

A liquid crystalline tetrathiafulvalenylphthalocyanine

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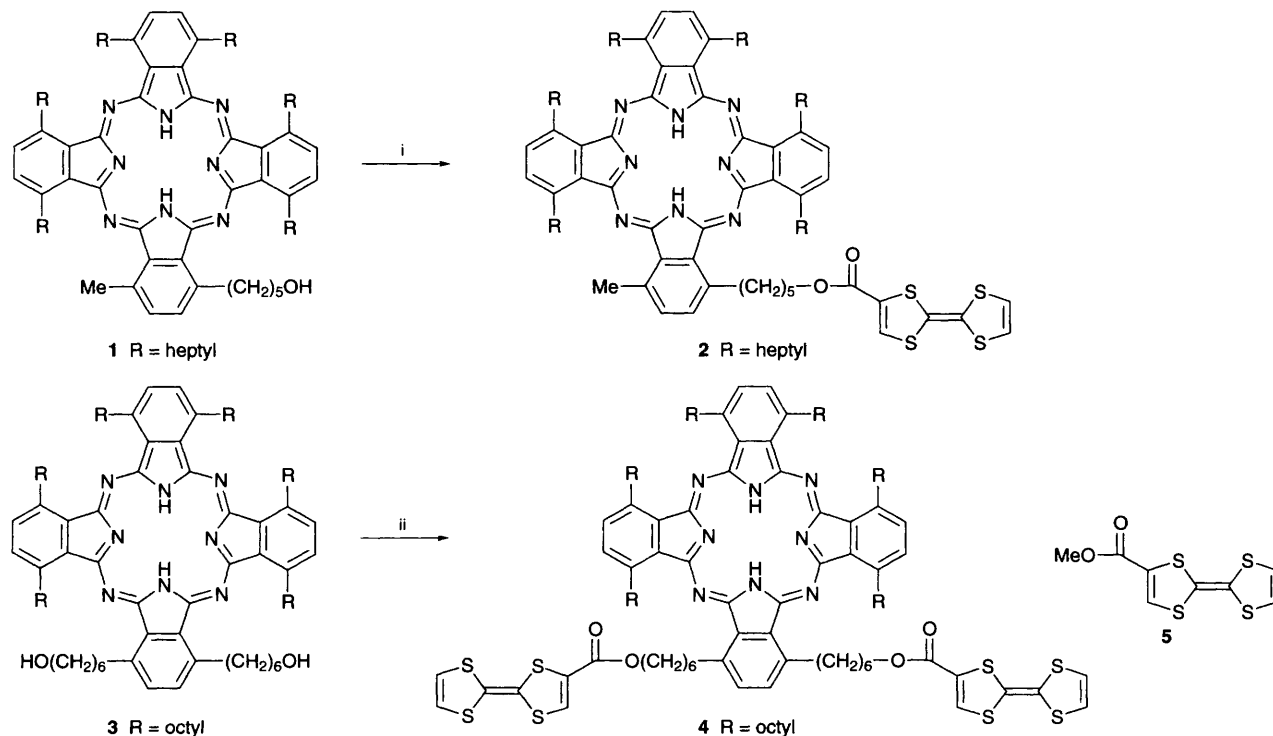
The synthesis and characterisation of the first discotic liquid crystalline tetrathiafulvalenylphthalocyanine is described.

Tetrathiafulvalene (TTF) derivatives have played an important role in the development of new molecular conductors.¹ In recent years there has been considerable interest in producing molecular assemblies of the TTF moiety displaying increased intermolecular interactions and dimensionality, in endeavours to suppress the onset of the Peierls distortion.² Chalcogen-chalcogen³ and hydrogen bonding interactions⁴ are in the forefront of recent attention. A possible progression in this area would be to attach the TTF unit to a discotic phthalocyanine liquid crystalline centre; the columnar stacking exhibited within the mesophase region should ensure highly ordered supramolecules in which the molecular architecture can be varied with temperature. Furthermore, the intermolecular spacing between the phthalocyanine rings (*ca.* 3.3 Å) in the mesophase region is comparable with the intermolecular spacing between TTF molecules in the highly conducting complex with TCNQ (*ca.* 3.4 Å), which could promote favourable intermolecular orbital overlap and interstack interactions.⁵

