

Thiophenotribenzoporphyrazines: novel near-IR absorbing dyes

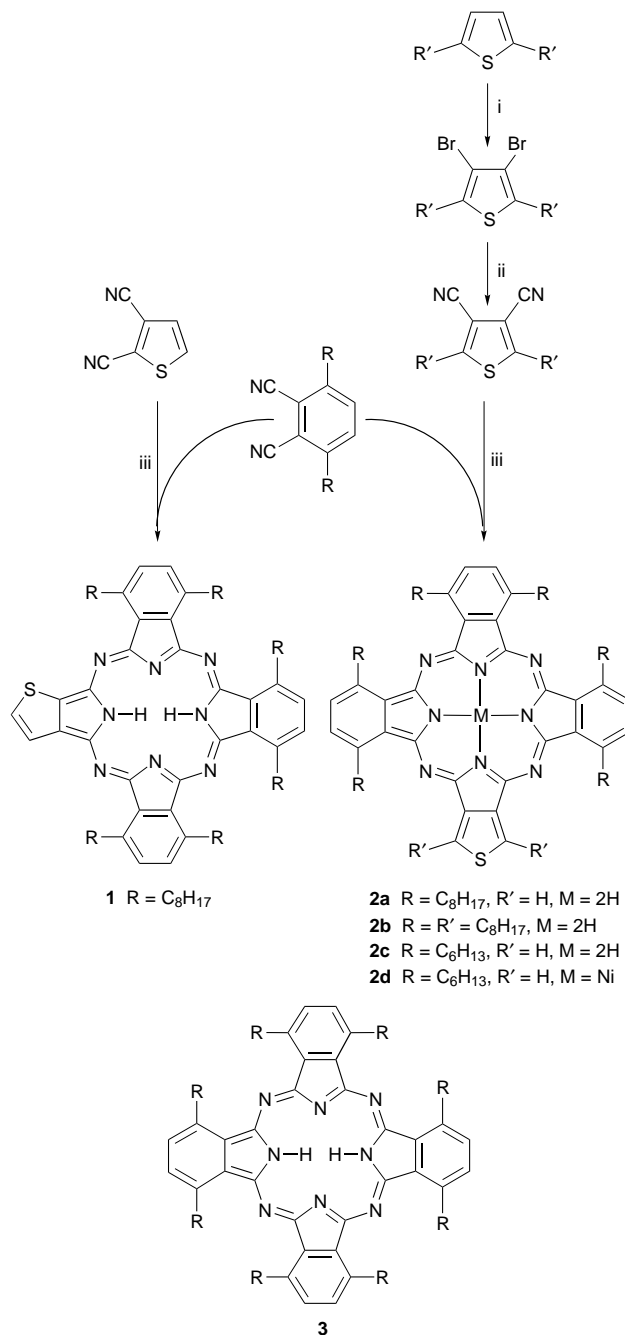
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The first examples of thiophenotribenzoporphyrazines have been synthesised. The compounds obtained bear either six or eight alkyl chains and show Q-band absorptions which are red shifted relative to analogous phthalocyanine derivatives. Their formulations as spin coated films show broad band absorption extending into the near IR. The compounds exhibit discotic mesophase behaviour.

Phthalocyanines (Pcs) show interesting optoelectronic and photophysical properties, many of which are associated with the intense and relatively narrow-band absorption in the visible region spectrum, the Q-band.¹ Manipulation of the energy levels of the π orbitals associated with the Q-band through the incorporation of ring substituents or benzofusion (as in the naphthalocyanines) provides access to far-red–near IR absorbing dyes.² Such materials have potential in medical applications such as photodynamic therapy³ and in optical data storage devices.⁴ Here we describe the first examples of the related thiophenotribenzoporphyrazine system and demonstrate significant red shifting of the Q-band which arises on replacement of one of the benzenoid rings of the Pc core with a thiophene unit. Furthermore, the distortion of the π system in the new series of macrocycles may lead to interesting nonlinear optic (NLO) behaviour and, as shown here, gives rise to a broad band absorption which may render the new materials beneficial for applications requiring light harvesting within the far-red–near IR region of the spectrum.⁵

