

## Synthesis, electrochemistry and photoconductivity of oligo- and poly-(1,1'-dihexylferrocenylenes)

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Oligo- and poly-(1,1'-dihexylferrocenylenes), more soluble than unsubstituted oligo- and poly-(1,1'-ferrocenylenes), were synthesized by reaction of dihexylfulvalene dianion with  $[\text{FeCl}_2(\text{thf})_2]$  (thf = tetrahydrofuran). Electrochemical properties of pentamers and a hexamer were revealed and compared with theory for a system with a linear combination of redox centres. Charge-transfer complexes of poly(dihexylferrocenylene) ( $M = 5000$ ,  $M/M_n = 1.2$ ) with tetracyanoethylene and 7,7,8,8-tetracyanoquinodimethane exhibit photoconductivity.

Poly(1,1'-ferrocenylene) is a representative organometallic polymer in which there is electronic communication between metal sites along the linear polymeric chain. Many synthetic routes for it have been developed and its physical properties investigated both experimentally<sup>1</sup> and theoretically.<sup>2</sup> For example, electrochemical properties of oligoferrocenylenes have been examined up to a tetramer,<sup>3</sup> showing the same number of one-electron oxidation waves as that of ferrocene units in a molecule due to the formation of mixed valence states. Cyclic voltammetry of low-molecular-weight poly(ferrocenylene) ( $M = \text{ca. } 900$ ) dissolved in  $\text{CH}_2\text{Cl}_2$  and electrodeposited on Pt gives a broad redox wave with two (or three) peaks between 0.2 and 0.8 V vs. saturated sodium chloride calomel electrode (SSCE).<sup>4</sup> The electrical conductivity of poly(ferrocenylene) has been reported by Pittman and Sasaki<sup>5</sup> and Sanechika *et al.*<sup>6</sup> to be increased significantly up to  $4 \times 10^{-2} \text{ S cm}^{-1}$  on forming complexes with organic  $\pi$  acceptors such as 7,7,8,8-tetracyanoquinodimethane (tcnq). It should be noted, however, that the poor solubility of unsubstituted poly(1,1'-ferrocenylene) is a major problem in studying its fundamental properties and practical application.

On the other hand, Aoki and Chen<sup>7</sup> have recently given a theoretical insight on the redox properties of a linearly combined multiredox system based on the interaction energy between the neighbouring redox sites. This theory predicts that a system with an odd number of redox centres,  $n = 2m + 1$  ( $m \geq 1$ ) gives three redox waves involving  $m$ , 1 and  $m$  electrons, and one with an even number of redox sites  $n = 2m + 2$  ( $m \geq 1$ ), gives four redox waves involving  $m$ , 1, 1 and  $m$  electrons, and consequently the number of waves converges to two when  $m$  approaches infinity. A series of oligo- and poly-ferrocenylenes is one of the best systems to examine this prediction if the solubility is sufficient for electrochemical analysis and this prompted us to synthesize soluble derivatives. Attachment of long alkyl chains is a typical method to increase the solubility of insoluble linear polymers.<sup>8</sup> In this study, we have synthesized oligo- and poly-(1,1'-dihexylferrocenylenes) from dihexylfulvalene\* ion and  $[\text{FeCl}_2(\text{thf})_2]$  (thf = tetrahydrofuran), and isolated oligo(dihexylferrocenylenes) up to a hexamer by the recycling GPC method. We report the electrochemical properties of the penta- and hexa-(ferrocenylene) derivatives. We have also found that charge-transfer complexes of poly(dihexylferro-

cenylene) with organic acceptors, tcnq and tetracyanoethylene (tcne), exhibit photoconductivity.

### Experimental

Sodium *n*-hexylcyclopentadienide was prepared as described previously.<sup>9</sup> Anhydrous solvents were obtained from Kanto Chemicals. Tetra-*n*-butylammonium perchlorate was obtained from Tomiyama Chemicals as lithium battery grade. Dichloromethane used for electrochemical measurements was a HPLC grade chemical from Kanto Chemicals. Interdigitated microarray (IDA) electrodes with 100 fingers, finger length 2 mm, finger width 5  $\mu\text{m}$  and finger gap 10  $\mu\text{m}$  and made of indium tin oxide (ITO) were a generous gift from NTT Basic Research Laboratories.<sup>10</sup> Plates of *n*-GaAs and *p*-GaAs were a generous gift from Fujitsu Laboratories Ltd.<sup>10</sup> Infrared, UV/VIS, <sup>1</sup>H NMR and electron-impact (EI) mass spectra were recorded with Shimadzu FT-IR 8100M, JASCO V-570, JEOL GX400 and Hitachi M-80B spectrometers, respectively. Measurements of field-desorption (FD) mass spectra for higher oligoferrocenylenes were carried out at UBE Scientific Analytical Laboratory.

