

Internally referenced analysis of charge-transfer reactions in a new ferrocenyl bithiophenic conducting polymer through cyclic voltammetry†

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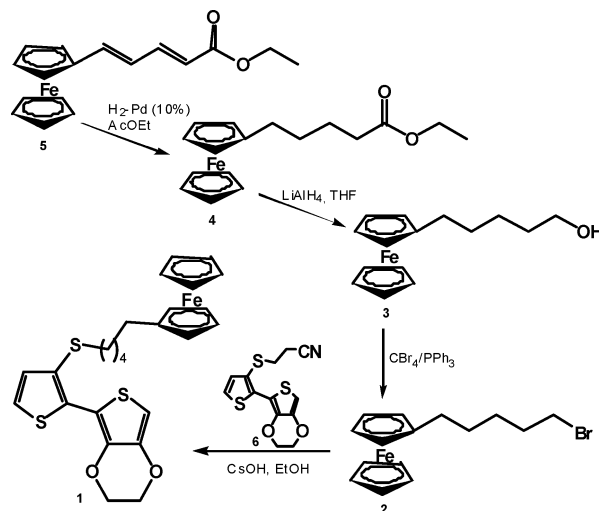
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A new ferrocenyl bithiophenic polymer has enabled the first demonstration of internally referenced quantitative analysis of charge-transfer reactions, which may enable better understanding and applications of conducting polymers in *e.g.* supercapacitors.

The peculiar charge-transfer reaction in conducting polymers results in interesting properties such as large pseudocapacitance and converse piezoelectric effect, leading to applications in electrochemical capacitors and actuators.^{1–3} Thus, the amount of charge, α , transferred to or from each monomer unit (or the reciprocal of the number of monomer units to donate or accept one electron) in the polymer is of both theoretical and practical importance.

For instance, a previous report has assumed $\alpha = 0.25$ to estimate the ratio of two components in a copolymer of polypyrrole and ferrocene-substituted polypyrrole,^{4a} although the work would have been more reliable if α was accurately measured. The electrochemical quartz crystal microbalance (EQCM) has the dual function of recording charge and mass changes in electro-polymerisation and detecting the equivalent polymer mass deposited per electron.⁵ By doing so, the specific capacitance (C_M , F g⁻¹) of the polymer can be derived, which is directly linked to α . However, the accuracy of the EQCM highly depends on the thickness of the deposited polymer film and also the experimental conditions such as the frequencies of individual crystals used. A further point is that due to the solvation of counter ions, which intercalate into the polymer during oxidation, the measured mass is a sum of the intercalated ions and the solvents. Thus, the reliability of the α value derived from the EQCM is compromised.

Conducting polymers functionalised by metallocenes, particularly ferrocene (Fc), were recently synthesised, showing the redox properties of both groups.⁶ Their potential applications include, for example, metal cation recognition,^{6b} and the reference electrode.^{6c} In principle, the redox chemistry of the



Scheme 1 Synthesis of the ferrocenyl bithiophenic monomer 1.

metallocene can function as an internal reference for more reliable determination of α values of the parent polymers, but such an opportunity has not yet been explored in the literature.

Herein, we report the synthesis and electro-polymerisation of a new ferrocenyl (Fc) bithiophenic (BTh) monomer 1 (Scheme 1), and the analysis of charge-transfer reactions in the obtained conducting polymer by cyclic voltammetry (CV), particularly to determine α , using the Fc group as an internal reference. As an example for application, the obtained α values are used to derive the C_M value of the BTh chains in the polymer with the results compared with those in the literature.

The synthesis chemistry is summarised in Scheme 1 and below with more details given in the ESI†. Precursor 5 was obtained by a Wittig–Horner reaction between 1-formylferrocene and substituted phosphonate anion derived from the diethylphosphonocrotonate. The catalytic hydrogenation of the double bonds in 5 with palladium-on-charcoal produced compound 4 in quantitative yield. The hydroxypropyl ferrocene 3 was classically prepared by reduction of the carboxylic ester in 4 with AlLiH₄. Finally, deprotection of the thiolate group in precursor 6, 2-(3,4-ethylenedioxythienyl)-3-(2-cyanoethylsulfanyl)thiophene,^{7a,b} by caesium hydroxide followed by reaction with 2 produced the target monomer 1 in 97% yield.

