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Macrodiscotic liquid crystals derived from planar phthalocyanine oligomers

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Abstract—A novel unsymmetrically substituted phthalocyanine, which contains an extended planar core and a pair of adjacent peripheral hydroxyl groups is synthesised and used to prepare planar phthalocyanine oligomers. These materials act as macrodiscotic liquid crystals giving a columnar mesophase, which is stable over a large temperature range.

Materials that form columnar liquid crystals are generally composed of disk-shaped molecules with rigid aromatic cores and peripheral alkyl chains.[1–3] On heating, such molecules self-assemble into individual molecular columns. Such materials are of interest for the anisotropic transport of electronic charge or light energy (via excitons).[4,5] Columnar liquid crystals based on phthalocyanine (Pc) derivatives are especially interesting due to their intense light absorption between 300–800 nm, their relatively small HOMO–LUMO gaps (1.5–2.0 eV), and their ability to display ordered columnar mesophases over a very broad temperature range (>200 °C).[6–10] In general, extending the planarity of an aromatic core increases the ordering within the columnar mesophase and extends the thermal range over which they are stable. The associated enhanced overlap of π-orbitals of the aromatic system is expected to increase charge carrier mobility along the axis of the columns. Previously, several types of macrodiscotic mesogens have been reported. For example, Müllen and co-workers prepared mesogens composed of discrete fragments of graphite such as hexaalkyl substituted hexabenzocoronene derivatives[4] and extended triphenylenes.[11] Previously, we have described a novel synthetic approach towards macrodiscotic materials involving the preparation of two-dimensional sheet polymers by the assembly of phthalocyanine components using dioxane linkages.[12] In the present study, discrete phthalocyanine-containing oligomers (dimer **1** and a trimer **2**) are assembled using the same dioxane-forming double aromatic nucleophilic substitution.[13] For each of these oligo-mers the nonperipheral substitution of flexible alkyl chains (R—dodecyl) is designed to ensure that they form columnar liquid crystals on heating. The choice of the Zn^{2+} as resident metal ion for the central cavity of the phthalocyanine units is also designed to enhance columnar mesophase formation.[6]

The synthetic route to the dioxane-linked dimer **1** and hexaazatrinaphthylene-centred trimer **2** are given in Schemes 2 and 3, respectively. Both routes involve the initial preparation of an unsymmetrical phthalocyanine **6** containing a reactive *ortho*-dihydroxy moiety as shown in Scheme 1. For this phthalocyanine, the two phthalonitrile starting materials are 4,5-dimethoxyphthalonitrile[8] **3** and 2,3-dicyano-6,9-didodecyldibenzodioxane[12,14,15] **4** both of which are readily prepared following literature methods. The formation of the non-uniformly substituted phthalocyanine **5**, which contains two methyloxy groups, is achieved by the mixed cyclotetramerisation reaction of **4** and **3** in a 1:5 molar ratio

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Keywords: Phthalocyanine; Discotic liquid crystal; Nucleophilic aromatic substitution.