### Synthesis of oligo- and poly-(ferrocenylenes)

All manipulations were carried out under nitrogen except as otherwise stated. To a 10 dm<sup>3</sup> thf solution of sodium *n*-hexylcyclopentadienide (1.0 g, 5.8 mmol) at  $-63^\circ\text{C}$  was added dropwise a thf solution (10 dm<sup>3</sup>) of I<sub>2</sub> (1.7 g, 2.9 mmol) and stirred for 1 h. A hexane solution (3.6 dm<sup>3</sup>) of *n*-butyllithium (1.62 mol dm<sup>-3</sup>) was slowly added and stirred at  $-63^\circ\text{C}$  for 1 h. The temperature was raised to  $-29^\circ\text{C}$ , then a thf solution (5 dm<sup>3</sup>) of  $[\text{FeCl}_2(\text{thf})_2]$  (0.79 g, 2.9 mmol) was slowly added followed by stirring for 20 h and allowing the temperature to increase to room temperature. After addition of water (30 dm<sup>3</sup>) the mixture was exposed to the air and transferred to a separatory funnel. The product was extracted with hexane (20 dm<sup>3</sup>) seven times, and the extract dried with sodium sulfate, filtered through a membrane filter (pore size 0.45  $\mu\text{m}$ ), and the solvent distilled off under vacuum. The oily residue was dissolved in toluene and separated into a lower-molecular-weight component (molecular weight < 4000 based on the polystyrene standard) and a higher one, 7 (molecular weight > 4000), with a JAI LC-908 recycling HPLC apparatus with JAIGEL 2H and 3H columns. The latter component was further separated into monomeric and oligomeric ferrocenylenes, **1a**, **1b**, **2a**, **2b**, **3a**, **3b**, **4a**, **4b**, **5a**, **5b** and **6b** using the

\* Fulvalene = 5-(cyclopenta-2,4-dien-1-ylidene)cyclopenta-1,3-diene.