Instead and co-workers obtained tetrathiophenoporphyrazine, presumably as an isomeric mixture, from 2,3-dicyanothiophene during their classic studies of phthalocyanines in the 1930's, describing the product as being greener than phthalocyanine itself.⁶ The thiophenotribenzoporphyrazines described here, containing just one thiophene unit, have been obtained by reacting both 3,4- and 2,3-dicyanothiophene,⁷ as well as the 2,5-dioctyl derivative of the former, with an excess of a 3,6-dialkylphthalonitrile⁸ (Scheme 1). The required products were obtained by conventional workup as the metal-free analogues **1** (7%), **2a** (12%), **2b** (1%) and **2c** (11%) after separation (column chromatography over silica) from by-products, the major one being the octaalkyl Pc **3**. The metallated analogue **2d** was prepared from **2c** by reaction with nickel acetate in pentanol solution heated to reflux. Each compound gave satisfactory analytical data, and the ¹H NMR spectra of the metal-free compounds gave signals readily interpreted in terms of their structure (Table 1). Compound **2d** showed a satisfactory low resolution FAB-MS but the metal-free derivatives were prone to fragmentation. The compounds are soluble in solvents such as THF, toluene and cyclohexane, a property attributable to the presence of the long alkyl chains. The latter also promote columnar mesophase behaviour (Scheme 2); polarised light microscopy shows that each compound gives rise to a mesophase with a fan type structure on cooling from the isotropic liquid (I). This is characteristic of the hexagonal columnar mesophase (D_{hd}) also exhibited by non-peripherally octaalkyl-substituted phthalocyanines of series **3**.^{9a} Compounds **2b** and **2d** also



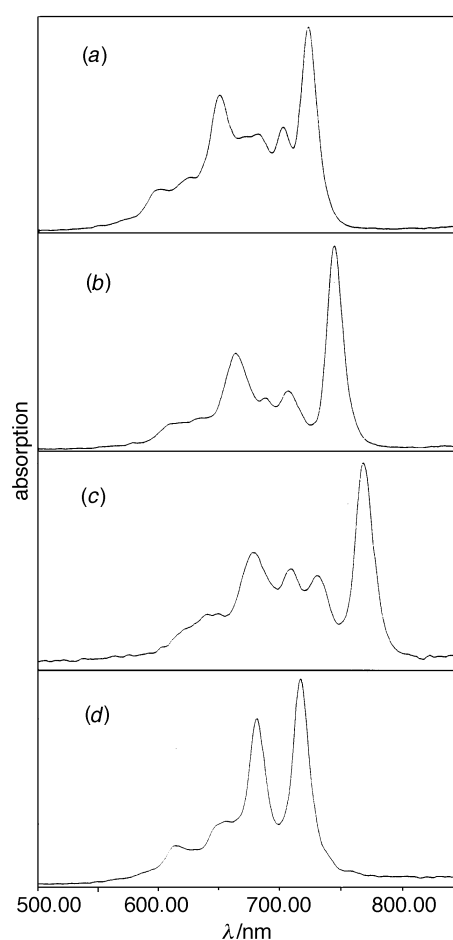
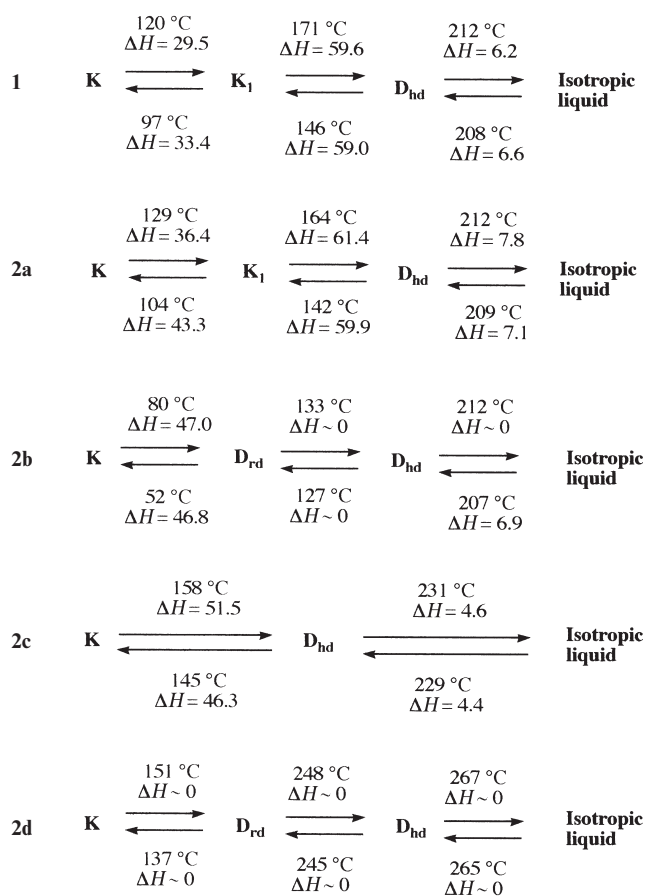
Scheme 1 Reagents and conditions: i, Br₂, MeCO₂H, -5 °C, 18 h; ii, CuCN, DMF, 6 h; iii, LiOC₅H₁₁-C₅H₁₁OH, AcOH [followed by M(OAc)₂ for the metallated derivative]

