

## Columnar Liquid Crystals Based on 2,3-Naphthalocyanine Core

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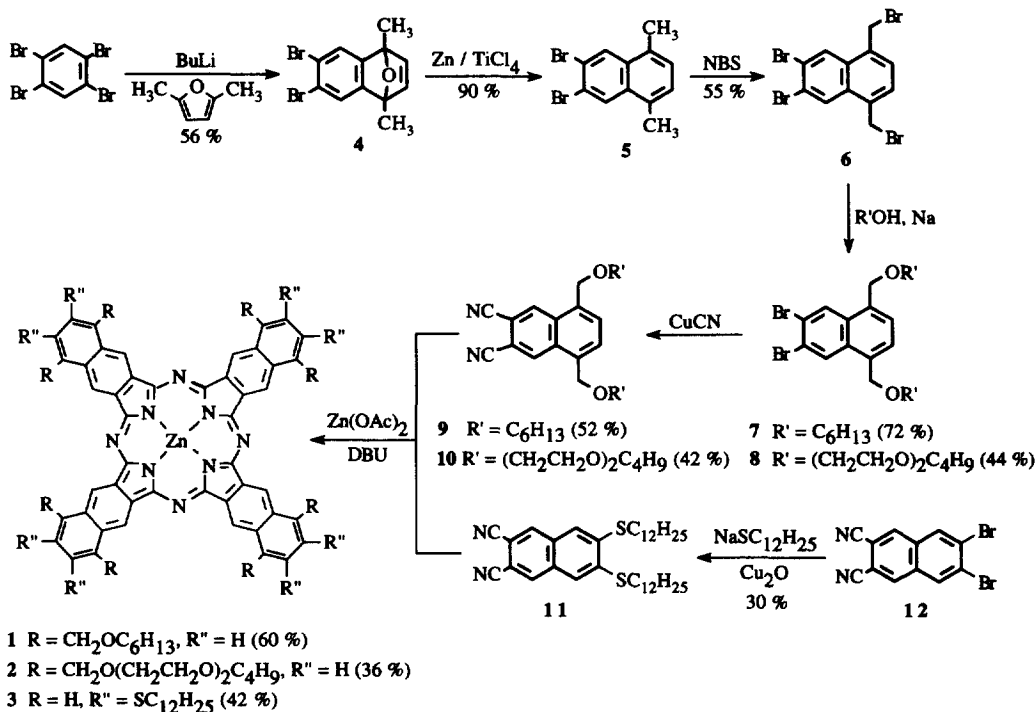
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**Abstract:** The first example of octasubstituted 2,3-naphthalocyanines showing discotic mesophase behaviour is described. © 1997 Elsevier Science Ltd.

Interest in phthalocyanines has increased enormously in recent years owing to their intriguing electrical, optical, photochemical and catalytic properties.<sup>1</sup> While there have been extensive studies of the chemistry, properties and applications of this fascinating class of compounds, there has been much less work carried out on the related 2,3-naphthalocyanine system.<sup>2</sup> The benzofusion on the macrocyclic core renders these compounds absorbing strongly in the near-IR region and exhibiting superior electrical properties compared with phthalocyanines,<sup>3</sup> that have also been supported by theoretical calculations.<sup>4</sup> Substituted 2,3-naphthalocyanines in particular are rare which may be due to the lack of convenient synthetic routes to their precursors 2,3-dicyanonaphthalenes. Considerable progress has only been made in this respect very recently.<sup>5</sup> Here we describe two synthetic pathways to differently substituted 2,3-naphthalocyanines **1-3**. These macrocycles incorporated with eight long-chain substituents exhibit liquid crystalline properties. Although phthalocyanine-based liquid crystals are well-documented,<sup>6</sup> to our knowledge, the compounds **1-3** represent the first discotic mesogens based on 2,3-naphthalocyanine core.

The synthetic routes to octasubstituted zinc naphthalocyanines **1-3** are shown in Scheme 1.<sup>7,8</sup> Treatment of 1,2,4,5-tetrabromobenzene with butyl lithium and 2,5-dimethylfuran gave the endoxide **4**, which underwent deoxygenation yielding the dibromonaphthalene **5**. Benzylic bromination followed by alkoxylation introduced two long-chain substituents to the naphthalene ring. The dibromides **7** and **8** were then converted to the respective dinitriles **9** and **10** by using the Rosenmund-von Braun reaction. The 6,7-disubstituted 2,3-dicyanonaphthalene **11** was prepared by a different strategy which involved the aromatic nucleophilic substitution of **12** with thiolate NaSC<sub>12</sub>H<sub>25</sub>. This dinitrile was described previously and was converted to the corresponding metal-free and copper naphthalocyanines.<sup>9</sup> Cyclisation of dicyanonaphthalenes **9-11** with zinc acetate and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in 1-hexanol led to the formation of **1-3**, respectively, in moderate yields. All of these macrocycles possess good solubility in common organic solvents and were purified mainly by column chromatography with hexane or toluene mixed with tetrahydrofuran (THF) as eluent. The latter was employed in order to disrupt the molecular aggregation associated with the large  $\pi$ -system.

