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Liquid Crystals

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Ferrocene-based liquid-crystalline compounds

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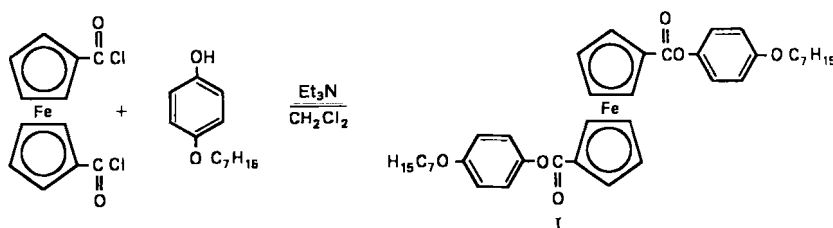
Three new ferrocene-based compounds were prepared which formed liquid crystalline phases in the melt, as follows: 1,1'-bis(*p*-heptoxyphenyl)ferrocene dicarboxylate, I; 1,1'-bis(*p*-decyloxyphenyl)ferrocene dicarboxylate, III; and 1-(*p*-decyloxyphenyl)-1'-(*p*-hydroxyphenyl)ferrocene dicarboxylate, IV. All three were characterized for their liquid-crystalline properties by polarized light microscopy, DSC and wide-angle X-ray diffraction.

1. Introduction

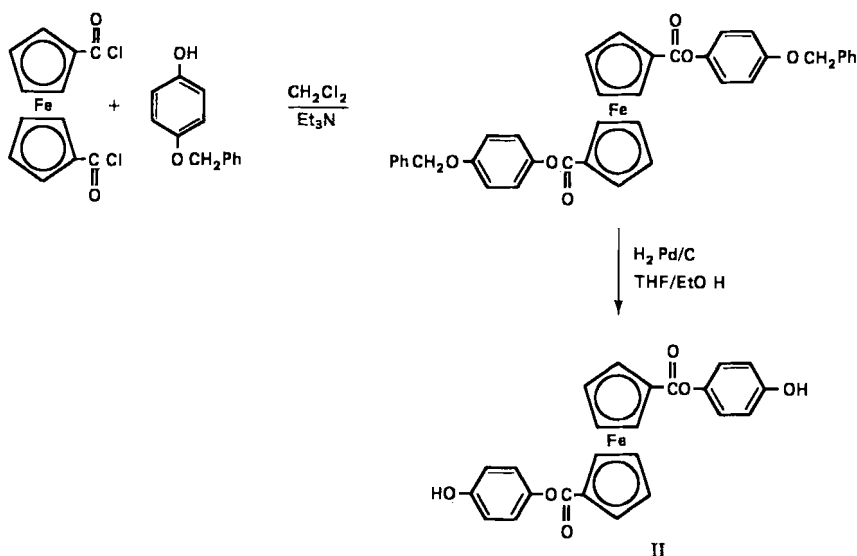
To our knowledge, there has not been an experimental verification that ferrocene could serve as the basis for a mesogenic group in a liquid crystalline compound. In principle it would seem possible that 1,1'-disubstituted ferrocene rings could impart both rigidity and collinearity as the central structural unit of a potential mesogen if additional substituents are present which are also linear and rigid [1]. Some bis(4-alkoxy-4'-biphenyl) ferrocene 1,1'-diesters were recently reported [2] to be liquid-crystalline, but it was implied that the ferrocene unit did not in itself contribute to mesophase formation. To test our hypothesis, we have, therefore, prepared a series of new linearly substituted ferrocene-containing compounds and examined them for the ability to organize spontaneously into liquid-crystalline phases.

