Synthesis and characterisation of some novel phthalocyanines containing both oligo(ethyleneoxy) and alkyl or alkoxy side-chains: novel unsymmetrical discotic mesogens

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The synthesis of unsymmetrical, peripherally octa-substituted phthalocyanines which contain a combination of 1,4,7,10-tetraoxaundecyl and hexadecyl or dodecyloxy side-chains is described. These compounds were prepared by mixed phthalonitrile cyclotetramisations or by the self-condensation of an unsymmetrical phthalonitrile containing both dodecyloxy and 1,4,7,10-tetraoxaundecyl groups. Separation of phthalocyanine products was achieved by simple column chromatography. A number of isomeric phthalocyanines, separated as single compounds, are reported. All of the phthalocyanines possess thermotropic columnar liquid crystallinity and a brief summary of their mesogenic properties is given.

The phthalocyanine (Pc) macrocycle is of considerable interest owing to its fascinating electronic and optical properties. In recent years a large number of derivatives have been prepared to facilitate the exploitation of these properties in gas sensors, electrophotography, fuel cells, solar energy conversion, non-linear optics, catalysis and the photodynamic therapy of cancer.[1] For example, there has been a considerable effort to fabricate materials in which the orientation and self-association properties of the Pc ring can be controlled. This includes the development of derivatives which possess liquid crystallinity (thermotropic or lyotropic)[2] or that are capable of forming well ordered Langmuir-Blodgett (LB) multi-layer films.[3] Pcs that are designed to be compatible with both methods of materials fabrication are of particular interest.[4]

The ability to form thermotropic columnar liquid crystals can be induced by the peripheral (2,3,9,10,16,17,23,24) substitution of Pc with eight alkyl[5] (*e.g.* Pc 1), alkoxy[6] (*e.g.* Pc 7), alkoxymethyl[7] or oligo(ethyleneoxy)[8] (*e.g.* Pc 6) side-chains. Similar behaviour is demonstrated by derivatives with eight alkyl[9] or alkoxymethyl[10] substitution at the non-peripheral (1,4,8,11,15,18,22,25) sites. In addition, a number of unsymmetrically substituted Pcs have been shown to form thermotropic liquid crystals.[11] This has led to mesogenic derivatives which can be incorporated into oligomers[12] and polymers,[13] or which possess an amphiphilic structure and thus the ability to form well-ordered LB films.[4]

The introduction of water-solubilising groups onto the peripheral sites of the Pc gives rise to lyotropic liquid crystallinity owing to the formation of columnar aggregates in concentrated aqueous solution.[14] Recently, for example, research in our laboratories has shown that peripherally attached oligo(ethyleneoxy) moieties produce Pcs which form columnar lyotropic mesophases in pure water in addition to thermotropic columnar phases.[15] Oligo(ethyleneoxy) substituted Pcs are also of interest as ionic conducting materials.[2]

This paper describes the synthesis of a number of novel unsymmetrical Pc mesogens substituted in the peripheral sites by a combination of hydrophobic hexadecyl or dodecyloxy side-chains and hydrophilic 1,4,7,10-tetraoxaundecyl substituents (Pc structures 2–5, 8–15). This allows us to test whether combinations of polar and non-polar side chains are compatible with the formation of columnar liquid crystals and thus, produce mesogenic Pcs with a non-ionic amphiphilic character and the potential for ionic conductivity.
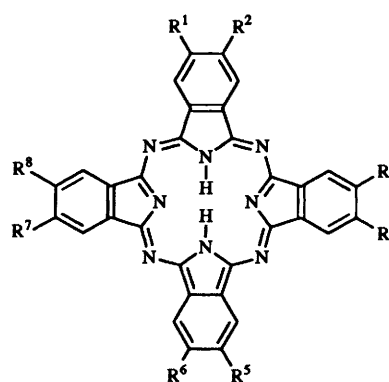
	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8
1	HD	HD	HD	HD	HD	HD	HD	HD
2	TOU	TOU	HD	HD	HD	HD	HD	HD
3	TOU	TOU	TOU	TOU	HD	HD	HD	HD
4	TOU	TOU	HD	HD	TOU	TOU	HD	HD
5	TOU	TOU	TOU	TOU	TOU	TOU	HD	HD
6	TOU	TOU	TOU	TOU	TOU	TOU	TOU	TOU
7	DDO	DDO	DDO	DDO	DDO	DDO	DDO	DDO
8	TOU	TOU	DDO	DDO	DDO	DDO	DDO	DDO
9	TOU	TOU	TOU	TOU	DDO	DDO	DDO	DDO
10	TOU	TOU	DDO	DDO	TOU	TOU	DDO	DDO
11	TOU	TOU	TOU	TOU	TOU	TOU	DDO	DDO
12	TOU	DDO	TOU	DDO	TOU	DDO	TOU	DDO
13	TOU	DDO	DDO	TOU	TOU	DDO	TOU	DDO
14	TOU	DDO	DDO	TOU	DDO	TOU	TOU	DDO
15	TOU	DDO	DDO	TOU	TOU	DDO	DDO	TOU

$HD = -C_{16}H_{33}$, $DDO = -OC_{12}H_{25}$, $TOU = -O(CH_2CH_2O)_3-CH_3$
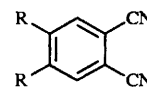

16 $R = C_{16}H_{33}-$
17 $R = C_{12}H_{25}O-$
18 $R = CH_3(OCH_2CH_2)_3O-$

Synthesis of compounds

The required precursors to the Pcs 1–11, 4,5-bis(hexadecyl)-phthalonitrile 16,[5] 4,5-bis(dodecyloxy)phthalonitrile 17[16] and 4,5-bis(1,4,7,10-tetraoxaundecyl)phthalonitrile 18,[17] were prepared using only slight modifications to literature methods. The novel 4-dodecyloxy-5-(1,4,7,10-tetraoxaundecyl)phthalonitrile