Scheme 1



The  $^1\text{H}$  NMR spectra of 1-3 in benzene- $d_6$  showed only broad bands due to the aliphatic side chains, while the aromatic signals were not observed because of the strong aggregation tendency of these molecules. Addition of a small amount of pyridine- $d_5$ , however, led to the appearance of two highly deshielded broad signals in the regions  $\delta$  9.53-10.08 and 7.85-8.27 assignable to the ring protons of two different groups; the signals due to the side chains were also sharpened.<sup>10</sup> This indicated clearly that pyridine, apart from THF, can also break the intermolecular  $\pi$ - $\pi$  interactions to some extent. The UV-Vis spectra of 1-3 in THF displayed a B band at 336-347 nm and an intense Q band at 756-780 nm which are typical of those of 2,3-naphthalocyanines.<sup>11</sup>

The mesophase behaviour of 1-3 was studied by differential scanning calorimetry (DSC) and polarised optical microscopy. The results are listed in Table 1. The DSC thermograms of 1 and 3 showed only a single endothermic peak within the range of 25-300°C, corresponding to the crystalline to mesophase transition. No well-defined transition peak was observed for 2, which is soft and rubbery at room temperature. Upon heating above the transition temperature or *ca.* 150°C in the case of 2, the melt of these compounds was very viscous and the birefringence formed slowly as viewed through a polarised microscope. The optical texture of the mesophase of 2 was fan-shape, which is characteristic of a discotic columnar (disordered) mesophase with hexagonal symmetry, denoted as  $D_{\text{hd}}$ , and is commonly observed for substituted phthalocyanines.<sup>12</sup> No characteristic texture, however, could be observed for compounds 1 and 3. As the isotropic phase could not be

reached up to 300°C at which decomposition of the compounds began, the mesophase was observed on heating from their crystalline phase rather than cooling from the isotropic phase. The samples were thus annealed at elevated temperature for 2-4 days prior to microscopic investigation. This is analogous to octasubstituted phthalocyanines with substituents of similar chain length such as  $H_2[Pc'(CH_2OR)_8]$  ( $R = C_6H_{13}, C_{10}H_{21}$ ),<sup>13</sup>  $Cu\{Pc''[O(CH_2CH_2O)_3CH_3]_8\}$ <sup>14</sup> and  $M[Pc''(OC_{12}H_{25})_8]$  ( $M = H_2,^{15} Pt^{16}$ ) of which the clearing temperature is higher than the decomposition temperature (>250°C).<sup>17</sup>

**Table 1** Thermal behaviour of 1 and 3

Compound	Transition	T / °C	$\Delta H / kJ mol^{-1}$
1	K - D	133	16.7
3	K - D	100	52.1

In summary, we have synthesised three octasubstituted 2,3-naphthalocyanines which exhibit mesomorphic properties. The synthetic routes are general and it can be envisaged that a wide range of substituents can be introduced to the naphthalocyanine core by coupling with the versatile precursors 6 and 12.

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7. Compounds 1-10 are new compounds and were fully characterised by elemental analysis, <sup>1</sup>H and <sup>13</sup>C NMR, IR and EI- or LSI-MS.
8. Selected data for the precursors 4-10: 4, mp 98-100°C; <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  7.33 (s, 2 H, ArH), 6.74 (s, 2 H, =CH), 1.85 (s, 6 H, CH<sub>3</sub>). 5, mp 88-90°C; <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  8.21 (s, 2 H, ArH), 7.19 (s, 2 H, ArH), 2.57 (s, 6 H, CH<sub>3</sub>). 6, mp 218-220°C (decomp.); <sup>1</sup>H NMR (250 MHz,

