

A Liquid Crystalline Ferrocenyl-phthalocyanine

Michael J. Cook,* Graeme Cooke* and Ali Jafari-Fini

School of Chemical Sciences, University of East Anglia, Norwich, UK NR4 7TJ

The synthesis and characterisation of the first discotic liquid crystalline derivative of ferrocene are described.

The attachment of the ferrocenyl core to various moieties commonly associated with cholesteric¹ and calamitic² liquid crystals has provided a number of ferrocene derivatives which exhibit mesophases. However, we are unaware of any examples where the ferrocene unit has been incorporated into discotic columnar liquid crystals. The dimensions of the ferrocene molecule suggest that its attachment to structures giving rise to discotic columnar mesophase behaviour, *e.g.* octasubstituted phthalocyanines,³ might have one of two effects. The bulky unit could severely disrupt columnar packing to the extent that the new material would exhibit no mesophase behaviour. Alternatively, because of the distance of *ca.* 3.3 Å between the two cyclopentadienyl rings is close to the intermolecular spacing of phthalocyanine molecules within mesophase stacks, a purpose designed derivative might allow the ferrocenyl unit to be readily accommodated into the mesophase packing to provide a supramolecular formulation of two intrinsically interesting moieties.

Here we have attached a ferrocenyl group to the liquid crystalline phthalocyanine **1**³ to afford the novel ferrocenyl-phthalocyanine system **2**. This compound was chosen because the absence of a long alkyl chain at one of the eight substituent positions on the phthalocyanine ring should provide a series of spaces in the columnar stack. In principle, these spaces could be occupied by the unsubstituted cyclopentadienyl ring of the ferrocene groups of neighbouring molecules in the stack.

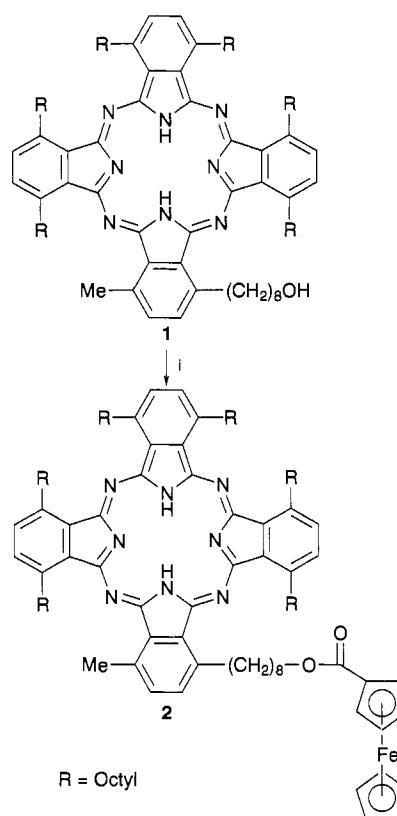
The synthesis of the target compound **2** was accomplished by treating compound **1** with a twofold excess of ferrocenecarbonyl chloride⁴ in dichloromethane at 25 °C, in the presence of a stoichiometric amount of pyridine (Scheme 1). After 5 h, the reaction was judged to have ceased (TLC, silica gel, toluene; $R_f = 0.6$). Compound **2** was obtained in 38% yield, together with ferrocenecarbonyl chloride and unreacted **1**, which could be reused. Isolation of compound **2** was achieved by column chromatography (silica gel, toluene). The compound gave satisfactory elemental analysis, low resolution mass spectrum and ¹H NMR spectrum.† The solution UV–VIS spectrum (THF) of **2** showed the presence of absorptions at 725, 695, 636, 391, 358 and 310 nm for the phthalocyanine moiety and 238 nm for the ferrocene group.