19, precursor to isomeric Pcs 12–15, was prepared using the route depicted in Scheme 1. Thus, 2-dodecyloxyphenol, a by-

$R^1 = C_{12}H_{25}$
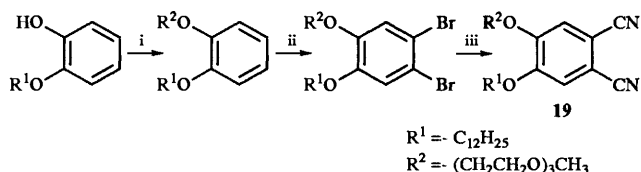
$R^2 = (CH_2CH_2O)_3CH_3$

Scheme 1 *Reagents and conditions:* i, $CH_3(OCH_2CH_2O)_3OTs$, acetone, anhydrous K_2CO_3; ii, Br_2, CH_2Cl_2; iii, CuCN, DMF, 150 °C

product from the first step in the preparation of phthalonitrile 17 from catechol,[5] was treated, under basic conditions, with 3,6,9-trioxadecyl tosylate. Subsequent bromination, followed by cyanide displacement of bromine using copper(I) cyanide in refluxing dimethylformamide (DMF), yielded the required phthalonitrile 19.

The symmetrical Pc 1 was readily prepared by the cyclo-tetramisation of the phthalonitrile 16 in refluxing pentanol, catalysed by lithium pentoxide. In a recent publication it was reported that the use of this method to prepare the symmetrical Pc 6 from the phthalonitrile 18 had resulted in partial transetherification of the 1,4,7,10-tetraoxaundecyl side-chains by the pentanolate anion and thus the formation of a mixture of Pc products.[17] This was confirmed by our own investigations. A similar side-reaction was described in the synthesis of octaalkoxyphthalocyanines substituted in the non-peripheral sites.[18] Thus, we prepared the Pc 6 by the lithium-catalysed cyclotetramisation of the phthalonitrile 18 using 3,6,9-trioxadecan-1-ol (triethylene glycol mono-methyl ether) as solvent. In this case transetherification does not effect the final product. This procedure was also used in the mixed cyclotetramisations[19] of a 1 : 1 molar ratio of the phthalonitriles 16 and 18 to give the Pcs 2–5 together with trace amounts of the symmetrical Pcs 1 and 6 (Scheme 2). In order to avoid

$R^1 = C_{16}H_{34}–$ $R^2 = CH_3(OCH_2CH_2)_3O–$
or = $C_{12}H_{26}O–$
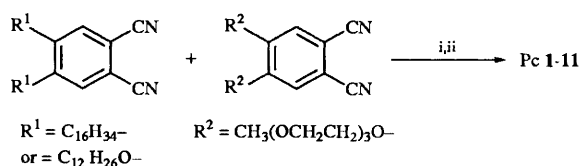
Scheme 2 *Reagents and conditions:* i, $LiOC_5H_{11}–C_5H_{11}OH$, 135 °C; ii, AcOH

transetherification, the Pcs 8–12 were synthesised, in poor yield, from a 1 : 1 molar mixture of the phthalonitriles 17 and 18 using ammonia as catalyst and N,N-dimethlyaminoethanol as the solvent. The Pcs produced by this method showed no evidence of transetherification. The Pcs 12–15 were also prepared, in low yield but without transetherification, by the ammonia-catalysed cyclotetramisation of the phthalonitrile 19 in N,N-dimethyl-aminoethanol.

Separation of the Pcs from the product mixture was achieved by column chromatography (silica gel as substrate, toluene–THF as eluent). The solubility of the Pcs 1–4 in the eluting solvent mixture is poor at room temperature, consequently, the separation of these compounds had to be carried out at 50 °C by use of a heated chromatographic column. Generally, Pcs which have a greater number of relatively polar tetraoxaundecyl side chains are substantially slower to elute through the silica column. In addition, Pcs 3 and 9, in which the four tetraoxaundecyl side-chains are located on adjacent benzo portions, are retained longer on the silica than the respective isomeric Pcs 4 and 10, in which the tetraoxaundecyl chains are placed on opposite benzo moieties. This is a rare demonstration

of Pc isomer separation and is remarkable in that only simple column chromatography is required.[20,21] The purity of each Pc was confirmed by fast atom bombardment mass spectroscopy (FABMS), elemental analysis, ^{1}H NMR (500 MHz) and thin layer chromatography (TLC). Owing to the difficulty in differentiating the isomeric Pcs by FABMS and elemental analysis, we also tested the purity of these compounds using analytical HPLC to confirm that there was no cross-contamination of isomers. The very different retention times under the same elution conditions for Pcs 3, 4, 9 and 10 are reported in the Experimental section.

Pcs 1, 2, 3, 4, 5 and 8 could be obtained pure by simple recrystallisation but the other Pcs tended to form oils using this technique, probably owing to their low melting points. Instead these Pcs were purified by repeated reprecipitation from a good solvent into a poor solvent.

Surprisingly, three distinct Pc fractions were obtained, after column chromatography, from the product mixture of the ammonia-catalysed cyclotetramisation of the phthalonitrile 19. These three fractions were denoted A, B and C in order of their elution from the column. A discussion of the likely structures of the isolated fractions, with respect to the expected four regioisomers (Pcs 12–15), is given below.

