

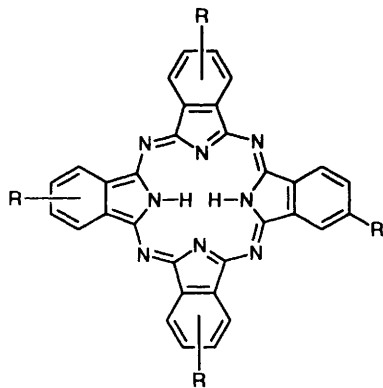
Lyotropic and Thermotropic Mesophase Formation of Novel Tetra-[oligo(ethyleneoxy)]-substituted Phthalocyanines

Neil B. McKeown* and James Painter

Department of Chemistry, University of Manchester, Manchester, UK M13 9PL

The synthesis of tetra[oligo(ethyleneoxy)]phthalocyanines is described. Preliminary characterization of both thermotropic and lyotropic mesophases obtained from examples of this series are reported.

The phthalocyanine (Pc) macrocycle is of considerable interest due to its fascinating electronic and optical properties, which have been exploited in a large number of applications.¹ In recent years there has been a considerable effort to fabricate self-organized Pc-based materials. For example Pc, when peripherally substituted with alkyl groups, forms thermotropic discotic liquid crystals.^{2–4} Similarly, water soluble tetra-2,9(10),16(17),23(24) or octa-carboxyphthalocyanines exhibit lyotropic mesophases in aqueous solution.^{5,6} However, to date, there are no reports of Pc derivatives that possess both lyotropic and thermotropic mesophase behaviour. Indeed, disc-shaped (discotic) mesogens that form both lyotropic and thermotropic liquid crystals are extremely rare.⁷ Octa-2,3,9,10,16,17,23,24-[oligo(ethyleneoxy)]phthalocyanines have been prepared previously and found to possess a columnar thermotropic mesophase but lyotropic mesophase formation was not investigated.^{8,9} This preliminary communication describes the synthesis and basic mesophase properties, both lyotropic and thermotropic, of Pcs substituted by only four methyl-terminated oligoethyleneoxy side-chains.



1 R = $-\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$
2 R = $-\text{O}(\text{CH}_2\text{CH}_2\text{O})_8\text{CH}_3$

Metal free tetra(1,4,7,10-tetraoxaundecyl)phthalocyanine (**1**) and tetra-(1,4,7,10,13,16,19,22,25-nonaohexacosyl)phthalocyanine (**2**) were prepared using the synthetic route depicted in Scheme 1. Commercially available triethylene glycol monomethyl ether and poly(ethyleneoxy) monomethyl ether (nominal average molecular weight=350) were used as starting

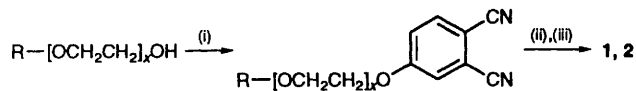
materials for **1** and **2**, respectively. These alcohols reacted with 4-nitrophthalonitrile *via* a base-catalysed nitro-displacement reaction¹⁰ to afford the precursor methoxyoligo-(ethyleneoxy)phthalonitriles. Remarkably, the precursor to **2** could be isolated by column chromatography (silica gel) from the product mixture formed from poly(ethyleneoxy) monomethyl ether ($M_n=350$) and 4-nitrophthalonitrile, using ethyl acetate as the eluent. Elemental analysis; and nuclear magnetic resonance (NMR), and mass spectrometry (MS) confirmed that the 4-(1,4,7,10,13,16,19,22,25-nonaohexacosyl)phthalonitrile was uncontaminated by significant quantities of other oligo(ethyleneoxy) phthalonitriles. Cyclotetramerization of these phthalonitriles to produce **1** and **2** was achieved using lithium pentaoxide catalysis in refluxing pentanol. The blue products were isolated by column chromatography. Purity was established by thin-layer chromatography (single spot) and by satisfactory elemental analysis.[†] The structures of the resultant Pcs were confirmed by fast atom bombardment (FAB) MS[†], NMR, ultraviolet-visible (UV-VIS) and infrared (IR) spectroscopy. We expect that **1** and **2** were prepared as a statistical mixture of four regioisomers owing to the various possible positions of the oligo(ethyleneoxy) side-chains relative to one another. The four probable isomers can be designated by their molecular symmetry as D_{4h} , C_{4h} , C_{2v} and C_s and each isomer would be prepared, assuming a statistical distribution, in a relative yield of 1:1:2:4 respectively.¹¹ No attempt was made to separate the isomers of **1** and **2**.

