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Some *in situ* reflectance Fourier transform infrared studies of electrochemically prepared polybenzo[*c*]thiophene and poly-5-fluorobenzo[*c*]thiophene films†

Christopher L. Jones,[a] Simon J. Higgins*[a] and Paul A. Christensen[b]

[a]*Department of Chemistry, University of Liverpool, Crown Street, Liverpool, UK L69 7ZD.*
E-mail: shiggins@liv.ac.uk
[b]*Department of Chemistry, University of Newcastle upon Tyne, Newcastle, UK NE1 7RU*

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Electrogenerated films of polybenzo[*c*]thiophene (PBCT) and poly-5-fluorobenzo[*c*]thiophene (PFBCT) have been studied *in situ* under potential control using reflectance FTIR spectroscopy. For PBCT, the onset of oxidation (p-doping) results in the appearance of infrared activated vibrations (IRAVs), which are very similar to those observed earlier during photoinduced IRAV experiments. However, at more positive potentials, the spectra become more complex, as a new charge carrier evolves, and positive of +0.5 V (*vs.* SCE), the features due to the first charge carrier are lost. This change in behaviour is compared with the results of earlier *in situ* data obtained using electronic and EPR spectroscopies. Although *peak* potentials for the p-doping process are only slightly more positive for PFBCT than for PBCT, it is clear from the IR data that the *onset* of p-doping occurs at a potential *ca.* 0.4 V more positive for PFBCT than for PBCT. In other respects, the evolution of charge carriers in PFBCT films is similar to that in PBCT. Some unusual bands at *ca.* 1700 cm^{-1} in the spectra of both polymers are attributed to chain-terminating carbonyl groups in this quinoid polymer. The reduction of PBCT and PFBCT to the n-doped conducting state has also been examined. Interestingly, the IRAVs which develop as the film becomes n-doped are very similar to those of the first stage of p-doping. The onset of n-doping, deduced from the appearance of the characteristic electronic band in the IR spectrum, occurs at a potential 0.5 V more positive for PFBCT than for PBCT. Thus, the relatively trivial substitution of one F at C5 has a remarkable effect on the redox potentials for n- and p-doping in PBCTs.

Introduction

There is currently a great deal of interest in the use of conjugated polymers in novel electronic devices and in molecular electronics.[1,2] One important feature of conjugated materials is that, by appropriate choice of monomer structure, control can be exerted over the band gap and the redox properties of the polymer. In this respect, much work has been reported on polythiophenes.[3–5] For example, colour control in polythiophene-based light-emitting diodes (LEDs) has been demonstrated, using poly-3-alkylthiophenes and poly-3,4-dialkylthiophenes in which the degree of inter-ring twisting, and hence effective conjugation, was tuned by altering the steric bulk of the alkyl groups.[6] A good example of using substituents to control redox properties is the use of a cyano-substituted polyphenylenevinylene (PPV) next to the cathode in PPV-based LEDs, in which the HOMO energy is lowered by the electron-withdrawing group relative to unsubstituted PPV, reducing the barrier to electron injection into the organic material.[7]

An important target in conjugated polymer science has been the design and synthesis of materials with low band gaps.[5] In principle, if the band gap could be reduced to zero, the conjugated material would be an organic metal without the need for oxidative or reductive doping. In practice, it is more likely that reduction of the band gap would result in significant thermal population of the conduction band, and hence intrinsic semiconducting behaviour. An early success in this field was the demonstration that, whereas polythiophene has a band gap of *ca.* 2 eV, polybenzo[*c*]thiophene (poly-**1**) has a band gap of *ca.* 1 eV.[8–10] This reduction arises because the major contributor to the existence of a band gap in these polymers is a type of Peierls instability, the size of which is related to the degree of bond alternation in the polymer structure.[5] In polythiophene, the most stable resonance form of the polymer is the aromatic structure, in which the inter-ring C–C bond is considerably longer than the intra-ring bonds (Scheme 1). The quinoid form is much higher in energy. However, in polybenzo[*c*]thiophene, whereas the quinoid form is generally accepted as the most stable resonance form of the polymer,[11] the aromatic form is closer in energy, and so the degree of bond alternation is lessened.

One consequence of band gap reduction which is important in its own right is the stabilization of the negatively-charged (n-doped) form of the polymer.[5] This is a most important target for the design of organic bipolar electronic devices.[12] For example, while polythiophene itself is oxidized to its p-doped, conducting form beginning at *ca.* $E = +0.3$ V (*vs.* SCE), it is not reduced to its n-doped conducting form until $\leqslant -1.8$ V, and the n-doped form is both extremely sensitive to traces of moisture or oxygen, and inherently rather unstable.[4] Polybenzo[*c*]thiophene can be reversibly n-doped at significantly more positive potentials (*ca.* -1.1 V).[13]