same apparatus as noted above: **1a** (77 mg, 5.2%) [Found: C, 79.15; H, 10.1%;  $m/z$  (EI) 502 ( $M^+$ ).  $C_{33}H_{50}Fe$  requires C, 78.9; H, 10.0%;  $M$ , 502];  $\delta_H$ (CDCl<sub>3</sub>) 6.6–6.2 (4 H, m, CH of the end  $C_5H_4C_6H_{13}$  group), 4.1–3.4 (7 H, m, CH of  $\eta^5$ -hexylcyclopentadienyl groups), 2.5–1.6 (6 H, m, terminal CH<sub>2</sub> of  $C_6H_{13}$ ), 1.6–1.0 (24 H, m, CH<sub>2</sub> of  $C_6H_{13}$ ) and 1.0–0.6 (9 H, m, CH<sub>3</sub>); **1b** (53 mg, 2.8%) [Found: C, 81.3; H, 10.2%;  $m/z$  (EI) 650 ( $M^+$ ).  $C_{44}H_{66}Fe$  requires C, 81.2; H, 10.2%;  $M$ , 650];  $\delta_H$ (CDCl<sub>3</sub>) 6.6–6.2 (8 H, m, CH of end  $C_5H_4C_6H_{13}$ ), 4.1–3.4 (6 H, m, CH of  $\eta^5$ -hexylcyclopentadienyl groups), 2.5–1.6 (8 H, m, terminal CH<sub>2</sub> of  $C_6H_{13}$ ), 1.6–1.0 (32 H, m, CH<sub>2</sub> of  $C_6H_{13}$ ) and 1.0–0.6 (12 H, m, CH<sub>3</sub>); **2a** (42 mg, 3.4%) [Found: C, 77.5; H, 9.8%;  $m/z$  (EI) 854 ( $M^+$ ).  $C_{55}H_{82}Fe_2$  requires C, 77.3; H, 9.7%;  $M$ , 854];  $\delta_H$ (CDCl<sub>3</sub>) 6.6–6.1 (4 H, m, CH of end  $C_5H_4C_6H_{13}$ ), 4.3–3.2 (13 H, m, CH of  $\eta^5$ -hexylcyclopentadienyl groups), 2.6–1.6 (10 H, m, terminal CH<sub>2</sub> of  $C_6H_{13}$ ), 1.6–1.0 (40 H, m, CH<sub>2</sub> of  $C_6H_{13}$ ) and 1.0–0.6 (15 H, m, CH<sub>3</sub>); **2b** (61 mg, 4.2%) [Found: C, 78.9; H, 9.7%;  $m/z$  (EI) 1002 ( $M^+$ ).  $C_{66}H_{98}Fe_2$  requires C, 79.0; H, 9.85%;  $M$ , 1002];  $\delta_H$ (CDCl<sub>3</sub>) 6.6–6.1 (8 H, m, CH of end  $C_5H_4C_6H_{13}$ ), 4.3–3.2 (12 H, m, CH of  $\eta^5$ -hexylcyclopentadienyl groups), 2.6–1.6 (12 H, m, terminal CH<sub>2</sub> of  $C_6H_{13}$ ), 1.6–1.0 (48 H, m, CH<sub>2</sub> of  $C_6H_{13}$ ) and 1.0–0.6 (18 H, m, CH<sub>3</sub>); **3a** (20 mg, 1.7%) [Found: C, 76.5; H, 9.6%;  $m/z$  (EI) 1207 ( $M^+$ ).  $C_{77}H_{114}Fe_3$  requires C, 76.6; H, 9.5%;  $M$ , 1207];  $\delta_H$ (CDCl<sub>3</sub>) 6.6–6.1 (4 H, m, CH of the end  $C_5H_4C_6H_{13}$ ), 4.3–3.2 (19 H, m, CH of  $\eta^5$ -hexylcyclopentadienyl groups), 2.5–1.6 (14 H, m, terminal CH<sub>2</sub> of  $C_6H_{13}$ ), 1.26 (56 H, m, CH<sub>2</sub> of  $C_6H_{13}$ ) and 1.0–0.6 (21 H, m, CH<sub>3</sub>); **3b** (32 mg, 2.5%) [Found: C, 78.2; H, 9.5%;  $m/z$  (EI) 1355 ( $M^+$ ).  $C_{88}H_{130}Fe_3$  requires C, 78.0; H, 9.7%;  $M$ , 1355];  $\delta_H$ (CDCl<sub>3</sub>) 6.6–6.1 (8 H, m, CH of end  $C_5H_4C_6H_{13}$  groups), 4.3–3.2 (18 H, m, CH of  $\eta^5$ -hexylcyclopentadienyl groups), 2.5–1.6 (16 H, m, terminal CH<sub>2</sub> of  $C_6H_{13}$ ), 1.26 (64 H, m, CH<sub>2</sub> of  $C_6H_{13}$ ) and 1.0–0.6 (24 H, m, CH<sub>3</sub>); **4a** (6 mg, 0.5%) (Found: C, 76.5; H, 9.4.  $C_{99}H_{146}Fe_4$  requires C, 76.2; H, 9.4%);  $\delta_H$ (CDCl<sub>3</sub>) 6.6–6.1 (4 H, m, CH of end  $C_5H_4C_6H_{13}$ ), 4.4–3.1 (25 H, m, CH of  $\eta^5$ -hexylcyclopentadienyl groups), 2.5–1.6 (18 H, m, terminal CH<sub>2</sub> of  $C_6H_{13}$ ), 1.26 (72 H, m, CH<sub>2</sub> of  $C_6H_{13}$ ) and 0.88 (27 H, m, CH<sub>3</sub>); **4b** (22 mg, 1.7%) (Found: C, 77.55; H, 9.7.  $C_{110}H_{162}Fe_4$  requires C, 77.4; H, 9.6%);  $\delta_H$ (CDCl<sub>3</sub>) 6.6–6.1 (8 H, m, CH of end  $C_5H_4C_6H_{13}$ ), 4.4–3.1 (24 H, m, CH of  $\eta^5$ -hexylcyclopentadienyl groups), 2.5–1.6 (20 H, m, terminal CH<sub>2</sub> of  $C_6H_{13}$ ), 1.26 (80 H, m, CH<sub>2</sub> of  $C_6H_{13}$ ) and 1.0–0.6 (30 H, m, CH<sub>3</sub>); **5a** (4 mg, 0.4%) [Found: C, 77.5; H, 9.6%;  $m/z$  (FD) 1912 ( $M^+$ ).  $C_{121}H_{178}Fe_5$  requires C, 76.0; H, 9.4%;  $M$ , 1912];  $\delta_H$ (CDCl<sub>3</sub>) 6.6–6.1 (4 H, m, CH of the end  $C_5H_4C_6H_{13}$ ), 4.3–3.1 (31 H, m, CH of  $\eta^5$ -hexylcyclopentadienyl groups), 2.5–1.6 (22 H, m, terminal CH<sub>2</sub> of  $C_6H_{13}$ ), 1.26 (88 H, m, CH<sub>2</sub> of  $C_6H_{13}$ ) and 0.89 (33 H, m, CH<sub>3</sub>); **5b** (12 mg, 1.0%) [Found: C, 76.7; H, 9.7%;  $m/z$  (FD) 2060 ( $M^+$ ).  $C_{132}H_{194}Fe_5$  requires C, 77.0; H, 9.5%;  $M$ , 2060];  $\delta_H$ (CDCl<sub>3</sub>) 6.6–6.1 (8 H, m, CH of end  $C_5H_4C_6H_{13}$ ), 4.4–3.1 (30 H, m, CH of  $\eta^5$ -hexylcyclopentadienyl groups), 2.5–1.6 (24 H, m, terminal CH<sub>2</sub> of  $C_6H_{13}$ ), 1.25 (96 H, m, CH<sub>2</sub> of  $C_6H_{13}$ ) and 0.89 (36 H, m, CH<sub>3</sub>); **6b** (6 mg, 0.5%) [Found: C, 76.9; H, 9.55%;  $m/z$  (FD) 2412 ( $M^+$ ).  $C_{154}H_{226}Fe_6$  requires C, 76.7; H, 9.4%;  $M$ , 2412];  $\delta_H$ (CDCl<sub>3</sub>) 6.6–6.1 (8 H, m, CH of end  $C_5H_4C_6H_{13}$ ), 4.4–3.1 (36 H, m, CH of  $\eta^5$ -hexylcyclopentadienyl group), 2.5–1.7 (28 H, m, terminal CH<sub>2</sub> of  $C_6H_{13}$ ), 1.26 (112 H, m, CH<sub>2</sub> of  $C_6H_{13}$ ) and 0.88 (42 H, m, CH<sub>3</sub>); **7** (17 mg, 2%) (Found: C, 75.8; H, 9.4.  $C_{22}H_{32}Fe$  requires C, 75.0; H, 9.15%).

