JOURNAL OF
Materials
CHEMISTRY

Synthetic strategies towards macrodiscotic materials. Can a new dimension be added to liquid crystal polymers?†

Kadhum Msayib, Saad Makhseed and Neil B. McKeown*

The Innovation Centre for Organic Materials, Department of Chemistry, University of Manchester, UK M13 9PL. E-mail: neil.mckeown@man.ac.uk

Received 6th April 2001, Accepted 31st May 2001
First published as an Advance Article on the web 26th September 2001

Macrodiscotic materials are liquid crystalline systems composed of an extended planar structure. It is anticipated that the self-ordering of such materials will result in interesting mechanical and electronic properties. Two synthetic strategies for the realisation of macrodiscotic materials are reviewed: firstly, the preparation of molecules which possess a single extended discotic core and secondly, the assembly of rigid, planar macromolecules composed of a random array of fused discotic units. Oxanthrene-based phthalonitrile precursors, prepared by high yielding reactions between catechols and 4,5-dichlorophthalonitrile, are used to explore both strategies for the synthesis of macrodiscotic materials that incorporate phthalocyanine (Pc) as the discotic unit.

The first well-defined examples of disc-shaped (discotic) liquid crystals, hexa-substituted benzenes, were reported in 1977 by Chadrasekhar.[1,2] However, before this important disclosure, a liquid crystalline state composed of discotic molecular components was observed during the high temperature carbonisation of petroleum residues to form graphite.[3] This observation led directly to the development of high-performance fibres by the melt-spinning of 'mesophase pitch' prepared from aromatic hydrocarbons.[4–6] The resultant carbon fibres differ from those produced by the thermal treatment of polyacrylonitrile in that they are composed of extended graphitic sheets that are oriented by the shear field during the spinning process.[7] Many high performance polymers such as poly(*p*-phenyleneterephthalamide) (Kevlar®) and liquid crystal polyesters gain their mechanical strength from a similar orientation of their lyotropic or thermotropic mesophase during fibre formation. Thus, mesophase pitch can be considered as a two-dimensional or discotic equivalent of main-chain calamitic liquid crystal polymers. Clearly, carbonisation is a drastic and limited chemical conversion. Thus, it is interesting to consider the synthesis of extended sheet-like (macrodiscotic) molecules using conventional synthetic chemistry.

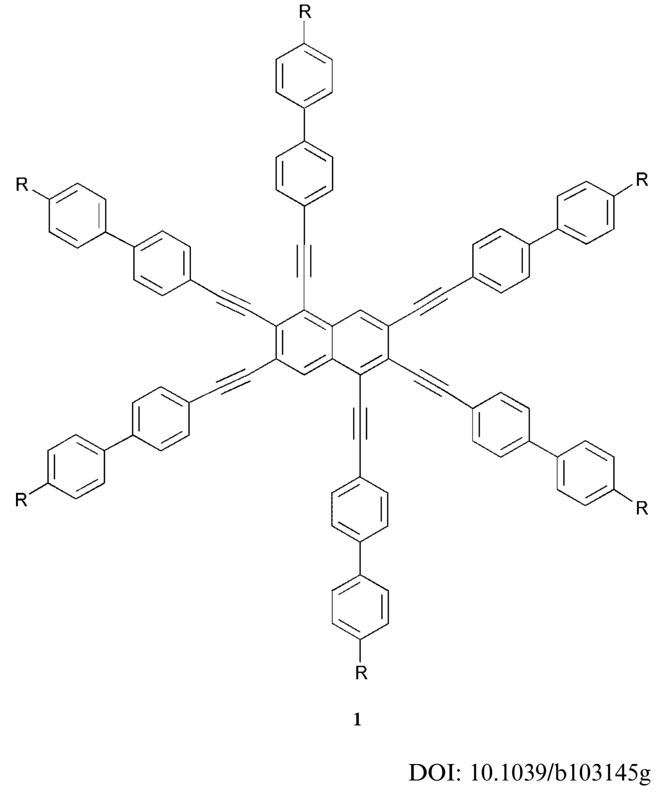
This paper will consider two synthetic strategies for the realisation of macrodiscotic materials: firstly, the preparation of molecules which possess a single extended discotic core and secondly, the assembly of rigid, planar macromolecules composed of a random array of fused discotic units. For both strategies, a novel and high yielding reaction between catechols and 4,5-dichlorophthalonitrile to give benzodioxine-containing precursors is employed.

Results and discussion

Strategy 1: the synthesis of mesogens with extended discotic cores

Several types of macrodiscotic mesogens have been reported previously. Praefcke *et al.* used the term macrodiscotic to describe large planar molecules composed of a benzene or naphthalene core radially substituted with biphenylylethynyl units (*e.g.* **1**; R = alkyl)[8] and also multinuclear palladium complexes derived from hexaalkoxyaldobisimines.[8,9] Elegant work by Müllen *et al.* has involved the preparation of mesogens composed of discrete fragments of graphite such as hexaalkyl substituted hexabenzocoronene derivatives (*e.g.* **2**; R R = alkyl)[10,11] and extended triphenylenes (*e.g.* **3**; R = alkyl).[12]

