

Electrochemical oxidation of double-stranded polybisenorbornenes containing linearly aligned ferrocene linkers†

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Received (in Cambridge, UK) 27th May 2008, Accepted 16th June 2008

First published as an Advance Article on the web 30th July 2008

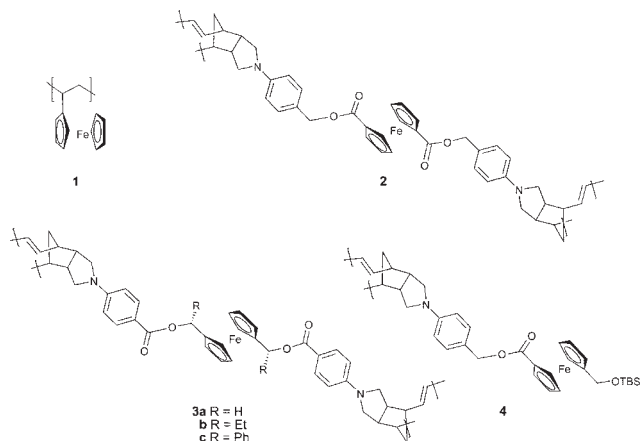
DOI: 10.1039/b808958b

Seventy percent of the ferrocene moieties in double-stranded polybisenorbornenes containing linearly aligned ferrocene linkers are oxidised and each of the neighbouring monomeric units in these polymers may strongly interact with each other; the oxidised form of **3c** has been shown to be antiferromagnetic.

There has been ever burgeoning interest on the electrochemistry of macromolecules containing multiple electroactive centers.^{1–4} Multielectron transfer is common in these polymers and their voltammetric curves are occasionally similar to those of one-electron transfer reactions.¹ The electrochemical behaviour of these polymers depends on whether interactions between these electroactive groups are present or not.^{1,2} For example, in the oxidation of poly(vinylferrocene) **1**, all the ferrocene groups are oxidised at one potential and it is believed that there is little interaction between these iron-containing sandwich pending groups.¹ On the other hand, when the ferrocene moieties are part of the polymeric backbone separated by different types of linkers, two reversible oxidation waves are in general observed.² Similar behaviour is also found in ferrocene-containing dendrimers.³ We recently reported the first DNA-like double-stranded bispolybisenorbornenes **2** using covalent ferrocene linkers.⁵ The spacing occupied by each of the monomeric unit is about 5.5 Å based on scanning tunneling microscopic images of **2**⁵ and on the X-ray structure of a related monomer.⁶ Unlike those ferrocene-containing polymers in the literature, which are somewhat fluxional, **2** is more rigid and the ferrocene moieties in **2** are aligned essentially in eclipsed manner with a fixed distance. It is envisaged that interactions between the ferrocene units in **2** might be reflected by their electrochemical behaviour.

Since the oxidation potentials of the ferrocenedicarboxylate and the 4-aminobenzyl moieties in **2** were very close, and the 4-aminobenzyl moiety in **2** would be very labile and susceptible to hydrolysis,⁷ we decided to tackle the electrochemistry of **3** containing a linear array of ferrocene derivatives. The ferrocene moiety and 4-aminobenzoate groups in **3** would show very different oxidation potentials. In addition, the aminobenzoate moiety would be more stable than the aminobenzyl entity under various conditions. The syntheses of **3**

essentially followed a similar strategy as described for **2**⁵ and the details will be described elsewhere.



Results of the cyclic voltammetry of **3a–c** are summarised in Table 1, and the cyclic voltammograms are shown in Fig. 1. A redox pair around 100 mV (with reference to the ferrocene–ferrocenium couple) was assigned to the redox of ferrocene moieties in **3**. The irreversible electrochemical oxidation of the aminobenzoate moiety in **3** gave an anodic peak around 650 mV. As shown in Table 1, the i_{pc}/i_{pa} ratios were close to unity (where i_{pc} and i_{pa} are the cathodic and anodic peak currents, respectively) indicating that the redox behaviour of the ferrocene moieties in **3** would be reversible (Fig. 1, solid line).

In order to investigate the oxidation characteristics of ferrocene moieties in **3**, a fixed potential at 350 mV was employed for bulk electrolysis. The results are listed in Table 2. It is interesting to note that about 70% of ferrocene moieties in **3** were oxidised. When single stranded polymer **4** was used for the electrolysis

Table 1 Cyclic voltammetric results of **3** in CH₂Cl₂ containing 0.1 M Bu₄NPF₆

Compound	E_{pa}^a/V	E_{pc}^a/V	$\Delta E_p/V$	i_{pc}/i_{pa}
3a	0.112	0.078	0.034	0.84
3b	0.062	0.022	0.040	0.94
3c	0.147	0.071	0.076	0.99

^a Peak potentials determined from cyclic voltammograms with potential scans involving the redox reactions of the ferrocene moieties only. The electrochemical potentials are reported relative to the ferrocene/ferrocenium redox couple measured after every experiment.