#### Electrochemical measurements

A glassy carbon rod (outside diameter 5 mm) (Tokai Carbon GC-20) was embedded in Pyrex glass and the cross-section used as a working electrode. Cyclic voltammetry and Osteryoung square-wave voltammetry were carried out in a standard one-compartment cell equipped with a platinum-wire counter electrode and an Ag–Ag<sup>+</sup> reference electrode [10 mmol dm<sup>-3</sup> AgClO<sub>4</sub> in 0.1 mol dm<sup>-3</sup> NBu<sub>4</sub>ClO<sub>4</sub>–MeCN,

$E^\circ$  (ferrocenium–ferrocene) = 0.21 V] with a BAS CV-50W voltammetric analyser. The computer software, DIGISIM2 (BAS) of Rudolph *et al.*,<sup>11</sup> was used for simulation of cyclic voltammograms.

#### Photoconductivity measurements

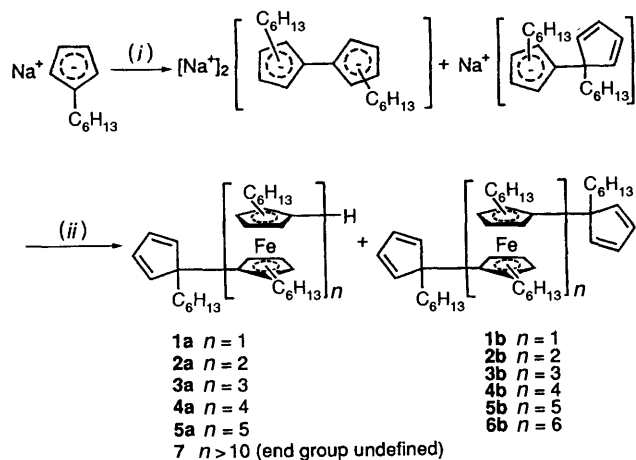
An acetonitrile solution containing compound **7** and an organic  $\pi$  acceptor such as 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (ddbq), tcne, tcnq, tetrachloro-1,4-benzoquinone or 2,6-dichloro-*p*-benzoquinone (dbq) in a given ratio was drop-coated on an ITO-IDA electrode. Sandwich devices for the tcne complex of **7** (abbreviated as **7**·tcne), *n*-GaAs/**7**·tcne/ITO and *p*-GaAs/**7**·tcne/ITO, were also fabricated by the drop-coating method. Photoirradiation was carried out with a 500 W xenon lamp through an IR-cut filter under nitrogen.

## Results and Discussion

### Synthesis of oligo- and poly-(dihexylferrocenylene)

Reductive coupling of 1,1'-dihalogenoferrocene with Mg, Mg plus a nickel(II) complex catalyst or nickel(0) complexes are typical methods to prepare poly(1,1'-ferrocenylenes).<sup>1,6</sup> Based on these methods our preliminary attempts to synthesize poly(dihexylferrocenylene) from 1,1'-dichloro-2,2'-dihexylferrocene, 1,1'-dichloro-3,3'-dihexylferrocene or 1,1'-dibromo-3,3'-dihexylferrocene have not given satisfactory results; *e.g.* a polymeric product ( $M > 4000$ ) was obtained in less than 1% yield in the reaction of 1,1'-dibromo-3,3'-dihexylferrocene with [Ni(cod)<sub>2</sub>] (cod = cycloocta-1,5-diene) in thf. This would be due to the weaker reducibility of the hexyl derivatives than unalkylated dibromoferrocene. Thus we employed a reaction of dihexylfulvalene ion with an iron(II) complex, [FeCl<sub>2</sub>(thf)<sub>2</sub>], which was originally developed for the synthesis of bis(fulvalene)diiron.<sup>12</sup> We, however, could not obtain a significant amount of bis(dihexylfulvalene)diiron probably because of the steric effect of the *n*-hexyl group on the cyclopentadienyl rings, preventing a face-to-face configuration for unco-ordinated rings which is indispensable to formation of the second ferrocene moiety when the first ferrocene is made from two fulvalene ions. The polymerization degree of the product was widely distributed, indicating that this method is not suitable for the preparation of a high-molecular-weight polymer but effective for oligomer synthesis. The product was first separated by GPC into a polymeric component, **7**, with molecular weight > 4000 based on the polystyrene standard, and other oligomeric components. The polymer ( $M = 5000$ ,  $M/M_n = 1.2$ ) is a brown tar soluble in common organic solvents such as hexane, benzene, dichloromethane or thf. Oligomers were separated into several fractions by recycling GPC. Isolation of higher oligomers is more difficult due to a decrease in the retention time difference with increasing molecular weight, and in this study we have isolated up to a hexamer. Purification of compound **5a** was not achieved as indicated by elemental analysis owing to low yield and because its GPC peak is not clearly isolated from a larger peak of **4b**. The purity of other isolated oligomers was checked by GPC, mass spectra and elemental analysis and found to be high enough for electrochemical analysis. All the oligomers are oily and they are light orange to brown with increasing molecular weight.