2. Results and discussion

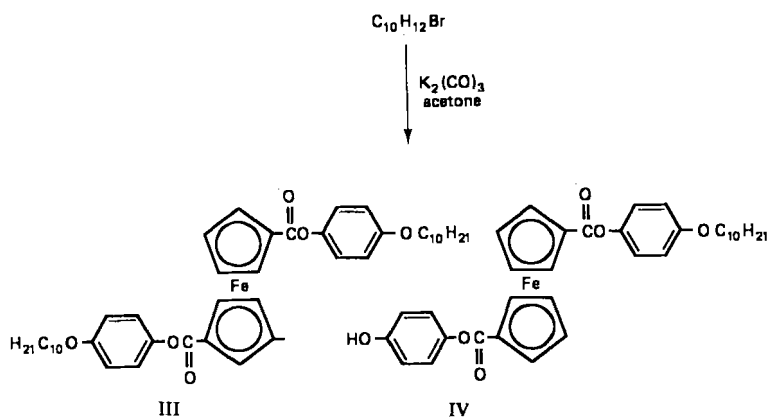
The first compound of the series was obtained from the reaction of 1,1'-bis(chlorocarbonyl)ferrocene [3] with *p*-heptoxyphenol using triethylamine as a base and methylene chloride as the solvent. The product, 1,1'-bis(*p*-heptoxyphenyl)ferrocene dicarboxylate, I, was obtained in 82 per cent yield, as shown below:



Two other compounds in this series were prepared from 1,1'-bis(*p*-hydroxyphenyl)ferrocene dicarboxylate, II, which in turn was obtained in two steps from the reaction between 1,1'-bis(chlorocarbonyl)ferrocene and 4-benzyloxyphenol followed by debenzoylation by hydrogenolysis, as follows:



A subsequent reaction between II and *n*-decyl bromide led to a mixture of products. The desired disubstituted compound, 1,1'-bis(*p*-decyloxyphenyl)ferrocene dicarboxylate, III, was obtained in only low yield. The major product was the monosubstituted compound, 1-(*p*-decyloxyphenyl)-1'-(*p*-hydroxyphenyl)ferrocene dicarboxylate, IV, as shown below:



These three compounds were characterized for their possible liquid-crystalline behaviour by optical microscopy and DSC. The DSC thermogram of I contained a shoulder on the melting endotherm which could be indicative of mesogenic behaviour, but if so, the temperature range of the liquid-crystalline phase was too small to permit observation of this behaviour on the polarizing microscope in the heating cycle. In contrast, the DSC thermogram of IV in figure 2 clearly showed the presence of multiple endotherms, which could be indicative of the formation of liquid-crystalline phases.

Compound I appeared to form only an isotropic melt when heated on a hot stage placed on a polarizing microscope, but on cooling at 2°/min a texture was observed for