Table 1 summarizes the thermotropic mesophase properties of **1** and **2**, investigated by optical microscopy and differential scanning calorimetry. We believe that these are the first examples reported of tetra-substituted Pc thermotropic mesogens.¹² Both **1** and **2** exhibit thermally stable mesophases, which have an optical texture characteristic of a columnar hexagonal mesophase in which the Pc macrocycles have periodic positional order along the columnar axis (D_{ho} , Fig. 1).¹³ The formation of digitate stars on cooling **2** from its isotropic melt is also indicative of the D_{ho} mesophase.¹⁴ This structure is commonly found in Pc thermotropic meso-

[†] **1**, FAB-MS $\text{C}_{60}\text{H}_{74}\text{N}_8\text{O}_{16}$; $(M+H)^+$ 1163. Elemental analysis, found: C, 61.95; H, 6.50; N, 9.50%. $\text{C}_{60}\text{H}_{74}\text{N}_8\text{O}_{16}$ requires C, 61.95; H, 6.41; N, 9.63%. **2**, FAB-MS $^{13}\text{C}_{99}\text{H}_{154}\text{N}_8\text{O}_{36}$; $(M+H)^+$ 2044. Elemental analysis, found: C, 58.45; H, 7.90; N, 5.49%. $\text{C}_{100}\text{H}_{154}\text{N}_8\text{O}_{36}$ requires C, 58.75; H, 7.59; N, 5.48%.

Table 1. Thermotropic mesomorphism of **1** and **2**

Pc	transition	$T/^\circ\text{C}$	$\Delta H/\text{J g}^{-1}$
1	solid $\rightarrow D_{ho}$	78	24.7
	$D_{ho} \rightarrow$ isotropic	> 300	—
2	solid $\rightarrow D_{ho}$	11	47.4
	$D_{ho} \rightarrow$ isotropic	170–180	<0.2



Scheme 1 Reagents and conditions: (i) 4-nitrophthalonitrile, N,N-dimethylformamide, anhydrous K_2CO_3 ; (ii) $\text{LiOC}_5\text{H}_{11}-\text{C}_5\text{H}_{11}\text{OH}$, 135°C ; (iii) AcOH

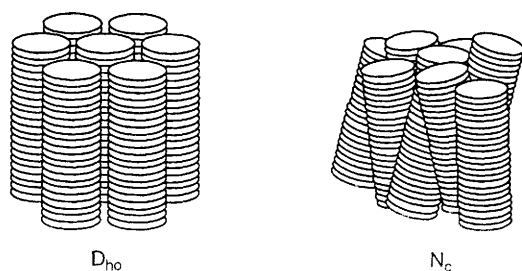


Fig. 1 Structure within the columnar hexagonal (D_{ho}) and columnar nematic (N_c) mesophases

gens.^{3,14} **2** is of interest in that it is a rare example of a Pc derivative with a stable thermotropic mesophase at ambient temperature.^{8,15}

Both **1** and **2** gave broad UV-VIS absorption spectra ($\lambda_{max}=630$ nm) in ethanol even at very low concentration, typical of that obtained from Pc aggregation.⁶ Preliminary investigation of possible lyotropic mesophases of **1** and **2**, as a result of the formation of columnar aggregates, was investi-

gated by placing a drop of dilute isotropic Pc solution between a microscope slide and cover slip and allowing time for partial evaporation of the solvent from the edge of the solution. In this way a concentration gradient was created with a higher concentration of material at the edge of the slide (at the top of Plates 1–3).