The monomers and oligomers were characterized by <sup>1</sup>H NMR, IR, UV/VIS and mass spectroscopy and elemental analysis. The end groups of the complexes are 1-hexylcyclopenta-2,4-dien-1-yl or H (Scheme 1) according to the spectroscopic and elemental analysis data. Formation of one-side substituted complexes (*i.e.* one of the end groups is H and denoted by **a** in the compound numbering) requires not only dihexylfulvalene ion but also hexylcyclopentadienide ion remaining in the solution. The hexyl group in the end



**Scheme 1** (i) (a) I<sub>2</sub>, thf; (b) LiBu<sup>n</sup>, C<sub>6</sub>H<sub>14</sub>; (ii) [FeCl<sub>2</sub>(thf)<sub>2</sub>], thf

hexylcyclopentadienyl group is ascertained to be at the 1 position from the <sup>1</sup>H NMR data (see Experimental section); the ratio of the number of protons giving signals at δ 3.1–4.4 (for the η<sup>5</sup>-hexylcyclopentadienyl group) to those at δ 6.1–6.6 (from olefinic carbons in the end C<sub>5</sub>H<sub>4</sub>C<sub>6</sub>H<sub>13</sub>) is (6n + 1):4 for the one-side substituted complexes with n ferrocenylene units, and 6n:8 for the both-side substituted complexes (denoted by **b** in the compound numbering), and no signal due to H at an aliphatic carbon in the end hexylcyclopentadienyl group is observed. This end-group structure is reasonable because it cannot be deprotonated by a treatment with LiBu<sup>n</sup> in the step which forms the fulvalene dianion (see Scheme 1) and thus the monoanion formed terminates the polymerization process. The oligomers are thermally stable, implying that the dimerization reaction of cyclopentadiene can hardly occur for the end C<sub>5</sub>H<sub>4</sub>C<sub>6</sub>H<sub>13</sub> group.

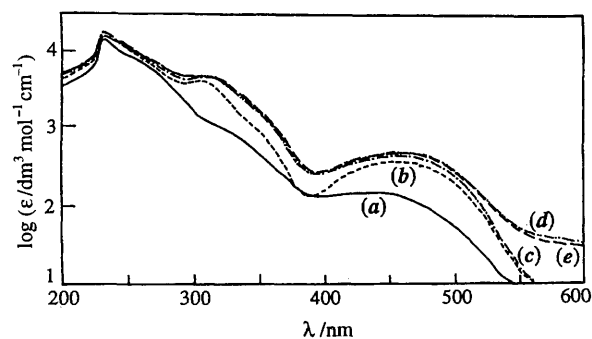
There remains a possibility of several geometric isomers for each oligomeric component due to different locations of the hexyl groups on the cyclopentadienyl ring because the formation of dihexylfulvalene ion from hexylcyclopentadienide ion would not occur stereoselectively. At present it is difficult to elucidate these positions from the spectroscopic data and we should assume a mixture when considering the physical properties. However, the electrochemical properties of each oligomer can be treated as that of a single redox molecule as described below.

The UV/VIS spectra of compounds **1b–5b** are given in Fig. 1. A peak appears at 310–325 nm when n ≥ 2 and the peak increment saturates when n ≥ 3. This is in accordance with the behaviour of unsubstituted oligo(1,1'-ferrocenylene),<sup>13</sup> and indicates weak electronic delocalization consistent with theoretical calculation.<sup>2</sup> There appear to be no significant differences in the effect of n on the spectrum between one-end substituted and both-end substituted complexes.