Characterisation of the Pcs

Each of the Pcs gave a satisfactory elemental analysis and, with the exception of Pc 1, a molecular ion peak using FABMS that was consistent with their proposed molecular formula. Visible region absorption spectra of dilute solutions of the Pcs display the characteristic split Q-band absorption of non-aggregated metal-free Pcs. More concentrated Pc solutions all display a broad band centred at 646 nm which is characteristic of intermolecular aggregation. Routine NMR characterisation (200 MHz at room temperature) gave only broadened spectra due to aggregation of the Pcs in [$^2H_6$]benzene solution. However, low concentration (1 mg cm^{-3}), elevated temperature (60 °C) and the use of a high resolution spectrometer (500 MHz) enabled well resolved spectra to be obtained. These high resolution spectra were particularly useful for the differen-tiation of the isomers of tetra(hexadecyl)tetra(1,4,7,10-tetraoxaundecyl)-Pc (3 and 4), and the isomers of tetra-(dodecyloxy)tetra(1,4,7,10-tetraoxaundecyl)-Pc 9, 10, 12–15 (see Figs. 1 and 2). The regioisomers 4 and 10, in which the 1,4,7,10-tetraoxaundecyl chains are attached to benzo subunits on opposite sides of the macrocycle ring, display only one resonance for each of the methylenes of the ethyleneoxy group closest to the Pc. Similarly, only one signal is observed for the first methylene of the hexadecyl chains of Pc 4 and the dodecyloxy chains of Pc 10. In addition, only two types of proton are present in the aromatic region for Pcs 4 and 10. The less symmetrical isomers 3 and 9, which possess tetraoxaundecyl side-chains on adjacent benzo moieties, give two sets of methylene resonances consistent with the two distinct magnetic environments of these substituents. In addition, the aromatic regions of the NMR spectra from Pc 3 and 9 have four well defined proton resonances.

A FABMS analysis of the three fractions (A, B and C) obtained from the cyclotetramerisation of the unsymmetrical phthalonitrile 19 all gave molecular ion peaks consistent with the expected molecular formula ($C_{108}H_{170}N_8O_{20}$). However, each fraction exhibited a different ^{1}H NMR spectrum with no evidence of cross contamination. In addition, no cross contamination was apparent by HPLC analysis of the three fractions (retention times and elution conditions for each fraction are given in the Experimental section). We believe that the three Pc products represent a partial separation of the expected mixture of four regioisomers (Pc structures 12–15) obtained due to the various possible positions of the two types
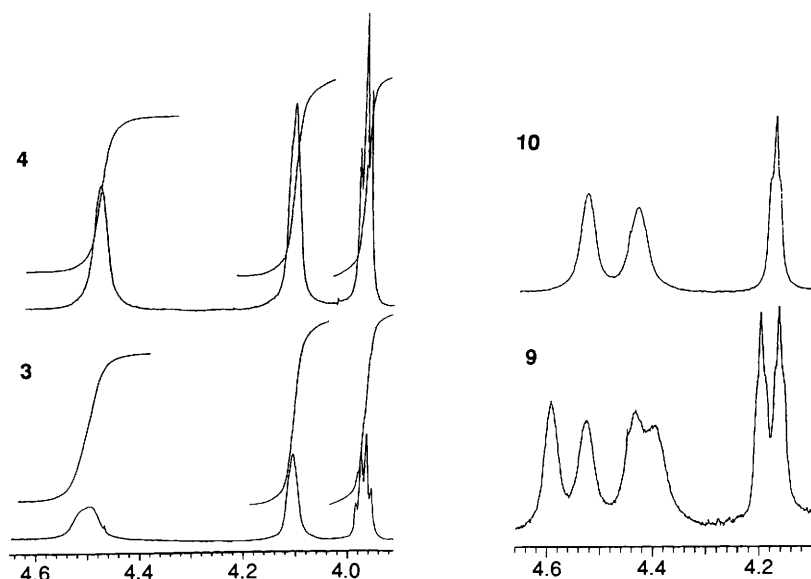
Fig. 1 Detail of ^{1}H NMR (500 Mz) spectra of Pcs 3 and 4, 9 and 10 showing the resonances associated with the methylene groups closest to the Pc core. Magnetic non-equivalence of side-chains is evident for Pcs 3 and 9. Note broadening due to aggregation.

Assignments for Pc 3: δ 4.45 [OCH_2CH$_2$(OCH$_2$CH$_2$)$_2$OCH$_3$, (two broad overlapped peaks), 4.11 [OCH$_2$CH_2(OCH$_2$CH$_2$)$_2$OCH$_3$] and 3.97 [OCH$_2$CH$_2$OCH_2CH$_2$OCH$_2$CH$_2$OCH$_3$, quadruplet due to two overlapped triplets]. Assignments for Pc 4: δ 4.44 [OCH_2CH$_2$(OCH$_2$CH$_2$)$_2$-OCH$_3$], 4.10, [OCH$_2$CH_2(OCH$_2$CH$_2$)$_2$OCH$_3$] and 3.98 [OCH$_2$CH$_2$OCH_2CH$_2$OCH$_2$CH$_2$OCH$_3$]. Assignments for Pc 9: δ 4.60 + 4.53 [OCH_2CH$_2$(OCH$_2$CH$_2$)$_2$OCH$_3$], 4.45 + 4.41 (OCH_2-C$_{11}$H$_{23}$) and 4.20 + 4.16 [OCH$_2$CH_2(OCH$_2$CH$_2$)$_2$OCH$_3$]. Assignments for Pc 10: δ 4.54 [OCH_2CH$_2$(OCH$_2$CH$_2$)$_2$OCH$_3$], 4.44 (OCH_2-C$_{11}$H$_{23}$) and 4.15 [OCH$_2$CH_2(OCH$_2$CH$_2$)$_2$OCH$_3$].