We therefore investigated the syntheses, electrochemical polymerization and characterization of the novel substituted benzo[*c*]thiophenes **2–5** to examine whether electron-withdrawing substituents would stabilize the n-doped form of their polymers, and whether substituents affected the band gap.[14,15] Theoretical predictions had suggested that substituents would have a minor effect upon band gap.[16] We showed that the onset potentials for n-doping were remarkably sensitive to

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†Electronic supplementary information (ESI) available: schematic representation of the energy levels of polybenzothiophenes, CVs and FTIR spectra. See http://www.rsc.org/suppdata/jm/b1/b108054g/

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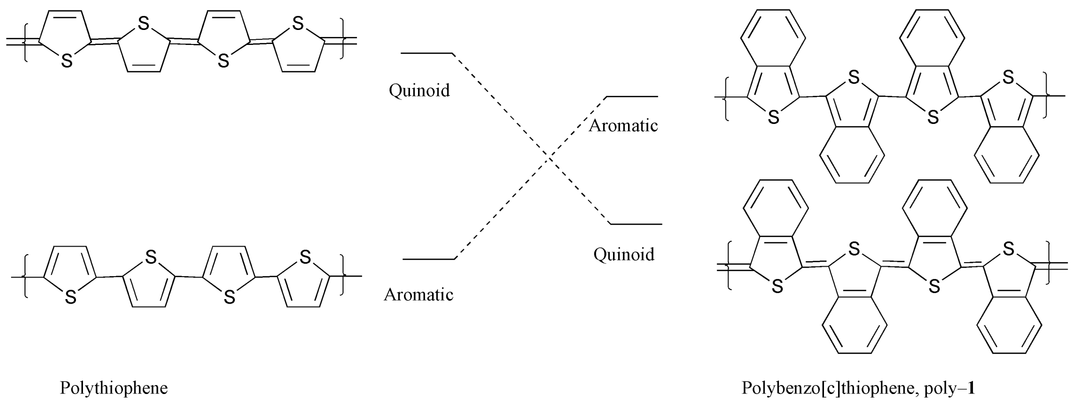


Scheme 1 Effect on the aromatic and quinoid forms of polythiophene (poly-**1**) of grafting butadiene fragments onto the thiophene rings, to create polybenzo[*c*]thiophene.

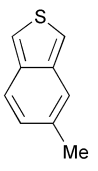
substituent effects. Whereas poly-**2** was n-doped beginning at $E \leqslant -1.1$ V, poly-**3** was n-doped from $E \leqslant -0.6$ V and poly-**4** from $E \leqslant -0.2$ V. Steric effects clearly have a very marked influence on band gap; the band gap of poly-**5** was increased compared with poly-**1**, although **5**, like **3**, has a single fluorine substituent.[14] But in poly-**5**, the 4-substituent leads to greater inter-ring twisting and hence, an increased band gap. Since the *peak* potentials for the p-doping process(es) did not drastically differ as a function of substituent, it appeared that the band gaps of poly-**3** and poly-**4** might have been significantly reduced compared with that of poly-**1**. We were obliged to use the p-doping peak potentials since it was very difficult to determine the onset potential for p-doping because the redox waves were broad. Although the band gap of poly-**3**, determined spectroscopically from the low-energy edge of the π–π* absorption of the neutral form of the polymer, was slightly lower than that of poly-**2**, the difference was far too small to account for the electrochemical data.[17]

We have found *in situ* reflectance FTIR spectroscopy to be a valuable tool for characterizing electrogenerated polythiophenes.[18–22] Some time ago, we undertook preliminary work with polybenzo[*c*]thiophene (PBCT) films, but found it difficult to grow reproducible and adherent films of sufficient thickness to obtain good data.[23] We have since found that much smoother, thicker and more adherent films of PBCTs may be grown using toluenesulfonate as the dopant anion instead of 'spherical' anions such as BF_4^- or ClO_4^-.[24] This allowed us to prepare films suitable for electrical measurements,[25,26] and it has now allowed us to deposit films of both poly-**1** (PBCT) and poly-**3** (PFBCT) on highly-polished electrodes suitable for *in situ* reflectance FTIR studies. We report the results of this study here.