Deaerated acetonitrile solutions of tetrabutylammonium or lithium perchlorate (TBAClO₄ or LiClO₄, 0.1 ~ 0.5 mol L⁻¹) were used as the supporting electrolyte for recording cyclic voltammograms (CVs). The working electrode was a platinum (Pt) disc (inset photo, Fig. 1a) with an Ag/AgCl reference

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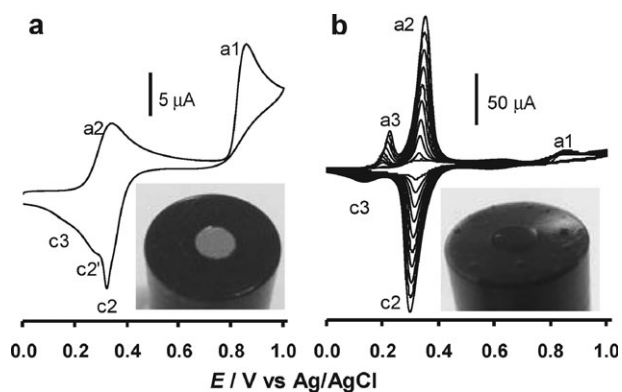


Fig. 1 The first (a) and consecutive cyclic voltammograms of 10 potential cycles (b) of an acetonitrile solution of 5.0 mmol L⁻¹ monomer **1** and 0.5 mol L⁻¹ LiClO₄. Scan rate: 20 mV s⁻¹. The inset photos show the Pt disc (1.6 mm diameter) working electrode before (a) and after (b) recording the CVs in both (a) and (b).

electrode and a Pt mesh counter-electrode. As shown in Fig. 1a, the CV of **1** (5.0 mmol L⁻¹) in the potential range of 0–1.0 V (vs. Ag/AgCl) exhibits two main oxidation processes, represented by peaks a1 and a2 (0.85 and 0.34 V vs. Ag/AgCl). The BTh and Fc groups in **1** can both undergo oxidation as previously reported and hence account for a1 and a2, respectively.^{6d,e} The oxidation of BTh leads to the deposition of the polymer and explains the irreversibility of a1. Note that although each BTh has two different thiophenic rings, direct charge transfer between the two may occur,^{4b} and account for a1 being a single peak. It is worth mentioning that the potential of a1 is very similar to that found for **6** under the same conditions.^{7b} The same is true for a2 in comparison with an alkyl-substituted ferrocene.^{6a,7c} These findings suggest insignificant intramolecular interactions, if any, between the Fc and BTh groups, which are almost electrostatically isolated from each other by the long alkyl chain in **1**.^{7c}

Interestingly, Fig. 1a shows a major reduction peak c2 (0.33 V) and two small but recognisable shoulders, c2' (ca. 0.27 V) and c3 (ca. 0.18 V). As discussed below, c2 and c3 correspond to the reduction of the oxidised Fc (Fc⁺) and BPh (BPh^{z+}) groups in the deposited polymer. Thus, c2' must have resulted from the reduction of the Fc⁺ group in the monomer in solution, and can be explained as follow. When the negative scan reached between 0.80 and 0.45 V, the potential was too low to oxidise BPh, but high enough to oxidise Fc. Such partially oxidised monomers remained in solution and were reduced at less positive potentials to give rise to c2'. Further evidence comes from the fact that a2 and c2' are separated by ca. 70 mV as expected from the quasi-reversible one-electron oxidation of an alkyl-substituted ferrocene in acetonitrile.^{6a}

Repetitive potential cycling (Fig. 1b, 10 cycles) led to two fast increasing peak couples, a2/c2 and a3/c3, which are strong evidence of continuous deposition of a conducting polymer on the Pt electrode. The deposit was further confirmed by visual observation (inset photo in Fig. 1b). Comparing with Fig. 1a, a2/c2 and a3/c3 on the consecutive CVs can be, respectively attributed to the Fc groups and the BTh chains in the deposit. Note that c2' is not visible in Fig. 1b, apparently due to it being engulfed in the much larger c2.