Here we attached tetrathiafulvalenyl groups to the previously described liquid crystalline phthalocyanine derivatives **1** and **3**⁶ to afford the novel tetrathiafulvalenylphthalocyanines **2** and **4** respectively.† The syntheses of **2** (75% yield) and **4** (79% yield) were accomplished by reacting the precursor phthalocyanines with excess 4-carboxytetrathiafulvalene,⁷ DCC and DMAP in

THF at 25 °C, Scheme 1, followed by chromatographic separation (silica gel, toluene). Both gave satisfactory elemental analyses and low resolution FAB mass spectra.‡ UV-VIS spectra (cyclohexane, 25 °C) of **1** and **3** are typical of phthalocyanines which are essentially non-aggregated in the solution phase. The TTF derivatives **2** and **4**, however, show lower intensity Q-bands (λ_{\max} 726 and 695 nm) and increase absorption to the blue indicative of an enhanced aggregation of the phthalocyanine moieties in these compounds. This argues against π stacking involving interleaving of the phthalocyanine and TTF subunits in the solution phase. ¹H NMR spectra also support this view; the TTF protons for **2** [δ 5.26 (s, 2 H) and 6.48 (s, 1 H)] and for **4** [δ 5.24 (s, 2 H) and 6.54 (s, 1 H)] are marginally shielded relative to those of **5** [δ 5.33 (s, 2 H) and 6.60 (s, 1 H)]‡ possibly indicating some limited degree of π stacking involving the TTF units with each other rather than residing over the phthalocyanine cores.§ The fluorescence spectra of compounds **1–4** (2.1×10^{-6} mol dm⁻³ solutions in cyclohexane) revealed that the emission intensity at 732 nm (excited at 693 nm) for **2** and **4** was approximately half that of the parent phthalocyanine.

Cyclic voltammetric (CV) data were obtained for compounds **1–5** and are presented in Table 1. The data for the parent phthalocyanines **1** and **3** reveal that both phthalocyanines undergo essentially identical reversible oxidations at *ca.* 0.69 and 0.95 V. The oxidation waves for the phthalocyanine component of compounds **2** and **4** are similar to that observed for the parent compounds. The oxidation waves for the TTF



Scheme 1 Reagents and conditions: i, 4-carboxytetrathiafulvalene (2 equiv.), DCC, DMAP, THF, then aqueous work-up; ii, 4-carboxytetrathiafulvalene (4 equiv.), DCC, DMAP, THF, then aqueous work-up

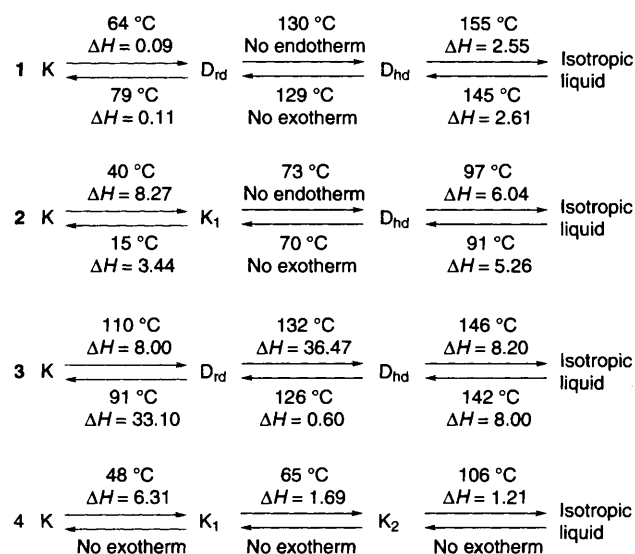
derivatives are partly masked by the phthalocyanine oxidations; only the first oxidation corresponding to the formation of the TTFC(O)OR radical cation are observed for derivatives **2** and **4**. The first oxidation for the phthalocyanine moiety in compound **4** appears to be irreversible.

The compounds were examined for mesophase behaviour using polarised light microscopy and differential scanning calorimetry, data from which are summarised in Scheme 2. Compound **2** exhibits a mesophase, assigned tentatively as D_{hd} from the fan-type birefringence texture observed by microscopy. In contrast the incorporation of the two TTF units in **4** suppresses the mesophase behaviour exhibited by its precursor, **3**. The temperature range of the mesophase of **2**, ca. 24 °C, is significantly less than that of its precursor phthalocyanine **1**, ca. 90 °C.

