Synthesis and liquid crystal properties of phthalocyanine derivatives containing both alkyl and readily oxidised phenolic substituents†

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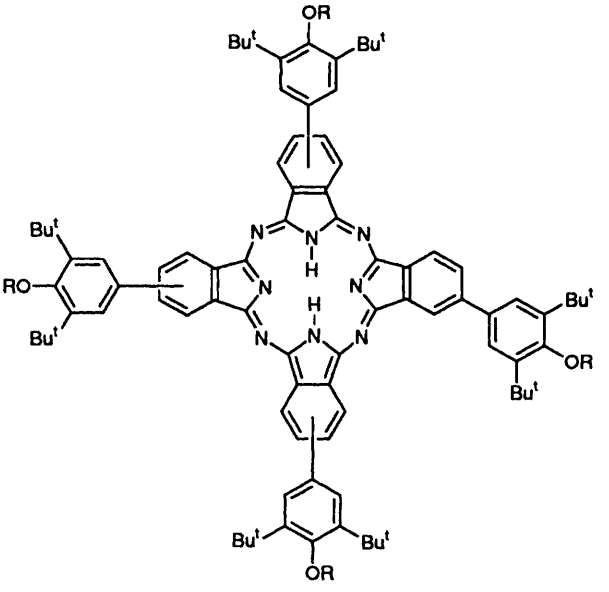
The synthesis, using a mixed phthalonitrile cyclotetramisation, of phthalocyanine derivatives containing both long alkyl side-chains and redox-active, sterically hindered phenolic (3,5-di-*tert*-butyl-4-hydroxyphenyl) substituents is described. A detailed structural characterisation, including high resolution NMR spectroscopy, revealed that the statistically predicted amounts of regioisomers were prepared for each compound. Some isomers could be isolated using a combination of column chromatography and HPLC. A detailed investigation of their thermotropic mesophase behaviour is reported, including X-ray diffraction structure determination. These compounds are designed to combine interesting oxidative behaviour with liquid crystalline properties.

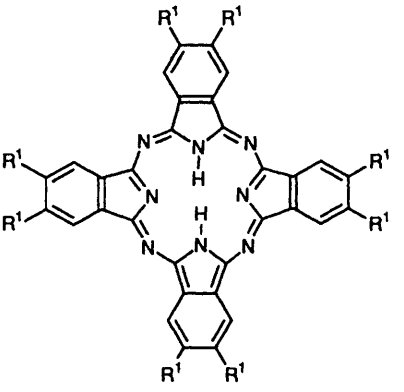
Since their discovery in 1977,[1] columnar mesophases derived from aromatic cores substituted with flexible side-chains have been of great interest due to the possibility of producing materials with anisotropic electronic conductivity.[2] For example, recent work with aligned triphenylene mesophases doped with strong oxidants have revealed that conductivity along the axes of the columns is at least three orders of magnitude greater than that across the columns.[3] In addition, the photoconductivity of a related system was shown to be remarkably efficient.[4] Columnar mesogens with phthalocyanine (Pc) as the aromatic core[5] are particularly relevant to this field of study due to the well-known electronic conductivity of this macrocycle when doped with oxidants[6] and its widespread use as a photoconductor in xerography.[7] However, Pcs require strong oxidants, such as iodine, to produce the conductive state and it would be desirable to produce more easily oxidisable Pc mesogens for anisotropic conductivity measurements.

Recently, we have explored the concept of using redox-active, sterically hindered phenols, specifically 3,5-di-(*tert*-butyl-4-hydroxyphenyl) (DTBHP) substituents, in order to modify the electronic properties of the Pc ring.[8] This research was prompted by previous studies on *meso*-tetra(DTBHP)-porphyrin which revealed a rich oxidative chemistry.[9–11] Our initial investigations indicate that DTBHP substituents can also cooperate with the Pc macrocycle in a number of interesting oxidative processes. For example, non-mesogenic tetra(DTBHP)phthalocyanine (Pc **1**) oxidises in aerated and basified toluene solution to form stable and delocalised radical species and ultimately, benzoquinone containing Pc derivatives.[8] The exciting redox behaviour of Pc **1** is incontrast to that observed for dodecachlorotetra(DTBHP)phthalocyanine (Pc **2**), previously studied by Milaeva *et al.*,[12] in which the steric effects of the adjacent chlorine atoms effectively hinders coplanarity, and thus strong π–π orbital interactions, between the Pc ring and DTBHP substituents. This also explains the reported absence of a significant bathochromic shift of the visible absorption band (Q-band) of Pc **2** on deprotonation of the DTBHP moieties. A large bathochromic shift of the Q-band is observed for a solution of Pc **1** on addition of a base (Fig. 2), illustrating the strong electronic interaction between the deprotonated DTBHP substituents and the Pc core—a prerequisite for cooperative oxidative processes.

The aim of the work reported in this paper was to prepareun-symmetrically substituted Pc derivatives (Pcs **5**, **7**, **9** and **11**), containing both DTBHP and flexible alkyl substituents, which we hoped would combine interesting oxidative behaviour with liquid crystalline properties. Previous studies have shown that octa-alkyl substitution (*e.g.* Pc **4**) leads to columnar mesophase forming Pcs[13–15] and that unsymmetrical substitution patterns need not preclude liquid crystallinity.[15–18]



Pc **1**, R = H
Pc **2**, R = H, all Pc benzo sites substituted with Cl
Pc **3**, R = $CH_2OCH_2CH_2OCH_3$



Pc **4**, R^1 = $-C_{16}H_{33}$

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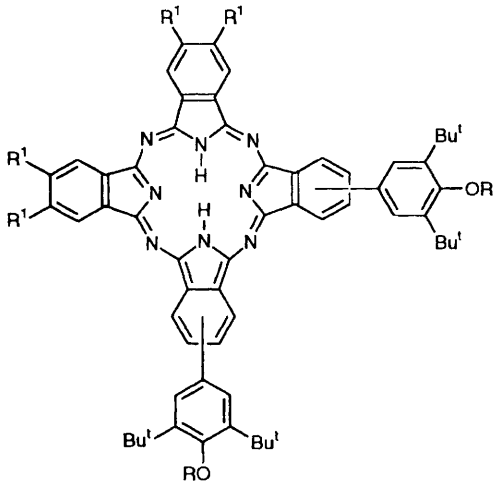
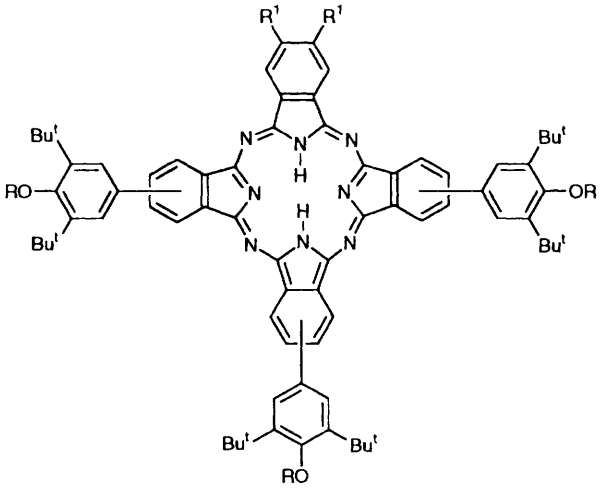
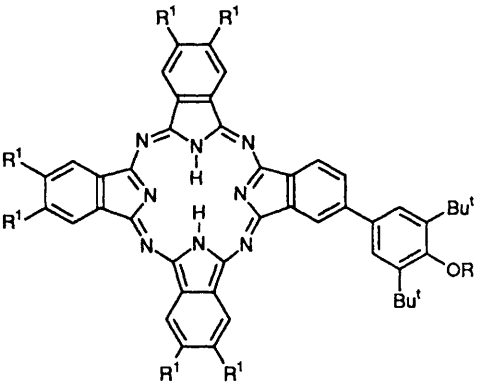