develop a second, lower temperature liquid crystal phase characterised by a needle-like texture; this we tentatively assign to a columnar mesophase having rectangular symmetry, *i.e.* D_{rd}.

The Q-band absorptions in the visible region spectra of solutions in cyclohexane at *ca.* 1 × 10⁻⁶ M are given in Table 1 and examples are displayed in Fig. 1. The band shapes of **1**, **2a** and **2b** are more complex than for metal-free and metallated

Table 1 Characterisation data for thiophenotribenzoporphyrazines

compound	molecular formula Found; C, H, N (required)	¹ H NMR δ _H (270 MHz, C ₆ D ₆)	λ _{max} (ε × 10 ⁵) for solutions in cyclohexane [λ _{max} (relative peak intensity) of the spin-coated films]
1	C ₇₈ H ₁₁₂ N ₈ S 78.50 9.24 9.39 (78.47 9.46 9.39)	−1.32 (s, 2H), 0.8–1.0 (m, 18H), 1.2–1.9 (m, 56H), 1.9–2.08 (t, 2H), 2.08–2.25 (t, 2H), 2.3–2.6 (m, 12H), 4.35 (t, 4H), 4.58 (t, 4H), 4.70 (t, 4H), 7.54 (d, 1H), 7.77 (m, 4H), 7.94 (s, 2H), 8.40 (d, 1H).	720 (1.64), 700 (0.85), 679 (0.80), 648 (1.11), 347 (0.79) [784 (0.57), 624 (0.68), 334 (1.0)]
2a	C ₇₈ H ₁₁₂ N ₈ S 78.48 9.55 9.26 (78.47 9.46 9.39)	−0.58 (s, 2H), 0.8–0.95 (m, 18H), 1.2–2.0 (m, 60H), 2.28–2.45 (m, 12H), 4.34 (t, 4H), 4.62–4.72 (m, 8H), 7.79–7.90 (m, 6H), 8.28 (s, 2H).	742 (2.40), 705 (0.71), 687 (0.63), 663 (1.15), 333 (0.78) [793 (0.68), 658 (0.63), 334 (1.0)]
2b	C ₉₄ H ₁₄₄ N ₈ S 79.59 10.37 7.75 (79.61 10.23 7.90)	−0.17 (s, 2H), 0.87 (t, 24H), 1.2–1.9 (m, 80H), 2.11 (t, 4H), 2.2–2.4 (m, 12H), 3.82 (t, 4H), 4.27 (t, 4H), 4.56–4.67 (m, 8H), 7.7–7.84 (m, 6H).	768 (1.39), 729 (0.63), 708 (0.68), 677 (0.79), 337 (0.75), 307 (0.69), 284 (0.6) [817 (0.55), 657 (0.61), 341 (1.0)]
2c	C ₆₆ N ₈₈ N ₈ S 76.99 8.64 10.90 (77.29 8.65 10.93)	−1.27 (s, 2H), 0.92 (m, 18H), 1.2–2.0 (m, 36H), 2.1–2.4 (m, 4H), 4.03 (m, 4H), 4.49 (m, 4H), 4.60 (m, 4H), 7.64–7.67 (d, 2H), 7.74–7.78 (d, 2H), 7.83 (s, 2H), 8.03 (s, 2H).	742 (1.81); 705 (0.54); 687 (0.48), 662(0.88), 386 (0.36), 336 (0.56) [795 (0.99), 657 (0.69), 371 (0.91), 328 (1.0)]
2d	C ₆₆ H ₈₆ N ₈ SNi 73.22 7.89 10.40 (73.25 8.01 10.35)	0.91 (m, 18H), 1.05–1.85 (m, 36H), 2.15–2.35 (m, 12H), 3.95 (m, 4H), 4.39 (m, 4H), 4.53 (m, 4H), 7.50–7.54 (d, 2H), 7.60–7.64 (d, 2H), 7.8 (s, 2H), 8.07 (s, 2H).	716 (2.35), 681 (1.89), 614 (0.43), 333 (0.6), 298 (1.1) [765 (1.0), 660 (0.77), 335 (0.85)]