- CDCl<sub>3</sub>) δ 8.46 (s, 2 H, ArH), 7.50 (s, 2 H, ArH), 4.83 (s, 4 H, ArCH<sub>2</sub>). **7**, <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ 8.45 (s, 2 H, ArH), 7.44 (s, 2 H, ArH), 4.84 (s, 4 H, ArCH<sub>2</sub>), 3.52 (t, *J* = 6.4 Hz, 4 H, OCH<sub>2</sub>), 1.56-1.68 (m, 4 H, CH<sub>2</sub>), 1.22-1.40 (m, 12 H, CH<sub>2</sub>), 0.87 (t, *J* = 6.7 Hz, 6 H, CH<sub>3</sub>). **8**, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.48 (s, 2 H, ArH), 7.45 (s, 2 H, ArH), 4.92 (s, 4 H, ArCH<sub>2</sub>), 3.58-3.69 (m, 16 H, OCH<sub>2</sub>), 3.45 (t, *J* = 6.7 Hz, 4 H, OCH<sub>2</sub>), 1.55 (quintet, *J* = 6.7 Hz, 4 H, CH<sub>2</sub>), 1.34 (sextet, *J* = 7.4 Hz, 4 H, CH<sub>2</sub>), 0.89 (t, *J* = 7.2 Hz, 6 H, CH<sub>3</sub>). **9**, mp 86-88°C; <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ 8.69 (s, 2 H, ArH), 7.70 (s, 2 H, ArH), 4.90 (s, 4 H, ArCH<sub>2</sub>), 3.55 (t, *J* = 6.6 Hz, 4 H, OCH<sub>2</sub>), 1.57-1.65 (m, 4 H, CH<sub>2</sub>), 1.25-1.41 (m, 12 H, CH<sub>2</sub>), 0.87 (t, *J* = 6.7 Hz, 6 H, CH<sub>3</sub>). **10**, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.76 (s, 2 H, ArH), 7.69 (s, 2 H, ArH), 4.99 (s, 4 H, ArCH<sub>2</sub>), 3.60-3.72 (m, 16 H, OCH<sub>2</sub>), 3.46 (t, *J* = 6.8 Hz, 4 H, OCH<sub>2</sub>), 1.55 (quintet, *J* = 6.8 Hz, 4 H, CH<sub>2</sub>), 1.33 (sextet, *J* = 7.5 Hz, 4 H, CH<sub>2</sub>), 0.88 (t, *J* = 7.4 Hz, 6 H, CH<sub>3</sub>).
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  10. <sup>1</sup>H NMR [300 MHz, C<sub>6</sub>D<sub>6</sub> / C<sub>5</sub>D<sub>5</sub>N (v/v 3:1)] data for **1**: δ 10.00 (br s, 8 H, ArH), 7.92 (br s, 8 H, ArH), 5.39 (br s, 16 H, ArCH<sub>2</sub>), 3.84 (br s, 16 H, OCH<sub>2</sub>), 1.87-1.97 (m, 16 H, CH<sub>2</sub>), 1.57-1.70 (m, 16 H, CH<sub>2</sub>), 1.15-1.45 (m, 32 H, CH<sub>2</sub>), 0.83 (t, *J* = 6.8 Hz, 24 H, CH<sub>3</sub>); for **2**: δ 10.08 (br s, 8 H, ArH), 7.85 (br s, 8 H, ArH), 5.42 (br s, 16 H, ArCH<sub>2</sub>), 4.03 (br s, 16 H, OCH<sub>2</sub>), 3.93 (br s, 16 H, OCH<sub>2</sub>), 3.79-3.83 (m, 16 H, OCH<sub>2</sub>), 3.56-3.60 (m, 16 H, OCH<sub>2</sub>), 3.29 (t, *J* = 6.4 Hz, 16 H, OCH<sub>2</sub>), 1.38-1.48 (m, 16 H, CH<sub>2</sub>), 1.24-1.34 (m, 16 H, CH<sub>2</sub>), 0.78 (t, *J* = 7.3 Hz, 24 H, CH<sub>3</sub>); for **3**: δ 9.53 (br s, 8 H, ArH), 8.27 (br s, 8 H, ArH), 3.29 (br s, 16 H, SCH<sub>2</sub>), 2.05 (br s, 16 H, CH<sub>2</sub>), 1.70 (br s, 16 H, CH<sub>2</sub>), 1.20-1.60 (m, 128 H, CH<sub>2</sub>), 0.90 (t, *J* = 6.7 Hz, 24 H, CH<sub>3</sub>).
  11. The spectra are concentration dependent due to the molecular aggregation. Although the Q band absorption maxima remain virtually unshifted, the corresponding molar absorptivities increase upon dilution. The data given below are very close to those due to the monomeric species. UV-Vis (THF) [ $\lambda_{\max}$  / nm (log  $\epsilon$ )] data for **1** (4.26 x 10<sup>-7</sup> M): 336 (5.55), 676 (5.35), 721 (5.32), 756 (6.22); for **2** (4.79 x 10<sup>-7</sup> M): 336 (5.40), 678 (5.15), 722 (5.14), 757 (5.94); for **3** (1.85 x 10<sup>-7</sup> M): 347 (5.49), 697 (5.13), 743 (5.16), 780 (5.92).
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  17. Pc' = 1,4,8,11,15,18,22,25-octasubstituted phthalocyaninate; Pc'' = 2,3,9,10,16,17,23,24-octasubstituted phthalocyaninate.