The first liquid crystalline derivatives of Pc, a macrocycle noted for its interesting electronic and optical properties,[13] were described by Simon *et al.* in 1982.[14] Since that time hundreds of mesogenic Pc derivatives have been reported.[13] Peripheral substitution of the Pc macrocycle with *n*-alkyl,[15,16] *n*-alkyloxy[17] or *n*-alkyloxymethyl[14,18,19] (*n*-alkyl = hexyl to dodecyl) side-chains typically results in liquid crystalline materials which do not become isotropic liquids (clear) below their decomposition temperatures (> 300 °C).[15] The exceptional thermal stability of the columnar mesophase of Pc

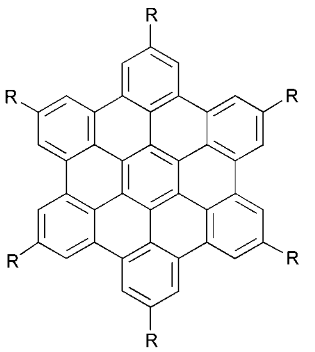


1

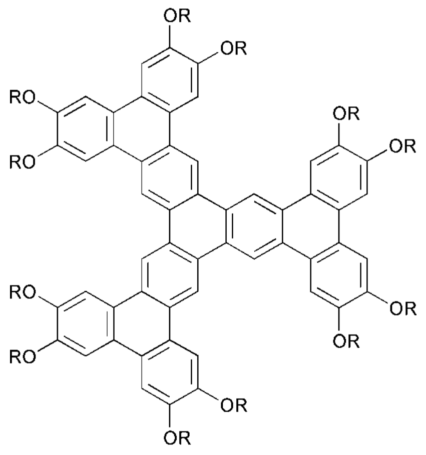
---

†Basis of a presentation given at Materials Discussion No. 4, 11–14 September 2001, Grasmere, UK.

DOI: 10.1039/b103145g

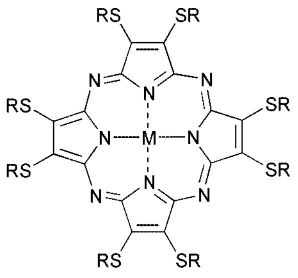


2

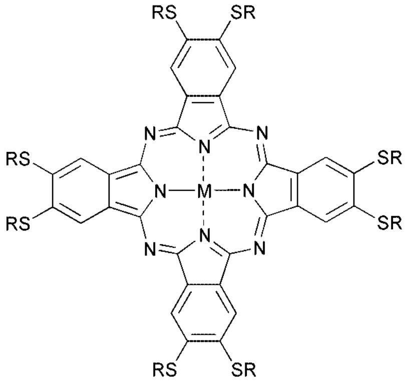


3

derivatives is due to the pronounced shape anisotropy afforded by the planar aromatic core (diameter ~1.6 nm; width ~0.4 nm). Thus, it is arguable that Pc derivatives may be considered as a class of macrodiscotic material. Supporting evidence for this comes from a comparison between the thermal stability of the columnar mesophase of tetraazaporphyrin derivatives (*e.g.* **4**) with those of related Pcs (*e.g.* **5**). It has been established that the length of the alkyl side chain,[13,20] the group that links it to the macrocyclic ring[13] and the central metal ion (M)[21] all have a profound influence over the thermal stability of the columnar mesophase. Thus, to compare the effect of the size of the macrocycle, the macrocycles must have the same peripheral side-chains and the same central metal ion. A survey of the literature provides only one opportunity for a direct comparison between the two systems. The tetraazaporphyrin **4**($R = $ alkyl; $M = Cu^{2+}$)[22] has a much lower clearing point of ~102 °C than the Pc **5**($R = $ alkyl; $M = Cu^{2+}$) (>300 °C).[23] The difference in clearing temperatures for the two systems can be estimated at ~280 °C by comparing the clearing temperature of 292 °C for **5**($M = 2H^+$) with the virtual clearing point of ~10 °C for **4**($M = 2H^+$). This latter figure is obtained by an extrapolation of the data for the shorter chained members of the homologous series whose clearing points lie above their melting points. Predictably, the equivalent naphthalocyanine derivative **6**($R = $ alkyl; $M = Zn^{2+}$) has a clearing point above its decomposition temperature (>300 °C).[24,25] The largest macrodiscotic compound based on a Pc-type structure, reported to date, is the tetrapyrazinoporphyrazine **7**($R = C_{12}H_{25}$) described by Ohta *et al.* that has a rigid core of diameter ~2.4 nm.[26] This material displays a columnar mesophase which is stable over the entire accessible temperature range (< -100 to >300 °C). Its deviation from a disc-like shape appears to result in a highly ordered mesophase of rectangular symmetry as deduced from X-ray diffraction (XRD) studies.