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† Electronic supplementary information (ESI) available: Details of electrochemical experiments and frontier orbitals from the DFT calculations. See DOI: 10.1039/b808958b

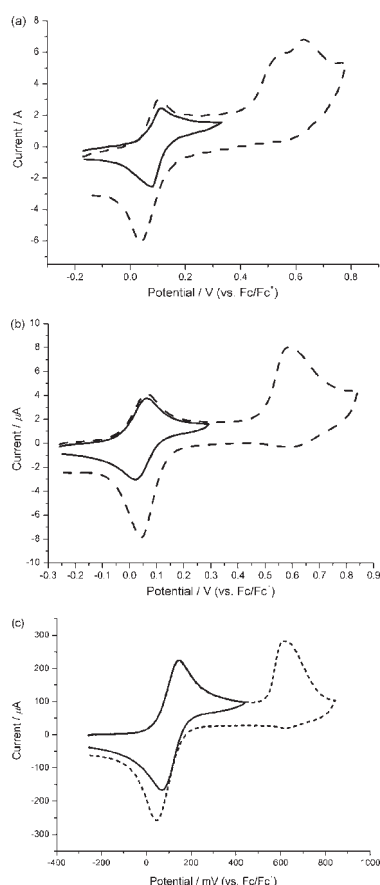


Fig. 1 Cyclic voltammograms of (a) **3a**, (b) **3b** and (c) **3c** in CH_2Cl_2 containing 0.1 M Bu_4NPF_6 . Scan rate = 100 mV s^{-1} . The adsorption of oxidised polymers onto the electrode surface may result in the appearance of larger i_{pc} of the ferrocene moieties.

experiment, a similar percentage of ferrocene groups were oxidised. It is noteworthy that the pending ferrocene moieties in **4** have been shown to align essentially in the same manner as those of **3**. As shown in Table 1, differences of some of the redox peak potentials of these polymers, ΔE_p , were somewhat smaller than 59 mV. It is noteworthy that each of these apparent redox pairs would represent a summation of multiple electron transfer processes in each of these polymers. Because of such strong overlaps among individual redox processes, the apparent ΔE_p of these polymers might appear to be smaller than 59 mV.

Table 2 Electron transfer ratios of the ferrocene moieties in the polymers estimated by bulk-electrolysis (BE) experiments and by chronoamperometry at a microelectrode (CM)

	M_n	n_p	Electron transfer ratio ^a (%)	
			BE	CM
3a	13 700	19	75	—
3b	31 100	40	68	70
3c	31 200	36	69	—
3c	37 600	43	—	74
4	1 700	8	105	—
4	11 900	20	69	70

^a The percentage of ferrocene units in a polymer that undergo electron transfer during the bulk-electrolysis process.

It is well documented that the ferrocene moieties in **1** were fully oxidised under similar conditions.¹ We have reexamined the octamer **1** and found complete oxidation of the ferrocene moieties. Apparently, the relative orientation of ferrocene moieties in **1** and those in **3** and **4** would be very different.

Electron transfer numbers of the ferrocene moieties in **3b**, **3c** and **4** were also examined by the chronoamperometric method on an microelectrode,^{1a} and the results are also summarised in Table 2. On the average, there were around 70% of the total ferrocene units in these polymers were electrochemically oxidised during a potential-step process. The results obtained by this protocol were consistent with those acquired by bulk-electrolysis experiments described above.

The oxidised **3c** was subjected to magnetic measurements, and the magnetic susceptibilities at different temperatures thus obtained are shown in Fig. 2. The molar magnetic susceptibility, χ_M , was calculated based on the contribution of ten ferrocene-containing monomers; the spin only $\chi_M T$ value of one unpaired electron ($S = 1/2$) should be $0.375 \text{ cm}^3 \text{ K mol}^{-1}$.⁸ Accordingly, the measured $\chi_M T$ value at 295 K of $2.62 \text{ cm}^3 \text{ K mol}^{-1}$ would suggest that roughly seven ferrocene out of every 10 monomers being oxidised. In other words, there would be 70% of the ferrocenium moieties, which is supposed to have one unpaired electron, in the oxidised **3c**. This result agreed nicely with those from the electrochemical measurements. Moreover, the $\chi_M T$ increases with temperature from 2 to 300 K, which indicates the strong antiferromagnetic coupling among the oxidised monomers.⁹

The oxidation behaviours of **3** and **4** are apparently very different from those of **1** and the sulfur- or silylene-spaced ferrocene copolymers.² The structural uniqueness of **3** and **4** may play a pivotal role in this electrochemical oxidation process. That 70% of the ferrocene moieties in **3** and **4** were oxidised suggest that each of the neighbouring monomeric units may strongly couple with each other, which can be evidenced by the antiferromagnetic interactions observed in magnetic susceptibility measurements. However, due to the electrostatic repulsion, the ferrocene linkers in **3** and **4** cannot be fully oxidised. It is noteworthy that the oxidised form of **3** and **4** appeared to be fairly stable under ambient conditions.