Pc **1** is insoluble in water and anhydrous ethanol, however, it is readily soluble in 95% ethanol. Plate 1 shows the *schlieren* texture, which formed at the boundary between the pure material and its isotropic dilute ethanolic solution at room temperature. This is indicative of the formation of a lyotropic columnar nematic mesophase (N_c) in which columnar aggregates possess partial orientational order (Fig. 1).¹⁶ Ethanolic solutions with 11–45% concentrations of **1**, by weight, show this fluid phase. Less concentrated solutions are isotropic, whereas solutions of greater than 50% concentration exhibit an optical texture consistent with hexagonal order.

Pc **2** is highly water soluble. Edge evaporation of a dilute aqueous solution of **2** gave a mesophase with an optical texture identical to that shown by the D_{ho} mesophase of the pure material (Plate 2). However, on heating to 50 °C a *schlieren* texture formed at the boundary between that of D_{ho} and the isotropic solution (Plate 3). Examination of a range

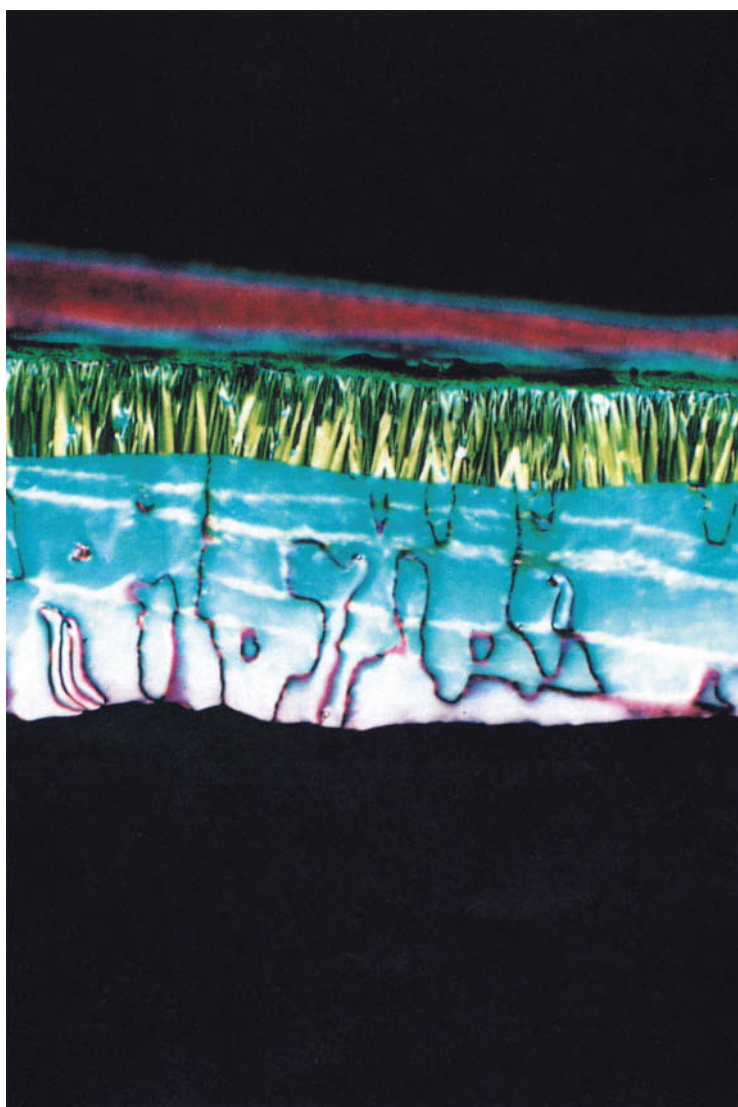


Plate 1 Photomicrograph of the texture of the lyotropic mesophases of **1** at 20 °C. A concentration gradient was established by evaporation of an ethanolic solution of the Pc from the edge of the microscope slide. A columnar hexagonal phase (D_{ho}) has formed at the most concentrated region and a columnar nematic (*schlieren* texture) lies between the D_{ho} and isotropic solution. Magnification $\times 50$.