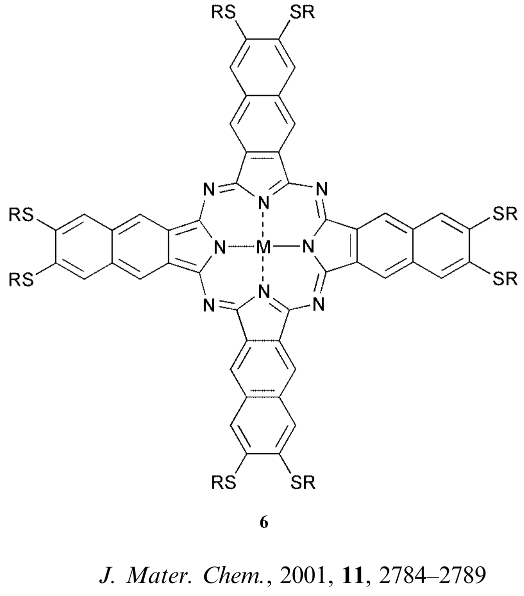
4



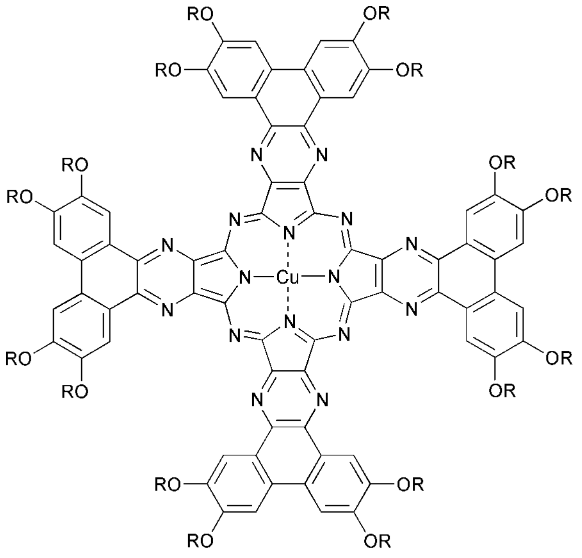
5

We report here some preliminary work on the extension of the Pc core by the use of benzodioxine subunits. Initially, this may seem an unusual choice in order to obtain a *planar* structure. However, the X-ray crystal structure of the parent compound, oxanthrene (dibenzodioxine), and those of a number of other substituted derivatives show no significant deviation from planarity.[27] Thus, although there may be some fluctuation between non-planar conformations, it can be assumed that the benzodioxine is, on average, coplanar with the Pc core. The chosen target was Pc **8** for which the eight 'non-peripheral' dodecyl side-chains (R) were anticipated to help reduce the transitions temperatures so that the clearing point would lie below the decomposition temperature.

The important step of the synthetic route to Pc **8** (Scheme 1) is the aromatic nucleophilic substitution reaction between 3,6-didodecylcatechol and 4,5-dichlorophthalonitrile. The latter compound has been used by Wöhrle for the synthesis of a series of 4,5-bis(phenyloxy)phthalonitriles using similar reaction conditions.[28] The formation of the desired 2,3-dicyano-6,9-didodecyloxanthrene **9** is achieved without contamination from 4,5-bis(2′,5′-didodecyl-6′-hydroxyphenyloxy)phthalonitrile. This confirms the greater efficiency of the intramolecular substitution reaction within the 4-chloro-5-(2′,5′-didodecyl-6′-hydroxyphenyloxy)phthalonitrile intermediate in comparison



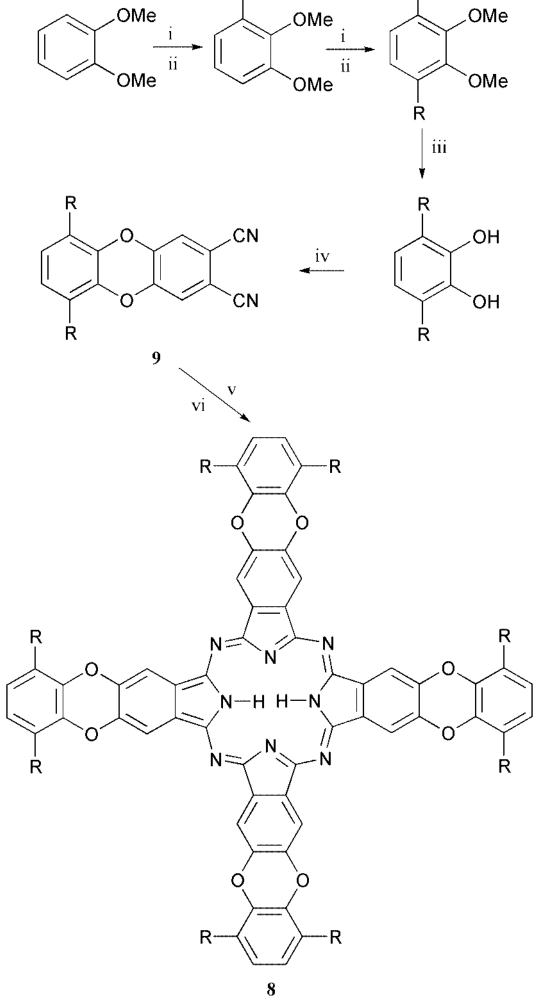
6



7

with a second intermolecular reaction.[29] Pc formation was achieved by the cyclotetramerisation of the resulting phthalonitrile.

Polarising optical microscopy (POM) confirms that Pc **8** becomes a birefringent, fluid mesophase at just above room temperature (~45 °C) and becomes isotropic at 258–262 °C. The focal conic optical texture observed, on cooling the isotropic liquid, is typical of the hexagonal columnar mesophase with the texture growing as dendritic shapes with six-fold symmetry.[30] The relatively low clearing point of Pc **8** as compared to those of other Pc mesogens with alkyl side-chains of similar length is related to the non-peripheral position of the alkyl side-chains. For comparison, Pc **10** which also possesses eight non-peripheral side-chains has a clearing point of 115 °C.[20,31,32] Therefore, it can be concluded that the extension of the Pc core by the benzodioxine groups significantly improves the thermal range of stability for the columnar mesophase.