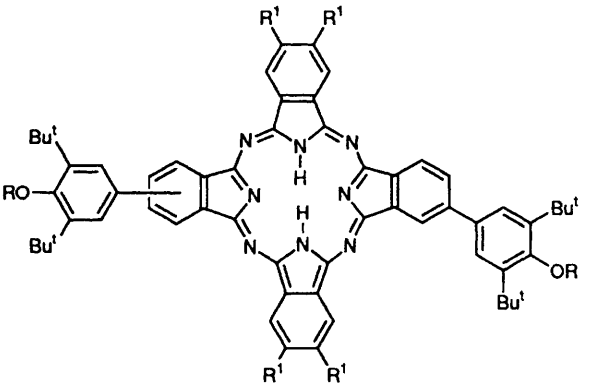
Pc **9**, R = H, $R^1 = -C_{16}H_{33}$
Pc **10**, R = $-CH_2OCH_2CH_2OCH_3$, $R^1 = -C_{16}H_{33}$



Pc **11**, R = H, $R^1 = -C_{16}H_{33}$
Pc **12**, R = $-CH_2OCH_2CH_2OCH_3$, $R^1 = -C_{16}H_{33}$



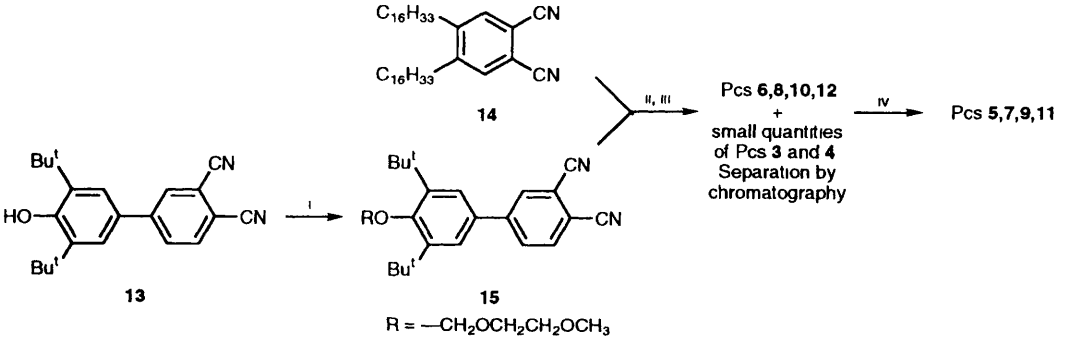
Pc **5**, R = H, $R^1 = -C_{16}H_{33}$
Pc **6**, R = $-CH_2OCH_2CH_2OCH_3$, $R^1 = -C_{16}H_{33}$



Pc **7**, R = H, $R^1 = -C_{16}H_{33}$
Pc **8**, R = $-CH_2OCH_2CH_2OCH_3$, $R^1 = -C_{16}H_{33}$

Synthesis of phthalocyanines

Symmetrically substituted Pcs **1** and **4** have been synthesised previously by the lithium pentyloxide catalysed cyclotetramisation of 4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)phthalonitrile **13** and 4,5-bis(hexadecyl)phthalonitrile **14**, respectively [8 15] Similarly, non-uniformly substituted Pcs can be prepared by mixed phthalonitrile cyclotetramisations, although a complex Pc product mixture is obtained which requires separation by chromatography [15 19 21] Unfortunately, both Pcs **1** and **4** have similar chromatographic properties as exemplified by their TLC R_f values 0 8 and 0 7, respectively, using toluene as eluent and silica gel as substrate Therefore, it was envisaged that a mixed cyclotetramisation reaction between phthalonitriles **13** and **14** would result in an inseparable product mixture of Pcs **1**, **4**, **5**, **7**, **9**, **11** Recent work in our laboratory has shown that the combined use of oligo(ethyleneoxy) and alkyl substituents allows excellent separation of complex Pc mixtures, including opposite and adjacent regioisomers, by the use of simple column chromatography [15] Generally, the greater the number of polar oligo(ethyleneoxy) side-chains attached to the Pc, the longer the compound is retained on the silica column Thus, we predicted that an oligo(ethyleneoxy) substituent attached to the DTBHP moiety of phthalonitrile **13**, prior to the mixed cyclotetramisation with phthalonitrile **14**, would allow subsequent separation of the resultant Pc products The methoxy-



Scheme 1 *Reagents and conditions* i, NaH, MEM–Cl, THF, 48 h, ii, $LiOC_5H_{11}$–$C_5H_{11}OH$, 135 °C, 4 h, iii, H_2O, iv, pyridinium toluene-*p*-sulfonate, $C_5H_{11}OH$, 135 °C, 4 h

(ethoxy)methylene (MEM) group, an often used protecting group for hydroxy functionality,[22] was chosen as the oligo-(ethyleneoxy) side-chain due to its stability to strongly basic conditions and ease of removal.

Thus, the target Pcs **5**, **7**, **9** and **11** were prepared by the route shown in Scheme 1. An efficient reaction between phthalonitrile **13** and MEM chloride prepared 4-[3,5-di-*tert*-butyl-4-(1,3,6-trioxaheptyl)phenyl]phthalonitrile **15**. Phthalonitriles **14** and **15** reacted together successfully in a mixed cyclotetramisation reaction, catalysed by lithium pentyloxide, in refluxing pentanol. Simple column chromatography separated the Pcs **3**, **4**, **6**, **8** (the opposite di-DTBHP precursor), **10** (the adjacent di-DTBHP precursor) and **12**. In addition, HPLC chromatography was successful in isolating, on a small scale, each of the three isomers of the adjacent di-DTBHP substitued Pc **10**. The structural assignment, using high resolution ^{1}H NMR, of these isolated compounds to the expected three regioisomers (**10a**, **10b**, **10c**) will be discussed in the next section. Removal of the MEM groups from **6**, **8**, **10** and **12** to reveal Pcs **5**, **7**, **9** and **11**, respectively, was achieved in high yield by the action of pyridinium toluene-*p*-sulfonate.[22] Final purification of Pcs **3**–**12** involved recrystallisation from an appropriate solvent.