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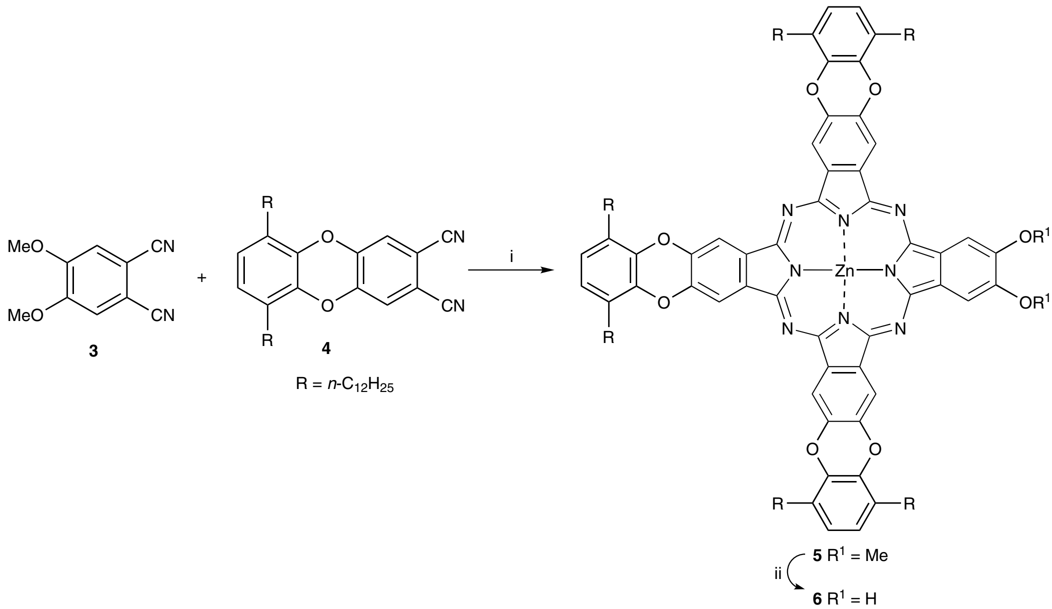
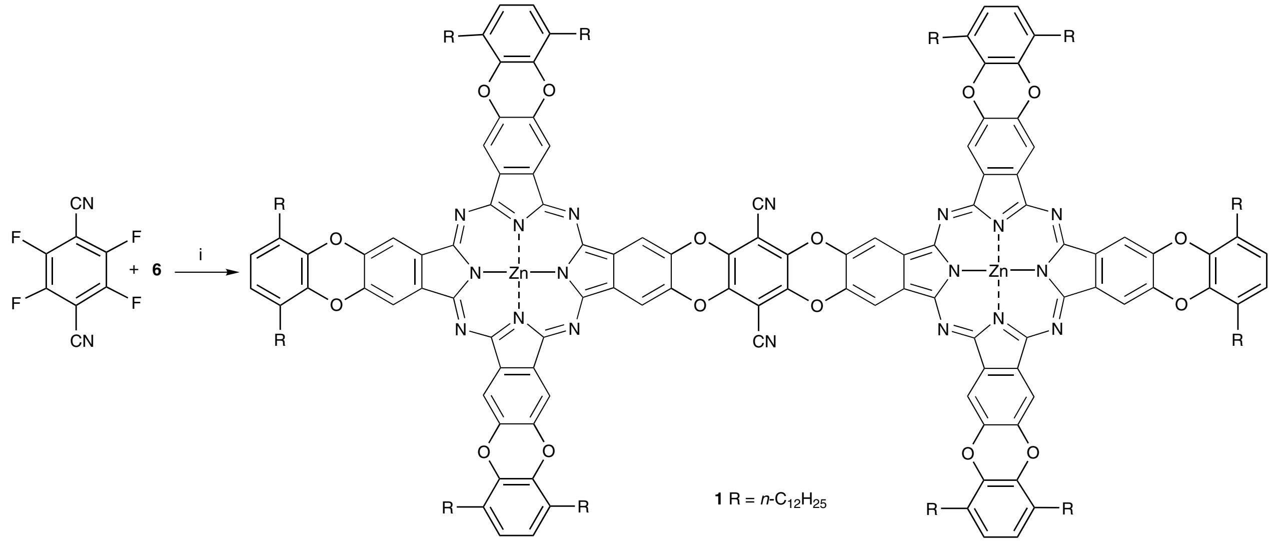