Plate 2 Photomicrograph of the texture of the lyotropic mesophase formed from an aqueous solution of **2**. At 20 °C only a D_{ho} mesophase has formed. Magnification $\times 50$.

of aqueous solutions shows that concentrations of **2** of between 30 and 50%, by weight, form D_{ho} at room temperature and an N_c phase at temperatures in excess of 50 °C. Solutions of **2** of greater than 50% concentration show only D_{ho} textures, even at more elevated temperatures (at 80 °C aqueous solutions of **2** display a cloud-point at which the Pc precipitates from solution). The lyotropic mesophases exhibited by the tetra[oligo(ethyleneoxy)]phthalocyanines described in this communication appear to be analogous to well characterized phases found in aqueous solutions of other discotic compounds; for example, the columnar hexagonal and columnar nematic mesophases produced by hexa[oligo(ethyleneoxy)]-triphenylenes and designated C_H and N_C , respectively, by Boden *et al.*¹⁶ In addition, obvious similarities exist between the mesophases obtained from aqueous solutions of octa-2,3,9,10,16,17,23,24-carboxyphthalocyanine, designated N (columnar nematic) and M (columnar hexagonal) by Usoltseva *et al.*⁶

Work is in progress to extend the range of oligo(oxyethylene)-substituted Pcs produced and to examine in more detail their lyotropic and thermotropic mesomorphic behaviour.

References

- 1 *Phthalocyanines: Properties and Applications*, ed. C. C. Leznoff and A. B. P. Lever, VCH, New York, vols. 1 and 2, 1992 and 1993.
- 2 C. Piechocki, J. Simon, A. Skoulios, D. Guillon and P. Weber, *J. Am. Chem. Soc.*, 1982, **104**, 5245.
- 3 K. Ohta, L. Jacquemin, C. Sirlin, L. Bosio and J. Simon, *New J. Chem.*, 1988, **12**, 751.
- 4 M. J. Cook, M. F. Daniel, K. J. Harrison, N. B. McKeown and A. J. Thompson, *J. Chem. Soc., Chem. Commun.*, 1987, 1086.
- 5 S. Gasperd, A. Hochapfel and R. Viovy, *C.R. Acad. Sci., Paris, Ser. C*, 1979, **289**, 387.
- 6 N. V. Usoltseva, V. V. Bykova, N. M. Kormilitsyn, G. A. Ananieva and V. E. Maizlish, *Il Nuovo Cimento*, 1990, **12**, 1237.
- 7 H. Zimmerman, R. Poupko, Z. Luz and J. Billard, *Liq. Cryst.*, 1989, **6**, 151.
- 8 D. Guillon, P. Weber, A. Skoulios, C. Piechocki and J. Simon, *Mol. Cryst. Liq. Cryst.*, 1985, **130**, 223.
- 9 C. Piechocki and J. Simon, *New J. Chem.*, 1985, **9**, 159.
- 10 T. W. Hall, S. Greenberg, C. R. McArthur, B. Khouw and C. C. Leznoff, *New J. Chem.*, 1982, **6**, 653.
- 11 M. Hanack, G. Schmid and M. Sommerauer, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1422.
- 12 J. Simon and P. Bassoul, in *Phthalocyanines: Properties and*



Plate 3 As above, except that the sample has been heated to 50°C. The *schlieren* texture indicates that a columnar nematic mesophase has formed. Magnification $\times 50$.

- Applications* ed. C. C. Leznoff and A. B. P. Lever, VCH, New York, vol. 2, 1992, p. 223.
- 13 C. Destrade, P. Foucher, H. Gasparoux and N. H. Tinh, *Mol. Cryst. Liq. Cryst.*, 1984, **106**, 121.
 - 14 J. F. van der Pol, E. Neeleman, J. C. van Miltenburg, J. W. Zwikker, R. J. M. Nolte and W. Drenth, *Macromolecules*, 1990, **23**, 155.
 - 15 A. N. Cammidge, M. J. Cook, K. J. Harrison, and N. B. McKeown, *J. Chem. Soc., Perkin Trans. 1*, 1991, 3053.
 - 16 N. Boden, R. J. Bushby, L. Ferris, C. Hardy and F. Sixl, *Liq. Cryst.*, 1986, **1**, 109.

Communication 4/02100B; Received 8th April, 1994