of side-chain relative to one another.[20,21] The four isomers can be designated by their molecular symmetry as C_{4h} (12), C_s (13), C_{2v} (14) and D_{2h} (15) and each isomer would be prepared, assuming a statistical distribution, in a relative yield of 1:4:2:1 respectively. For Pcs with equal numbers of each type of side chain, we believe that the relative elution time is dependant on the number of neighbouring tetraoxaundecyl substituents on adjacent benzo moieties. A clear example of this is the greater elution time of Pcs 3 and 9 (four tetraoxaundecyl chains adjacent to one another) compared to Pcs 4 and 10 (two neighbouring tetraoxaundecyl groups on opposite benzo subunits). Considering structures 12–15; Pc 12 has no neighbouring tetraoxaundecyl side-chains, 13 and 14 have one, and 15 has two such arrangements. Based on this analysis we conclude that fraction A (fastest elution time) is composed of Pc 12, fraction B is a mixture of Pcs 13 and 14, and fraction C (slowest elution time) is composed of Pc 15. ^{1}H NMR supports this conclusion. The spectra of fractions A and C each show magnetically equivalent tetraoxaundecyl side-chains and also dodecyloxy groups, consistent with the relatively symmetrical structures of Pcs 12 (C_{4h}) and 15 (D_{2h}); whereas the spectrum of B shows two sets of resonances for each type of side-chain, consistent with the lower symmetry of the Pcs 13 (C_s) and 14 (C_{2v}). The isolated yields of the Pc fractions also supports the above assignments. The expected ratio of compounds 12, 13 plus 14, and 15 would be 1:6:1 which compares well with the mass ratio of the isolated fractions A, B and C (1:6:1.3). A careful analysis by HPLC of fraction B showed no separation of Pc 13 from Pc 14. Interestingly, the isomer, 15 (fraction C), has a sharp, relatively high melting point into the columnar mesophase (80 °C) whereas the other fractions are mesogenic at room temperature.

Mesophase properties

As characterised by polarised optical microscopy and differential scanning calorimetry (DSC), all of the Pcs 1–15 possess at least one mesophase [see Figs. 3(a) and (b)]. A few general trends can be observed by examination of the melting

behaviour of these compounds. Firstly, a greater degree of tetraoxaundecyl substitution generally results in lower crystal to mesophases transition temperatures. In contrast, the clearing temperatures for Pcs 1–6 show an increase on substitution of the hexadecyl side-chain for tetraoxaundecyl moieties [Fig. 3(a)]. This can be attributed to the greater length (by five atoms) of the alkyl chain compared to the oligo(ethyleneoxy) chain. It is now well documented for Pc mesogens that increasing the length of alkyl substituent results in a decrease in the clearing temperature.[9] It is remarkable that, despite the very different substitution patterns of Pcs 8–15, all have a similar clearing temperature (295–315 °C). This may be explained by the fact that there is only two atoms difference in length between the two types of substituents (dodecyloxy and tetraoxaundecyl) and that both side-chains have an oxygen linkage to the Pc ring.

The symmetrical Pc 7 has previously been shown, by an X-ray diffraction study, to possess a columnar mesophase of hexagonal symmetry in which the molecules are periodically spaced (hexagonal ordered—D_{ho}) along the columns.[5,6,22] Although the Pcs 6–15 possess much less symmetrical substitution patterns, they display a mesophase of an identical appearance (broken fan optical texture), when viewed by optical microscopy, to the D_{ho} phase of 7. In particular, the hexagonal symmetry of this mesophase is evident by the formation of digitate stars (best observed with parallel polarisers) on slow cooling from the isotropic phase.

Pcs 1–3 and 5 show two distinct phases. The higher temperature mesophase has a fan-like texture characteristic of a hexagonal columnar phase in which there is no periodicity associated with the molecular positions within the column (hexagonal disordered—D_{hd}). We have confirmed this mesophase structure for Pc 1 by a X-ray diffraction study. The lower temperature mesophase has a distinctive finger print optical texture which has been previously assigned to a columnar mesophase of rectangular symmetry (D_{rd}).[23] Compound 4 is very much an oddity amongst Pc mesogens as it possesses no hexagonal mesophase but instead shows only a
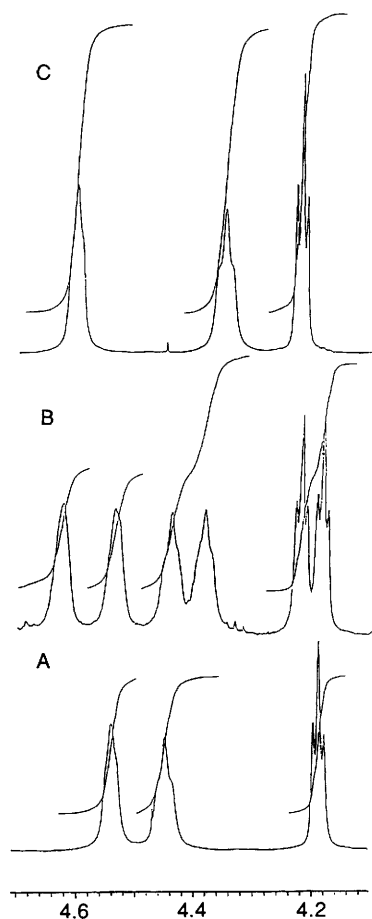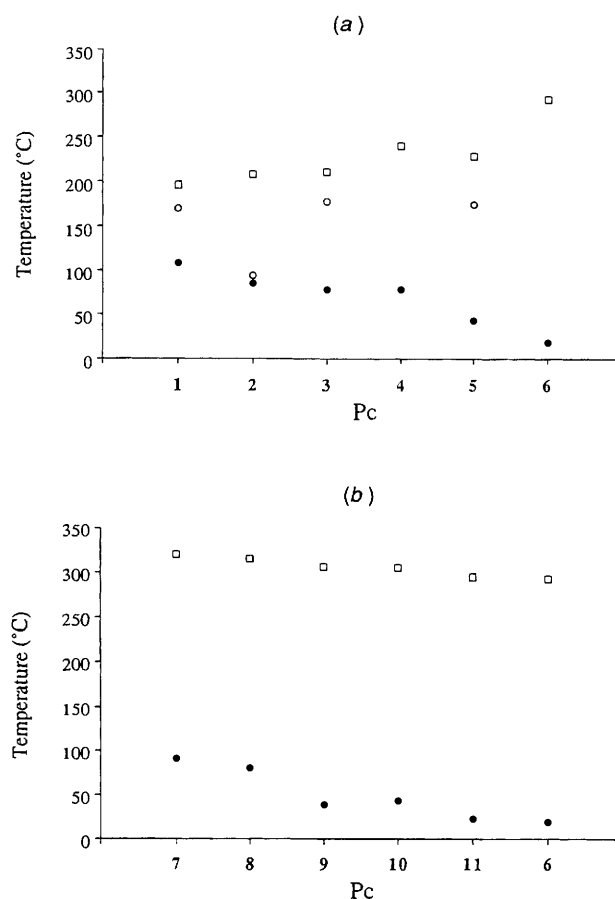
Fig. 2 Detail of ^{1}H NMR (500 Mz) spectra of Pc fractions A, B, and C obtained from the cyclotetramisation of 4-dodecyloxy-5-(1,4,7,10-tetraoxaundecyl)phthalonitrile showing the resonances associated with the methylene groups closest to the Pc core. Magnetic equivalence of side-chains is evident for fractions A and C

