestingly, there was little difference in the onset

potentials for film growth for **1a-e** (Table 1). Growth was stopped when coverage of *ca.* 10⁻⁸ (mol redox sites) cm⁻² was obtained. On removal from solution with the potential held at the negative limit, neutral films of **1c** and **d** (Pt electrodes) were emerald green by reflected light. The other films appeared blue. The modified electrodes were washed with MeCN and stored in a dry, dust-free environment.

The cyclic voltammograms (CV) of films of **1b-e** in the p-doping region were then examined in monomer-free electrolyte. No significant difference between the first and subsequent scans was noticed, and all the polymers were stable to repeated (10-20) cycles at 0.05 V s⁻¹, without the need for the conditioning process cited as necessary for films of **1a**.⁶ Several other useful pieces of information emerge from these experiments. Firstly, all the CVs of **1b-e** show a broad,



Scheme 1 Reagents and conditions: i, LiAlH₄, THF; ii, EtOAc, then 0.1 mol dm⁻³ HCl; iii, 48% HBr, reflux; iv, Na₂S·9H₂O, 5:1 EtOH:H₂O, reflux; v, NaIO₄, H₂O, 25 °C

Table 1 Onset potentials for electrochemical oxidation of **2a-e** to **1a-e**, anodic peak potentials for **1a-e** p-doping processes and onset potentials for **1a-e** n-doping process

Monomer/ polymer	$E_{\text{onset 2} \rightarrow \text{1}}/\text{V}^a$	$E_{p_a(1)}/\text{V}^b$	$E_{p_a(2)}/\text{V}^b$	$E_{\text{onset n-doping}}/\text{V}$
2a/1a	1.04	0.45	0.85	-1.10
2b/1b	1.25	0.72	0.98	-0.35
2c/1c	1.15 ^c	0.50 ^c	0.78 ^c	-0.70 ^c
2d/1d	1.15	0.80	1.00	
2e/1e	0.95	0.50	0.77	-1.20

^a Potential where current for oxidation of **2** reaches 20 μA cm⁻² on Pt disc electrodes (first scan) except where stated otherwise. ^b Peak potentials for first and second anodic waves as seen in Fig. 1 for **1c**. ^c ITO electrode.

symmetrical redox process at lower potentials, and a sharper, less symmetrical, feature at higher potentials (Fig. 1), very similar to that seen for **1a**.^{6,13} All films showed peak currents linear with scan rate between 0.010 and 0.150 V s⁻¹ for both anodic and cathodic peaks, as expected for surface-localised redox processes. *In situ* FTIR and ellipsometric measurements on films of **1a** on Pt have been interpreted in terms of the first, broad, wave being due to polaron formation, and the second wave to bipolaron formation.¹³ Secondly, for the monosubstituted examples **1c–e** no overall trend can be discerned in the peak potentials; only in the case of **1b** is there an experimentally significant positive shift in the p-doping potentials. Finally, all the films underwent a reversible colour change from dark-blue or blue-green (neutral form) to transparent (conducting form), as expected for these materials.¹⁴

The negative potential limit was then extended progressively until the n-doping process was evident. Providing that moisture was rigorously excluded from the cell, and the films had previously been cycled between the neutral and p-doped form, all films showed an accessible n-doping process. However, in contrast to p-doping, this was very dependant upon the substituent (Table 1; Fig. 1). It is very clear that the presence of electron-withdrawing group(s) makes n-doping easier to achieve. In particular, the extremely mild potential at which **1b** is fully n-doped (−0.7 V) is very notable; films of **1b** becomes transparent at ≤ −0.5 V. Thus, the substituents shift the n-doping process some 0.65 V cathodic of that for **1a**.⁶ The CV seen in Fig. 1 showed *ca.* 7% diminution in current after 10 cycles, but its appearance was otherwise unchanged. Clearly, a significant portion of the charge injected on n-doping is not recovered until p-doping potentials are reached; this is entirely consistent with results for polythiophenes and **1a**.^{2,3,6}

The smaller difference between n- and p-doping onset

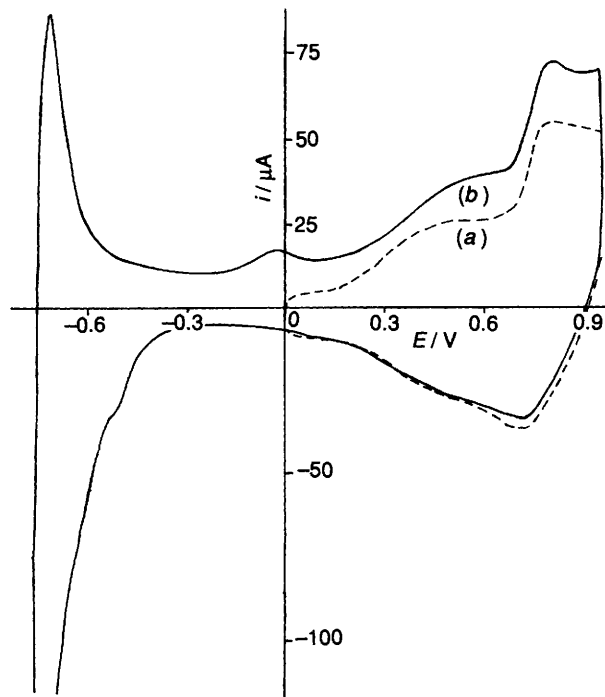


Fig. 1 CV for a film of **1c** on ITO glass, (a) between 0.00 and 1.0 V at 0.050 V s⁻¹ and (b) a subsequent scan from 0.00 to −0.75 to +1.00 to 0.00 V. The n-doping peak current (measured separately) was 280 μA.

potentials for **1b–d** implies a lower band gap. In principle, electronic spectroscopy can provide an independent measure of the band gap.⁶ The UV–VIS–near IR spectra of neutral films of **1b–e** on ITO glass were examined *ex situ*. All films showed a peak near 700 nm, with a shoulder to lower energy, and were similar in appearance to published *in situ* spectra of **1a** held at potentials where the film is partially p-doped.¹⁵ Thus, although our films were removed from solution under potential control in the fully undoped state, partial p-doping (presumably by oxygen) occurred.

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Footnotes

† All potentials quoted are with respect to the SCE.

‡ Selected spectroscopic data: for **2b**: ¹H NMR (250 MHz, CDCl₃) (vs. internal CHCl₃) δ 7.63 (s) 7.75 (s); IR ν/cm⁻¹ (KBr disc) 3100m, 3050w, 3030w (aromatic C-H); MS (EI) *m/z* 202 (M:100), 167 (M – Cl: 28.5).

2c: ¹H NMR δ 6.90 (m, 1 H), 7.17 (m, 1 H), 7.55 (m, 2 H), 7.68 (m, 1 H); MS *m/z* 152 (M: 100).

2d: ¹H NMR δ 6.68 (m, 1 H, *J*_{5,6} 7.7, *J*_{5,F} 11 Hz, 5-H), 6.99 (m, 1 H, *J*_{6,7} 8.8 Hz, 6-H), 7.39 (d, 1 H, 7-H), 7.72 (overlapping dd, 1 H, *J*_{1,3} 3.3, *J*_{3,F} 3.3 Hz, 3-H), 7.81 (dd, 1 H, *J*_{1,F} 1.1 Hz, 1-H); MS *m/z* 152 (M: 100).

2e: ¹H NMR: decomposed too rapidly for satisfactory spectra; MS *m/z* 148 (M: 100).

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