Experimental

General

The precursors, 1,3-dihydrobenzo[*c*]thiophene 2-oxide and 1,3-dihydro-5-fluorobenzo[*c*]thiophene 2-oxide, were prepared as described earlier.[14] The electrochemical cell and FTIR instrumentation, and general methods, were as described recently.[27] We used a BioRad FTS-60 spectrometer, operating with a resolution of 8 cm^{-1}, in these experiments. The tetraethylammonium toluene-*p*-sulfonate (TEATos) electrolyte was dried by melting under vacuum for 2 hours. The benzo[*c*]thiophenes were freshly prepared by thermal dehydration of the precursors[14] immediately prior to preparing the electrolytes for film growth. All electrolyte solutions were prepared under Schlenk conditions in flame-dried glassware, and were injected into the cell under nitrogen. The reference electrode (Ag/AgCl) was separated from the sample compartment by a salt bridge containing the same electrolyte as used in the sample compartment. All potentials quoted in this paper are *vs.* Ag/AgCl. PBCT and PFBCT films were grown on bulk platinum disk working electrodes in the spectroelectrochemical cell, with the working electrode pulled back from the IR-transparent window, by potential cycling in 0.2 M TEATos/acetonitrile, using the protocol outlined earlier.[24] The films were then maintained at −0.4 V (PBCT) or −0.2 V (PFBCT) for five minutes. Subsequently, the growth solution was flushed from the cell using fresh 0.2 M tetraethylammonium tetrafluoroborate (TEAT) in acetonitrile, and the polymer film was subjected to potential cycles over the p-doping region (*i.e.* up to +1.0 V) at 0.1 V s^{-1} until the voltammogram was constant (two to five cycles sufficed). The modified electrode was then pushed against the IR-transparent window. A spectrum was collected with the working electrode held at −0.4 V (poly-**1**) or −0.2 V (poly-**3**), and the potential was then progressively stepped 0.1 V more positive, a spectrum being collected each time, up to +1.1 V (poly-**1**) or +0.9 V (poly-**3**). The potential was then stepped back in 0.1 V increments, again with a spectrum being collected at each point, until the starting potential was reached. After the exploration of the p-doping region in this fashion, the electrodes were then progressively stepped to more negative potentials in the same manner, to investigate the n-doping process.



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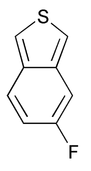

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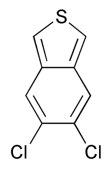

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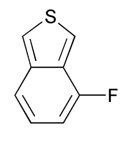

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In this paper, spectra are presented as log (S_P/S_R), where S_P is the spectrum collected at the potential *P* V, and S_R is the spectrum collected at the reference potential *R* V. Peaks pointing down (*i.e.* to negative log (S_P/S_R)) are therefore due to features gained, and peaks pointing up (*i.e.* to positive log (S_P/S_R)) are due to features lost, on changing the potential from *R* to *P*.

Results and discussion

Benzo[*c*]thiophene film oxidation

An intense π–π* transition dominates the visible region of the electronic spectrum for the neutral form of polythiophenes (see diagram S1 in the Electronic Supplementary Information; ESI†). In PBCTs, this band is in the red region of the spectrum,[9,13] and hence the neutral polymers are blue or blue-green. On removal of an electron from the HOMO of a polymer chain (oxidation, or so-called p-doping), the new π SOMO moves up in energy, and the corresponding π* orbital moves down, into the gap.[7] For polythiophenes, there has been much controversy over whether the removal of further electrons results in the generation of further SOMO's (polaron carriers), or whether spinless, dicationic charge carriers (bipolarons) are formed, in which case the intragap levels are both empty.[28–31] More recently, oligothiophene studies have shown that it is also possible for polarons on neighboring chains to form π-dimers, which are also spinless.[32] It is becoming clear that the preferred carrier for a given polymer (polaron, bipolaron, polaron π-dimer) is a function of criteria such as the structure of the polymer and how it was synthesised (*e.g.* chemically or electrochemically by oxidative coupling, or by organometallic aryl–aryl coupling).[4] It may also depend upon how the carrier is generated (*e.g.* whether by electrochemical or chemical oxidation with the consequent uptake of an anion, or by photoexcitation), and the phase (solid or solution).[29,30] For example, we have found significant differences between polymers generated from the electrooxidation of thiophene or 3-methylthiophene, and that generated by electrooxidation of 2,2′-bithiophene.[18,21,33] More recently, we have compared electrogenerated poly-3-methylthiophene with its copolymers with 3-alkylthiophenes bearing pendant metal complexes.[18,21]

In the spectral region accessible in our experiments (*ca.* 900–6000 cm^{-1}), a strong electronic band (or its low-energy edge) is generally observed during the oxidation of a conducting polymer film, owing to the lowest-energy transition (marked '1' in ESI Fig. S1) regardless of the identity of the charge carrier in the doped polymer. In addition, the movement of charge carriers along polymer chains gives rise to large dipole changes in those vibrations that can couple to the carrier motion (the so-called T modes).[34] The corresponding infrared bands are selectively enhanced, such that difference spectra such as those presented herein usually show only the gain of these very intense infra red activated vibrations (IRAV's).

Fig. 1 shows the cyclic voltammogram in the p-doping potential region of a PBCT film, recorded prior to the collection of the infrared data, shown in Fig. 2. It is immediately apparent that although this PBCT film shows two broad redox processes, one below and one above +0.6 V (Fig. 1), the major changes to the electronic bands occur prior to +0.5 V (Fig. 2).