8

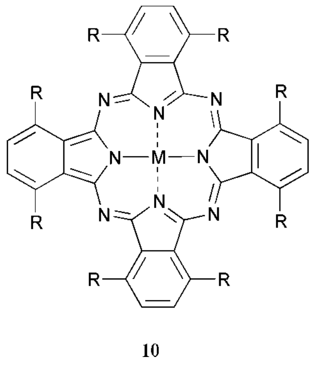
Scheme 1 *Reagents and conditions*: i, *n*-BuLi, THF, reflux; ii, 1-bromodecane, THF reflux; iii, BBr_3, CH_2Cl_2; iv, 4,5-dichlorophthalonitrile, K_2CO_3, DMF, 60 °C; v, lithium, pentanol, reflux; vi, AcOH.

Strategy 2: the synthesis of planar macromolecules

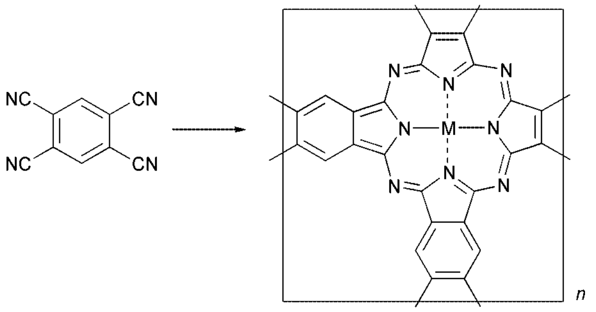
Despite a plethora of crystalline 2-dimensional (2D) 'polymer' motifs obtained through non-covalent interactions, there are few reports of well-characterised synthetic 2D *covalent* polymers other than Müllen's extended graphitic fragments.[33–35] In particular, the concept of linking discotic cores to form a sheet polymer has not been explored.

Any efficient step-growth polymerisation involving monomers containing more than two reactive groups will lead to a cross-linked network. However, in most cases a three-dimensional network will be the inevitable result. There have been a number of interesting attempts to prepare 2D polymers by confining network formation within a lamellar superstructure such as a smectic liquid crystal or a Langmuir–Blodgett (LB) multilayer film.[36] For example, a porphyrin-based sheet polymer has been prepared, albeit in minute quantities, by confinement of network formation within a LB film.[37] An alternative to the 2D physical confinement of the polymerisation is the use of a reaction that ensures the planar propagation of the polymer network. This can be achieved by the formation of rigid cyclic structures between the discotic units using similar chemistry to that used for the synthesis of linear ladder polymers. In addition, the formation of the discotic unit itself is a suitable reaction for 2D polymerisation—but only if the structure of the monomer ensures co-planarity between the resulting discotic groups.

The suitability of the Pc-forming reaction for the assembly of 2D polymers was recognised many years ago with the synthesis of poly(phthalocyanine) **11** from suitable precursors (*e.g.* 1,2,4,5-tetracyanobenzene).[38] However, even for carefully controlled cyclotetramerisation reactions, the degree of polymerisation of PPc appears small (*i.e.* only a few Pc subunits per molecule).[39] The possibility exists of strong electronic conjugation between the aromatic subunits of polymer **11** but this interesting feature adds an additional element of structural uncertainly to what is clearly a highly inhomogeneous material.[40] In addition, **11** is difficult to characterise because of its complete lack of solubility. Indeed, even rigid planar structures of modest size (*e.g.* unsubstituted Pc) are generally insoluble.[13] Without suitable precautions, such as the incorporation of solubilising groups, this will present serious problems for both the solution phase synthesis and characterisation of 2D polymers.