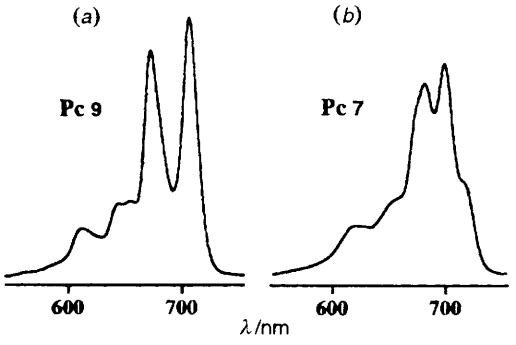


Fig. 1 Visible absorption spectra of Pcs **9**(*a*) and **7**(*b*)

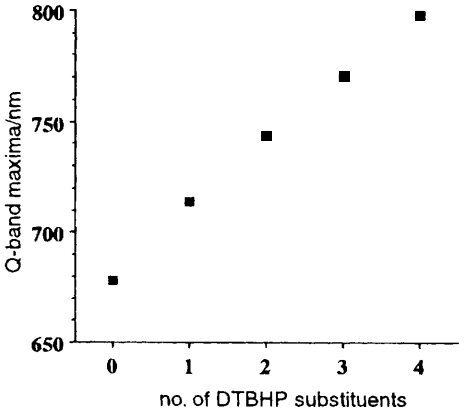


Fig. 2 Position of Q-band absorption (nm) on addition of excess base (tetrabutylammonium hydroxide) for Pcs with 0 (Pc **4**), 1 (Pc **5**), 2 (Pc **7**), 3 (Pc **11**) and 4 (Pc **1**) DTBHP substituents

Structural characterisation of phthalocyanines

Each of the isolated Pcs gave elemental analyses and fast atom bombardment (FAB) mass spectra consistent with their proposed structures (with the exception of Pcs **5** and **6** which did not display molecular ion peaks). Visible region absorption spectra of dilute toluene solutions of Pcs **5**, **9**, **11** and **6**, **10**, **12** display the characteristic split Q-band of non-aggregated metal-free Pcs [*e.g.* Fig. 1(*a*)]. However, Pcs **7** and **8** have a very different appearance [*e.g.* Fig. 1(*b*)], analogous to similar Q-band splitting effects observed in other Pc derivatives with opposite substitution patterns.[20,21] Addition of base (tetrabutylammonium hydroxide) to toluene solutions of Pcs **5**, **7**, **9**, **11** produces a bathochromic shift of the Q-band which is proportional to the number of DTBHP substituents (Fig. 2). This illustrates that, as expected, the strong electronic interaction between the phenolic groups and the Pc ring, necessary for cooperative oxidative chemistry, is not affected by the presence of the hexadecyl side-chains. No such shift is seen with the analogous visible spectra of the MEM precursors, Pcs **6**, **8**, **10**, **12**.

Excellent quality NMR spectra, with no evidence of broaden-

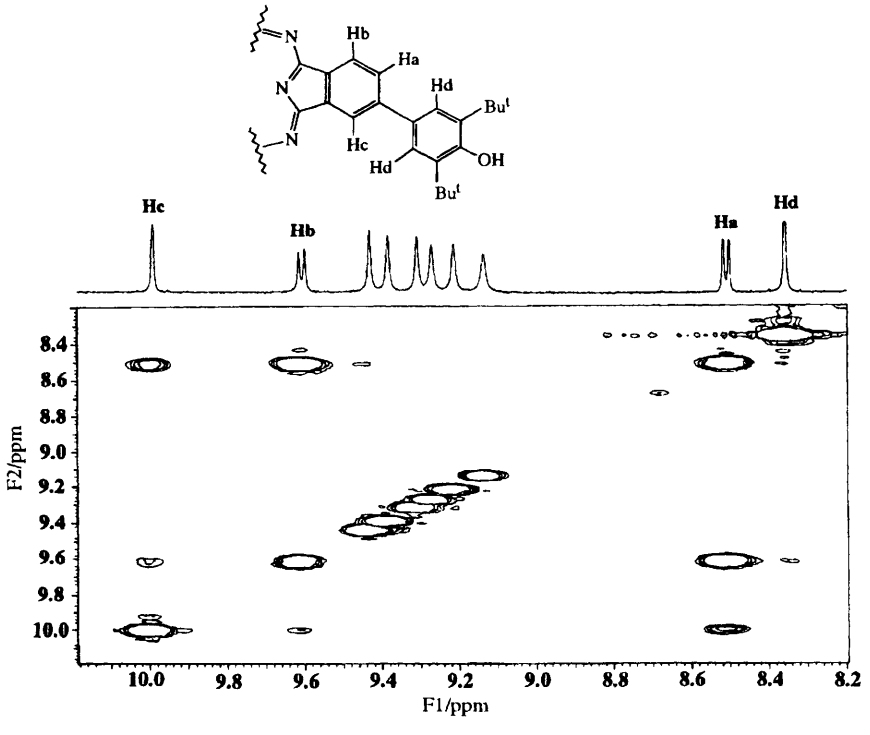


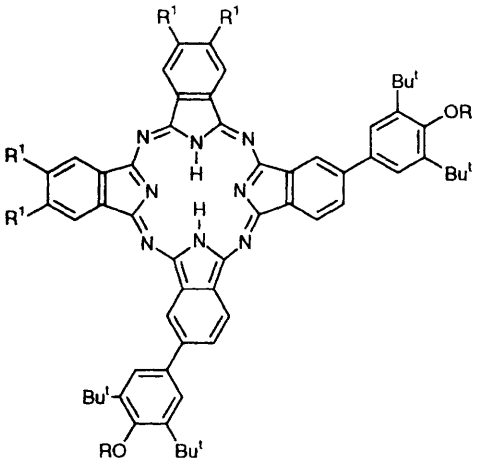
Fig. 3 COSY ^{1}H NMR spectrum of the aromatic region of Pc **6**. The assignments, labelled Ha–Hd, refer to the partial general structure shown. The *ortho* coupling between Ha and Hb, and the *meta* coupling between Ha and Hc are clearly discernible.

ing due to intermolecular aggregation, could be obtained for each Pc product from a dilute solution (1 mg per cm^3, in [$^2H_6$]benzene), at elevated temperature (60 °C), using a high resolution spectrometer (500 MHz). The NMR spectra are, in each case, consistent with the proposed structures. A COSY analysis of the aromatic region of the spectrum for Pc **6** (Fig. 3) helped to assign the protons attached to the same benzo subunit as the DTBHP moiety (see partial structure). Proton Ha (δ 8.51) is relatively shielded because of its peripheral location[23] and proton Hb (δ 9.61) can be assigned due to its strong *ortho* coupling ($J_{Ha\text{-}Hb}$ 10 Hz) with Ha. The *meta* coupling ($J_{Ha\text{-}Hc}$ 2 Hz) between protons Ha and Hc allows us to assign Hc (δ 10.00). The six other benzo protons, adjacent to the hexadecyl side-chains, give rise to six discrete singlets between δ 9.0 and 9.5 and the two aromatic protons of the DTBHP substituent (Hd) resonate at δ 8.35 ppm. The aromatic region of Pc **5** is very similar to that of its MEM derivative Pc **6**, however, the higher field region has a sharp singlet (δ 5.32, 1 H) originating from the phenolic hydroxy group whereas that of Pc **6** has peaks consistent with the MEM functionality (δ 5.41, singlet, 2 H; 4.12, triplet, 2 H; 3.63, triplet, 2 H; 3.37, singlet, 3 H).