Dealing with the early stages of film oxidation first, Fig. 2a shows the evolution of the infrared spectrum from −0.3 V up to +0.6 V, referenced to the spectrum taken at −0.4 V. The

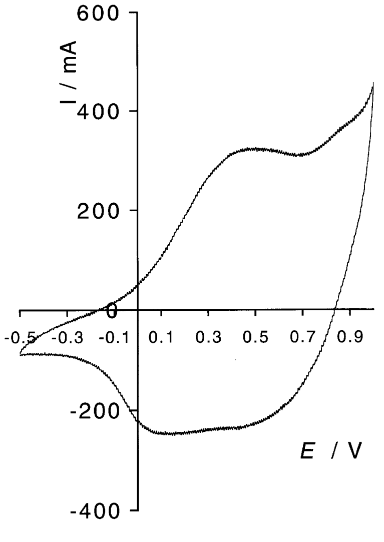


Fig. 1 Cyclic voltammogram (p-doping potential region) of PBCT film grown in the *in situ* FTIR cell, immediately prior to the film being pushed against the cell window for the p-doping experiment depicted in Fig. 3. Scan rate 98 mV s^{-1}.

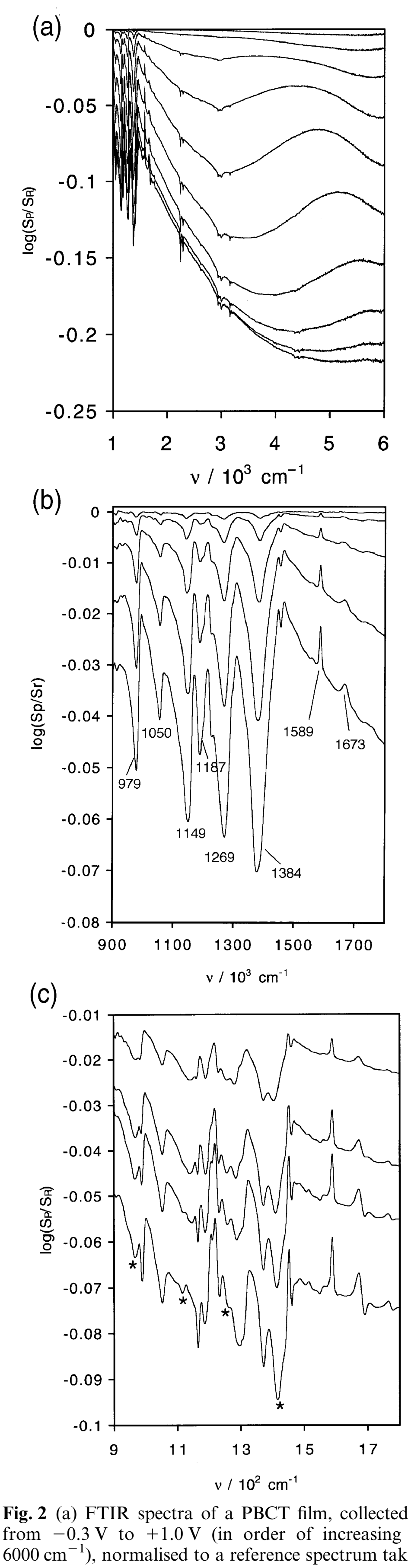


Fig. 2 (a) FTIR spectra of a PBCT film, collected at 0.1 V intervals from −0.3 V to +1.0 V (in order of increasing band intensity at 6000 cm^{-1}), normalised to a reference spectrum taken at −0.4 V (only the spectra collected up to +0.6 V are shown here, since little further evolution of the electronic bands occurred from +0.6 to +1.0 V; see text) (b) the region from 900–1800 cm^{-1}, for spectra taken from −0.3 to +0.1 V (in order of increasing peak size), normalised to the −0.4 V reference spectrum, (c) spectra taken from +0.2 to +0.5 V inclusive, normalised to the spectrum taken at +0.1 V; the spectrum at +0.5 V is offset by an additional −0.015 for clarity.

two broad features seen early in the oxidation, centred around 3000 and $>5500\ \mathrm{cm}^{-1}$, are electronic transitions involving the charge carriers in the polymer. These are discussed below. The sharp peaks below $1500\ \mathrm{cm}^{-1}$ are mainly due to the IRAV modes; the non-IRAV features are also discussed later. Fig. 2b shows the IRAV region, in the potential range from −0.3 to +0.1 V, referenced to the spectrum taken at −0.4 V. The positions of the IRAVs closely match those observed by Poplawski *et al.* in photoinduced doping experiments on PBCT,[35] *viz.* (literature values in parentheses) 1384 (1377), 1269 (1258), 1187 (1188), 1149 (1140) and 979 (972) cm^{-1}. There is an additional weak feature at $1050\ \mathrm{cm}^{-1}$ in our films, which is tentatively assigned to the BF_4^- ion, given the behaviour of the spectra on n-doping (*q.v.*). These T-mode frequencies for PBCT can be compared with those for polythiophene; 1330, 1200, 1120, 1030 cm^{-1}.[18] The differences can be accounted for by the greater quinoid character of PBCT, which will change the relative strengths of the intra- and inter-ring bonds. Interestingly, there is no evident IRAV enhancement of any benzenoid vibrations.