Assignments for fraction A: δ 4.54 [$OCH_2CH_2(OCH_2CH_2)_2OCH_3$], 4.45 ($OCH_2C_{11}H_{23}$) and 4.19 [$OCH_2CH_2(OCH_2CH_2)_2OCH_3$]. Assignments for fraction B: δ 4.63 + 4.53, [$OCH_2CH_2(OCH_2)_2OCH_3$], 4.45 + 4.38 (OCH_2-$C_{11}H_{23}$) and 4.22 + 4.18 [OCH_2-$CH_2(OCH_2CH_2)_2OCH_3$]. Assignments for fraction C: δ 4.63 [$OCH_2CH_2(OCH_2CH_2)_2OCH_3$], 4.37 ($OCH_2$-$C_{11}H_{23}$) and 4.24 [$OCH_2CH_2(OCH_2CH_2)_2OCH_3$].

Fig. 3 Transition temperatures for the Pc derivatives. Pcs are listed, from left to right, in order of increasing tetraoxaundecyl substitution for hexadecyl side-chains (graph a) and dodecyloxy side-chains (graph b). Pcs 3 and 4 in graph a and Pcs 9 and 10 in graph b are isomeric. Note: ● Indicates crystal to mesophase transition, □ indicates mesophase to isotropic liquid transition and ○ shows mesophase to mesophase transition. See text for discussion.

rectangular columnar mesophase. However, the isomeric Pc 5 has both a hexagonal and a rectangular mesophase. This marked difference in thermal behaviour between these isomers may be due to either their dissimilar shapes or dipole moments. It is in contrast to the very similar thermal properties of the isomeric Pcs 9 and 10 which possess side-chains (dodecyloxy and tetraoxaundecyl) of similar length and the same oxygen linkage to the Pc ring.

The symmetrical Pc 6 is water soluble and displays aqueous lyotropic and thermotropic mesogenicity. This is indicated by a distinct *schlieren* optical texture which has been assigned, previously,[14,15] to the nematic columnar phase. This behaviour illustrates the hydrophilic character of the 1,4,7,10-tetra-oxaundecyl substituent and therefore the potential of the unsymmetrical Pcs 2–5 and 8–15 as non-ionic amphiphiles.

In conclusion, the combination of oligo(ethyleneoxy) and alkyl substituents allows for excellent separation of the Pc product mixture from mixed phthalonitrile reactions. It is also compatible with the formation of thermally stable columnar mesophases. This work reveals that the incorporation of oligo(ethyleneoxy) in place of alkoxy side-chains of similar length results in a marked reduction of the crystal to mesophase

transition temperatures but has very little effect on the clearing temperatures.

A full account of the mesophase properties, including detailed X-ray diffraction analysis, and the LB film forming capabilities of these compounds will be given in future publications.

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 path-length 10 mm. Elemental analyses were obtained using a Carlo Erba Instruments CHNS-O EA 108 Elemental Analyser. Routine low-resolution chemical ionisation (CI) and electron ionisation (EI) mass spectra were obtained using a Fisons Instruments Trio 2000. Pc fast atom bombardment (FAB) spectra were recorded on a Kratos Concept spectrometer. Routine melting point determination was carried out with a Gallenkemp melting point apparatus and are uncorrected. Determination of transition temperatures, crystal (K) to mesophase (D_{ho}, D_{hd}, D_{rd}) to isotropic liquid (I) 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. Bulb-to-bulb distillation was achieved by use of a Kugelrohr apparatus. Analytical HPLC was carried out using a silica resolve cartridge fitted with Perkin-Elmer Diode array LC-480 UV detector.

All solvents were dried and purified as described in Perrin and Armarego.[24] Silica gel (60 Merck 9385) was used in the separation and purification of Pcs by column chromatography.

Preparation of 4-dodecyloxy-5-(1,4,7,10-tetraoxaundecyl)-phthalonitrile 19

(i) 2-Dodecyloxyphenol. A mixture of pyrocatechol (11 g, 100 mmol), bromododecane (32.4 g, 130 mmol) and potassium carbonate (18.2 g, 130 mmol) in dry dimethylformamide (DMF) (100 cm^3) was stirred and heated at 60 °C for 48 h and then poured into water (500 cm^3) and extracted with diethyl ether (3 × 100 cm^3). The combined extracts were washed with saturated brine (2 × 100 cm^3), dried (MgSO$_4$), and evaporated to give a solid. Distillation of this *in vacuo* gave the title compound (11.4 g, 41%), bp 175 °C/0.5 mmHg (Found: C, 77.8; H, 10.8. C$_{18}$H$_{30}$O$_2$ requires C, 77.65; H, 10.86%); *m/z* (CI) 296 (M$^+$ + NH$_4$$^+$); δ_H(200 MHz, CDCl$_3$) 0.90 (t, 3 H), 1.28 (br s, 18 H), 1.82 (q, 2 H), 4.04 (t, 2 H), 5.70 (s, 1 H) and 6.85 (m, 4 H) and *o*-phenylene didecyl ether (11.2 g, 25%), bp 225 °C/0.5 mmHg, mp 46 °C (lit.,[5] 46 °C).