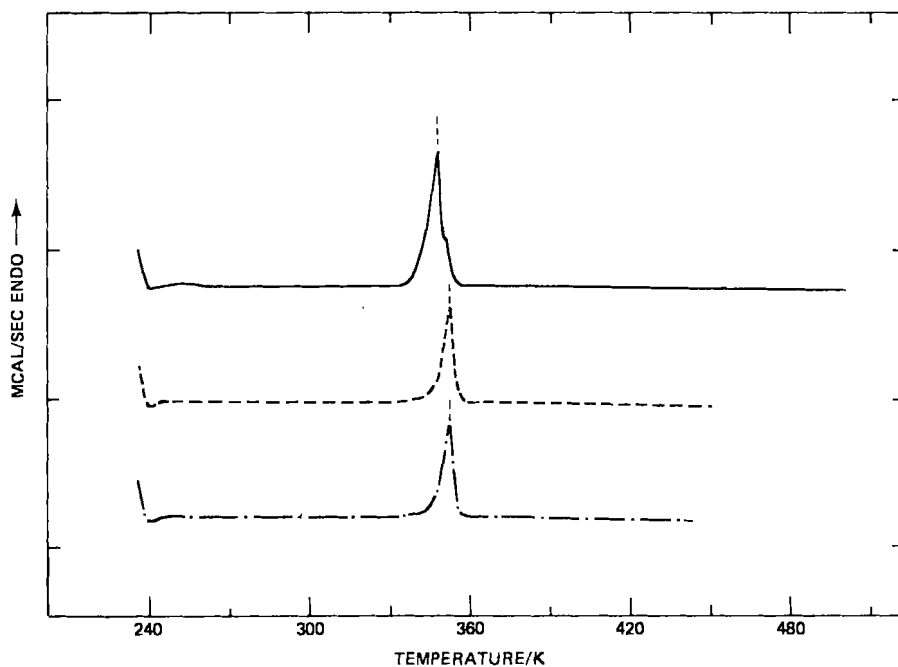


Figure 1. DSC thermograms of III: top, first heating cycle; middle, second heating cycle; bottom, third heating cycle.

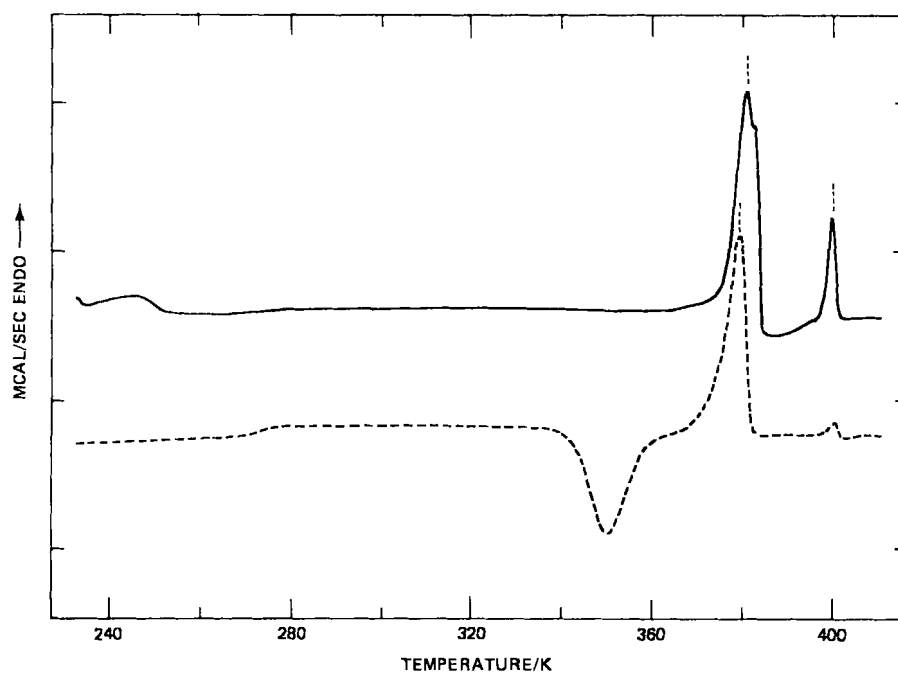


Figure 2. DSC thermograms of IV: top, first heating cycle; bottom, second heating cycle.