The obtained polymer-coated Pt electrode was rinsed with acetonitrile to remove adsorbed excess monomers and ions,

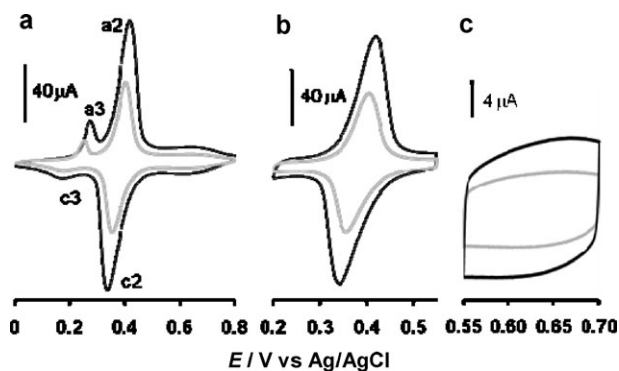


Fig. 2 Cyclic voltammograms of the electro-deposited polymer film (Fig. 1b) in the acetonitrile solution of 0.1 M TBAClO₄ between potentials of (a) 0–0.80 V, (b) 0.20–0.55 V, and (c) 0.55–0.70 V. Scan rate: 20 mV s⁻¹ (black line) and 10 mV s⁻¹ (grey line).

and then transferred into the monomer-free electrolyte. The CVs were recorded in the range of 0–0.80 V to avoid over-oxidation of the BTh chains, and are shown in Fig. 2a. It can be seen that the electro-deposited polymer alone also exhibits both redox reactions of the polymer chain, a3/c3, and the attached Fc, a2/c2. In particular, the oxidation peak potentials of the Fc group in the polymer (Fig. 2a) and in the monomer (Fig. 1a) are very close to each other, suggesting that the Fc in the polymer remains the same as it is in solution. This again agrees with the isolation effect of the long alkyl connector.

Peak couple a3/c3 corresponds to the conducting/insulating phase transition in the polymer,^{1a} but can be avoided by, for example, setting a less cathodic potential limit.^{2c} Fig. 2b shows indeed the disappearance of a3/c3 from the CV recorded in 0.20–0.55 V. At potentials higher than 0.50 V, the reduction of Fc⁺ would not occur and, as shown in Fig. 2c, the CVs are of the typical rectangular shape as expected from the pseudo-capacitance of the polymer chains.

CVs like those in Fig. 2b differentiate clearly the redox currents of the Fc/Fc⁺ couple from the pseudo-capacitive currents of the BTh chains. Integration of the currents before and after subtraction of the interpolated capacitive current gave the charges corresponding, respectively, to the Fc/Fc⁺ redox reaction and the pseudo-capacitance of the BTh chains (Autolab/General Purpose Electrochemical System 4.9). Some of the obtained charges are given in Table 1.

The positive and negative charges (Q_a and Q_c) for the Fc/Fc⁺ couple were almost equal with very small effects from the scan rate, in agreement with the nature of a pseudo-reversible one-electron transfer reaction. This fact and the non-interactive nature of the Fc group with the BTh chain as discussed above make the Fc a reliable internal reference for analysis of charge-transfer reactions in the polymer.

For the BTh chains, Q_a was similar to Q_c at the same scan rate, but both were about 8% smaller at 20 mV s⁻¹ than at 10 mV s⁻¹, which is similar to what has been observed in other conducting polymers, and can be interpreted by the charge-transfer kinetics.^{2d} This dependence of charge transfer on scan rate demonstrates the necessity and importance of using a reliable internal reference that is independent of the kinetics as a function of, e.g. the thickness and porosity of the conducting polymer film.