(ii) 1-Dodecyloxy-2-(1,4,7,10-tetraoxaundecyl)benzene. A mixture of 2-dodecyloxyphenol (4.75 g, 17.1 mmol), 3,6,9-trioxadecyl toluene-*p*-sulfonate[25] (6 g, 18.9 mmol), dry acetone (50 cm^3) and anhydrous potassium carbonate (2.6 g, 18.9 mmol) was stirred and heated to reflux under a nitrogen atmosphere for 48 h. Upon cooling the reaction mixture was filtered and the acetone removed under reduced pressure. Distillation of the resultant oil, *in vacuo*, gave 1-dodecyloxy-2-(1,4,7,10-tetraoxaundecyl)benzene as a clear oil (5.4 g, 74%), bp 245 °C/0.4 mmHg; *m/z* (CI) 442 (M$^+$ + NH$_4$); δ_H(200 MHz, CDCl$_3$) 0.88 (t, 3 H), 1.26 (br s, 18 H), 1.80 (q, 2 H), 3.38 (s, 3 H), 3.50–3.80 (m, 8 H), 3.87 (t, 2 H), 3.98 (t, 2 H), 4.17 (t, 2 H) and 6.90 (s, 4 H) which was used in the next step without further purification.

(iii) 1,2-Dibromo-4-dodecyloxy-5-(1,4,7,10-tetraoxaundecyl)-benzene. To a stirred solution of 1-dodecyloxy-2-(1,4,7,10-tetraoxaundecyl)benzene (5 g, 11.8 mmol) in dichloromethane (50 cm^3), cooled to 0 °C, was added a solution of bromine (3.95 g, 24.3 mmol) in dichloromethane (10 cm^3), dropwise. The reaction mixture was allowed to warm to room temperature after which it was washed with saturated aqueous sodium sulfite (2 × 20 cm^3), dried (MgSO$_4$) and evaporated to give the title compound as a clear oil (6.5 g, 95%) (Found C, 51.3; H, 7.5; C$_{25}$H$_{42}$Br$_2$O$_5$ requires C, 51.55; H, 7.27%); *m/z* (CI) 580 (M$^+$ +NH$_4$$^+$), 582 (M$^+$ + 2 + NH$_4$$^+$) and 584 (M$^+$ + 4 + NH$_4$$^+$); δ_H(200 MHz, CDCl$_3$) 0.88 (t, 3 H), 1.26 (br s, 18 H), 1.79 (q, 2 H), 3.38 (s, 3 H), 3.66 (m, 8 H), 3.85 (t, 2 H), 3.93 (t, 2 H), 4.13 (t, 2 H), 7.06 (s, 1 H), and 7.13 (s, 1 H) which was used in the next step without further purification.

(iv) 4-Dodecyloxy-5-(1,4,7,10-tetraoxaundecyl)phthalonitrile. A mixture of the preceding compound (4.5 g, 7.7 mmol) and copper(I) cyanide (2.1 g, 23 mmol) in anhydrous DMF (50 cm^3) was heated and stirred at 150 °C for 48 h under a nitrogen atmosphere. The mixture was carefully poured into rapidly stirred concentrated aqueous ammonia (300 cm^3) and, after 1 h, the resulting precipitate was filtered off and washed with ammonia solution (50 cm^3) and water (200 cm^3). The resultant solid was dried and then passed down a silica column (ethyl acetate–light petroleum 2:5) to give the title compound as white needles (1.7 g, 47%), mp 38–40 °C (recrystallised from methanol–water) (Found C, 68.2; H, 9.0; N, 6.1. C$_{27}$H$_{42}$N$_2$O$_5$ requires C, 68.32; H, 8.92; N, 5.90%); *m/z*(CI) 492 (M$^+$ + NH$_4$$^+$); δ_H(200 MHz, CDCl$_3$) 0.85 (t, 3 H), 1.23 (br s, 18 H),

1.83 (q, 2 H), 3.35 (s, 3 H), 3.63 (m, 8 H), 3.89 (t, 2 H), 4.03 (t, 2 H), 4.23 (t, 2 H), 7.12 (s, 1 H), and 7.23 (s, 1 H); and 4-*dode-cyloxy*-5-(1,4,7,10-*tetraoxaundecyl*)*phthalimide* (0.27 g, 6%) as small white needles, mp 73–74 °C (recrystallised from methanol–water) (Found: C, 65.7; H, 8.8; N, 2.7. C$_{27}$H$_{43}$NO$_7$ requires C, 65.69; H, 8.78; N, 2.70%); *m/z*(CI) 511 (M$^+$ + NH$_4$$^+$); δ_H(200 MHz, CDCl$_3$) 0.85 (t, 3 H), 1.27 (br s, 18 H), 1.85 (q, 2 H), 3.38 (s, 3 H), 3.66 (m, 8 H), 3.93 (t, 2 H), 4.09 (t, 2 H), 4.27 (t, 2 H), 7.27 (s, 1 H), 7.30 (s, 1 H) and 7.34 (s, 1 H).

Phthalocyanine preparation

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

(i) Single phthalonitrile cyclotetramerisations. 2,3,9,10,16,-17,23,24-*Octa*(*hexadecyl*)*phthalocyanine* 1.—A solution of 4,5-bis(hexadecyl)phthalonitrile (0.5 g, 0.87 mmol) in dry pentan-1-ol (2 cm^3) was heated to reflux and an excess of lithium metal (0.05 g, 8 mmol) was added to it. The solution turned blue immediately. Reflux was continued for 4 h. On cooling, the mixture was treated with acetone (20 cm^3) and acetic acid (2 cm^3) to give a blue precipitate which was filtered off and washed with acetone (100 cm^3). Upon recrystallisation from toluene it afforded the title compound 1 (210 mg, 42%); transition temperatures: 108 °C (*K-D$_{rd}$*), 170 °C (*D$_{rd}$-D$_{hd}$*), 196 °C (*D$_{hd}$-I*) (Found: C, 83.15; H, 11.8; N, 4.9. C$_{160}$H$_{274}$N$_8$ requires C, 83.2; H, 12.0; N 4.8%); λ_{max}(toluene)/nm 704, 668, 648, 608, 422 and 348; δ_H(500 MHz, solvent C$_6$D$_6$, 60 °C) −1.05 (2 H), 0.99 (24 H, t), 1.3–1.5 (192 H, m), 1.81, (16 H, m), 2.11 (16 H, m), 3.28 (16 H, t) and 9.62 (8 H, s).