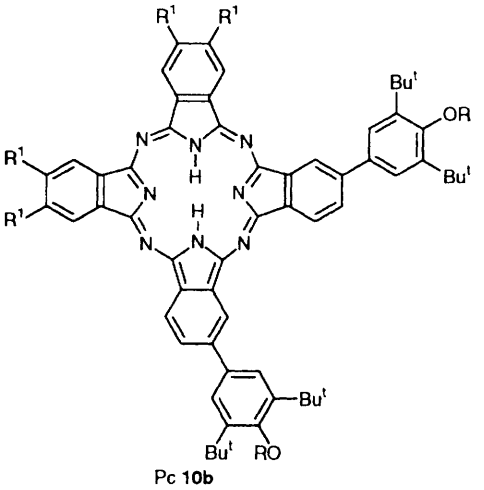
The ^{1}H NMR spectra of opposite di-DTBHP substituted Pcs **7** and **8** show clearly that they are both composed of two regioisomers present in roughly equal quantities. In particular there are two separate resonances associated with each of the protons (Ha, Hb and Hc) of the Pc benzo subunit attached to the DTBHP moiety. There are also two separate peaks of equal intensity for the aromatic protons, Hd, on the DTBHP substituent of Pc **7** (δ 8.30 and 8.35) and for the phenolic hydroxy proton (δ 5.31 and 5.30). HPLC analysis could not separate the two isomers of Pc **7** or **8**.

Three possible isomers are expected for adjacent di-DTBHP substituted Pcs **9** and **10** and three separate fractions were isolated, using column chromatography followed by preparative HPLC, from the mixed phthalonitrile reaction. Each of these fractions gave FAB mass spectra consistent with the molecular formula of Pc **10**. ^{1}H NMR of the aromatic region of each of the fractions of Pc **10** is given in Fig. 4 labelled with our tentative assignments. For the least symmetrical isomer, **10b**, the DTBHP moieties are not equivalent and this allows assignment to the middle fraction obtained by HPLC which has a ^{1}H NMR containing two well resolved sets of peaks for the protons Hd as well as the neighbouring benzo protons Hb and Hc. The correlation of isomer structures **10a** and **10c** with the NMR spectra of the two remaining fractions is more difficult as both show only the expected single set of peaks for these protons. Our assignment is based on the greater molecular dipole moment of **10c**, due to the similar relative orientation of the DTBHP substituents, which would account for the longer HPLC retention time observed for the third fraction. The shorter retention time of the first fraction and identical chemical shift (δ 9.24) for the four benzo protons adjacent to the hexadecyl side-chains are consistent with the expected low dipole moment of isomer **10a**. A comparison of the intensities of the peaks for each of the pure isomers isolated by HPLC, as compared with the isomeric mixture obtained only by column chromatography, indicates that **10a**, **10b** and **10c** were prepared in the statistically predicted ratio of 1:2:1, respectively. The liquid crystal transition temperature of the isomeric mixture, Pc **10**, appears to be dominated by the major isomer **10b** (Table 1) which possesses the highest clearing temperature of the three pure isomers. Due to the labourious separation of the isomers by preparative HPLC, it was decided to use only the isomerically mixed precursor, Pc **10**, to prepare the redox-active Pc **9**.

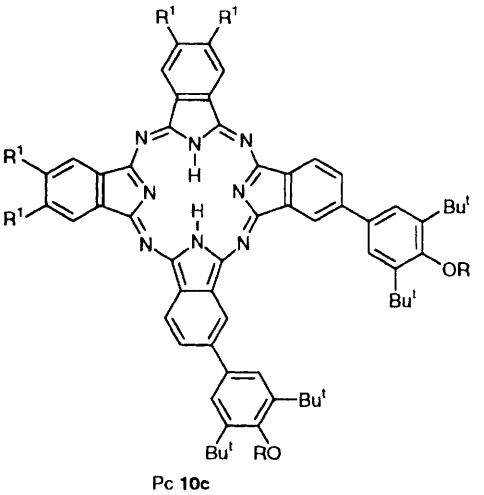
The tri-DTBHP substituted Pcs **11** and **12** gave, in each case, ^{1}H NMR spectra consistent with a mixture of four inseparable regioisomers.



Pc **10a**



Pc **10b**



Pc **10c**

R = —$CH_2OCH_2CH_2OCH_3$, R^1 = —$C_{16}H_{33}$

Mesomorphic properties

As characterised by polarised optical microscopy and differential scanning calorimetry (DSC), all of the Pcs **5**, **7**, **9**, **11** and their precursors, Pcs **6**, **8**, **10**, **12**, possess at least a single mesophase over a broad temperature range [Table 1 and Fig. 5(*a*) and (*b*)]. Each compound, on cooling from its isotropic phase, forms a fluid mesophase which is mainly homeotropic when viewed using a polarising microscope but displays birefringent fan-like defects (Fig. 6). This texture is characteristic of a columnar mesophase which has a two-dimensional lattice of hexagonal symmetry but in which there is no periodicity of

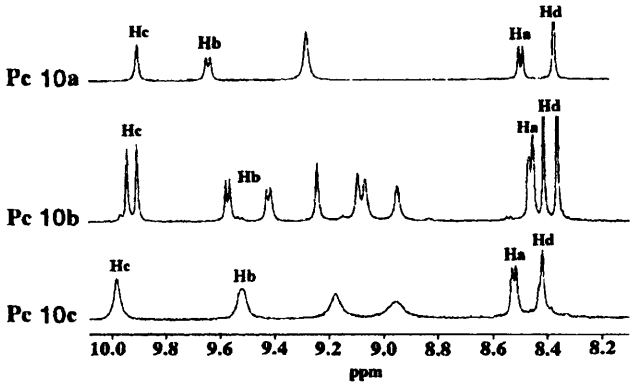


Fig. 4 ^{1}H NMR spectra of the aromatic region of the three isomers of the adjacent di-DTBHP substituted Pc **10**, isolated by HPLC. The labels Ha–Hd refer to the partial general structure shown in Fig. 3. Tentative assignment of these three fractions to the expected regioisomers **10a**, **10b** and **10c** is discussed in the text.

Table 1

	transition temperatures[a]/°C (ΔH/J g^{-1})				
Pc	K→D_x	K→D_{hd}	glass[b]→D_{hd}	D_x→D_{hd}	D_{hd}→I
4	108 (41.9)	—	—	170 (<1)	196 (2.6)
5	72 (46.5)	—	—	96 (c)	215 (3.0)
6	61 (37.3)	—	—	135 (c)	228 (3.8)
7	—	—	17	—	255 (2.2)
8	—	30 (13.1)	—	—	265 (2.5)
9	—	—	20	—	195 (1.3)
10	—	37 (8.3)	—	—	249 (3.3)
10a[d]	—	—	—	—	223
10b[d]	—	—	—	—	250
10c[d]	—	—	—	—	209
11	—	—	30	—	214 (0.9)
12	—	—	45	—	287 (2.3)

[a] Transition temperatures quoted are for heating cycle. Significant supercooling is observed for solid to mesophase transitions, on cooling, but only a small amount (<5 °C) occurs for the isotropic to D_{hd} transition. [b] Onset of glass transition, observed by DSC, on heating sample. [c] Transition not observed by DSC. [d] Transition temperatures measured only by optical microscopy due to insufficient material. Solid to mesophase transition is difficult to observe optically.

molecular spacing along the columnar axes (D_{hd}). The D_{hd} mesophase is commonly encountered for Pc mesogens especially those substituted by alkyl side-chains, such as the symmetrical by-product of the mixed phthalonitrile reaction, Pc **4**.[13–15] X-Ray diffraction studies of this mesophase were carried out for Pcs **5** and **11** which confirm its structure as D_{hd} with intercolumnar distances of 32.4 and 29.4 Å, respectively (Table 2). However, the lower degree of two-dimensional hexagonal ordering within the mesophase formed by Pc **11**, as compared with that of Pc **5**, is evident from the appearance of only lower order diffraction rings. However, the diffraction ring associated with the molecular ordering within the columns ($d \sim 3.6$ Å) is sharper for the mesophase of Pc **11** than for Pc **5**.