10



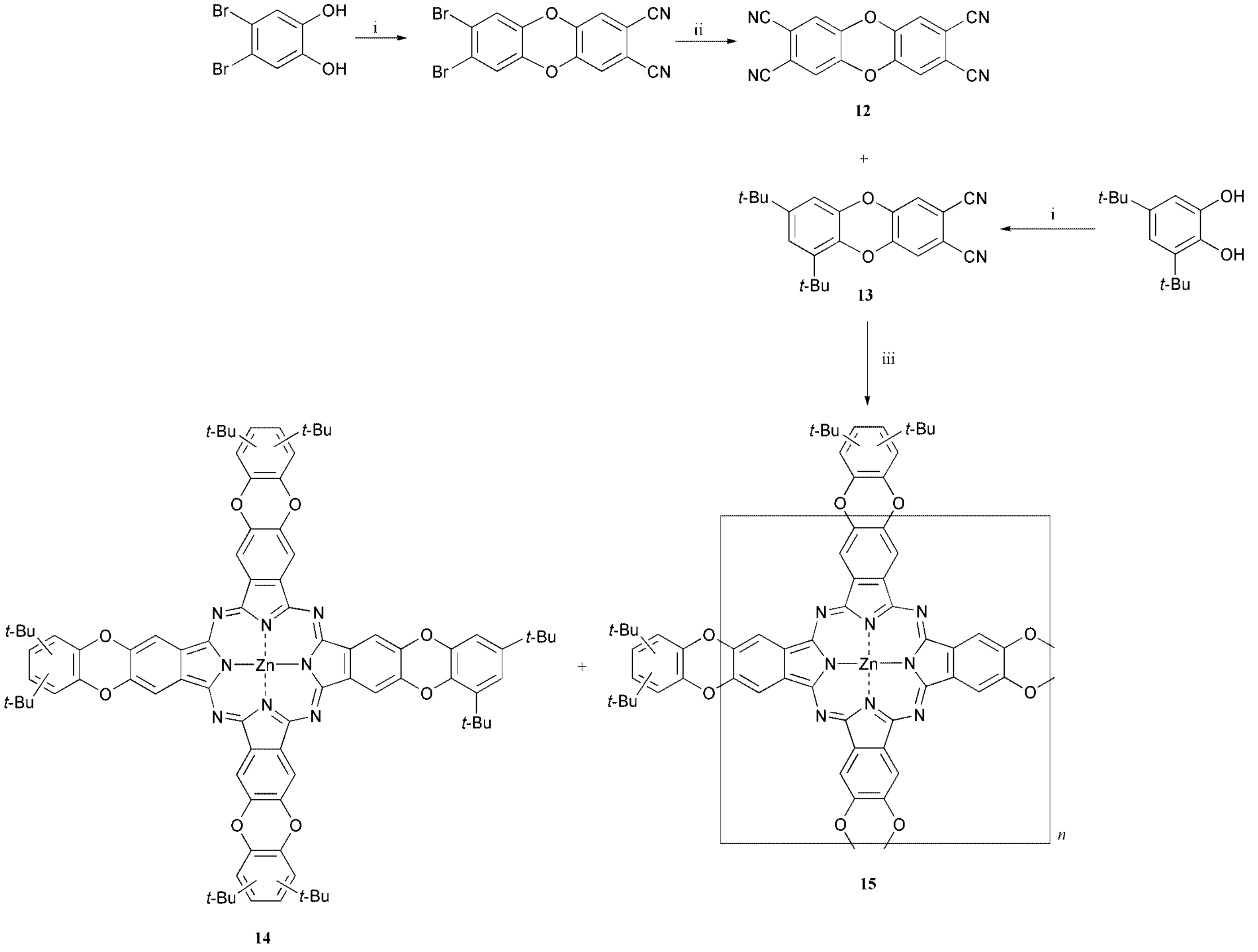
11

Many different monomers have been used for the synthesis of Pc-containing networks[40] but none, with the possible exception of 1,2,4,5-tetracyanobenzene, have ensured the co-planarity of neighbouring Pc units. It was anticipated that the bis(phthalonitrile) monomer 2,3,7,8-tetracyanooxanthrene **12**, would result in a planar Pc network on cyclotetramerisation of the phthalonitrile units. Unlike polymer **11**, there is no possibility of significant electronic conjugation between the Pc units of the resulting network, which avoids some structural inhomogeneity. Monomer **12** is prepared readily by the reaction between 4,5-dibromocatechol and 4,5-dichlorophthalonitrile followed by a Rosenmund von Braun reaction to replace the two bromines with nitrile groups (Scheme 2).

It was expected that the network derived from **12** would be insoluble and precipitate out of the reaction mixture prior to the formation of a network of high molecular mass. Therefore, a mono-functional phthalonitrile that contains *tert*-butyl solubilising groups was added to the polymerisation mixture in order to maintain the growing hyperbranched macromolecule in solution and facilitate solution-based characterisation of the resulting material. This phthalonitrile, 1,3-di-*tert*-butyl-7,8-dicyanooxanthrene **13**, prepared by the reaction between 4,5-dichlorophthalonitrile and 3,5-di-*tert*-butylcatechol (Scheme 2), was selected as the mono-functional phthalonitrile due to the excellent solubility of Pc **14** in organic solvents (*e.g.* hexane). In addition, it was expected that **13** would possess similar reactivity as **12** towards Pc formation.

A mixture containing a **13** and **12** (1 : 1 molar ratio) was reacted at 220 °C in quinoline solution in the presence of zinc acetate (Scheme 2). Purification of the resulting polymer involves initial precipitation onto methanol and then continual extraction of the solid with methanol in a Soxhlet extractor to remove polar impurities. Subsequent extraction with hexane removes the symmetrical Pc **14** formed from the cyclotetramerisation of phthalonitrile **13** and some oligomeric material. When the solvent was changed to THF an intensely green polymer **15** was extracted which is fully soluble in DMAc and sparingly soluble in cold $CHCl_3$ or THF. Some material remained in the extraction thimble and this proved only sparingly soluble in hot DMAc. Reaction mixtures that contain a smaller molar ration of **13** relative to **12** result in the rapid precipitation of very insoluble material.

The soluble polymer **15** was examined using gel permeation chromatography (GPC) as a solution in DMAc. It possesses a wide molecular mass distribution with a range commencing at



Scheme 2 *Reagents and conditions*: i, 4,5-dichlorophthalonitrile, K_2CO_3, DMF, 60 °C; ii, CuCN, DMF, 130 °C; iii, $Zn(OAc)_2$, quinoline, 200 °C.

$\sim 10 \times 10^3$ amu and continuing up to the exclusion limit of the GPC column ($\sim 100 \times 10^3$ amu). This vast polydispersity ($M_w/M_n > 10$) is typical for a hyperbranched polymer. ^{1}H NMR analysis fails to provide evidence for any structural component of the polymer except for a broad peak in a position consistent with the *tert*-butyl solubilising groups. This observation is expected for a large rigid polymer such as **15** and the absence of any sharp peaks in the spectrum suggests that the material is free from low molar mass impurities. An IR spectrum reveals the absence of a peak at ~ 2220 cm^{-1} which is consistent with an efficient conversion of phthalonitrile to Pc. UV-Vis spectroscopy shows adsorption bands at 670 nm and 630 nm originating from the Q-band of isolated and cofacially associated Pc units, respectively.