Table 1 Cyclic voltammetric data

Compound	$E_1^{1/2}/V$	$E_2^{1/2}/V$	$E_3^{1/2}/V$
1	0.69	0.95	
2	0.57	0.73	0.99
3	0.70	0.95	
4	0.56	0.70 ^a	0.92
5	0.58	0.89	

Measurements were performed in dry degassed CH_2Cl_2 under argon at 20 °C; scan range 0 to +1.75 V at a scan rate of 100 mV s⁻¹; electrolyte $Et_4N^+ClO_4^-$ (ca. 1×10^{-1} mol dm⁻³), compounds (ca. 1×10^{-5} mol dm⁻³), data were recorded vs. Ag/AgCl, Pt working electrode, using a BAS 50W electrochemical analyser. ^a An irreversible oxidation.



Scheme 2 Phase transitions determined by DSC and optical microscopy. Entropy measurements were determined by DSC (ΔH in J g⁻¹).

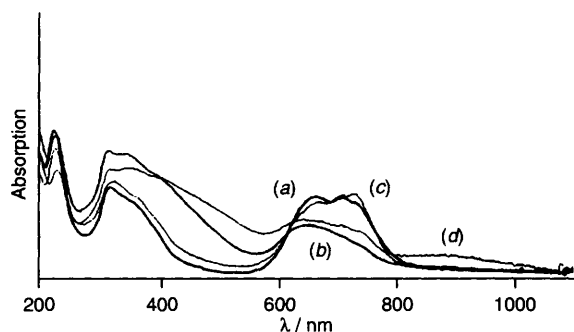


Fig. 1 UV-VIS spectra of spin coated films of compounds **2** and **4** deposited onto quartz: (a) **2** as deposited; (b) **2** immediately after oxidation with iodine; (c) **4** as deposited; (d) **4** immediately after oxidation with iodine

The long chain substituents in **2** and **4** confer solubility in organic solvents, a pre-requisite for fabricating materials as thin films by the spin coating technique. Earlier work from these laboratories⁸ has demonstrated that octa-substituted phthalocyanines form good quality spin coated films and this property is shared by the more complex derivatives **2** and **4**. A drop of a solution of **2** or **4** in THF applied to the centre of a rotating glass slide (2000 rpm) produced, after evaporation of solvent, a film which showed uniform absorbance at various locations and no evidence of crystallites. In contrast, TTF and its derivative **5** failed to generate satisfactory films under the same conditions.

Fig. 1 depicts the UV-VIS spectra of newly fabricated films of **2** and **4** and the same films after exposure to iodine. The former show broad band absorption in the visible region, characteristic of thin films of other phthalocyanine derivatives. Exposure to iodine reduces the absorbance in this region and changes the shape of the band envelope, indicating that a change in the molecular packing has been induced. There is also enhanced absorption to shorter wavelengths and, in the case of **4**, a further weak, broad band absorption centred at ca. 900 nm. The latter is somewhat reminiscent of the near IR absorption observed for stacked arrangements of the TTF radical cations observed in oxidised films of amphiphilic TTF derivatives fabricated by the LB method.⁹ After standing the oxidised films in air for 15 min their spectral bandshapes return to those of the original films. A further reversible reorganisation of the molecular packing of the film of the mesogenic derivatives **2** was achieved during a heating-cooling cycle during which a newly deposited film was heated to 80 °C, i.e. within the mesophase range of the compound as bulk material. At 80 °C the visible region becomes a little less broad with lower intensity in the 650–690 nm region.

Compound **2** is the first example of a discotic liquid crystalline tetrathiafulvalenylphthalocyanine derivative. UV-VIS spectroscopy of spin coated films reveals the molecular architecture of this material can be changed by oxidation with iodine vapour and heating to within the mesophase region.

We thank the EPSRC Mass Spectrometry Service Centre, University of Wales, Swansea and Professor M. R. Bryce, University of Durham, for help with CV measurements.

Footnotes

† Bryce and co-workers have recently reported a phthalocyanine bearing eight TTF units, which apparently does not exhibit liquid crystalline properties.¹⁰

‡ Spectroscopic data will be published elsewhere.

§ All spectra measured under identical conditions (270 MHz, C₆D₆) and concentrations.

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Received, 21st May 1996; Com. 6/03549C