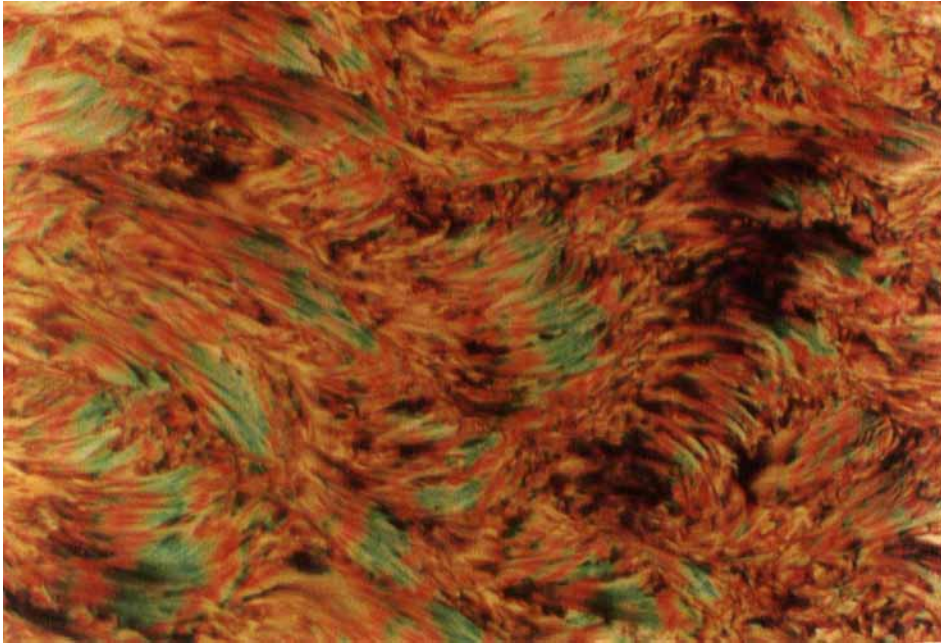


Figure 3. Photomicrograph of I at 77°C on cooling from the isotropic melt (magnification $\times 200$).

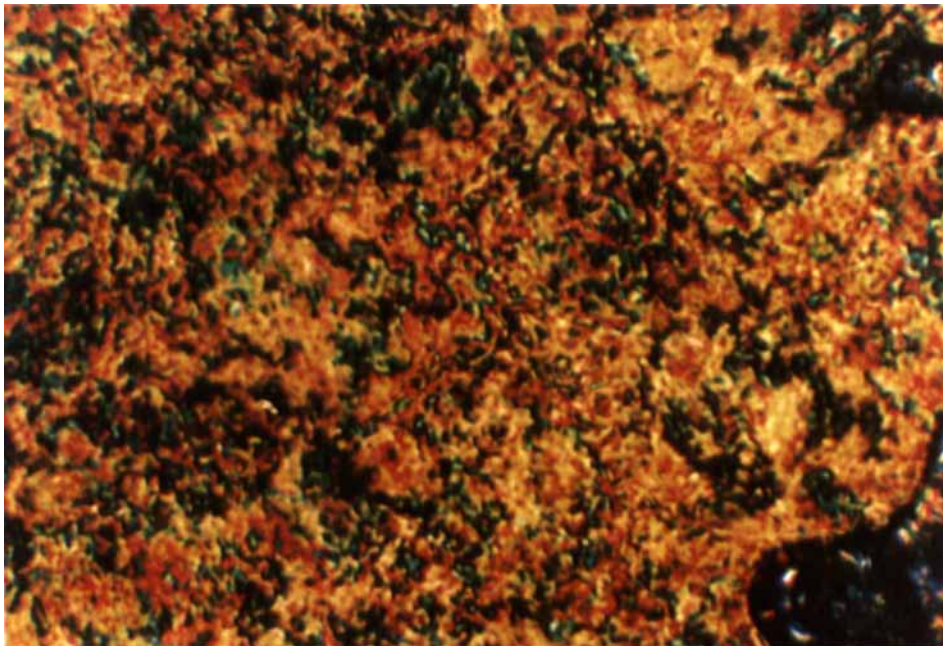


Figure 4. Photomicrograph of III at 78°C on heating from the crystalline state (magnification $\times 200$).

