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Design and synthesis of liquid crystalline phthalocyanines: combinations of substituents that promote the discotic nematic mesophase

Andrew D. Garland, Isabelle Chambrier, Andrew N. Cammidge*, Michael J. Cook*

School of Chemistry, University of East Anglia, Norwich Research Park, Norwich, NR4 7TJ, UK

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ABSTRACT

A homologous series of fourteen metal-free 1,4,8,11,15,18-hexakis(alkyl)-22-methyl-25-hydroxyalkylphthalocyanine derivatives has been investigated to interrogate the interplay of the roles of the six alkyl chains and the length of the hydroxyalkyl chain in promoting thermotropic nematic liquid crystalline behaviour. All but two of the compounds form mesophases. Eight of the remaining compounds exhibit only columnar mesophases, which is common among liquid crystalline phthalocyanines. However, four examples form the rare discotic nematic mesophase. A general structural feature is deduced in that this rare phase is favoured when the number of linking atoms in the hydroxyalkyl chain exceeds twice the number of carbon atoms in any one of the six common alkyl chains, disrupting the columnar packing arrangement. In addition, zinc and copper metallated examples of one of the metal-free discotic nematic compounds were prepared, of which the zinc metallated compound formed a nematic phase whereas the copper containing analogue favoured columnar mesophase formation.

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1. Introduction

Phthalocyanines (Pcs) are highly stable man-made macrocycles. They are typically blue–green in colour and for many decades have been used as commercial dyes and pigments. The relative ease of incorporating substituents onto the macrocyclic ring and introducing a metal ion or metalloid element into the core of the macrocyclic ligand allows tuning of the properties of the system, not simply the colour but a range of interesting photophysical and semi-conducting properties. They are thus important in the area of organic materials development, building on their successfully established applications as charge carriers in photocopiers,¹ as dyes in laser/LED printing² and as laser light absorbers for optical data storage in certain CD-ROMs.³ Other Pcs show promise for exploitation in organic based solar cells⁴ and their photoexcited state properties, tunable by structure variation, has provided materials suitable for optical limiting⁵ and as singlet oxygen photosensitizers for photodynamic therapy of particular cancers.⁶ In one developing area, a number of Pcs that exhibit liquid crystal properties show enhanced semiconducting behaviour in the temperature range where the liquid crystal state (mesophase) occurs.^{7–10}

Simon et al. discovered the first liquid crystalline Pcs in 1982,¹¹ so adding new examples to the then recently identified class of so-called 'discotic' liquid crystals. Discotic liquid crystals typically possess near planar (often aromatic) cores and bear a number of paraffinic chains. Simon's Pcs carried eight alkoxyethyl chains at the peripheral (2,3,9,10,16,17,23,24-) sites of the Pc ring.^{11–14} The UEA group then reported new examples bearing eight medium length alkyl^{15–18} or alkoxyethyl groups^{19,20} located at the alternative non-peripheral (1,4,8,11,15,18,22,25-) positions of the macrocycle, substitution type A in Fig. 1. The group then extended the range of liquid crystalline Pcs to include non-uniformly substituted compounds such as those depicted as type B in Fig. 1.^{21–25} All the liquid crystalline examples referred to above exhibit columnar mesophase behaviour, see Fig. 2, and is discussed later. Our recent preliminary study²⁶ probed how a combination of particular ring substituents on the Pc core of type C metal-free compounds also promotes mesophase formation. R groups were pentyl and the hydroxyalkyl group chainlength was varied from $n=9$ to 12. Pentyl groups were chosen in light of an earlier study that showed that eight pentyl groups alone in the type A structure were insufficient to promote mesophase generation.^{15,16} It was found that type C compounds with six pentyl groups, a methyl group and a long hydroxyalkyl chain exhibited not merely liquid crystallinity, but either columnar or the rare nematic mesophase (see Fig. 2) depending upon the length of the hydroxyalkyl chain. The present paper reports

* Corresponding authors. Tel.: +44 (0)1603 592011; fax: +44 (0)1603 592003; e-mail addresses: a.cammidge@uea.ac.uk (A.N. Cammidge), m.cook@uea.ac.uk (M.J. Cook).

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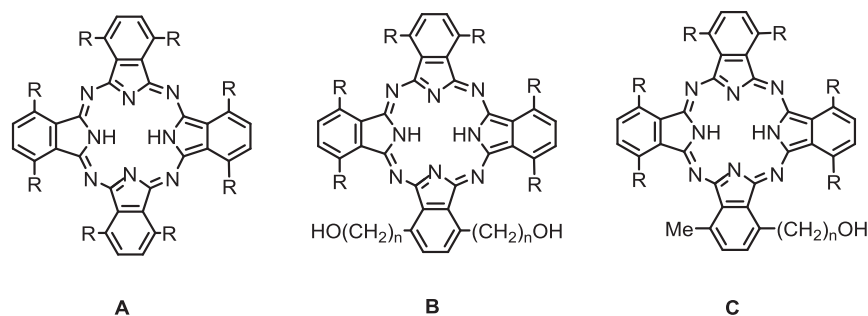


Fig. 1. Examples of series of substituted phthalocyanines, R=alkyl, as metal-free derivatives, that exhibit liquid crystal behaviour.