The compound was examined for mesophase behaviour using polarised light microscopy and differential scanning calorimetry, DSC. Scheme 2 summarises phase transition data for compound **2**; these are compared with those for compound **1**. Compound **2** exhibited a single mesophase which was characterised by its fan type birefringence texture as a discotic columnar mesophase of hexagonal symmetry with disordered spacing within the columns, D_{hd} . Its behaviour differs from that of compound **1** which showed two mesophases, the higher temperature phase is D_{hd} and the lower one is D_{rd} .³

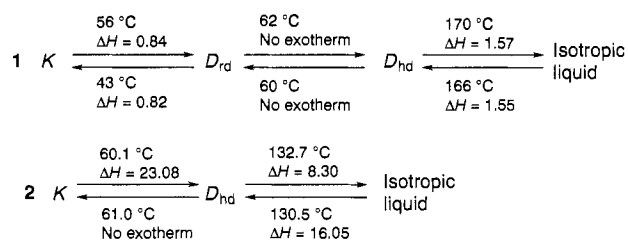
Spin coating of a drop of a saturated solution of **2** in THF onto the centre of a rotating glass slide (2000 rpm) produced, after evaporation of solvent, thin films of excellent quality, as judged by uniform absorbance measured at different parts of the film.⁵ It is well established that the band shape of the visible region absorption envelope of phthalocyanines in the solid state is very sensitive to molecular packing.⁶ Fig. 1(a) shows the spectrum of the film, and the corresponding spectrum of the spin coated film of the phthalocyanine precursor **1**, (b). The two are remarkably similar and suggests that the incorporation of the ferrocenyl group into **2** does not significantly modify the packing of the phthalocyanine cores. The film was then heated in a hotstage contained within the sample compartment of the spectrometer

and the spectrum was recorded at 80 °C, *i.e.* in the mesophase range of the material, (c). The band envelope has narrowed but the change is reversible, the band shape returning to that of the original spectrum on cooling. Oxidation of the film of **2** with iodine changes the colour of the film from green to brown and involves a further reorganisation of the phthalocyanine moieties resulting in enhanced intensity to the blue end of the visible region band, and the appearance of a shoulder at *ca.* 470 nm, (d). On standing the film in air for 40 min., the green colour returns and the visible region spectrum is superimposable upon that of the original film. The 470 nm band, however, is retained.

Compound **2** is thus the first example of a liquid crystalline ferrocenyl-phthalocyanine derivative and its ready formulation as a thin film offers the prospect of convenient studies of its



Scheme 1 Reagents and conditions: i, ferrocenecarbonyl chloride, pyridine, dry DCM, then aqueous workup



Scheme 2 ΔH in kcal mol⁻¹ (1 cal = 4.184 J)

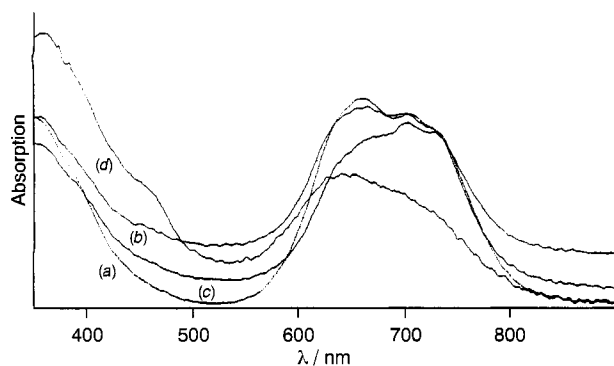


Fig. 1 UV-VIS spectra of spin coated films of compounds **1** and **2**: (a), **2** as deposited; (b) **1** as deposited; (c), compound **2** in the mesophase region (80 °C); (d), **2** immediately after oxidation with iodine

redox properties, both in the solid state and in the liquid crystal phase.

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Footnote

† Yield 38% (Anal. found: C, 77.99; H, 9.00; N, 6.98; $C_{100}H_{140}FeN_8O_2$ requires C, 77.89; H, 9.15; N, 7.27). FAB-MS (LSIMS) m/z 1542. IR (Nujol) ν/cm^{-1} 3304, 2925, 2854, 1719, 1461, 1477, 1262, 1098, 1024, 861, 804 and 762; 1H NMR (270 MHz, C_6D_6) δ 7.85 (m, 4 H), 7.62 (d, 1 H), 7.57 (d, 2 H), 7.44 (d, 1 H), 4.80 (t, 2 H), 4.69 (t, 4 H), 4.56 (t, 4 H), 4.45 (m, 4 H), 4.13 (t, 4 H), 3.95 (t, 2 H), 3.93 (s, 5 H), 3.51 (s, 3 H), 2.40–2.0 (m, 14 H), 1.85–1.20 (m, 70 H), 0.85 (m, 18 H) and –0.8 (s, 2 H).

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