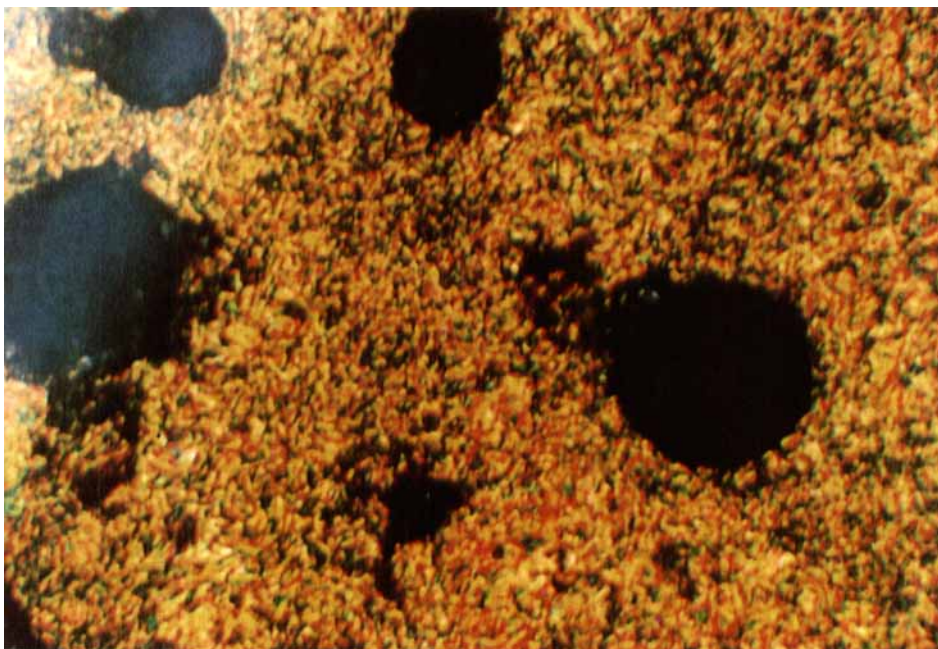


Figure 5. Photomicrograph of IV at 115°C on heating from the crystalline state (magnification $\times 200$).

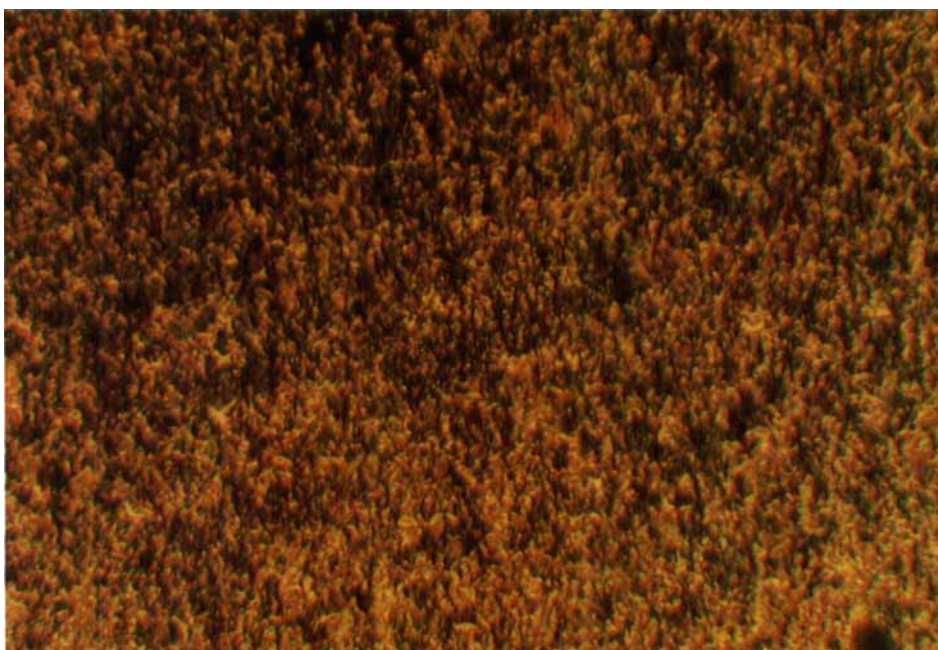


Figure 6. Photomicrograph of IV after 24 hours at room temperature (magnification $\times 200$).

this compound which is indicative of the formation of a smectic liquid-crystalline phase, as shown in figure 3. However, the specific phase could not be verified by miscibility tests with known smectics, including S_A , S_B and S_C compounds, and wide-angle X-ray diffraction of the melt also gave patterns which did not appear to be those of typical smectics.

Figure 4 is a photomicrograph of the texture formed by III as observed between 78°C (T_m) and 79°C (T_i) during the heating cycle on the polarizing microscope. However, the nematic texture seen in this figure did not develop again on cooling from the isotropic phase.

