MATERIALS CHEMISTRY COMMUNICATION

Pyridino[3,4]tribenzoporphyrazines: edge-to-face *versus* face-to-face assemblies among phthalocyanine analogues

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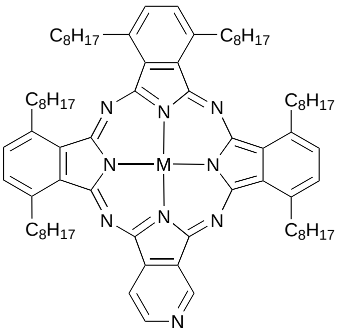
The metal-free and nickel derivatives of hexaoctylpyridino[3,4]tribenzoporphyrazine generate conventional face-to-face aggregates in solution, exhibit columnar mesophases and form columnar assemblies upon evaporation of solutions. By contrast, the zinc derivative forms alternative edge-to-face complexes through axial ligation of one molecule to the zinc atom of another, a process which inhibits mesophase behaviour and leads to new types of visible region absorption signatures.



1a M + H,H
b M = Ni
c M = Zn

Phthalocyanines (Pcs) in condensed phases possess interesting optical absorption signatures, semiconductivity and optoelectronic properties[1] which are often sensitive to molecular packing. Normally, the planar molecules are prone to form co-facial or near co-facial assemblies. These 'face-to-face' structures include the simple aggregates found in solution,[2] the longer columnar stacks in the liquid crystal phases of mesogenic derivatives,[3] and the classic 'herring bone' columnar packing in the most common polymorphs of the unsubstituted compounds.[4] Polymeric columnar structures include the 'shish-kebab' polymers formed when the central metal atoms of neighbouring Pc units are covalently or coordinatively linked *via* bridging atoms or molecules.[5]

In the present communication we report an investigation of organic solvent soluble pyridino[3,4]tribenzoporphyrazines **1** in which one benzenoid ring of the Pc nucleus has been replaced by a pyridinoid ring. Such compounds provide for the generation of 'edge-to-face' assemblies *via* metal–nitrogen coordination involving the pyridyl nitrogen atom of one molecule and the metal ion of a second molecule. Although edge-to-face assemblies have been constructed earlier using porphyrin derivatives,[6] they had not as yet been realised within the Pc series.

Linstead[7] first demonstrated the replacement of all four benzene rings of the Pc nucleus by pyridine in his classic investigations in the 1930s, obtaining a mixture of insoluble isomeric dyes from 2,3-dicyanopyridine. Subsequently, Shibamiya and co-workers prepared unsubstituted macrocycles containing combinations of both benzenoid and pyridinoid rings.[8] In the present study, the novel macrocyclic derivative **1a** was obtained by reaction of 3,4-dicyanopyridine with excess 3,6-dioctylphthalonitrile[9] under basic ($C_5H_{11}OLi$) conditions. Following conventional workup, **1a** (10%) was separated chromatographically from the principal by-product, 1,4,8,11,15,18,22,25-octaoctylphthalocyanine.[9] Reactions of **1a** with nickel acetate and zinc acetate in refluxing pentanol generated the corresponding metallated derivatives **1b** (53%) and **1c** (78%). Each gave a satisfactory elemental analysis† and low resolution FAB-MS. All three showed good solubility in solvents such as THF, toluene, cyclohexane and CH_2Cl_2.

The properties of the substituted pyridino[3,4]tribenzoporphyrazines **1** prove to be highly dependent upon the atom(s) at the centre of the macrocycle and reflect the individual compound's propensity for forming either face-to-face assemblies or edge-to-face complexes. The Q-band absorptions in the visible region spectra of solutions of **1a** and **1b** in cyclohexane at *ca.* 1×10^{-6} M are shown in Fig. 1. The two component Q-band of **1a** [Fig. 1(*a*)] is similar to that of a metal-free Pc. The Q-band of **1b** [Fig. 1(*b*)] is also split (λ_{max} 694 and 679 nm) differing from that of simple metallated Pcs but consistent with the lower symmetry of the system.[10] Otherwise, the high extinction coefficients of the Q-bands (see legend to Fig. 1) and the very low intensity absorptions to the blue, are characteristic of Pc compounds which are essentially non-aggregated. At higher concentrations, however, face-to-face type aggregation becomes apparent, manifested by the characteristic enhanced absorption in the region 600 to 690 nm (see the inset spectra in Fig. 1) and the lower extinction coefficients of the lowest energy bands.

