Electron-transfer induced mesomorphism in the ferrocene–ferrocenium redox system: first ferrocenium-containing thermotropic liquid crystal

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Chemical oxidation (silver tosylate, acetone, room temperature) of a non-mesomorphic persubstituted ferrocene derivative leads to the corresponding ferrocenium species which exhibits a smectic A phase (polarized optical microscopy, differential scanning calorimetry, X-ray diffraction).

Owing to its remarkable electrochemical properties,[1] ferrocene has found widespread applications as an electroactive building-block for elaborating switchable molecular aggregates,[2] redox-active receptors,[3] redox-active polymeric ionomers[4] and conducting and magnetic materials.[5]

Efforts oriented towards the design of new metallomesogens[6] led to ferrocene derivatives displaying rich mesomorphism.[7] Recently, chiral[8] and polymeric[9] liquid-crystalline ferrocenyl systems with potential applications in the development of ferroelectric liquid-crystal devices and processable materials were described.

Mesomorphic ferrocenium structures have not yet been reported. Such compounds would be of fundamental importance to investigate magnetism in anisotropic fluids.[10] Furthermore, comparison of the mesogenic properties of ferrocenium complexes with those of the corresponding ferrocene derivatives would bring much novel information concerning the factors which are responsible for generating and engineering mesomorphism in the case of thermotropic metallocenes.

This communication describes the synthesis and thermal properties of the persubstituted ferrocene derivative **1** and of its oxidized complex **2**. The latter represents the first example of a ferrocenium-containing thermotropic liquid crystal. A peralkylated ferrocene derivative was selected as an electron donor because of the ease of oxidation of such a species (and related peralkylated compounds) in comparison with less substituted structures {[Fe(η-C_5H_5)$_2$] +0.44 V, [Fe(η-C_5H_5)(η-C_5Me_5)] +0.13 V, [Fe(η-C_5Me_5)$_2$] −0.12 V}.[5c]

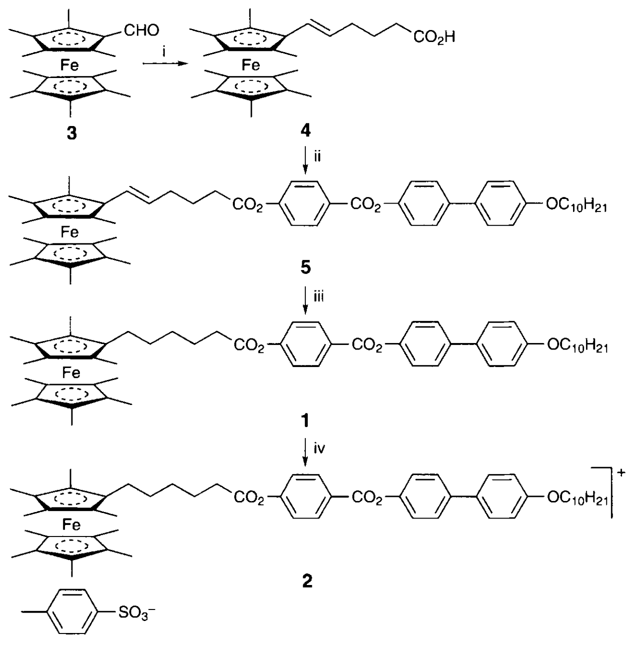
Compounds **1** and **2** were prepared as outlined in Scheme 1. Reaction of aldehyde derivative **3**[11] with (4-carboxybutyl)triphenylphosphonium bromide under Wittig reaction conditions[12] gave acid intermediate **4** [recovered by (i) addition of H_2O and diethyl ether, (ii) extraction (diethyl ether) of the acidified aqueous phase (dil. HCl solution), and (iii) crystallization from hexane]. Esterification of **4** with 4-decyloxybiphenyl-4-hydroxybenzoate, which was prepared from 4-(benzyloxy)benzoic acid and 4-decyloxy-4′-hydroxy biphenyl[13] following established procedures,[14] led to **5** (purified by crystallization from CH_2Cl_2–EtOH), the catalytic reduction of which furnished compound **1** as a yellow solid (purified by crystallization from acetone). Oxidation of **1** with silver tosylate yielded ferrocenium species **2** as a green solid (purified by crystallization from AcOEt). The structure and purity of **1**–**5** were confirmed by NMR spectroscopy and elemental analysis.†

Thermal and mesomorphic behaviour of **1** and **2** were investigated by polarized optical microscopy, differential scanning calorimetry (DSC) and X-ray diffraction studies.‡ The transition temperatures reported below were determined by DSC (onset temperature, rate 10 °C min^{-1} under N_2).

No mesomorphism was observed from ferrocene derivative **1**. When heated, **1** melted at 154 °C (ΔH = 41.5 kJ mol^{-1}, second heating run) into an isotropic fluid and, when cooled, crystallized from the isotropic melt at 137 °C (ΔH = 40.1 kJ mol^{-1}).