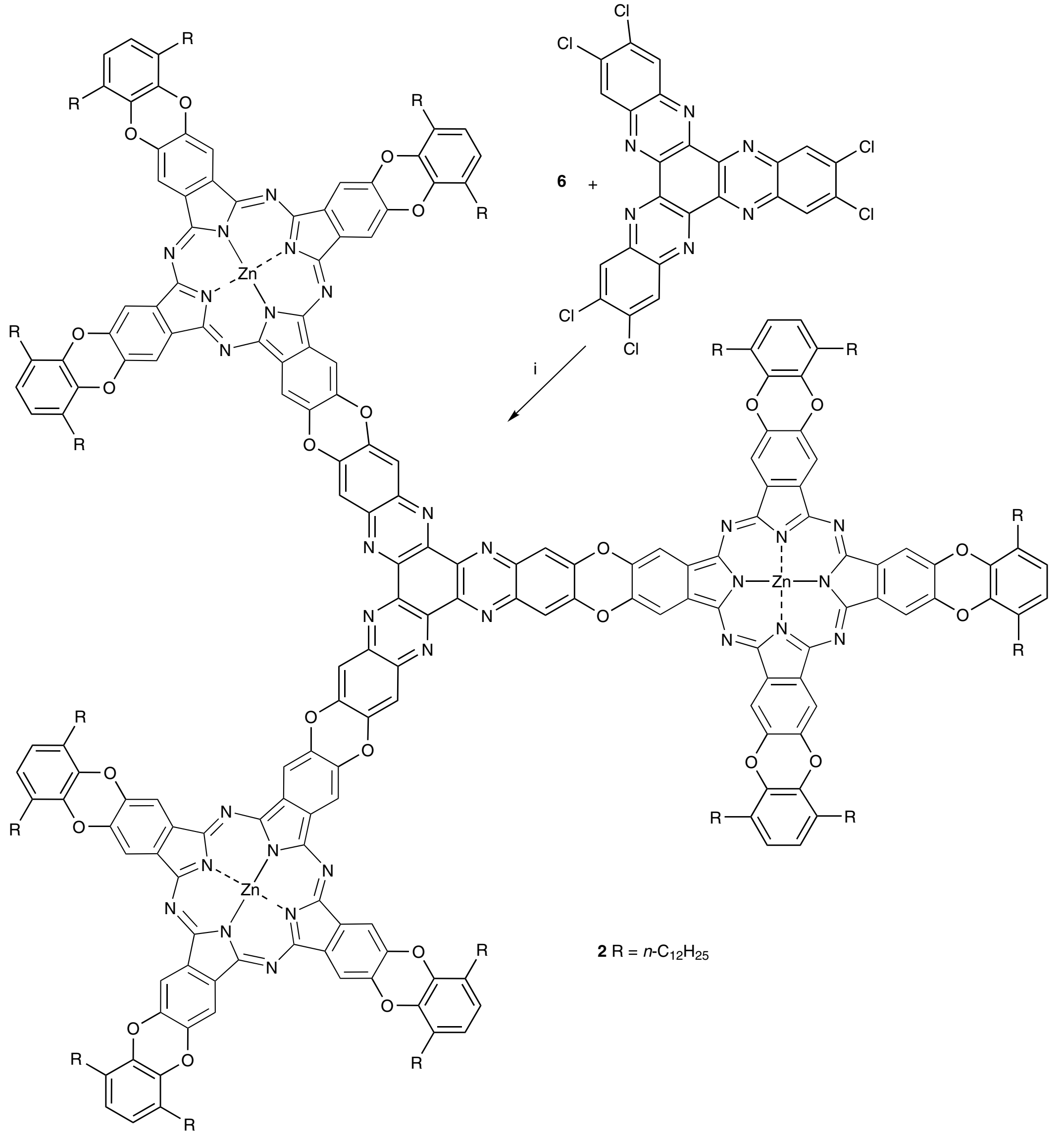
Scheme 1. Reagents and conditions: (i) $Zn(OAc)_2$, NMP, 160 °C, 2 h; (ii) BBr_3, DCM, 25 °C, 3 h.



Scheme 2. Reagents and conditions: (i) K_2CO_3, DMF, 60 °C, 24 h.

at 160 °C in the presence of zinc acetate, using NMP as solvent. The methoxy groups were removed from Pc **5** using boron tribromide to provide the dihydroxyphthalocyanine **6**. Separation of Pc **5** from the symmetrical phthalocyanine byproduct could not be achieved by column chromatography; therefore, the crude mixture of phthalocyanines was used in the demethylation reaction. However, once demethylation was achieved, the greater polarity of Pc **6** enabled its separation from the symmetric phthalocyanine by column chromatography.[16,17]

For the preparation of the benzodioxine-linked dimer **1**, a high yielding double aromatic nucleophilic substitution (S_NAr) reaction between the unsymmetrical Pc **6** and tetrafluoroterephthalonitrile was used.[15] The dimer can be purified and separated from excess Pc **6** using column chromatography and then recrystallised from ethyl acetate to give a green powder in good yield (85%). Similarly, the synthesis of trimer **2** involves the S_NAr reaction between a five-times molar excess of Pc **6** and 2,3,8,9,14,15-hexachloro-5,6,11,12,17,18-hexaazatrinaphthylene **7** (prepared using a literature method, based on the condensation of hexaoxocyclohexane octahydrate with 4,5-dichlorobenzene-1,2-diamine).[18] Purification of the resulting trimer **2** involves precipitation from methanol and then continual extraction of the solid initially with methanol and acetone in a Soxhlet extractor to remove polar impurities and then with ethyl acetate to remove the excess of Pc **6**.



Scheme 3. Reagents and conditions: (i) K_2CO_3, DMF, 100 °C, 24 h.