Polymer **15** is a green, brittle solid at room temperature and thermal analysis by DSC and POM shows that it does not soften below its decomposition temperature (> 300 °C). The possibility of lyotropic mesophase formation was briefly examined using POM by observing small samples of **15** in contact with DMAc. The formation of soft, malleable material was observed at the boundary between the polymer and its isotropic solution. This material flowed when sheared; however, its intense colour prohibited the observation of an optical texture indicative of lyotropic mesophase formation. Further work, involving both the synthesis and characterisation of Pc hyperbranched polymers, is planned.

Conclusions

The efficient reaction between catechols and 4,5-dichlorophthalonitrile provides a route to precursors suitable for the preparation of Pc mesogens and hyperbranched polymers. The high thermal stability of the mesophase exhibited by the benzodioxine extended Pc **8** supports the evidence from previous structural studies that show planarity for the oxanthrene system. Hence, it is anticipated that the hyperbranched polymer **15** or similar materials will ultimately provide 2D liquid crystalline polymers, although no direct evidence for this has been obtained from the very preliminary investigations carried out to date.

Experimental

Equipment

Routine ^{1}H NMR spectra were measured at 300 MHz using a Inova 300 spectrometer. High resolution (500 MHz) ^{1}H NMR spectra were recorded using a Varian Unity 500 spectrometer. UV-visible spectra were recorded on a Shimadzu UV-260 spectrophotometer using cells of pathlength 10 mm. IR spectra were recorded on a ATI Mattson Genesis Series FTIR (KBr/Germanium beam splitter). Elemental analyses were obtained using a Carlo Erba Instruments CHNS-O EA 108 Elemental Analyser. Routine low resolution electron ionisation (EI) mass spectrometry were obtained using a Fisons Instruments Trio 2000. MALDI mass spectra were recorded on a Micromas Tof Spec 2E instrument using a dithranol matrix. GPC analysis was carried out using a Polymer Laboratories Mixed-E ($\times 4$) column with a Polymer Laboratories LC1200 UV detector and a Gibson 307 pump. Polystyrene standards were used for calibration. Differential scanning calorimetry measurements were made on a Seiko DSC 220C machine and calibrated using an indium standard. Polarising optical microscopy was carried out using a Nikon Optiphot-2 microscope with a Mettler FP80 HT Hot Stage.

Materials

The preparation of 3,6-didodecylcatechol from veratrole is summarised in Scheme 1 and was based upon the method of Schill *et al.*[41] 4,5-Dichlorophthalonitrile is commercially available (Aldrich) but is conveniently prepared in large quantities from 4,5-dichlorophthalic acid using the method of Wöhrle.[28] 4,5-Dibromocatechol was prepared by the bromination of catechol. Other materials were obtained from Aldrich and used as received unless stated otherwise. All solvents were dried and purified as described in Perrin and Armarego.[42] Silica gel (60 Merck 9385) was used in the separation and purification of compounds by column chromatography. Materials were heated at 80 °C under vacuum for 18 hours as the final step of purification.

2,3-Dicyano-6,9-didodecyloxanthrene (9). A mixture of anhydrous potassium carbonate, 3,6-didodecylcatechol (3.5 g, 7.85 mmol) and 4,5-dichlorophthalonitrile (2.5 g, 12 mmol) in dry DMF (50 mL) was stirred at 70 °C for 18 h. On cooling, the mixture was added to water (800 mL) and the crude product collected by filtration. Recrystallisation from ethanol gave **9** as a white solid. Yield = 3.6 g (80%); mp = 98–99 °C (Found C, 79.71; H, 9.67; N, 4.91%. $C_{38}H_{54}N_2O_2$ requires C, 79.94; H, 9.53; N, 4.91%); δ_H (300 MHz, CDCl$_3$): 0.90 (6H, t), 1.20–1.50 (36H, m), 1.55–1.70 (4H, br s), 2.59 (4H, t), 6.80 (2H, s), 7.28 (2H, s); *m*/*z* (CI) 570 (M$^+$), 588 (M$^+$ + NH$_4^+$).

The following two compounds were prepared using a similar procedure.

1,3-Di-*tert*-butyl-7,8-dicyanooxanthrene (13). From 3,5-di-*tert*-butylcatechol and 4,5-dichlorophthalonitrile. Yield = 3.0 g (50%); mp = 206 °C (Found C, 76.01; H, 6.35; N, 8.07%. $C_{22}H_{22}N_2O_2$ requires C, 76.27; H, 6.40; N, 8.09%); δ_H (300 MHz, CDCl$_3$): 1.31 (9H, s), 1.43 (9H, s), 6.83 (H, d), 7.04 (H, d), 7.21 (H, s), 7.30 (H, s); *m*/*z* (CI) 346 (M$^+$), 364 (M$^+$ + NH$_4^+$).