2,3,9,10,16,17,23,24-*Octa*(1,4,7,10-*tetraoxaundecyl*)*phthalo-cyanine* 6.—To a stirred solution of 4,5-bis(1,4,7,10-tetraoxaun-decyl)phthalonitrile (0.5 g, 1.1 mmol) in dry 3,6,9-trioxadecan-1-ol (1 cm^3) at 140 °C was added an excess of lithium metal (0.05 g). Heating was continued for 4 h after which acetic acid (0.5 cm^3) was added to the green reaction mixture. After cooling to room temperature, the reaction mixture was placed on a column of silica and washed with ethanol (100 cm^3), ethanol–water (1:1; 100 cm^3) and finally ethanol (100 cm^3). The green band was then eluted from the column with ethanol–dichloromethane (1:1; 50 cm^3). Evaporation of the fraction gave a dark-green oily solid which was dissolved in a minimum of dichloromethane and reprecipitated from hexane to give the title compound 6 as a dark-green oily solid (0.125 g, 25%); transition temperatures: 19 °C (*K-D$_{ho}$*), 293 °C (*D$_{ho}$-I*) (Found: C, 58.6; H, 7.00; N, 6.15. C$_{88}$H$_{130}$N$_8$O$_{32}$ requires C, 58.33; H, 7.23; N, 6.18%); λ_{max}(CH$_2$Cl$_2$)/nm 698, 664, 642, 600, 422, and 348; δ_H(500 MHz, solvent C$_6$D$_6$, 60 °C) −3.20 (2 H, br s), 3.37 (24 H, s), 3.64 (16 H, t), 3.82 (16 H, t), 3.93 (16 H, t), 4.08 (16 H, t), 4.25 (16 H, t), 4.61 (16 H, br t) and 8.71 (8 H, br s) [Found: *m/z*, 1813 [^{13}CC$_{87}$H$_{130}$N$_8$O$_{32}$ requires (M$^+$ + H$^+$), 1812].

(ii) Mixed phthalonitrile cyclotetramerisations. *Phthalo-cyanines* 2–5.—To a rapidly stirred mixture of 4,5-bis(1,4,7,10-tetraoxaundecyl)phthalonitrile (0.452 g, 1.00 mmol) and 4,5-di(hexadecyl)phthalonitrile (0.577 g, 1.00 mmol) in triethylene-glycol monomethyl ether (5 cm^3), at 140 °C under nitrogen, was added an excess of lithium metal (0.1 g). Heating and stirring were continued for 4 h. On cooling, the reaction mixture was treated with acetic acid (10 cm^3) and acetone (100 cm^3) and the resultant precipitate collected. The green product mixture was placed on a column of silica and washed with ethanol (100 cm^3), ethanol–water (1:1; 100 cm^3) and then ethanol (100 cm^3); the green fraction was removed from the column with dichloromethane–ethanol (1:1), at 50 °C. The product mixture was dissolved in a minimum of warm toluene (5 cm^3) and the solution applied to a column of silica gel from which, at 50 °C, it was eluted with an increasing amount of