Table 1 Positive (Q_a) and negative (Q_c) charges derived from Fig. 2b for the redox reactions of the Fc group and BTh chain^a

Redox active group	Q_a	Q_c
Fc, 20 mV s ⁻¹	3.36×10^{-4} C	3.36×10^{-4} C
Fc, 10 mV s ⁻¹	3.37×10^{-4} C	3.38×10^{-4} C
BTh chain, 0.20 ~ 0.55 V, 20 mV s ⁻¹	1.08×10^{-4} C, $\alpha = 0.32$	1.05×10^{-4} C, $\alpha = 0.31$
BTh Chain, 0.20 ~ 0.55 V, 10 mV s ⁻¹	1.17×10^{-4} C, $\alpha = 0.35$	1.14×10^{-4} C, $\alpha = 0.34$

^a The possible maximum error in the data was estimated to be $\pm 2\%$ based on three or more CV measurements.

The α value for each BTh unit (with two different thiophenic rings) is the same as the ratio of charges transferred to BTh and Fc. Fairly consistent results were obtained, as listed in Table 1. Note that these α values are for the potential range of 0.20–0.55 V, in which the BTh chains should only exhibit the pseudo-capacitance. The same analysis applies to charge transfer in other potential ranges. At 10 mV s⁻¹, for the insulating–conducting phase transition (peak a3 Fig. 2a),^{1a} subtracting the capacitive current led to $Q_a = 1.10 \times 10^{-4}$ C and $\alpha = 0.33$. Between 0 V and 0.80 V (Fig. 2a), $Q_a = 3.14 \times 10^{-4}$ C (excluding the charge of a2 for Fc oxidation), thus $\alpha = 0.93$.

The α value can be linked to the specific capacitance, C_M , of a conducting polymer by the following equation:

$$C_M = Q/(\Delta EM) = \alpha F/(\Delta EM) \quad (1)$$

where F is the Faraday constant, ΔE the potential range and M the molecular mass of the monomer unit in the polymer. For a hypothetical polymer composed of only the BTh chains with $\alpha = 0.93$ (note: each BTh unit has two different thiophenic rings), eqn (1) gives $C_M = 505 \text{ F g}^{-1}$ for the full oxidation of the polymer (0–0.8 V). Considering only the pseudo-capacitive current, $\alpha = 0.35$ (0.20–0.55 V) and $C_M = 435 \text{ F g}^{-1}$. As a further check, CVs were recorded in the range of 0.55–0.70 V (Fig. 2c, where Fc is fully oxidised and does not contribute further to the current) and exhibited highly capacitive behaviour,^{2d} with $Q_a = 5.55 \times 10^{-5}$ C (10 mV s⁻¹), $\alpha = 0.16$ and $C_M = 464 \text{ F g}^{-1}$.

The BTh chains are structurally intermediate between polythiophene (PTh) and poly(3,4-ethylenedioxythiophene) (PEDOT). The theoretical C_M values of PTh and PEDOT were claimed to be, respectively, 485 F g⁻¹ ($\Delta E = 0.8$ V) and 210 F g⁻¹ [$\Delta E = 1.2$ V, or 190 F g⁻¹ from eqn (1)], assuming $\alpha = 0.33$ for each thiophenic unit.^{2f} Others found much lower C_M values, 90–110 F g⁻¹, in CV and EQCM measurements of PEDOT.^{2c,5b} Comparing the molecular mass of the BTh unit (222) with that of two Th (168) or EDOT (280) units, the C_M values reported here are highly convincing and more reliable.

The above discussion also highlights an important cause for different C_M values reported for the same conducting polymer by different authors: the insulating–conducting phase transition.^{1a} This process occurs to a polymer in the reduced state, and increases significantly the overall charge capacity, but it is absent when the capacitance is measured by, for example, ac impedance or CV at more positive potentials.^{2d}

In summary, we have described the principle of internally referenced quantitative analysis of charge-transfer reactions in conducting polymers. For demonstration, a new ferrocenyl bithiophenic monomer has been synthesised and electro-polymerised as a conducting coating on a platinum electrode, which exhibits well distinguished voltammetric features

corresponding to, respectively, the ferrocenyl group and the polymer chains. The quasi-reversible one-electron transfer reaction of the ferrocenyl group provides a reliable and absolute internal reference for determination of the amount of charge involved in each of the bithiophenic units when the polymer undergoes the insulating–conducting phase transition and pseudo-capacitive charging in different potential ranges. We believe the findings reported here can assist better understanding and applications of conducting polymers, for example, in sensors and supercapacitors.

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