2,3-Dibromo-7,8-dicyanooxanthrene. From 4,5-dibromocatechol and 4,5-dichlorophthalonitrile. Yield = 5.1 g (90%); mp = > 300 °C (Found C, 42.66; H, 0.96; N, 6.99; Br, 40.72%. $C_{14}H_4Br_2N_2O_2$ requires C, 42.89; H, 1.03; N, 7.15; Br, 40.76%); δ_H (300 MHz, d$_6$-DMSO): 7.50 (2H, s), 7.90 (2H, s); *m*/*z* (CI) 390 (M$^+$), 392 (M$^+$ + 2), 408 (M$^+$ + NH$_4^+$), 410 (M$^+$ + 2 + NH$_4^+$).

2,3,7,8-Tetracyanooxanthrene (12). A mixture of 2,3-dibromo-7,8-dicyanooxanthrene (5.0 g, 13 mmol) and copper(I) cyanide (12.5 g, 140 mmol) in dry DMF (100 mL) was stirred at 130 °C for 18 h. On cooling, the mixture was added to water (100 mL) and the crude product collected by filtration. Recrystallisation from ethanol gave **12** as a white solid. Yield = 1.8 g (50%); mp = > 300 °C (Found C, 67.35; H, 1.47; N, 19.29%. $C_{16}H_4N_4O_2$ requires C, 67.61; H, 1.41; N, 19.72%); δ_H (300 MHz, d$_6$-DMSO): 7.95 (4H, s); *m*/*z* (CI) 284 (M$^+$), 302 (M$^+$ + NH$_4^+$).

1,4,10,13,19,22,28,31-Octadodecyltetrakis[1,4]benzodioxino-[2,3-*b*:2′,3′-*k*:2″,3″-*t*:2‴,3‴-*e*$_1$]phthalocyanine (8). Lithium metal (20 mg, 2.8 mmol) was added to a refluxing solution of **9** (250 mg, 0.49 mmol) in pentanol (2 mL). The solution was heated at reflux for 18 h. On cooling, acetic acid (0.2 mL) was added to the reaction mixture and the crude product was collected by centrifugation. The green material was purified by column chromatography (eluent: toluene) and by precipitation ($\times 3$) from CH$_2$Cl$_2$ solution into acetone to give a green wax. Yield = 25 mg (10%) (Found C, 78.75; H, 9.52; N, 4.73%. $C_{152}H_{218}N_8O_8$ requires C, 79.88; H, 9.62; N, 4.90%); λ_{max}: 703, 668, 638, 492 nm; δ_H(500 MHz, CDCl$_3$): 0.90 (24H, t), 1.00–1.80 (160H, m), 2.80 (16H, br t), 6.72 (8H, s), 7.95 (8H, br s); *m*/*z* (MALDI) 2284 (M$^+$).

1,3,10,12(11,13),19,21(20,22),28,30(29,31)-Octa-*tert*-butyltetrakis[1,4]benzodioxino[2,3-*b*:2′,3′-*k*:2″,3″-*t*:2‴,3‴-*e*$_1$]phthalocyanine (14). A mixture of **13** (5.3 g, 14.7 mmol) and zinc(II) acetate (1.6 g, 4.7 mmol) in quinoline (30 mL) was heated at 200 °C for 18 h. On cooling, MeOH (50 mL) was added and the precipitate collected by filtration. The green material was purified by column chromatography (eluent: CH_2Cl_2) and by precipitation (× 3) from CH_2Cl_2 solution into acetone to give a green wax. Yield = 1.4 g (25%) (Found C, 73.03; H, 6.16; N, 7.25%. $C_{88}H_{88}N_8O_8Zn$ requires C, 72.83; H, 6.11; N, 7.72%); λ_{max}: 680 nm; δ_H(500 MHz, $CDCl_3$): 1.50–2.00 (72H, m), 7.40–8.00 (8H, br m), 7.80–8.20 (8H, br m); *m*/*z* (MALDI) 1451 (M^+).

Polymer 15. A mixture of **12** (0.21 g, 0.74 mmol), **13** (0.25 g, 0.74 mmol) and zinc(II) acetate (0.14 g, 0.76 mmol) in quinoline (1 mL) was heated at 220 °C for 18 h. On cooling, MeOH (25 mL) was added and the precipitate collected by filtration. The resulting green solid was placed in a Soxhlet and washed with MeOH (18 h). The MeOH solvent was replaced with hexane and a significant quantity of green material (0.07 g) was obtained after 24 h. This proved to be mainly Pc **14** and oligomers by analysis with MALDI MS and GPC. On replacing the solvent with THF, a further 0.11 g of green material was extracted. The polymer precipitated from the THF solution on cooling and was collected by filtration (Found C, 76.27; H, 6.40; N, 8.0%); λ_{max}: 680, 640 nm; δ_H(500 MHz, d_6-DMSO): 2.0–2.5 (br s). The absence of small oligomers (*i.e.* dimers and trimers) was confirmed by MALDI MS. Some highly coloured material (0.14 g) remained in the extraction thimble and proved sparingly soluble in hot DMAc.

Acknowledgements

We thank the EPSRC (KM, SM) and Kuwait University (SM) for financial support.