During the first heating [Fig. 1(*a*)], **2** gave an endotherm at 132 °C (ΔH = 56.3 kJ mol^{-1}) which corresponded to the formation of an isotropic fluid. On cooling from the isotropic melt [Fig. 1(*b*)], an exotherm was detected at 83 °C (ΔH = 4.5 kJ mol^{-1}) followed by a glass transition temperature (T_g) at 33 °C. Polarized optical microscopy investigations revealed the formation of a liquid-crystalline phase from 83 °C. Examination of small droplets showed the formation of homeotropic and focal-conic textures. From these observations, the mesophase was identified as a monotropic smectic A phase. The high viscosity of the mesophase in the low-temperature region might have prevented crystallization of the sample. Such behaviour was recently reported for mesomorphic silver(I) complexes.[15] During the second heating [Fig. 1(*c*)], the liquid-crystalline phase formed at the glass transition temperature (*ca.* 37 °C) and cleared at 83 °C (ΔH = 5.1 kJ mol^{-1}).

X-Ray diffraction studies, which were performed upon cooling **2** from the isotropic liquid in a magnetic field of 1.7 T, gave patterns typical of a smectic A phase (the director is parallel to the magnetic field and the layer planes perpendicular to it) with a *d*-layer spacing of 39.5 Å. From CPK models, an



Scheme 1 *Reagents and conditions*: i, Bu^{t}OK (2 equiv.), (4-carboxybutyl)triphenylphosphonium bromide, thf, room temp., 2 h, 40%; ii, 4-decyloxybiphenyl-4-hydroxybenzoate, *N,N*′-dicyclohexylcarbodiimide (DCC), 4-pyrrolidinopyridine (Ppy), CH_2Cl_2, room temp., 3 h, 62%; iii, H_2, Pd (10%)/C, CH_2Cl_2–EtOH, room temp., 1 h, 80%; iv, $AgO_3SC_6H_4Me$ (0.9 equiv.), acetone, room temp., 30 min., 85%

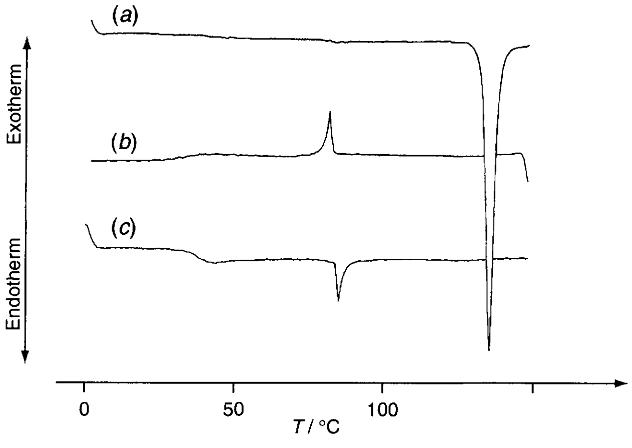


Fig. 1 Differential scanning calorimetry thermograms of **2** registered during the first heating (*a*), first cooling (*b*), and second heating run (*c*)

approximate molecular length *l* of 41 Å was measured for **2** in its fully extended conformation. The *d*/*l* ratio of 0.96 indicated a monomolecular organization of **2** within the mesophase. Upon long irradiation times, solidification of the sample was detected. This result was in agreement with the monotropic character of the mesophase.

Combination of a mesogenic structure with favourable electrostatic interactions is, most likely, at the origin of the liquid-crystalline behaviour observed for **2**. Electrostatic interactions should play a crucial role for generating mesomorphism since (neutral species) **1**, which did not show liquid-crystalline properties, and (ionic compound) **2** have the same basic structure. A detailed understanding of the influence of the structure, charge and counter ion on the thermal and mesomorphic properties requires the preparation and study of further ferrocenium complexes.

In conclusion, we have demonstrated that electron transfer can be exploited for controlling supramolecular organization within the liquid-crystalline state for the ferrocene–ferrocenium redox system.

Footnotes

† *Selected analytical data*: for **1** ^{1}H NMR (200 MHz, CD_2Cl_2), δ 0.85–1.15 (m, 30 H, C_5Me_5, C_5Me_4 and CH_3), 1.23 (m, 20 H, CH_2), 1.80 (m, 4 H, CH_2CH_2O and $CH_2CH_2CO_2R$), 2.62 (t, *J* 7.3 Hz, 2 H, CH_2CO_2R), 4.00 (t, *J* 6.5 Hz, 2 H, CH_2O), 6.98 (d, *J* 8.8 Hz, 2 H, H-arom), 7.26 (2 superimposed d, *J* 8.8 Hz, 4 H, H-arom), 7.55 (d, *J* 8.8 Hz, 2 H, H-arom), 7.62 (d, *J* 8.8 Hz, 2 H, H-arom), 8.23 (d, *J* 8.8 Hz, 2 H, H-arom). $C_{54}H_{70}FeO_5$ Anal. Calc. C, 75.86; H, 8.25. Found: C, 75.83; H, 8.18%.

For **2**: $C_{61}H_{77}FeO_8S$ Anal. Calc. C, 71.40; H, 7.56. Found: C, 71.53; H, 7.52%.

‡ For instrumentation, see (*a*) R. Deschenaux, I. Kosztics and B. Nicolet, *J. Mater. Chem.*, 1995, **5**, 2291; (*b*) A.-M. Levelut, Y. Fang and C. Destrade, *Liq. Cryst.*, 1989, **4**, 441.

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