From +0.2 V to +0.5 V, there is clearly a transition in behaviour, and this is highlighted in Fig. 2c by plotting the spectra obtained at +0.2 to +0.5 V with reference to the spectrum obtained at +0.1 V. While the IRAV features observed from −0.3 to +0.1 V continue to grow, each feature is shadowed by a new gain feature. Thus, the $979\ \mathrm{cm}^{-1}$ peak is accompanied by an additional peak at $964\ \mathrm{cm}^{-1}$, the $1149\ \mathrm{cm}^{-1}$ peak by one at $1114\ \mathrm{cm}^{-1}$, the $1269\ \mathrm{cm}^{-1}$ peak by one at $1257\ \mathrm{cm}^{-1}$, and the $1384\ \mathrm{cm}^{-1}$ peak by one at $1403\ \mathrm{cm}^{-1}$. The new peaks are starred in Fig. 2c. This could most readily be understood if a second charge carrier was evolving in this potential range, but co-existing with the continuing evolution of the first carrier. In this potential range, the electronic band continues to strengthen and move to higher energy.

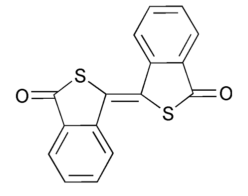
Positive of +0.5 V, the IRAVs due to the charge carrier generated in the early stages of oxidation are lost, while the new charge carriers, which start to form from +0.2 V, continue to be gained (Fig. S2; ESI). Meanwhile, examining the full spectral range, it is clear that, positive of +0.5 V, the electronic band continues to increase in intensity only at energies $\geqslant 5500\ \mathrm{cm}^{-1}$ (in fact there is some *loss* of electronic band intensity positive of +0.6 V at lower energy; not shown in Fig. 2a, for purposes of clarity).

These observations are consistent with other *in situ* spectroscopic studies of PBCT films. Hillman and co-workers have used both *in situ* electronic spectroscopy ($350 \leqslant \lambda \leqslant 820$ nm)[13] and EPR spectroscopy[36] of PBCT films (grown using tetrafluoroborate-containing electrolytes). They found that there was a definite change in the evolution of the electronic spectra at +0.55 V. The neutral polymer showed an intense π–π^* band centred around 700 nm, which steadily diminished in intensity, and shifted to higher energy, as the film was oxidized. However, positive of +0.55 V, the intensity at $\geqslant 700$ nm began to increase again, as a new feature at >820 nm began to grow. They also observed a maximum in the spin density in PBCT at around +0.65 V. Note that some differences would be expected between these films and the ones grown in our work, since Hillman *et al.* employed TEAT in CH_3CN to both grow and cycle their films, and they also employed a 'film conditioning' process to enhance the stability of their films to redox cycling. This consisted of one potential excursion up to +1.4 V at $10\ \mathrm{mV\ s}^{-1}$, which resulted in an irreversible oxidation wave and gave rise to a more intense π–π^* transition once the film was re-reduced to its neutral form. Similarly, Lapkowski *et al.* grew PBCT films by the electro-oxidation of 1,3-bis(*tert*-butyldimethylsilyl)benzo[*c*]thiophene, and observed isosbestic points (at 365 and 430 nm) in the electronic spectra of their films collected between −0.4 and +0.6 V, but not positive of this potential.[37]

We tentatively assign these observations to the formation of polaronic charge carriers from −0.4 to +0.5 V in our films. Beginning at *ca.* +0.2 V, another charge carrier starts to form. Since the EPR observations[36] indicate that these are spinless, they are either bipolarons or π-dimerised polarons. But since most evidence for π-dimers has been obtained on macroscopically ordered systems (*e.g.* chemically-generated polyalkylthiophenes, crystalline oligothiophenes),[3] and these electrochemically-generated films have a disordered morphology, π-dimerisation is less likely. In poly-3-methylthiophene (PMT) films, we also found evidence for a change in carrier identity, which we likewise assigned to a polaron–bipolaron change, but this occurred after a significantly smaller fraction of the total charge had been passed than in these polybenzo[*c*]thiophene films.[21] Since it is generally recognized that polarons tend to form to a greater extent in disordered films, with shorter mean conjugation lengths,[31] this indicates that electrogenerated PBCT is less ordered, and less conjugated, than electrogenerated PMT.

For a polymer film with a range of conjugation lengths, one would expect the longer conjugation lengths to be oxidized first. In a simple overlap model, the charge carriers so generated would be strongly stabilized by chain distortion, the SOMO would move substantially into the mid-gap, and hence the lowest-energy electronic absorption would be at higher energy. As more charge carriers are progressively generated, they should be less stabilized by chain distortion, and so move less far into the mid-gap, and therefore the electronic band increase should shift progressively to lower energy.[33] Clearly, when these PBCT films are p-doped, the energy of the electronic bands progressively increases. Similar observations have been noted for electrogenerated polythiophene films in *in situ* UV–vis–NIR spectroscopic studies.[38–40] There are many other factors (for example, relative permittivity changes[29–31] which can affect these absorption bands. Interestingly, we have also studied PBCT grown using Et_4NBF_4–CH_3CN electrolyte,[23,41] and in these films, the electronic band did move to slightly higher energies as the film was oxidized, so the behaviour of the electronic bands is clearly dependent upon the way in which the film is grown.