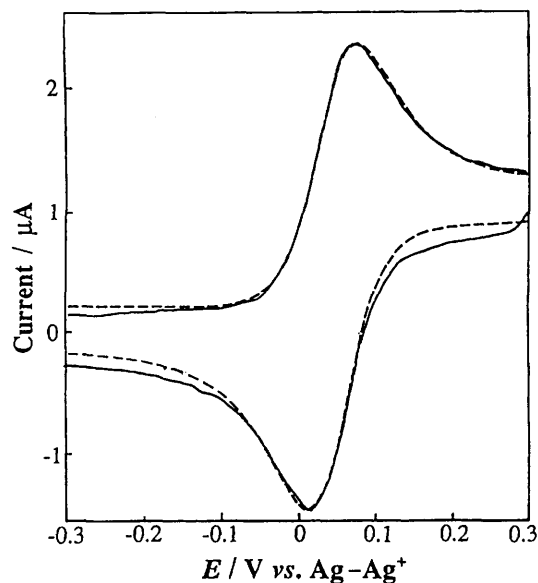
### Electrochemical properties

A cyclic voltammogram of compound **1a** and its simulation are displayed in Fig. 2. The peak-to-peak separation ΔE<sub>p</sub> = E<sub>pa</sub> – E<sub>pc</sub> is 60 mV and the curvature can be reproduced using a simple one-electron oxidation model. This implies that the redox behaviour of **1a** can be treated as that of a single species notwithstanding that there exists a possibility of several geometric isomers due to the difference in positions of the hexyl groups as noted above. Thus the difference in the location of the hexyl group on a cyclopentadienyl ring does not have a significant effect on E<sup>o</sup> for the ferrocenyl units, or less likely the hexyl group position is considerably regulated.

Some examples of cyclic voltammograms and square-wave voltammograms for oligomers are displayed in Figs. 3 and 4, respectively, and the results of both measurements are



**Fig. 1** The UV/VIS spectra of compounds **1b** (a), **2b** (b), **3b** (c), **4b** (d) and **5b** (e) in CH<sub>2</sub>Cl<sub>2</sub>



**Fig. 2** Cyclic voltammograms of 79.6 μmol dm<sup>-3</sup> compound **1a** (solid line) at glassy carbon (area 0.196 cm<sup>2</sup>) in 0.1 mol dm<sup>-3</sup> NBu<sub>4</sub>ClO<sub>4</sub>–CH<sub>2</sub>Cl<sub>2</sub> at a scan rate of 10 mV s<sup>-1</sup> at 25 °C and its simulation (broken line) based on the open-boundary finite-diffusion model using the following parameters: finite diffusion layer thickness, 0.41 mm; C<sub>dl</sub> 20 μF; E<sup>o</sup> 0.042 V; a 0.5; k<sub>s</sub> 0.020 cm<sup>2</sup> s<sup>-1</sup>; D<sub>R</sub> 2.9 × 10<sup>-5</sup> cm<sup>2</sup> s<sup>-1</sup>; D<sub>O</sub> 2.5 × 10<sup>-5</sup> cm<sup>2</sup> s<sup>-1</sup>

summarized in Table 1. A number, n, of reversible redox waves occur and the redox potential differences are almost in accordance with those for unsubstituted oligo(1,1'-ferrocenylenes) when n ≤ 4.<sup>3</sup>

Comparing the cyclic and square-wave voltammograms of compounds **5b** and **6b** shown in Figs. 3 and 4, respectively, with Aoki's theory,<sup>7</sup> both inconsistency and consistency are recognized. Inconsistent is the appearance of the same number of redox waves as for n even when n > 4. Consistent is the coarse dependency of E<sup>o</sup> values on n, especially the difference when n is odd or even. Conclusively, we can say that the first and third redox waves when n = 5 and first and fourth when n = 6 in the theory are separated into two one-electron peaks in the case of oligoferrocenylenes. A possible rationale to explain the experimental results is to take into account different values of the interaction parameter between neighbouring oxidized and reduced sites, U<sub>OR</sub>, depending on the location of the redox units because the substituents on the cyclopentadienyl rings are different for inside and outside ferrocenylene moieties on an oligomer chain. Another approach is the introduction of interaction parameters between more than two redox sites. This will be discussed theoretically by Aoki *et al.*<sup>14</sup> in another paper.

A cyclic voltammogram of poly(ferrocenylene), **7**, is given in Fig. 3. Three broad redox waves are seen at 0.03, 0.31 and 0.55 V, and the first one is much larger than the others. For a