The mono-DTBHP containing Pc **5** and its precursor Pc **6** also display a second mesophase at lower temperature which develops as radial striations on the fan defects of the D_{hd} mesophase (Fig. 7). This mesophase behaviour is also shown by the symmetrical Pc **4**. However, no associated thermal transition can be detected by DSC and it gives an identical diffraction pattern as the D_{hd} mesophase (Table 2). A similar mesophase has been reported for some 1,4,8,11,15,18,22,25-octaalkyl Pcs and was classified as D_{hd} on the basis of a detailed X-ray diffraction study,[13] although the optical texture is reminiscent of a mesophase with rectangular symmetry.[24] This mesophase is labelled as D_x in Table 1 and Fig. 5, however it is possible that it is simply a textural variation of the D_{hd}

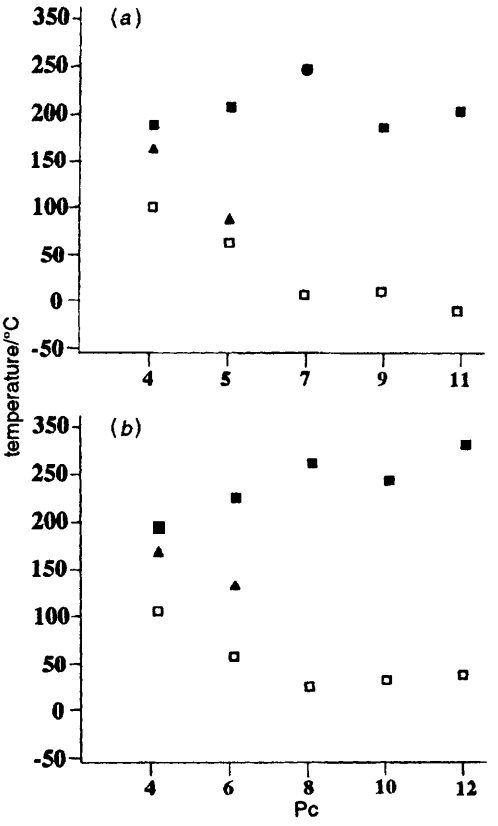


Fig. 5 Plot of the transition temperatures of (*a*) the DTBHP substituted Pcs **5**, **7**, **9** and **11** and (*b*) of the MEM-DTBHP substituted Pcs **6**, **8**, **10** and **12**. In both cases the symmetrical octahexadecyl derivative (Pc **4**) is included for comparison. □ indicates a solid to mesophase transition (crystal to D_x for Pcs **4**, **5** and **6**, glass to D_{hd} for Pcs **7**, **9**, **11** and **12** and crystal to D_{hd} for Pcs **8** and **10**. ▲ indicates a D_x to D_{hd} transition. ■ indicates a D_{hd} mesophase to isotropic liquid transition.

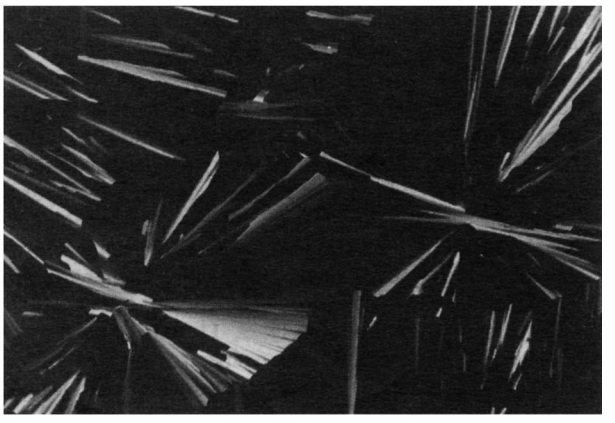


Fig. 6 Optical texture of the D_{hd} mesophase of Pc **5** (200× magnification, 190 °C)

mesophase. A high resolution X-ray diffraction study is planned to clarify the structure of the D_x mesophase.

Noting the unsymmetrical substitution patterns, the inflexible and bulky nature of the DTBHP substituent, and the different regioisomers present in most of the Pcs, it is quite remarkable that the DTBHP containing Pcs possess liquid crystallinity over such broad temperature ranges. These factors do seem to destroy the solid state crystallinity of Pcs **7**, **9**, **11**, **12** as they display only glass transitions (T_g) rather than true melting points. However, the glassy state exhibited by Pcs **7**, **9**, **11**, **12** may be a useful material property as it could be used to freeze the structure of the columnar mesophase into the solid state. Despite the obvious destabilisation of the

Table 2 Powder X-ray diffraction data

Pc	mesophase	D^a/Å	T/°C	Bragg spacing (d)	intensity	hexagonal lattice assignment (h,k)
5	D_{hd}	32.3	150	28.0	strong	1,0
				16.1	medium	1,1
				14.0	weak	2,0
				10.4	very weak	2,1
				4.8	broad, weak	—
				3.61	broad, weak	—
5	D_x	32.3	85	28.0	strong	1,0
				16.1	medium	1,1
				13.8	weak	2,0
				10.4	very weak	2,1
				4.6	broad	—
				3.61	broad, weak	—
11	D_{hd}	29.4	150	25.5	strong	1,0
				15.4	very weak	1,1
				4.8	broad	—
				3.6	medium	—

[a] Intercolumnar distances (D) calculated from 1,0 diffraction ring.

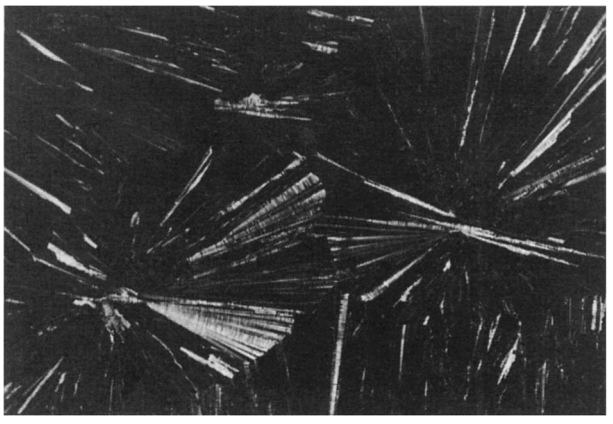


Fig. 7 Optical texture of the D_x mesophase of Pc **5** (200× magnification, 85 °C)

crystalline state by the DTBHP moieties, the well defined clearing points (mesophase to isotropic transition) of Pcs **5**, **7**, **9**, **11** are at least as high as that of the symmetrical Pc **4** which contains no DTBHP functionality. An interesting comparison can be made between the clearing temperatures of Pc **7** with that of the isomeric Pc **9** showing that the mesophase formed by the opposite isomer is stable up to 60 °C higher than that of the adjacent isomer.