There are some features, present in the range 900–$1800\ \mathrm{cm}^{-1}$, which are not seen in the photoinduced IRAV experiments.[35] There is a loss feature at $1673\ \mathrm{cm}^{-1}$ which grows during the first part of the oxidation (−0.3 to +0.5 V; Fig. 2b), and which is joined, from *ca.* +0.3 V, by a gain at $1693\ \mathrm{cm}^{-1}$ (Fig. 2c) thus giving the appearance of a bipolar band at higher potentials. The loss feature continues to increase in intensity throughout the entire oxidation process. In contrast, the second weak loss peak, at $1589\ \mathrm{cm}^{-1}$, only increases significantly up to +0.6 V. It is unusual to find loss features in conjugated polymer spectra because of the very considerable enhancement of intensity of the IRAV modes, and where loss features are observed, this is usually when IRAVs gained in one potential range are subsequently lost. Non-IRAV-related 'loss' features are usually, in fact,'ghost losses', where chromophores are progressively hidden from the probing IR beam with changing potential; the significant refractive index changes alter the reflectivity of the film surface.[19,33] We tentatively suggest that the $1585\ \mathrm{cm}^{-1}$ band may be due to a 'ghost loss' of a benzenoid C–C stretch of the neutral polymer; these bands can be very intense in fused ring systems.[42] The loss at $1673\ \mathrm{cm}^{-1}$ may be a similar 'ghost loss' of chain-terminating carbonyl groups, and the gain at $1693\ \mathrm{cm}^{-1}$ may arise when the polymer is sufficiently oxidized that the charge carriers extend onto the electron-deficient end groups. Electron-withdrawing substituents increase carbonyl stretching frequencies, and the p-doping of the polymer chain will make it, in effect, progressively more electron-withdrawing. Significantly, this gain peak is not seen during n-doping (*q.v.*). For comparison,



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the compound **6** has a carbonyl stretch at 1700 cm^{-1} in its IR spectrum.[43]

Significantly, none of the changes seen in the potential region −0.4 V to +1.0 V is irreversible, and when the potential was progressively stepped back from +1.0 V, the spectroscopic changes on film reduction exactly mirrored the changes seen on oxidation (not shown here, for brevity).

Effect of fluorine substitution on polybenzo[*c*]thiophene film oxidation

Fig. 3 shows the evolution of the FTIR spectra of a PFBCT film, recorded during the p-doping process. The corresponding cyclic voltammogram of this film (Fig. S3 in ESI) showed that the peak potential for the first oxidation wave, *ca.* +0.6 V, was only some 0.15 V more positive than the first oxidation wave seen for PBCT (Fig. 2).

There are two important findings from this data. Firstly, it is evident that significant formation of IRAVs and electronic band intensity is not seen for PFBCT until >0.0 V, that is, *ca.* 0.4 V more positive than for PBCT itself. Therefore, consistent with our *in situ* visible–near IR studies,[17] the presence of the substituent does *not* greatly alter the band gap, estimated electrochemically as described earlier,[14] but it *does* shift both the n-doping and p-doping onset potentials positive, by *ca.* 0.5 V for n-doping and 0.4 V for p-doping, a very considerable amount. Secondly, the IRAVs of PFBCT are similar to those of PBCT, except that the bands almost all show some splitting. This can be seen in the expansion of the 900–1800 cm^{-1} region (Fig. S4 and S5 in ESI). For example the IRAV seen at 1269 cm^{-1} in PBCT is seen at 1260 cm^{-1} in PFBCT and is accompanied by an additional, weaker, peak at 1295 cm^{-1}. This is probably due to the lower symmetry of the substituted polymer. Not only is the monomer asymmetrically substituted, but the electropolymerisation is likely to be regiorandom, with respect to the relative positioning of fluorine substituents on neighbouring monomer units.

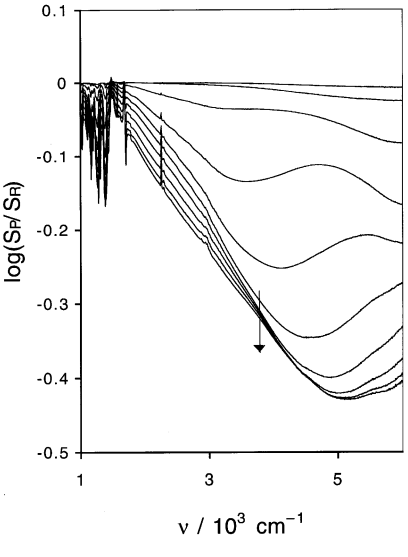

Fig. 3 FTIR spectra of a PFBCT film, collected at 0.1 V intervals from 0 V to +1.0 V (in order of increasing band intensity at 6000 cm^{-1}), normalised to a reference spectrum taken at −0.2 V.