All isolated phthalocyanine-based products **1**, **2** and **6** gave spectroscopic (UV/visible adsorption and MALDI-MS) and elemental analyses consistent with their proposed structures.[15–17] ^{1}H NMR spectroscopy gave only highly broadened peaks corresponding to the alkyl hydrogens due to aggregation. This broadening is severe and even the use of d_6-benzene (a solvent which usually reduces aggregation), elevated temperatures (60 °C) and the addition of d_5-pyridine (a potential axial ligand for the central zinc cation) did not sharpen the spectra sufficiently to unambiguously observe the aromatic hydrogens. Gel permeation chromatography (GPC) using THF as eluent also gives valuable information on the structure and purity of the products (see Fig. 1). For dimer **1** and trimer **2** the eluent peaks indicate that the products are monodisperse ($M_w/M_n = 1.05$–1.08), consistent with a pure single component system. Their apparent molecular masses (dimer $\mathbf{1} = 6400\,\mathrm{g\,mol^{-1}}$ and trimer $\mathbf{2} = 9290\,\mathrm{g\,mol^{-1}}$) relative to polystyrene calibration standards are significantly larger than their actual masses. This is consistent with the rigid and extended structures of the oligomers, which would give the oligomers a greater hydrodynamic volume per unit mass as compared with the random coil adopted by polystyrene in solution. Interestingly, GPC analysis of Pc **6** suggests that this compound appears to elute both as monomeric and aggregated species, which is likely to be due to hydrogen bonding enhancing the usual tendency of the phthalocyanine unit to undergo self-association. The MALDI-MS of Pc **6** supports this result by showing an additional strong peak matching the molar mass of this noncovalent dimer (at $m/z = 3876$) in addition to the parent ion ($M^+ = 1938$).

UV/visible absorption spectra of **1**, **2** and **6** in THF solution all show evidence of aggregation even at low concentrations. In each case a distinctive broad peak is obtained centred at 625 nm, in addition to the sharper Q-band at 690 nm, which is characteristic of co-facial (face-to-face) self-association.[19] The highly broadened

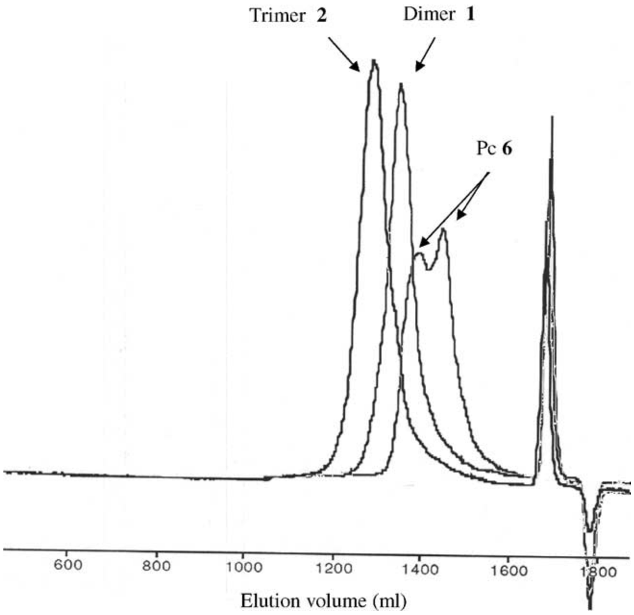


Figure 1. Superimposed GPC traces for dimer **1**, trimer **2** and intermediate Pc **6**.

^{1}H NMR spectra of the compounds is also consistent with aggregation.

A preliminary investigation of the liquid crystal behaviour of the dimer **1** and trimer **2** was performed by means of polarising optical microscopy. As expected for macrodiscotic materials,[11] both display birefringent textures consistent with a hexagonal columnar mesophase over a very wide temperature range (between 100 °C and their decomposition temperatures >300 °C).

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13. Dimer **1**: mp >300 °C.; ^{1}H NMR (500 MHz, C_6H_6, 60 °C) 0.85–2.5 (br m); *m/z* (MALDI) 3996 ($M^+ + H^+$). Anal. Calcd for $C_{252}H_{328}N_{18}O_{16}Zn_2$: C, 75.74; H, 8.27; N, 6.30; Zn, 3.27. Found: C, 75.33; H, 8.46; N, 6.11; Zn, 3.16%. UV/vis (THF, λ_{max}/nm): 680, 625, 358. Trimer **2**: mp >300 °C; ^{1}H NMR (500 MHz, C_6H_6, 60 °C): 0.9–2.5 (br m); *m/z* (MALDI) 6186 ($M^+ + H^+$). Anal. Calcd for $C_{390}H_{498}N_{30}O_{24}Zn_3$: C, 75.72; H, 8.12; N, 6.79; Zn, 3.17. Found: C, 75.22; H, 8.55; N, 6.41; Zn, 3.06%. UV/vis (THF, λ_{max}/nm): 686, 628, 360. Pc **6**: mp >300 °C; ^{1}H NMR (500 MHz, C_6H_6, 60 °C): 0.9–2.5 (br m); *m/z* (MALDI) 1938 ($M^+ + H^+$). Anal. Calcd for $C_{122}H_{16}N_8O_8Zn$: C, 75.60; H, 8.63; N, 5.78; Zn, 3.17. Found: C, 75.48; H, 8.76; N, 5.56; Zn, 3.30%. UV/vis (THF, λ_{max}/nm): 686, 628, 360.
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