Possible oxidation of Pcs **5**, **7**, **9**, **11** during heating was investigated by visible absorption spectroscopy of the Pcs subsequent to mesophase characterisation. No change in the spectrum was observed.

In conclusion, the combination of alkyl and redox-active DTBHP substitution of Pc is compatible with the formation of columnar mesophases over a broad range. More generally, this work suggests that the Pc core can tolerate a wide range of functional moieties in various substitution patterns and still maintain mesogenic potential. The redox properties of Pcs **5**, **7**, **9**, **11** are currently being investigated and will be presented in a future paper.

Experimental

Equipment and materials

Routine ^{1}H NMR spectra were measured at 200 MHz using a Varian Gemini 200 spectrometer. High resolution (500 MHz) ^{1}H NMR spectra were recorded using a Varian Unity 500 spectrometer. UV–VIS spectra were recorded on a Shimadzu UV-260 spectrophotometer from toluene or dichloromethane solutions using cells of pathlength 10 mm. Elemental analyses were obtained using a Carlo Erba Instruments CHNS-O EA 108 Elemental Analyser. Routine low resolution chemical ionisation (CI) were obtained using a Fisons Instruments Trio 2000. Pc fast atom bombardment (FAB) spectra were recorded on a Kratos Concept spectrometer. Routine melting point determinations were carried out with a Gallenkemp melting point apparatus and are uncorrected. Transition temperatures were obtained by optical microscopy using a Nikon Optiphot-2 microscope in conjunction with a Mettler FP82HT hot stage and were confirmed by differential scanning calorimetry (DSC) using a Seiko DSC 220C instrument. Temperature variable, small angle X-ray diffraction studies were carried out on a Philips PW1130/00 X-ray generator, using Cu-Kα radiation as the source, and the data collected on a photographic plate placed 60 mm away from the sample. Analytical HPLC was carried out using a silica Resolve cartridge (8SiO5μ) fitted with Perkin-Elmer Diode array LC-480 UV detector. Preparative HPLC was carried out on a Gilson unit using a Rainin Dynamax 60A silica column (21.4 × 250 mm) and a 115 Gilson UV detector at 255 nm.

All solvents were dried and purified as described in Perrin and Armarego.[25] Silica gel (60 Merck 9385) was used in the separation and purification of Pcs by column chromatography.

Preparation of 4-[3,5-di-*tert*-butyl-4-(1,3,6-trioxaheptyl) phenyl]phthalonitrile 15

To a stirred solution of 4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)phthalonitrile,[8] **13**, (2 g, 6.0 mmol) in dry tetrahydrofuran (THF) (20 cm^3), maintained at 0 °C, was added sodium hydride (0.28 g, 11.8 mmol). To this red solution was added MEM chloride (0.82 cm^3, 7.2 mmol) and the reaction was stirred under a nitrogen atmosphere for 48 h. The reaction mixture was then added to aqueous ammonia (30%,. 150 cm^3) and the product extracted with THF (3 × 50 cm^3). The combined THF extracts were washed with water (2 × 100 cm^3), dried with anhydrous magnesium sulfate and filtered. The THF was removed, under reduced pressure, and the resultant solid was passed through a silica column using dichloromethane as eluent. Evaporation of the solvent, followed by recrystallisation from ethanol, yielded pure 4-[3,5-*di*-tert-*butyl*-4-(1,3,6-*trioxaheptyl*)*phenyl*]*phthalonitrile* as white plates (1.9 g, 75%), mp, 130–131 °C; ν (evap. film)/cm^{-1} 2958, 2231 (CN), 1598 (Found: C, 74.4; H, 7.7; N, 6.5. $C_{26}H_{32}N_2O_3$ requires C, 74.3; H, 7.7; N, 6.7%); m/z (CI) 438 ($M+NH_4^+$); δ_H(200 MHz; $CDCl_3$) 1.5

(18 H, s), 3.45 (3 H, s), 3.65 (2 H, t), 4.02 (2 H, t), 5.05 (2 H, s), 7.45 (2 H, s), 7.8–8.0 (3 H, m).

Phthalocyanine preparation

Note: all Pc yields are based upon initial total weight of phthalonitrile precursors.