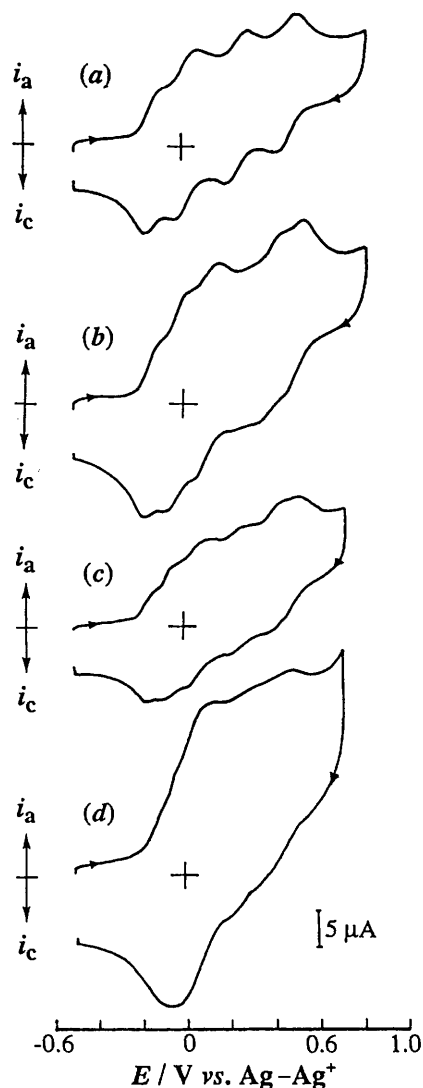


Fig. 3 Cyclic voltammograms of compounds **4b** (a), **5b** (b), **6b** (c) and **7** (d) at glassy carbon in  $0.1 \text{ mol dm}^{-3} \text{ NBu}_4\text{ClO}_4\text{-CH}_2\text{Cl}_2$  at a scan rate of  $100 \text{ mV s}^{-1}$

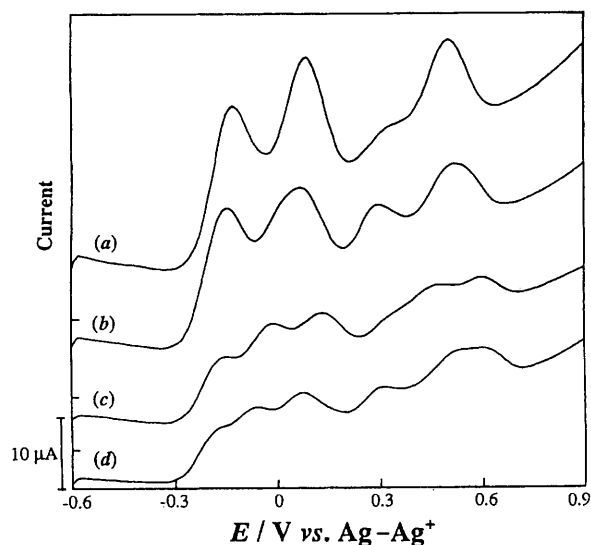


Fig. 4 Square-wave voltammograms of compounds **3b** (a), **4b** (b), **5b** (c) and **6b** (d) in  $0.1 \text{ mol dm}^{-3} \text{ NBu}_4\text{ClO}_4\text{-CH}_2\text{Cl}_2$  at a frequency of  $15 \text{ Hz}$  and a potential step of  $4 \text{ mV}$

sequence of oligomers, it is predicted that two waves appear at *ca.*  $-0.10$  and *ca.*  $0.55 \text{ V}$ .<sup>7</sup> However, the separation of the waves

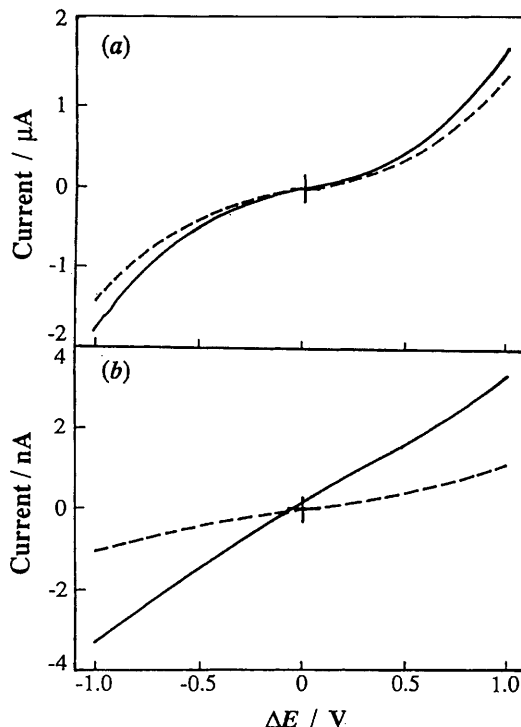


Fig. 5 Current vs.  $\Delta E$  curves for **7-tcnq** (a) and **7-tcne** (b) at ITO-IDA in the dark (broken lines) and under photoirradiation (solid lines) at a scan rate of  $2 \text{ mV s}^{-1}$

in the voltammogram in Fig. 3(d) is not well defined probably because the extent of polymerization is insufficient to afford the ideal voltammogram. It should be noted that Manners and co-workers<sup>15,16</sup> have reported the electrochemistry of oligo- and poly-(ferrocenylsilanes). They also observed that the number of oxidation waves depends on whether the number of ferrocenylene units is odd or even, while the  $\Delta E^{\circ'}$  values are quite different from those of oligoferrocenylenes.<sup>14</sup> They also showed that high-molecular-weight polymer gives two redox waves.<sup>15</sup>