In all other respects, the evolutions of both the electronic bands and the IRAV bands are quite similar for both polymers. Up to +0.5 V, the IRAVs increase in intensity in PFBCT (Fig. S4; ESI) just as they do in PBCT up to +0.2 V (Fig. 2b), and from +0.6 to +1.0 V, it appears that a second set of IRAVs grows with the first set (Fig. S5; ESI). Given the more positive p-doping onset for PFBCT, it is reasonable to suppose that, positive of +1.0 V, we could expect the same behaviour as for PBCT positive of +0.5 V, but we did not extend the potential limit further.

Another notable difference is that both the features due to chain-terminal carbonyl groups (loss seen at 1677 cm^{-1} and gain at 1702 cm^{-1}; Fig. S4; ESI) are relatively more intense in PFBCT, at +1.0 V, than these features in PBCT at the corresponding potential (*ca.* +0.6 V). If our assignment of these bands is correct, the interpretation must be that the average chain length in the fluoro-substituted polymer is shorter, making the carbonyl bands relatively more significant.

n-Doping of PBCT and PFBCT films

Fig. 4 shows the evolution of the infrared spectrum on stepping the PBCT film of Fig. 1 and 2 negative, from −0.6 V to −1.5 V.

The spectra in the IRAV region from −0.6 to *ca.* −0.9 V were very weak and are not shown in Fig. 4. Careful examination of these spectra showed that there is initially a slight *loss* in electronic band intensity as the reduction wave begins in the voltammogram. This is probably related to the elimination of trapped p-type charge carriers as the film regains electronic conductivity. The earliest potential at which the electronic band becomes a gain feature (albeit weak) is −1.0 V, representing the beginning of n-doping, hence these are the first spectra illustrated in Fig. 4. From −1.0 to −1.3 V (Fig. 4b), a set of IRAV bands very similar to that seen for PBCT p-doping (first stage) is observed, at 1385, 1270, 1194, 1138 and 970 cm^{-1}. (The only slight difference is that the 1138 cm^{-1} band shows a weaker feature at 1120 cm^{-1}, but close examination of the corresponding band in the p-doped film shows a definite shoulder at 1120 cm^{-1}). Negative of −1.3 V, the IRAV spectra become more complex, as another type of charge carrier evidently evolves, although the initial IRAV bands are still increasing in intensity (Fig. S6; ESI). The additional bands are not coincident with the second set of bands which evolve in the later stages of p-doping.

It is tempting to assign the initial charge carriers in the n-doped film as polarons, on the basis of the close similarity of the IRAVs to those seen during the onset of p-doping. While this is consistent with results from *in situ* electronic spectroscopy, albeit over a limited wavelength range,[13] it should be pointed out that *in situ* EPR spectra showed a maximum in spin density at −1.1 V during n-doping.[36]

Another feature worthy of comment is that the electronic band (Fig. 4a) strengthens and moves to higher energy during p-doping, whereas it shifts to lower energy on n-doping. Interestingly, examination of the electronic spectra in reference 13 shows that the π–π* transition for the remaining neutral form of the polymer shifts to higher energy during p-doping, but to lower energy on n-doping. Since our FTIR experiments strongly suggest the presence of terminal carbonyl groups, it is possible that these observations could be accounted for as follows. Clearly, a terminal benzo[*c*]thiophene bearing a conjugated carbonyl group will have a higher electron affinity than a benzo[*c*]thiophene within a polymer chain. Furthermore, if all the chain terminal groups are carbonyls, the *shorter* polymer chains will be more easily reduced.

Fig. 5 shows the evolution of the infrared spectrum on stepping the PFBCT film of Fig. 3 negative, from −0.4 V to −0.9 V, the spectra being referenced to that taken at −0.2 V. It can be seen here that the onset of n-doping, as defined by a gain

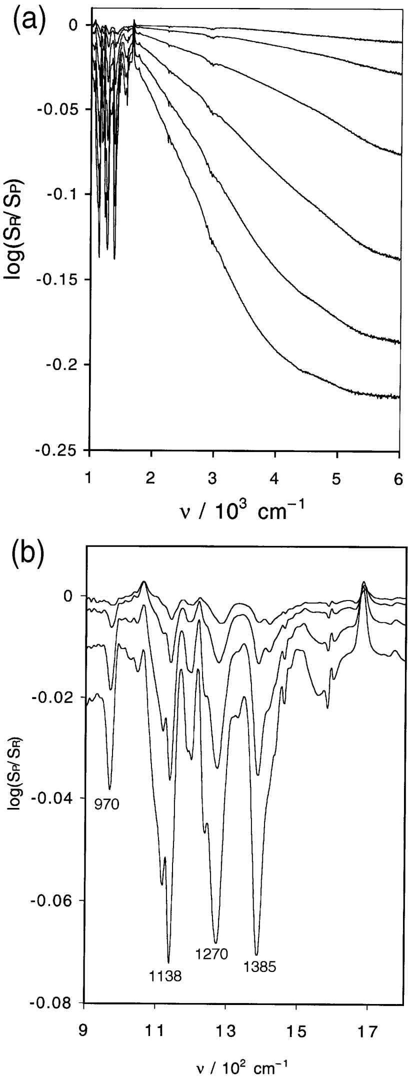

Fig. 4 (a) FTIR spectra of a PBCT film, collected at 0.1 V intervals from −0.6 V to −1.5 V (in order of increasing band intensity at 6000 cm^{-1}), normalised to a reference spectrum taken at −0.5 V (for clarity, only the spectra from −1.0 V are shown) (b) the region from 900–1800 cm^{-1}, for spectra taken from −1.0 to −1.3 V, normalised to the −0.5 V reference spectrum.