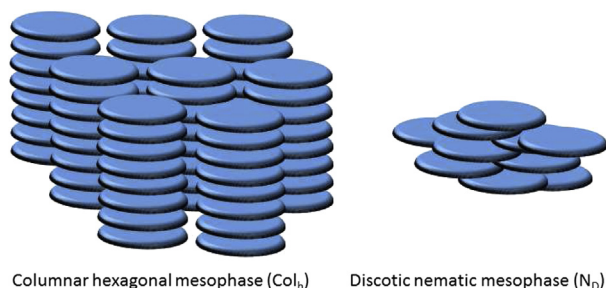


Fig. 2. Molecular arrangements in the (discotic) columnar mesophase and nematic mesophase N_d .

a comprehensive study into how mesophase type is indeed subtly, but somewhat predictably, dependent upon particular substituent combinations within type C structures and also extends the investigation to two examples of metallated Pc derivatives.

2. Results and discussion

2.1. Preparation of compounds

The present series of type C phthalocyanine derivatives investigated for liquid crystal behaviour was prepared according to the route shown in Scheme 1. The synthetic method was developed earlier by us to provide examples of homologues designed for other studies.^{22–25} In the present work, the mixed cyclisation of two phthalonitrile derivatives, i.e. a 3-methyl-6-(hydroxyalkyl) phthalonitrile and a 3,6-dialkylphthalonitrile, step iii in Scheme 1, produced the desired metal-free phthalocyanine compound. The principal side-product was the symmetrically substituted 1,4,8,11,15,18,22,25-octakis(alkyl)phthalocyanine; limited amounts of further unwanted cross-condensation products were also formed. In addition to fourteen type C metal-free derivatives, a zinc and a copper metallated example were also prepared by reacting metal-free derivative **5** with zinc acetate and copper acetate, respectively. Yields and characterisation data for novel compounds are collected in the Experimental section.

2.2. Mesophase behaviour

Typically, discotic liquid crystalline compounds exhibit the so-called columnar mesophase structure and, beyond phthalocyanines, much research has focussed in particular on triphenylenes and hexabenzocoronenes bearing flexible substituent chains. As the term implies, columnar mesophase formation involves a stacking of the cores of the molecules, providing a degree of order, with the stacks separated by the substituent chains. Thus, as the temperature is raised above the melting point of the crystalline material, stacking is largely maintained while the mobility of the chains

increases leading to disorder between the stacks. In short, the molecules display a positional short range order and an orientational long range order. An alternative packing arises in the much less common discotic nematic mesophase denoted as N_d .^{27,28} Here the columnar stacking is destabilised leading to translational and rotational freedom of the molecules about the axis perpendicular to the plane of the core. However, the cores remain broadly aligned parallel to each other, see Fig. 2. Among liquid crystalline phthalocyanines there have been no definitive reports of nematic mesophase formation prior to the present research program.²⁶

Mesophase behaviour of the Pc derivatives has been investigated using polarising optical microscopy (POM) and differential scanning calorimetry (DSC), and the results are summarized within Scheme 1. POM in particular provides a reliable and simple method for identifying the discotic mesophases and two representative images from the present work are shown in Fig. 3 for the columnar hexagonal phase and the discotic nematic phase (schlieren texture). The nematic mesophase is further characterized by its low viscosity compared to its columnar counterpart. The table within Scheme 1 illustrates how structural features of the Pcs, i.e. chain length of the six alkyl chains (R in structure C) and the length of the hydroxyalkyl chain, govern mesophase formation and the type of mesophase that is generated. Thus two examples bearing six butyl groups are non-liquid crystalline indicating that chains longer than these are essential for liquid crystallinity within the series. The liquid crystalline Pcs fall into two categories. On cooling from the isotropic liquid the majority follow the normal trend for Pcs in that they form columnar mesophases. Columnar hexagonal, Col_h , are solely formed for all such metal-free derivatives. Characteristic textures are formed (Fig. 3) that persist until a second transition occurs at lower temperatures. In some samples crystallization is clear, while others form a glassy phase where the viscosity of the system leads to partial crystallization and glass formation (denoted as X). The second category comprises a smaller subset of derivatives that display nematic mesophase behaviour on cooling. Again the nature of this low-viscosity phase is easily identified from POM. To the best of our knowledge this set of derivatives are the only Pcs known to form nematic phases and it is clear that the structural features leading to their formation are subtle and balanced. The hydrophilic end group of the hydroxyalkyl substituent is important for promoting formation of the nematic mesophase within this series of compounds. A related derivative where a $C_{12}H_{25}$ group replaces the $(CH_2)_{11}OH$ chain of compound **6** forms exclusively columnar mesophases.²⁶ Thus the presence of the terminal hydroxyl group is essential for promoting the nematic mesophase but it is only observed in a select subset of examples. Evidently, the relative lengths of the R chains and the hydroxyalkyl chain play a role in governing the type of mesophase that is formed. In those Pcs where the core–core separation in the columnar (Col) arrangement (ca. $2 \times$ length of the R chains) is as long as, or longer than, the hydroxyalkyl chain, then the latter can be accommodated within the columnar assembly and may even allow for the OH

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