The zinc derivative **1c** shows different behaviour. The spectrum of **1c** in cyclohexane [Fig. 1(*c*)] and in CH_2Cl_2 shows enhanced separation of the main Q-band components (λ_{max} 716 and 675 nm) within a band envelope which is essentially invariant over the concentration range *ca.* 1×10^{-4}–1×10^{-7} M. In particular, extinction coefficients remain high at the higher concentrations. Absence of face-to-face aggregation is signified by the lack of significant absorption in the visible region to the blue of these main bands. The gel permeation chromatogram obtained for elution of **1c** as a solution in CH_2Cl_2 through

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† *Selected data* for **1a**: Found: C, 79.54; H, 9.55; N, 10.65. $C_{79}H_{113}N_9$ requires: C, 79.82; H, 9.58; N, 10.60%. For **1b**: Found: C, 76.10; H, 9.00; N, 9.95. $C_{79}H_{111}N_9Ni$ requires: C, 76.18; H, 8.98; N, 10.12%. For **1c**: Found: C, 75.68; H, 8.78; N, 9.95. $C_{79}H_{111}N_9Zn$ requires: C, 75.78; H, 8.94; N, 10.07%.

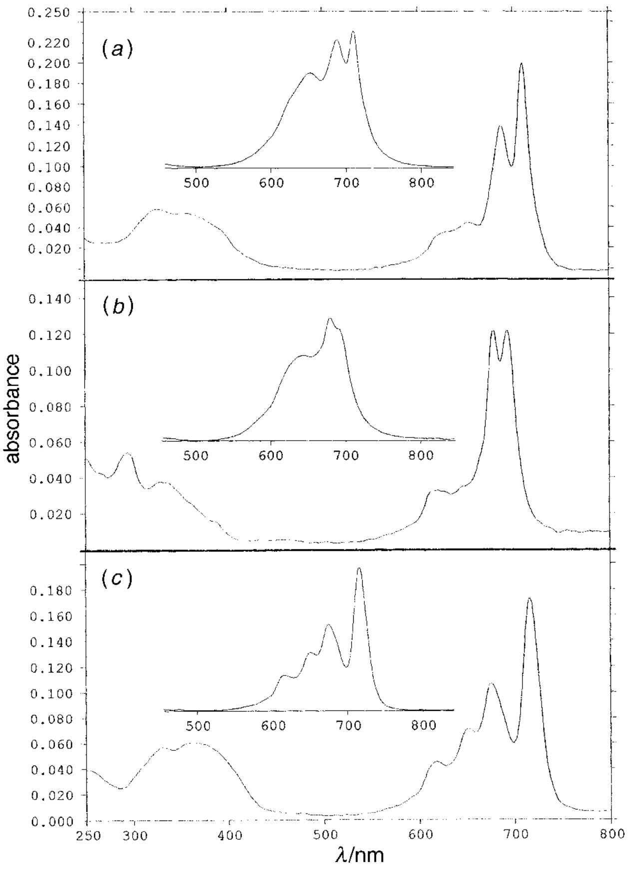

Fig. 1 (*a*) 250–800 nm spectrum of **1a** as a solution in cyclohexane at 1.46×10^{-6} M; λ_{max} 710 (ε 1.36×10^{5}) and 687 nm (0.95×10^{5}). Inset spectrum (scale not shown): Q-band absorption at 1.46×10^{-4} M; λ_{max} 709 (ε 6.23×10^{4}), 687 (5.85×10^{4}) and 652 nm (4.33×10^{4}). (*b*) As above but for **1b** at 1.04×10^{-6} M; λ_{max} 694 (ε 1.16×10^{5}) and 679 nm (1.17×10^{5}). Inset spectrum: Q-band absorption at 1.04×10^{-4} M; λ_{max} 690 (ε 5.61×10^{4}), 679 (6.15×10^{4}) and 643 nm (4.27×10^{4}). (*c*) As above but for **1c** at 1.24×10^{-6} M; λ_{max} 716 (ε 1.40×10^{5}) and 675 (0.86×10^{5}). Inset spectrum: Q-band absorption at 1.24×10^{-4} M; λ_{max} 715 (ε 1.25×10^{5}) and 675 nm (0.75 x 10^{5}).

PLgel (100 and 500 Å, 30 cm, 5 micron columns, calibrated against polystyrene) gives a peak molecular mass, *M*p, of 2050 (*M*w 1630 and *M*n 1390). Elution of three model phthalocyanine derivatives under the same conditions showed that the 'polystyrene equivalent' molecular masses for these macrocycles are consistently 20–25% lower than the actual molecular mass. Thus the *M*p obtained for **1c** suggests that, under the conditions of the GPC experiment, the material has formed a dimeric complex.