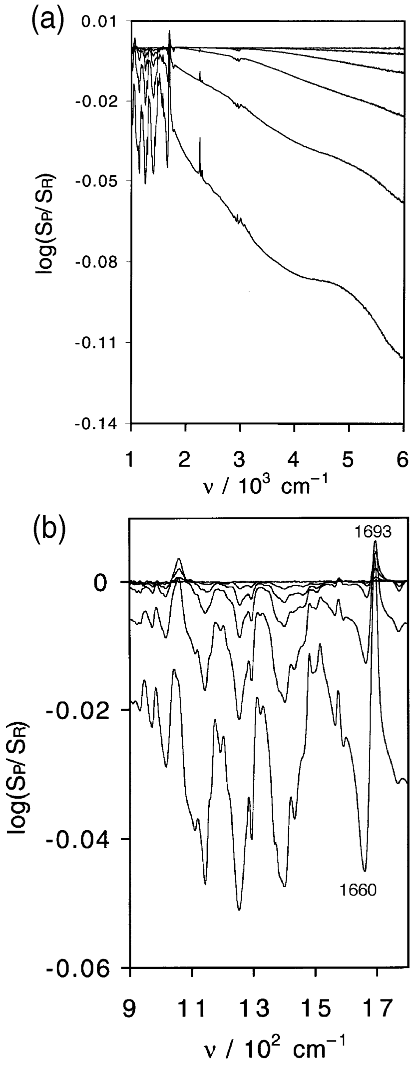

Fig. 5 (a) FTIR spectra of a PFBCT film, collected at 0.1 V intervals from −0.3 V to −0.9 V (in order of increasing band intensity at 6000 cm^{-1}), normalised to a reference spectrum taken at −0.2 V, (b) the region from 900–1800 cm^{-1}, expanded.

in IRAV and electronic band intensities, occurs at −0.4 V, 0.5 V positive of the onset of n-doping for PBCT.

Interestingly, for n-doped PFBCT, the IRAV bands look somewhat different from those seen in the early stage of p-doping. Indeed, they are much more like those observed in the second phase of p-doping, that from +0.6 to +0.9 V. This is particularly so for the highest-energy band centred at *ca.* 1400 cm^{-1} (compare Fig. 5b and Fig. S4, ESI). It is possible that the electron-withdrawing substituent changes the relative stability of the two charge carriers. As for PBCT, the electronic band intensity increases move steadily to lower energy with increased n-doping.

As noted for the p-doping experiments, the carbonyl features in n-doped PFBCT are relatively more intense than those in n-doped PBCT. On n-doping, we see a loss at *ca.* 1693 cm^{-1} and a gain at 1660 cm^{-1}. One would expect that, on reduction, the carbon–oxygen bonds will be weakened by the additional π-electron density, and this may explain the appearance of the band at 1660 cm^{-1}.

We have observed that, unless moisture and oxygen are rigorously excluded from the cell, there is considerable charge trapping in PBCTs when both the p- and n-doping potential regions are accessed. This manifests itself in pre-peaks, an oxidative one as the p-doping region is accessed after the n-doping region, and a reductive one immediately before n-doping when the film has previously been p-doped.[14] However, interestingly, in the FTIR experiments, we found that, for both polymers, >95% of the entire IRAV and electronic band intensity at the positive potential limit was re-lost upon stepping the potential back to the negative limit. Similarly, >95% of the entire IRAV and electronic band intensity, gained during the n-doping experiment at the negative potential limit used, was re-lost upon stepping the potential back to the positive limit.

Conclusions

The main conclusion from this study is that *in situ* reflectance FTIR spectroscopy has allowed us an independent assessment of the onset potentials for p- and n-doping in PBCT and PFBCT. This has confirmed that 5-fluoro-substitution has a surprisingly large effect upon the redox potentials of the polymer, but that any effect upon the band gap is of the order 0.1 V or less. We have found evidence for a change in charge carrier identity, probably from polaron to bipolaron, as PBCT and PFBCT films are oxidized, and we have correlated this with the voltammograms, and with previous *in situ* spectroscopic studies. Although the charge carrier during the early stage of

PBCT reduction is remarkably similar to that during the early stage of oxidation, this does not appear to be the case for PFBCT. Finally, we have found evidence for chain-terminating carbonyl groups in these electrogenerated quinoid conjugated polymers.

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