#### Photoconductivity of poly(dihexylferrocenylene)- $\pi$ -acceptor complexes

Photoconductivity of charge-transfer complexes of conducting polymers has recently received attention.<sup>17</sup> We carried out electrical conductivity measurements in the dark and under photoirradiation for mixtures of compound **7** with organic  $\pi$ -acceptors, ddbq ( $E^{\circ'} = 0.27 \text{ V}$ ), tcne ( $E^{\circ'} = -0.03 \text{ V}$ ), tcnq ( $E^{\circ'} = -0.11 \text{ V}$ ), chloranil ( $E^{\circ'} = -0.23 \text{ V}$ ) and dbq ( $E^{\circ'} = -0.42 \text{ V}$ ), in which the mole ratio of ferrocenylene units to acceptor was 1:1. Among them, the tcne and tcnq complexes exhibited significant conductivity and photoconductivity compared to **7** by itself as shown in Fig. 5. This indicates that the acceptors corresponding to the donating ability of **7** are necessary for generating charge carriers, which is in accordance with the fact that polyferrocenylenes become conductive in the mixed-valence, *i.e.* partially oxidized, state. Weaker acceptors such as chloranil and dbq do not oxidize **7**, and the strongest one, ddbq, may overoxidize and decompose **7** since it is known that the stability of the highly oxidized state is low for higher oligomers.<sup>3</sup>

The electrical conductivity of compound **7** is more enhanced when it forms a complex with tcnq than with tcne ( $\sigma = 2 \times 10^{-8}$  and  $1 \times 10^{-11} \text{ S cm}^{-1}$  at  $1 \text{ V}$ ), but the photoconductivity is more distinct in the latter case as shown in Fig. 5. It should be noted that steady-state *i vs. ΔE* curves are obtained when the voltage scan rate is low ( $2 \text{ mV s}^{-1}$ ), but a significant hysteresis due to the charging current is seen at fast scan rates such as  $0.1 \text{ V s}^{-1}$ . A sandwich cell, ITO/**7-tcne**/n-

**Table 1** Electrochemical properties of oligo(1,1'-dihexylferrocenylenes)

Compound	$E^{\circ}_1$	$E^{\circ}_2$	$E^{\circ}_3$	$E^{\circ}_4$	$E^{\circ}_5$	$E^{\circ}_6$
<b>1a</b>	0.04 <sup>a</sup> (0.048) <sup>b</sup>					
<b>1b</b>	-0.01 (0.000)					
<b>2a</b>	-0.07 (-0.064)	0.33 (0.332)				
<b>2b</b>	-0.10 (-0.088)	0.32 (0.316)				
<b>3a</b>	-0.10 (n.d.) <sup>c</sup>	0.12 (n.d.)	0.51 (n.d.)			
<b>3b</b>	-0.13 (-0.140)	0.09 (0.084)	0.51 (0.500)			
<b>4a</b>	-0.16 (-0.156)	0.05 (0.052)	0.30 (0.304)	0.54 (0.552)		
<b>4b</b>	-0.18 (-0.160)	0.03 (0.068)	0.30 (0.288)	0.57 (0.520)		
<b>5a</b>	-0.19 (n.d.)	-0.03 (n.d.)	0.15 (n.d.)	0.46 (n.d.)	0.58 (n.d.)	
<b>5b</b>	-0.19 (-0.180)	-0.05 (-0.028)	0.13 (0.140)	0.46 (0.452)	0.60 (0.608)	
<b>6b</b>	-0.21 (-0.201)	-0.08 (-0.068)	0.07 (0.076)	0.29 (0.300)	0.50 (0.515)	0.61 (0.624)

<sup>a</sup> Obtained from  $E^{\circ} = (E_{pa} + E_{pc})/2$  in a cyclic voltammogram. <sup>b</sup> Values in parentheses were obtained from the peak potential in square-wave voltammograms. The values are given in V vs. Ag-Ag<sup>+</sup>. <sup>c</sup> n.d. = Not determined.

GaAs, gave a photocurrent at zero bias but ITO/7-tcne/p-GaAs did not. This indicates that the tcne complex acts as a p-type semiconductor probably due to hole conduction along the polyferrocenylene chain. It should be noted that the photocurrent for ITO/7-tcne/n-GaAs is small probably because polarization can proceed due to migration of acceptor species in the non-rigid polymer matrix and consequently compensates the electric field formed by photoirradiation. This is supported by the fact that a significant charging current flows when the voltage scan rate is fast (0.1 V s<sup>-1</sup>) as mentioned above. Attempts to increase the photocurrent and a detailed quantitative analysis of the photoconductivity are now underway in our laboratory.

## Conclusion

In this study derivatives of oligo- and poly-(1,1'-ferrocenylenes) were prepared which are more soluble than unsubstituted ones. As a consequence the electrochemical properties of pentamers and a hexamer were revealed for the first time. The results are approximately consistent with Aoki's theory but require further modification of the theory. Charge-transfer complexes of polyferrocenylene with tcne and tcnq show photoconductivity and act as p-type semiconductors.

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