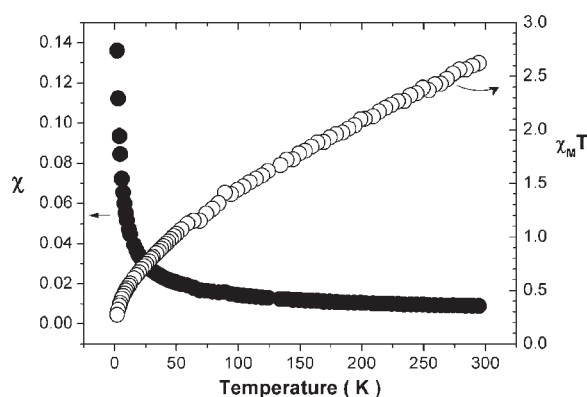
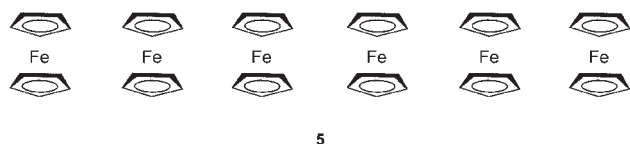


Fig. 2 Magnetic susceptibility of the oxidised **3c** as a function of temperature. The solid (χ) and open circle ($\chi_M T$) are experimental data based on ten monomeric units after correction on diamagnetism and normalization on the applied magnetic field.

Table 3 Hirshfeld charge analysis on **5** and **5ⁿ⁺** ($n = 4-6$)

Compound	Fe	Fe	Fe	Fe	Fe	Fe
5	0.0814	0.0867	0.0866	0.0866	0.0867	0.0814
5⁴⁺	1.2577	0.3469	0.1252	0.1252	0.3469	1.2577
5⁵⁺	1.6106	0.3590	0.1255	0.1255	0.3590	1.6106
5⁶⁺	1.9636	0.3710	0.1259	0.1259	0.3710	1.9636

As depicted earlier, the ferrocene moieties in **3** may be aligned coherently in essentially eclipsed manner with the spacing between neighbouring ferrocene moieties about 5.5 Å. In order to realise the charge distribution of the oxidised form of **3**, DFT calculations were undertaken on a model having six ferrocenes aligned linearly with a separation of 5.5 Å between the neighbouring ferrocenes, **5**. Each of the ferrocene moieties was assumed in D_{5h} point group and a C_{2v} symmetry was imposed on **5**.[‡] The calculation of neutral **5** was carried out in the restricted closed shell level. Four to six electrons were then removed from the HOMO to HOMO–2 of the neutral **5** to give the corresponding oxidised **5ⁿ⁺** ($n = 4-6$) and the charge densities on each ferrocene moiety in these ions were obtained.[‡] The Hirshfeld charge analysis¹⁰ at Fe atoms on **5** and **5ⁿ⁺** are summarised in Table 3. It is interesting to note that removal of electrons from **5** would yield uneven charge distribution among Fe atoms in oxidised forms of **5ⁿ⁺**. The majority of the charge is located at the terminal ferrocene moieties with minor charge resided at the interim ferrocene moieties. These results indicate the charges are delocalised and accumulated at the terminal ones to minimise the overall Coulombic interactions. The molecular orbital diagrams for HOMO to HOMO–5 and LUMO to LUMO + 1 are provided in the ESI.[†] Extensive oxidation up to the removal of five and six electrons from **5** may, however, result in too much charge localised at the terminal ferrocene moieties which may somewhat destabilise the system.



In summary, we have demonstrated the unique electrochemical properties of the ferrocene-containing double stranded bispolynorbornenes **3** and related polymer **4**. The antiferromagnetic character of the stable oxidised **3c** suggested strong coupling between the neighbouring ferrocene/ferrocenium moieties. The unusual structural feature and distinctive redox characteristics of these polymers may be useful for future applications in catalysis as well as in optoelectronic applications.

This work was supported by the National Science Council and the National Taiwan University of the Republic of China. We thank Professor Allen J. Bard for helpful discussions and NCHC for the support on the hardware and software for molecular orbital calculations.

Notes and references

[‡] The calculations were carried out by Amsterdam Density Functional 2006.01 (ADF)¹¹ with the generalised gradient approximation (GGA). The corrections of LDA and GGA parts were taken from VWN¹² and BP.^{13,14} The SCALAR ZORA was used for relativistic corrections. The triple zeta with two polarization function, TZ2P, Slater type basis sets were used for all atoms.

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