Fig. 1 The visible region spectra of (a) **1**, (b) **2a**, (c) **2b** and (d) **2d** as ca. 1×10^{-6} M solutions in cyclohexane

Pcs due to their lower symmetry.¹⁰ The λ_{\max} of the Q-band is sensitive to the type of thiophene fusion and to substituents. Thus the lowest energy component of the Q-band of **1** (λ_{\max} 720 nm) is marginally to the red of the Q-band of a similarly substituted hexaalkylphthalocyanine (Q_x 714, Q_y 676 nm).⁸ The corresponding band absorbs further to the red in the isomeric compound **2a** (λ_{\max} 742 nm) and further still upon addition of two alkyl chains onto the thiophene ring as in **2b** (λ_{\max} 768 nm). This is 40 nm to the red of the corresponding phthalocyanine derivative **3** (R=octyl). On traversing the series **1**, **2a** and **2b**, there is an increase in the spacing between the two main Q-band components. Upon metallation of **2c** to

give **2d**, the Q-band is blue shifted and the higher symmetry of the system (D_{2h}) leads to a simpler band structure which is reminiscent of that for metal-free Pcs such as **3**; these are also of D_{2h} symmetry.

Many actual or potential applications of Pc derivatives utilise the compounds in the solid state. We therefore formulated all five compounds as spin-coated films by administering a drop of a solution of each compound in THF (ca. 2 mg in 0.5 ml) onto a glass slide rotating at 2000 rpm.¹¹ Examples of the absorption spectra of the films obtained once the solvent had evaporated appear in Fig. 2 (see also Table 1). The spectra

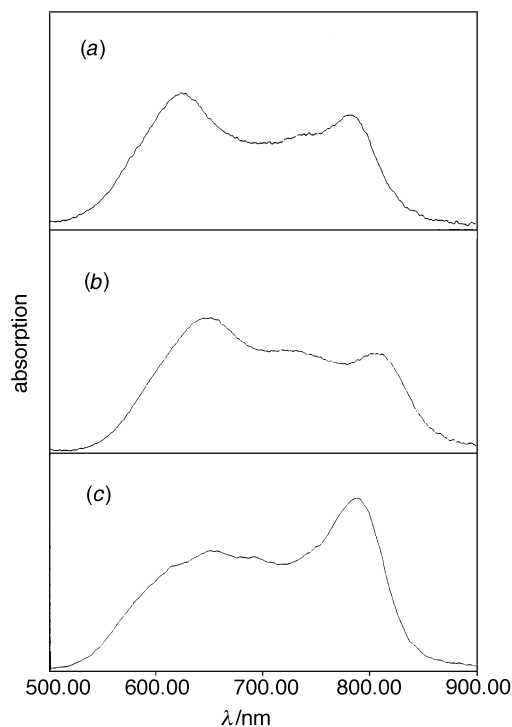


Fig. 2 The visible region spectra of spin coated films of (a) **1**, (b) **2b** and (c) **2c**

show unusually broad Q-band absorptions extending well into the near-IR region. The broadest band absorption is observed for the film of the octaoctyl substituted compound **2b**, which includes λ_{max} at 657 and 817 nm; the spin-coated film of the corresponding phthalocyanine **3** ($R = C_8H_{17}$) shows λ_{max} 635 and 765 nm.¹¹

In summary, we have obtained the first examples of some thiophenotribenzoporphyrzine derivatives. The site of fusion of the thiophene ring, substituents and incorporation of a metal ion provide a means of tuning the energy of the visible region absorption band and extending it into the far-red. Films fabricated by the spin coating technique show exceptional broad band absorption extending into the near IR. These

series of compounds are under further investigation in order to evaluate their efficiency as photoconducting materials.

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