Thus we assign the visible region spectrum of **1c** to a dimeric species (or lower oligomeric species) arising from intermolecular axial ligation of a pyridyl nitrogen of one macrocycle with the zinc atom of a second, to form an edge-to-face complex. In support of this, we note that addition of pyridine or THF changes the band shape to one closely resembling that of non-aggregated **1b**; this we attribute to disruption of the homoligated complex of **1c**. Similarly, excitation of **1c** (λ_{ex} 650 nm) as a solution in toluene at 1.2×10^{-5} M shows fluorescence emission at λ_{max} 731 nm. Addition of 100 µl pyridine raises the emission intensity by a factor of two and shifts the emission band to 720 nm. In contrast, **1a** under the same conditions shows λ_{em} 721 nm, essentially unchanged when pyridine is added.

Further confirmation of the formation of edge-to-face complexes by **1c** was obtained by ^{1}H NMR spectroscopy. The spectrum of **1c** in [^{2}H$_6$]benzene shows no signals downfield of δ 8.32. Upon addition of [^{2}H$_5$]pyridine, the spectrum simplifies and is very similar to that of **1a**. In particular, the pyridyl protons of **1c** now appear at δ 9.25, 9.43 and 11.12. We believe it likely that higher oligomers may be present at the higher solution concentrations used in the NMR experiment.

Fig. 2 Transmission electron micrograph of **1b** as a THF gel on a carbon coated copper grid. The field of view is 453 × 294 nm.

Transmission electron microscopy highlighted differences in packing in the condensed states of **1a**–**1c**. A drop of a solution of each compound in THF (2 mg ml^{-1}) was administered onto a copper grid, blotted dry, and viewed through a JEOL 100CX electron microscope as the solvent evaporated. Fig. 2 shows the micrograph obtained for **1b**. It clearly shows the generation of a columnar structure, formally analogous to the 'molecular wires' observed by Nolte and co-workers[11] for a more complex Pc derivative. Compound **1a** showed similar behaviour. The width of the assembly depicted in Fig. 2 is *ca.* 15 times the approximate diameter of the individual molecules of **1b**. In contrast, **1c** forms a distinctly different structure, the micrograph showing an apparently featureless film with no evidence of column formation.

These differences in molecular packing in the condensed phase lead to different behaviour on heating and cooling. Thus, compounds **1a** and **1b** exhibit thermotropic columnar mesophases; polarised light microscopy shows a fan type structure on cooling from the isotropic liquid consistent with the hexagonal columnar mesophase exhibited by other non-peripherally alkyl-substituted Pcs.[12] Phase transition data are reported in Scheme 1.

In contrast, **1c** does not exhibit a mesophase during either heating of the solid sample or upon cooling from the liquid phase; this we attribute to the orthogonal packing of adjacent molecules in the solid state and, presumably, in the liquid state just prior to crystallisation.

In conclusion, we have identified a phthalocyanine type macrocycle whose molecular packing is governed by the central metal ion. Both face-to-face and edge-to-face packing has been identified. The latter is promoted by the propensity for zinc to undergo strong axial ligation, and columnar liquid crystal behaviour, otherwise inherent within the series, is inhibited. Nickel complexes may also undergo weak axial ligation. However, **1b** at UV–VIS concentrations and in the liquid crystal phases favours face-to-face structures in which the Ni^{II} d^{8} ion is presumably in its favoured spin paired, square-planar four coordinate state.

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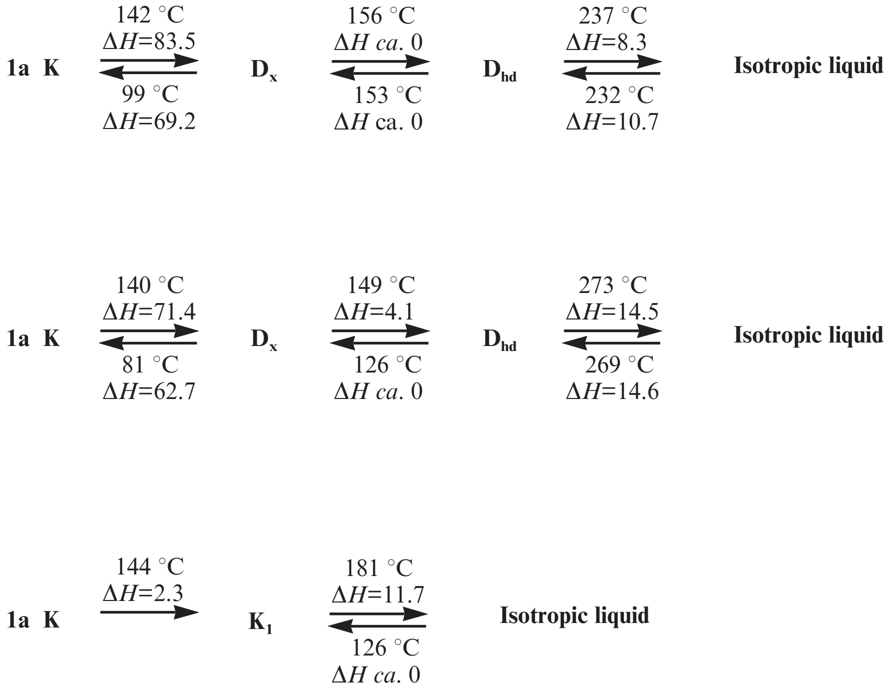