References

1 S. Chandrasekhar, *Liq. Cryst.*, 1993, **14**, 3.
2 S. Chandrasekhar, B. K. Sadashiva and K. A. Suresh, *Pramana*, 1977, **9**, 471.
3 J. D. Brooks and G. H. Taylor, in *Chemistry and Physics of Carbon*, ed. P. L. Walker, 1968.
4 L. S. Singer, US Patent 4 00 183, 1977.
5 I. Mochida, K. Shimizu, Y. Korai, T. Otsuka and S. Fujiyama, *Carbon*, 1988, **26**, 843.
6 T. Matsumoto, *Pure Appl. Chem.*, 1985, **57**, 1553.
7 J. J. McHugh and D. D. Edie, *Liq. Cryst.*, 1995, **18**, 327.
8 K. Praefcke, D. Singer, B. Gundogan, K. Gutbier and M. Langner, *Ber. Bunsen-Ges. Phys. Chem. Chem. Phys.*, 1994, **98**, 118.
9 B. B. Eran, D. Singer and K. Praefcke, *Eur. J. Inorg. Chem.*, 2001, 116.
10 P. Herwig, C. Kayser, H. W. Spiess and K. Müllen, *Adv. Mater.*, 1996, **8**, 510.
11 A. M. van de Craats, J. M. Warman, K. Müllen, Y. Geerts and J. D. Brand, *Adv. Mater.*, 1998, **10**, 36.
12 T. Yatabe, M. A. Harbison, J. D. Brand, M. Wagner, K. Müllen, P. Samori and J. P. Rabe, *J. Mater. Chem.*, 2000, **10**, 1519.
13 N. B. McKeown, *Phthalocyanine Materials: Synthesis, Structure and Function*, Cambridge University Press, Cambridge, 1998.
14 C. Piechocki, J. Simon, A. Skoulios, D. Guillon and P. Weber, *J. Am. Chem. Soc.*, 1982, **104**, 5245.
15 K. Ohta, L. Jacquemin, C. Sirlin, L. Bosio and J. Simon, *New J. Chem.*, 1988, **12**, 751.
16 M. K. Engel, P. Bassoul, L. Bosio, H. Lehmann, M. Hanack and J. Simon, *Liq. Cryst.*, 1993, **15**, 709.
17 J. F. Van der Pol, E. Neeleman, J. W. Zwikker, R. J. M. Nolte, W. Drenth, J. Aerts, R. Visser and S. J. Picken, *Liq. Cryst.*, 1989, **6**, 577.
18 D. Guillon, A. Skoulios, C. Piechocki, J. Simon and P. Weber, *Mol. Cryst. Liq. Cryst.*, 1983, **100**, 275.
19 D. Guillon, P. Weber, A. Skoulios, C. Piechocki and J. Simon, *Mol. Cryst. Liq. Cryst.*, 1985, **130**, 223.
20 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.
21 M. J. Cook, S. J. Cracknell and K. J. Harrison, *J. Mater. Chem.*, 1991, **1**, 703.
22 F. Lelj, G. Morelli, G. Ricciadi, A. Roviello and A. Sirigu, *Liq. Cryst.*, 1992, **12**, 941.
23 A. Lux, . G. G Rozenberg, K. Petritsch, S. C. Moratti, A. B. Holmes and R. H. Friend, *Synth. Met.*, 1999, **102**, 1527.
24 D. K. P. Ng, Y.-O. Yeung, W. K. Chan and S.-C. Yu, *Tetrahedron Lett.*, 1997, **38**, 6701.
25 K. Kitahara, T. Asano, K. Hamono, S. Tokita and H. Nishi, *J. Heterocycl. Chem.*, 1990, **27**, 2219.
26 B. Mohr, G. Wegner and K. Ohta, *J. Chem. Soc., Chem. Commun.*, 1995, 995.
27 A. W. Cordes and C. K. Fair, *Acta Crystallogr., Sect. B*, 1974, **B30**, 1621.
28 D. Wöhrle, M. Eskes, K. Shigehara and A. Yamada, *Synthesis*, 1993, 194.
29 G. C. Eastmond and J. Paprotny, *Chem. Lett.*, 1999, 479.
30 K. E. Treacher, G. J. Clarkson and N. B. McKeown, *Liq. Cryst.*, 1995, **19**, 887.
31 M. J. Cook, M. F. Daniel, K. J. Harrison, N. B. McKeown and A. J. Thomson, *J. Chem. Soc., Chem. Commun.*, 1987, 1086.
32 J. C. Swarts, E. H. G. Langner, N. Krokeide-Hove and M. J. Cook, *J. Mater. Chem.*, 2001, **11**, 434.
33 F. Morgenroth, E. Reuther and K. Müllen, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 631.
34 A. J. Berresheim, M. Muller and K. Müllen, *Chem. Rev.*, 1999, **99**, 1747 and references therein.
35 F. Dotz, J. D. Brand, S. Ito, L. Gherghel and K. Müllen, *J. Am. Chem. Soc.*, 2000, **122**, 7707.
36 S. I. Stupp and P. Osenar, in *Polymerization in Organized Media*, ed. A.-D. Schlüter, Weinheim, 1999.
37 D. Lefevre, F. Porteu, P. Balog, M. Roulliay, G. Zalczer and S. Palacin, *Langmuir*, 1993, **9**, 150.
38 A. Epstein and B. S. Wildi, *J. Chem. Phys.*, 1960, **32**, 324.
39 D. Wöhrle, U. Marose and R. Knoop, *Makromol. Chem.*, 1985, **186**, 2209.
40 N. B. McKeown, *J. Mater. Chem.*, 2000, **10**, 1979.
41 G. Schill, G. Doerjer, E. Logemann and W. Velter, *Chem. Ber.*, 1980, **113**, 3697.
42 D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*, Butterworth-Heinemann, Oxford, (3rd Edn.), 1988.