Figure 5 is a photomicrograph of the texture of compound IV at 115°C . This texture was observed to occur from 107°C (T_m) to 128°C (T_i) during the heating cycle, but as with III, on cooling the sample from the isotropic phase, the nematic texture was not seen to reform. Nevertheless, a nematic phase developed over 24 hours at room temperature, as seen in figure 6. The increased mesophase range of IV could result from the increase in the effective length of the molecule through intermolecular hydrogen bonding. The mixture of III and IV, isolated before column chromatographic separation, showed an unexpectedly broad nematic mesophase from about 110°C (T_m) to 170°C (T_i). The chromatographic separation indicated that the molar ratio of III:IV was *c.* 1:4.

In conclusion, these investigations have demonstrated that the ferrocene unit can be an effective component of a mesogen.

3. Experimental

Microanalyses were performed at the Microanalytical Labs at the University of Massachusetts, Amherst. DSC analyses were conducted on a Perkin-Elmer DSC-2 calorimeter interfaced with a thermal analysis data station. X-ray diffraction was done on a Statton diffractometer using a pinhole camera. $^1\text{H-NMR}$ spectra were recorded on Varian A-60, XLR-200 and XLR-300 spectrometers. Infrared spectra were obtained on either Beckman IR-10 or Perkin-Elmer 1310 IR spectrometers. All syntheses were carried out under prepurified nitrogen, which was further dried over P_2O_5 , and trace amounts of oxygen were removed with a BTS catalyst.

Ferrocene dicarbonyl chloride was prepared using a literature method [3, 4]. 4-Heptoxyphenol and decyl bromide were purchased from Aldrich Chemical Co. and used without any further purification.

3.1. Preparation of 1,1'-bis(*p*-heptoxyphenyl)ferrocene dicarboxylate (I)

A solution of ferrocene dicarbonyl chloride (1.24 g, 4.0 mmol) in methylene chloride (50 ml) was added to a stirred solution of *p*-heptoxyphenol (1.67 g, 8.0 mmol) and triethylamine (1.1 ml) in methylene chloride (100 ml) and the reaction mixture was refluxed for 16 hours. The cooled solution was washed successively with 0.1 N HCl, water, sodium bicarbonate solution, water and brine. The solvent was removed under high vacuum and the product crystallized from methylene chloride/pentane. mp. $87-88^\circ\text{C}$. Yield: 2.31 g, 92 per cent. IR(CH_2Cl_2): $\nu(\text{CO})$ 1735 cm^{-1} , $^1\text{H NMR}$ (CDCl_3): δ (ppm) 0.8–1.3 (methyl, methylene protons), 3.85 ($\text{CH}_2\text{-O-}$, methylene protons next to ether linkage), 4.5 and 5.0 (ferrocene protons), 6.9 (split doublets or aromatic protons). Found: C, 69.44; H, 7.31. $\text{C}_{38}\text{H}_{46}\text{O}_6\text{Fe}$ calcd.: C, 69.72; H, 7.08 per cent.

3.2. Preparation of 1,1'-bis(*p*-benzyloxyphenyl)ferrocene dicarboxylate

Ferrocene dicarbonyl chloride (3.12 g, 10 mmol) was refluxed for 24 hours with *p*-benzyloxyphenol (4.00 g, 20 mmol) and triethylamine (2.02 g, 20 mmol) in 200 ml of methylene chloride. The reaction mixture was cooled and washed successively with 0.1 N HCl, water, sodium bicarbonate solution, water, and brine. The methylene chloride layer was dried over anhydrous magnesium sulphate and the solvent removed under high vacuum. The residue was crystallized from methylene chloride/pentane to produce orange crystals of 1,1'-bis(*p*-benzyloxyphenyl)ferrocene dicarboxylate (5.25 g, 82 per cent). IR (CH₂Cl₂): $\nu(\text{CO})$ 1730 cm⁻¹. ¹H NMR (CDCl₃): δ (ppm) 6.9–7.5 (phenyl protons), 5.03 (s, Cp protons), 4.55 (t, methylene protons). Found: C, 71.40; H, 4.55. C₃₈H₃₀O₆Fe calcd.: C, 71.48; H, 4.73 per cent.