Scheme 1 Phase transitions determined by DSC and polarised optical microscopy. Enthalpy data (ΔH in J g^{-1}) were determined in a heating/cooling rate of 10 °C min^{-1}. **K** and **K$_1$** refer to crystal phases. The higher temperature mesophases of **1a** and **1b** give rise to a fan-like texure when viewed through a polarised light microscope, characteristic of a columnar mesophase with hexagonal cross sectional symmetry in which the columns are disordered, *i.e.* **D$_{hd}$**. The lower temperature mesophase **D$_x$** shows a needle type texture which we also tentatively assign as **D$_{hd}$** after ref. 12.

References

1 *Phthalocyanines—Properties and Applications,* ed. C. C. Leznoff and A. B. P. Lever, VCH, New York, 1989.

2 M. J. Cook, in *Spectroscopy of New Materials*, ed. R. J. H. Clark and R. E. Hester, Wiley, Chichester, 1993, p 87.

3 J. Simon and P. Bassoul, in *Phthalocyanines—Properties and Applications*, ed. C. C. Leznoff and A. B. P. Lever, VCH, New York, 1993, vol. 2, p 223.

4 See, for example, R. Mason, G. A. Williams and P. E. Fielding, *J. Chem. Soc., Dalton Trans.,* 1979, 676.

5 A. D. Pomogailo and D. Wöhrle, in *Macromolecule-Metal Complexes,* ed. F. Ciardelli, E. Tsuchida and D. Wöhrle, Springer, Berlin-Heidleberg, 1996, p 11; M. Hanack and M. Lang, *Adv. Mater.,* 1994, **6**, 819.

6 E.g. A. M. Shachter, E. B. Fleischer and R. C. Haltiwanger, *J. Chem. Soc., Chem. Commun.,* 1988, 960; E. B. Fleischer and A. M. Shachter, *Inorg. Chem.,* 1991, **30**, 3763; C. A. Hunter and L. D. Sarson, *J. Chem. Soc., Chem. Commun.*, 1994, **33,** 2313; K. Funatsu, A. Kimura, T. Immanura and Y. Sasaki, *Chem. Lett.*, 1995, 765; S. Anderson, H. L. Anderson, A. Bashall, M. McPartlin and J. K. M. Sanders, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1096; E. Alessio, M. Macchi, S. Heath and L. G. Marzilli, *Chem. Commun.,* 1996, 1411.

7 R. P. Linstead, E. G. Noble and J. M. Wright, *J. Chem. Soc.*, 1937, 911.

8 M. Yokote and F. Shibamiya, *Kogyo Kagaku Zasshi*, 1959, 62, 224 (*Chem. Abstr*., 1961, **55**, 24 019); M. Yokote, F. Shibamiya and H. Hayakawa, *Yuki Gosei Kagaka Kyokai-Shi,* 1965, **23**, 151 (*Chem. Abstr*., 1965, **62**, 14 859); K. Sakamoto, M. Yoshioka and F. Shibamiya, *J. Jpn. Soc. Colour Mater.,* 1985, **58**, 121 (*Chem. Abstr*., 1985, **103**, 38 688); K. Sakamoto and F. Shibamiya, *J. Jpn. Soc. Colour Mater.,* 1986, **59**, 517 (*Chem. Abstr*., 1987, **106**, 103 797).

9 I. Chambrier, M. J. Cook, S. J. Cracknell and J. McMurdo, *J. Mater. Chem.,* 1993, **3**, 841.

10 *Cf.* N. Kobayashi, M. Togashi, T. Osa, K. Ishii, S. Yamauchi and H. Hino, *J. Am. Chem. Soc*., 1996, **118**, 1073; M. J. Cook and A. Jafari-Fini, *J. Mater. Chem*., 1997, **7**, 5.

11 C. F. van Nostrum, S. J. Picken and R. J. M. Nolte, *Angew. Chem., Int. Ed. Engl*., 1994, **33,** 2173; C. F. van Nostrum, S. J. Picken, A-J. Schouten and R. J. M. Nolte, *J. Am. Chem. Soc*., 1995, **117,** 9957.

12 A. S. Cherodian, A. N. Davies, R. M. Richardson, M. J. Cook, N. B. McKeown, A. J. Thomson, J. Feijoo, G. Ungar and K. J. Harrison, *Mol. Cryst. Liq. Cryst*., 1991, **196**, 103.

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