Phthalocyanines 6, 8, 10, 12. To a rapidly stirred mixture of 4-[3,5-di-*tert*-butyl-4-(1,3,6-trioxaheptyl)phenyl]phthalonitrile, **15**, (0.72 g, 1.71 mmol) and 4,5-bis(hexadecyl)phthalonitrile, **14**, (1.0 g, 1.73 mmol) in refluxing pentanol (5 cm^3), under a nitrogen atmosphere, was added excess lithium metal (0.2 g). Heating and stirring were continued for 6 h. On cooling, water (30 cm^3) was added, and the reaction mixture heated to ensure complete Pc demetallisation. Evaporation of the water, under reduced pressure, left a green product mixture. The resultant solid was dissolved in toluene and passed through a silica column, at 50 °C, using an eluent composed of an increasing amount of THF relative to toluene. The first fraction (100 mg, 5.8%) (R_f=0.9, hot toluene) proved to be identical to a previously prepared sample of 2,3,9,10,16,17,23,24-*octakis(hexadecyl)phthalocyanine* **4**.[15] The second fraction was collected and applied to a fresh silica column (eluent: toluene–heptane, 1:1, 50 °C, R_f=0.4) and recrystallised from hot toluene to afford 2-(3,5-*di*-tert-*butyl*-4-(1,3,6-*trioxaheptyl*)*phenyl*]-9,10,16,17,23,24-*hexakis*(*hexadecyl*)*phthalocyanine* **6** as a blue solid (140 mg, 8.1%) (Found: C, 81.5; H, 11.15; N, 5.3. $C_{146}H_{238}N_8O_3$ requires C, 81.43; H, 11.14; N, 5.20%); λ_{max}(toluene)/nm 703, 671, 647, 610, 348; δ_H(500 MHz; C_6D_6; 60 °C) −1.3 (2 H, br s), 1.01 (18 H, br t), 1.22–1.7 (144 H, br m), 1.8 (12 H, br m), 1.92 (18 H, s), 2.1 (12 H, br m), 3.28 (12 H, br m), 3.38 (3 H, s), 3.65 (2 H, t), 4.12 (2 H, t), 5.37 (2 H, s), 8.35 (2 H, s) 8.51 (1 H, d), 9.15 (1 H, s), 9.23 (1 H, s), 9.29 (1 H, s), 9.33 (1 H, s), 9.4 (1 H, s), 9.45 (1 H, s), 9.62 (1 H, s), 10.0 (1 H, s). The third fraction was collected and applied to a fresh silica column (eluent: toluene–heptane, 9:1, 50 °C, R_f=0.25) and recrystallised from dichloromethane into ethanol (9:1) to afford 2,16(17)-*bis*[3,5-*di*-tert-*butyl*-4-(1,3,6-*trioxaheptyl*)*phenyl*]-9,10,23,24-*tetrakis*(*hexadecyl*)*phthalocyanine* **8** as a mixture of two isomers (60 mg, 3.5%) (Found: C, 79.2; H, 10.2; N, 5.6%. $C_{132}H_{202}N_8O_6$ requires C, 79.38; H, 10.20; N, 5.61%); λ_{max}(toluene)/nm 720, 695, 681, 651, 623, 387, 345; δ_H(500 MHz; C_6D_6; 60 °C) −1.41 (2 H, br s), 1.0 (12 H, br t), 1.2–1.85 (104 H, br m), 1.89 (36 H, s), 2.02–2.24 (8 H, br m), 3.1–3.33 (8 H, br m), 3.35 (3 H, s), 3.36 (4 H, m), 4.12 (4 H, m), 5.35 (2 H, s), 5.36 (2 H, s), 8.30 (2 H, s), 8.31 (2 H, s), 8.41 (1 H, d), 8.45 (1 H, d), 9.16 (1 H, br s), 9.28 (1 H, br s), 9.4 (1 H, br s), 9.46 (1 H, br s), 9.49 (1 H, br d), 9.59 (1 H, d), 9.89 (1 H, s), 9.95 (1 H, s) [Found: *m/z* 1998. $^{13}C_2C_{130}H_{202}N_8O_6$ ($M+H^+$) requires 1997]. The fourth fraction was collected and applied to a fresh silica column (eluent: toluene–THF, 40:1, 20 °C, R_f=0.2) and recrystallised from ethanol–dichloromethane (9:1) to afford, as a mixture of three isomers, 2(3),9(10)-*bis*[3,5-*di*-tert-*butyl*-4-(1,3,6-*trioxaheptyl*)-*phenyl*]-16,17,23,24-*tetrakis*(*hexadecyl*)*phthalocyanine* **10** as a blue–green waxy solid (120 mg, 7.0%) (Found C, 79.4; H, 10.1; N, 5.6. $C_{132}H_{202}N_8O_6$ requires C, 79.38; H, 10.20; N, 5.61%); λ_{max}(dichloromethane)/nm 707, 674, 645, 612, 345; δ_H(500 MHz; C_6D_6; 60 °C) −1.2 (2 H, br s), 1.0 (12 H, m), 1.2–1.84 (104 H, br m), 1.89 (9 H, s), 1.90 (9 H, s), 1.92 (9 H, s), 1.95 (9 H, s), 2.0–2.2 (8 H, br m), 3.1–3.31 (8 H, br m), 3.35 (3 H, s), 3.36 (3 H, s), 3.64 (4 H, m), 4.11 (4 H, m), 5.35 (1 H, s), 5.36 (1 H, s), 5.37 (1 H, s), 5.38 (1 H, s), 8.31, 8.32, 8.38, 8.41 (4 H, s), 8.52 (2 H, m), 9.0–9.48 (4 H, br m), 9.5–9.76 (2 H, br m), 9.84–10.14 (2 H, m) [Found: *m/z* 1998. $^{13}C_2C_{130}H_{202}N_8O_6$ ($M+H^+$) requires, 1997].

These three isomers were separated by preparative HPLC, to afford firstly 2,10-*bis*[3,5-*di*-tert-*butyl*-4-(1,3,6-*trioxaheptyl*)-*phenyl*]-16,17,23,24-*tetrakis*(*hexadecyl*)*phthalocyanine* **10a**, HPLC retention time (t_r)=244 s (eluent: hexane–ethyl acetate, 8:1, 20 °C); δ_H(500 MHz; C_6D_6; 60 °C) −1.7 (2 H, br s), 1.0 (12 H, m), 1.2–1.86 (104 H, br m), 1.93 (36 H, br s), 2.11 (8 H, m), 3.26 (8 H, m), 3.37 (6 H, s), 3.66 (4 H, t), 4.13 (4 H, t), 5.39 (4 H, s), 8.33 (4 H, s), 8.46 (2 H, d), 9.24 (4 H, br s), 9.6 (2 H, br d), 9.86 (2 H, br s). Secondly, 2,9-*bis*(3,5-*di*-tert-*butyl*-4-[1,3,6-*trioxaheptyl*)*phenyl*]-16,17,23,24-*tetrakis*(*hexadecyl*)*phthalocyanine* **10b**, HPLC retention time (t_r)=429 s (eluent: hexane–ethyl acetate, 8:1, 20 °C); δ_H(500 MHz; C_6D_6; 60 °C) −1.74 (2 H, br s), 1.0 (12 H, m), 1.2–1.88 (104 H, br m), 1.94 (18 H, s), 1.96 (18 H, s), 2.12 (8 H, m), 3.1–3.3 (8 H, br m), 3.364, 3.366, 3.373, 3.375 (6 H, s), 3.66 (4 H, m), 4.14 (4 H, m), 5.4 (4 H, s), 8.35 (2 H, s), 8.41 (2 H, s), 8.45 (2 H, br d), 8.94 (1 H, br s), 9.07 (2 H, br d), 9.23 (1 H, br s), 9.42 (1 H, br d), 9.57 (1 H, br d), 9.90 (1 H, s), 9.94 (1 H, s) and finally 3,9-*bis*[3,5-*di*-tert-*butyl*-4-(1,3,6-*trioxaheptyl*)*phenyl*]-16,17,23,24-*tetrakis*(*hexadecyl*)*phthalocyanine* **10c**, HPLC retention time (t_r)=596 s (eluent: hexane–ethyl acetate, 8:1, 20 °C); δ_H(500 MHz; C_6D_6; 60 °C) −1.7 (2 H, br s), 1.0 (12 H, t), 1.2–1.86 (104 H, br m), 1.98 (36 H, s), 2.13 (8 H, m), 3.08–3.28 (8 H, br m), 3.37 (6 H, s), 3.66 (4 H, t), 4.14 (4 H, t), 5.40 (4 H, s), 8.43 (4 H, s), 8.54 (2 H, br d), 8.97 (2 H, br s), 9.19 (2 H, br s), 9.54 (2 H, br s), 10.0 (2 H, br s).