3.3. Preparation of 1,1'-Bis(*p*-hydroxyphenyl)ferrocene dicarboxylate (II)

1,1'-Bis(*p*-benzyloxyphenyl)ferrocene dicarboxylate (3.59 g, 5.6 mmol) was shaken mechanically with hydrogen under pressure (38–40 psi) for 24 hours in the presence of 10 per cent palladium on activated charcoal (0.75 g) in a 50 : 50 mixture of THF and 100 per cent ethanol. The catalyst was removed by filtration through a Celite column and the solvent was removed under vacuum. The orange residue was crystallized from THF/pentane in the following manner to avoid decomposition. The residue was dissolved in a minimum amount of hot THF. Part of the THF was removed using a rotary evaporator and pentane was added to the cooled solution. The orange crystals that formed were filtered, washed with pentane and dried in a vacuum oven for 24 hours. Yield: 2.5 g, 98 per cent. IR (CH₂Cl₂): $\nu(\text{CO})$ 1735 cm⁻¹; $\nu(\text{OH})$ 3300 cm⁻¹. Found: C, 63.00; H, 3.89. C₂₄H₁₈O₆Fe calcd.: C, 62.90; H, 3.96 per cent.

3.4. 1,1'-Bis(*p*-decyloxyphenyl)ferrocene dicarboxylate (III) and 1-(*p*-decyloxyphenyl)-1'-(*p*-hydroxyphenyl)ferrocene dicarboxylate (IV)

A solution of 1,1'-bis(*p*-hydroxyphenyl)ferrocene dicarboxylate (0.60 g, 1.3 mmol), *n*-decyl bromide (0.54 ml, 2.6 mmol) and anhydrous potassium carbonate (0.36 g, 2.6 mmol) in 100 ml of 10 per cent aqueous acetone was refluxed for 12 hours. The cooled solution was filtered and the solvent removed under high vacuum. The residue was taken up in methylene chloride and washed successively with water, aqueous sodium bicarbonate, 0.2 N HCl, water and brine. The solution was dried over anhydrous magnesium sulphate and crystallized from methylene chloride-pentane. Thin layer chromatography on silica gel indicated the presence of two compounds. The compounds were separated by flash column chromatography on silica gel using (1) 1 : 1 chloroform/pentane, and (2) chloroform. They were both recrystallized from methylene chloride-pentane. Compound III: Yield 0.1 g, 10 per cent, mp 86°C. IR (CH₂Cl₂): $\nu(\text{CO})$ 1735 cm⁻¹. ¹H NMR (CDCl₃): δ (ppm) 0.3–1.8 (38 H, methyl, methylene protons), 3.95 (4 H, methylene protons next to ether linkage), 4.60 and 5.05 (8 H, ferrocene protons), 7.0 (8 H, split doublets of aromatic protons). Found: (C, 71.36; H, 8.09. C₄₄H₅₈O₆Fe calcd.: C, 71.53; H, 7.91 per cent). Compound IV: Yield 0.3 g, 39 per cent, mp 98°C. IR (CH₂Cl₂): $\nu(\text{CO})$ 1735 cm⁻¹. ¹H NMR (CDCl₃): δ (ppm) 0.3–1.8 (19 H, methyl, methylene protons), 3.95 (2 H, methylene protons next to ether linkage), 4.60 and 5.05 (8 H, ferrocene protons), 5.45 (1 H, phenolic proton), 6.6–7.2 (8 H, multiplet, aromatic protons). Found: C, 68.05; H, 6.67. C₃₄H₃₈O₆Fe calcd.: C, 68.23; H, 6.40 per cent.

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