The fifth fraction was collected and applied to a fresh silica column (eluent: toluene–THF, 20:1, 20 °C, R_f=0.1) and recrystallised from ethanol–dichloromethane (9:1) to afford, as a mixture of four isomers, 2(3),9(10),16(17)-*tris*[3,5-*di*-tert-*butyl*-4-(1,3,6-*trioxaheptyl*)*phenyl*]-23,24-*bis*(*hexadecyl*)*phthalocyanine* **12** as a blue–green solid (80 mg, 4.7%) (Found: C, 77.1; H, 9.0; N, 6.2. $C_{118}H_{166}N_8O_9$ requires C, 77.00; H, 9.10; N, 6.10%); λ_{max}(toluene)/nm 707, 676, 648, 614, 355; δ_H(500 MHz; C_6D_6; 60 °C) −1.4 (2 H, br s), 0.99 (6 H, m), 1.28–1.82 (52 H, br m), 1.91 (54 H, m), 2.05 (4 H, m), 3.1–3.31 (4 H, br m), 3.35 (9 H, br s), 3.64 (6 H, br t), 4.12 (6 H, br t), 5.3–5.42 (6 H, br m), 8.1–8.62 (9 H, br m), 8.84–10.1 (8 H, br m) [Found: *m/z* 1841. $^{13}CC_{117}H_{166}N_8O_9$ ($M+H^+$) requires 1841]. The sixth fraction was collected and applied to a fresh silica column (eluent: toluene–THF, 10:1, 20 °C, R_f=0.05) and reprecipitated from ethanol–dichloromethane (9:1) to afford, as a mixture of four isomers, 2,9(10),16(17),23,(24)-*tetrakis*[3,5-*di*-tert-*butyl*-4-(1,3,6- *trioxaheptyl*)*phenyl*]*phthalocyanine* **3** as a green solid. (75 mg, 4.4%) (Found: C, 73.9; H, 8.1; N, 6.7. $C_{104}H_{130}N_8O_{12}$ requires C, 74.16; H, 7.78; N, 6.65%); λ_{max}(toluene)/nm 712, 678, 651, 614, 418, 360; δ_H(500 MHz; C_6D_6; 60 °C) −1.2 (2 H, br s), 1.91 (72 H, br s), 3.35 (12 H, br s), 3.64 (8 H, br t), 4.11 (8 H, br t), 5.36 (8 H, br s), 8.14–8.64 (12 H, br m), 9.1–10.04 (8 H, br m) [Found: *m/z* 1685. $^{13}CC_{103}H_{130}N_8O_{12}$ ($M+H^+$) requires, 1684].

Preparation of phthalocyanines 5, 7, 9, 11

General procedure for the removal of the MEM group.

2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-9,10,16,17,23,24-hexakis(hexadecyl)phthalocyanine 5. A mixture of 2-(3,5-*di*-tert-*butyl*-4-[1,3,6-*trioxaheptyl*]*phenyl*]-9, 10, 16, 17, 23, 24-*hexakis*(*hexadecyl*)*phthalocyanine* **6** (57 mg, 0.03 mmol) and pyridinium toluene-*p*-sulfonate (38 mg, 0.15 mmol) in pentanol (1 cm^3) was stirred at reflux under a nitrogen atmosphere for 4 h. The pentanol was removed, under reduced pressure, to give a blue solid which was recrystallised from toluene to give 2-(3, 5-*di*-tert-*butyl*-4-*hydroxyphenyl*)-9, 10, 16, 17, 23, 24-*hexakis*(*hexadecyl*)*phthalocyanine* **5** as a blue solid (46 mg, 84%) (R_f=1.0, hot toluene) (Found: C, 82.6; H, 11.25; N, 5.5. $C_{142}H_{230}N_8O$ requires C, 82.57; H, 11.23; N, 5.43%); λ_{max}(toluene)/nm 705, 672, 647, 610, 346; δ_H(500 MHz; C_6D_6; 60 °C) −1.28 (2 H, br s), 1.01 (18 H, br t), 1.3–1.9 (156 H, br m), 1.77 (18 H, s), 2.14 (12 H, br m), 3.27 (12 H, br m), 5.32 (1 H, s), 8.23 (2 H, s), 8.51 (1 H, d), 9.15 (1 H, s), 9.25 (1 H, s),

9.26 (1 H, s), 9.33 (1 H, s), 9 37 (1 H, s), 9 41 (1 H, s), 9.61 (1 H, d), 9.99 (1 H, s).

The following Pcs were prepared by the same methodology

2,16(17)-*Bis*(3, 5-*di*-tert-*butyl*-4-*hydroxyphenyl*)-9, 10, 23, 24-*tetrakis*(*hexadecyl*)*phthalocyanine* **7** (*from Pc* **8**). Reprecipitated from toluene into ethanol to give a green waxy solid (87%) (R_f=0.85; toluene–hexane, 1 . 2, 20 °C) (Found C, 81.5; H, 9.95, N, 6 1. $C_{124}H_{186}N_8O_2$ requires C, 81.79; H, 10 30; N, 6 16%), λ_{max}(toluene)/nm 721, 700, 681, 650, 617, 388, 353; δ_H(500 MHz; C_6D_6, 60 °C) −1.6 (2 H, br s), 1.0 (12 H, t), 1.2–1 8 (104 H, br m), 1 75 (18 H, s), 1 76 (18 H, s), 2.09 (8 H, m), 3.2 (8 H, m), 5.31 (1 H, s), 5.32 (1 H, s), 8.18 (4 H, br s), 8.40 (1 H, d), 8.44 (1 H, d), 9.08 (1 H, br s), 9.17 (1 H, br s), 9 27 (1 H, br s), 9 33 (1 H, br s), 9.46 (1 H, br s), 9.56 (1 H, br s), 9.84 (1 H, br s), 9.91 (1 H, br s) [Found: *m/z* 1821 $^{13}CC_{123}H_{186}N_8O_2$ ($M+H^+$) requires 1820]

2(3),9(10)-*Bis*(3,5-*di*-tert-*butyl*-4-*hydroxphenyl*)-16,17,23,24-*tetrakis*(*hexadecyl*)*phthalocyanine* **9** (*from Pc* **10**) Reprecipitated from toluene into ethanol to give a green waxy solid (79%) (R_f = 0.48; toluene–hexane, 1:2, 20 °C) (Found. C, 82.0; H, 10.5, N, 6.0. $C_{124}H_{186}N_8O_2$ requires C, 81 79; H, 10.30; N, 6.16%); λ_{max}(toluene)/nm 709, 674, 643, 611, 350, δ_H(500 MHz; C_6D_6; 60 °C) −1.3 (2 H, br s), 1.0 (12 H, m), 1.2–1.7 (104 H, br m), 1.75, 1.76, 1 78, 1.81 (36 H, s), 2 08 (8 H, m), 3.23 (8 H, m), 5.32, 5.33, 5.34 (2 H, s), 8 19, 8 20, 8.27, 8.30 (4 H, s), 8.4–8.6 (2 H, br m), 8.9–9.78 (6 H, br m), 9 86–10 1 (2 H, br m) [Found. *m/z* 1821. $^{13}CC_{123}H_{186}N_8O_2$ ($M+H^+$) requires 1820].

2(3),9(10),16(17)-*Tris*(3,5-*di*-tert-*butyl*-4-*hydroxyphenyl*-23,24-*bis*(*hexadecyl*)*phthalocyanine* **11** (*from Pc* **12**) Reprecipitated from toluene into ethanol to give a green waxy solid (85%) (Found. C, 80 5; H, 9.45, N, 7 0 $C_{106}H_{142}N_8O_3$ requires C, 80.76; H, 9.08; N, 7.11%); λ_{max}(toluene)/nm 710, 679, 653, 616, 348; δ_H(500 MHz; C_6D_6, 60 °C) −1 5 (2 H, br s), 0.99 (6 H, t), 1.2–1.65 (52 H, br m), 1.76 (54 H, m), 1 8–2 2 (4 H, br m), 3.3 (4 H, br m), 5 24–5.4 (6 H, br m), 8 0–8.6 (9 H, br m), 8.8–10 1 (8 H, br m) [Found: *m/z* 1576. $^{13}CC_{105}H_{142}N_8O_3$ ($M+H^+$) requires 1576]

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