THF relative to toluene. The first fraction (15 mg, 1.5%) was collected and found to be identical (R_f 0.8, toluene) with a previously prepared sample of the phthalocyanine **1**. The second fraction was collected and applied to a fresh silica column (eluent: toluene–THF, 4:1, 50 °C, R_f 0.5) and recrystallised from hexane–dichloromethane (9:1) to afford 2,3,9,10,16,17-*hexa*(*hexadecyl*)-23,24-*bis*(1,4,7,10-*tetraoxaundecyl*)*phthalocyanine* **2** (100 mg, 10%); transition temperatures: 85 °C (K-D_{rd}), 94 °C (D_{rd}-D_{hd}) and 208 °C (D_{hd}-I) (Found C, 77.5; H, 10.8; N, 5.05. $C_{160}H_{274}N_8O_8$ requires C, 78.0; H, 11.0; N 5.1%); λ_{max}(toluene)/nm 704, 668, 648, 608, 422 and 348; δ_H-(500 MHz, solvent C_6D_6, 60 °C) -0.5 (2 H, br s), 1.00 (18 H, t), 1.3–1.8 (144 H, m), 1.78 (12 H, m), 2.13 (12 H, br s), 3.31 (18 H, m), 3.58 (4 H, t), 3.75 (4 H, m), 3.82 (4 H, t), 3.92 (4 H, t), 4.04 (4 H, t), 4.45 (4 H, br s), 9.12 (2 H, s), 9.4–9.8 (6 H, br m) [Found: m/z 2185. $^{13}C_2C_{158}H_{274}N_8O_8$ requires ($M^+ + H^+$), 2185]. The third fraction was collected and applied to a fresh silica column (eluent: heptane–THF, 1:1, 50 °C, R_fv 0.4) and re-crystallised from hexane–dichloromethane (9:1) to afford 2,3,-16,17-*tetra*(*hexadecyl*)-9,10,23,24-*tetra* (1,4,7,10-*tetraoxaun-decyl*)-*phthalocyanine* **4** (24 mg, 2.4%); t_R (HPLC) 122 s (eluent: MeOH–CH_2Cl_2, 1:9); transition temperatures: 78 °C (K-D_{rd}), 240 °C (D_{rd}-I) (Found C, 72.3; H, 9.9; N, 5.4. $C_{124}H_{202}N_8O_{16}$ requires C, 72.3; H, 9.9; N 5.4%); λ_{max}(toluene)/nm 704, 668, 648, 608, 422 and 348; δ_H(500 MHz, solvent C_6D_6, 60 °C) -1.4 (2 H, br s), 1.00 (12 H, t), 1.3–1.8 (96 H, m), 1.78 (8 H, m), 2.12 (8 H, br s), 3.26 (8 H, br s), 3.31 (12 H, s), 3.61 (8 H, t), 3.79 (8 H, t), 3.87 (8 H, t), 3.99 (8 H, t), 4.13 (8 H, br t), 4.50 (8 H, br s), 9.05 (4 H, br s) and 9.29 (4 H, br s) [Found: m/z 2060. $^{13}CC_{123}H_{202}$-N_8O_{16} requires ($M^+ + H^+$), 2060]. The fourth fraction was collected and applied to a fresh silica column (eluent: hexane–THF, 1:4, 20 °C, R_f 0.6) and recrystallised from hexane–dichloromethane (9:1) to afford 2,3,9,10-*tetra*(*hexadecyl*)-16,-17,23,24-*tetra*(1,4,7,10-*tetraoxaundecyl*)*phthalocyanine* **3** (52 mg, 5.2%); t_R (HPLC) = 190 s (eluent: MeOH–CH_2Cl_2 1:9); transition temperatures: 78 °C (K-D_{rd}), 178 °C (D_{rd}-D_{hd}) and 211 °C (D_{hd}-I) (Found: C, 72.4; H, 9.9; N, 5.35. $C_{124}H_{202}N_8O_{16}$ requires C, 72.3; H, 9.9; N 5.4%); λ_{max}(toluene) 704, 668, 648, 608, 422 and 348; δ_H(500 MHz, solvent C_6D_6, 60 °C) -1.3 (2 H, br s), 1.00 (12 H, t), 1.3–1.8 (96 H, m), 1.82 (8 H, m), 2.16 (8 H, br s), 3.3–3.4 (20 H, m), 3.59 (8 H, m), 3.76 (8 H, m), 3.86 (8 H, m), 3.97 (8 H, m), 4.11 (8 H, br t), 4.45–4.55 (8 H, br m), 8.95 (4 H, br m) and 9.4–9.6 (4 H, br t) [Found: m/z, 2060. $^{13}CC_{123}H_{202}N_8O_{16}$ requires ($M^+ + H^+$), 2060]. The fifth fraction was collected and applied to a fresh silica column (eluent: toluene–THF, 1:4, 20 °C, R_f 0.2) and recrystallised from hexane to afford 2,3-(*hexadecyl*)-9,10,16,17,23,24-*hexa*(1,4,7,10-*tetraoxaundecyl*)*phthalocyanine* **5** (25 mg, 2.5%), t_R (HPLC) 280 s (eluent: MeOH–CH_2Cl_2, 1:9); transition temperatures: 43 °C (K-D_{rd}), 175 °C (D_{rd}-D_{hd}) and 229 °C (D_{hd}-I) (Found C, 65.7; H, 8.6; N, 5.6. $C_{106}H_{166}N_8O_{24}$ requires C, 65.8; H, 8.6; N, 5.8%); λ_{max}(toluene)/nm 704, 668, 648, 608, 422 and 348; δ_H(500 MHz, solvent C_6D_6, 60 °C): -1.9 (2 H, br s), 1.00 (6 H, t), 1.2–1.75 (48 H, m), 1.83 (4 H, m), 2.18 (4 H, br s), 3.3–3.4 (22 H, br m), 3.61 (12 H, m), 3.79 (12 H, m), 3.89 (12 H, m), 4.01 (12 H, m), 4.16 (12 H, br t), 4.5–4.6 (12 H, br m), 8.6–9.1 (6 H, br m) and 9.41 (2 H, br m) [Found: m/z, 1936. $^{13}CC_{105}H_{166}N_8O_{24}$ requires ($M^+ + H^+$), 1936]. A sixth fraction (R_f 0.1, eluent THF) proved to be a trace amount of 2,3,9,10,16,17,23,24-octa(1,4,7,10-trioxaundecyl)phthalocyanine **6**.

Phthalocyanines 8–11. Dry ammonia gas was bubbled through a stirred solution of 4,5-di(1,4,7,10-tetraoxaundecyl)-phthalonitrile (0.5 g, 1.1 mmol), 4,5-di(dodecyloxy)phthalo-nitrile (0.55 g, 1.1 mmol) and sodium methoxide (5 mg) in dry 2-dimethylaminoethanol (5 cm³), at 60 °C, for 2 h. The temperature of the reaction mixture was then raised to 130 °C for 24 h. On cooling, the green product mixture was placed on a

column of silica and washed with ethanol (100 cm³), ethanol–water (1:1; 100 cm³) and ethanol (100 cm³); after this the green fraction was removed from the column with dichloromethane–ethanol (1:1). The resultant green mixture was then applied to a fresh column of silica and eluted with an increasing amount of THF relative to toluene. The first fraction (15 mg, 1.4% yield) was collected and found to be identical (R_f 0.8, toluene) with a previously prepared sample of 2,3,9,10,16,17,23,24-octa(dodecy-loxy)phthalocyanine **7**. The second fraction was collected and applied to a fresh silica column (eluent: toluene–THF, 4:1) and was reprecipitated from toluene into MeOH and then recrystallised from CH_2Cl_2–hexane to give 2,3,9,10,16,17-*hexa*(*dodecyloxy*)-23,34-*di*(1,4,7,10-*tetraoxyundecyl*)*phthalo-cyanine* **8** as a green solid (3.2 mg, 0.3%); transition temperatures: 80 °C (K-D_{ho}) and 315 °C (D_{ho}-I) (Found: C, 72.9; H, 9.7; N, 5.8. $C_{118}H_{190}N_8O_{14}$ requires C, 72.87; H, 9.85; N, 5.76%); λ_{max}(CH_2Cl_2)/nm 700, 664, 602, 426 and 348; δ_H(500 MHz, solvent C_6D_6, 60 °C) -2.50 (2 H, br s), 1.05 (18 H, t), 1.42–1.72 (96 H, m), 1.86 (12 H, pent), 2.23 (12 H, m), 3.32 (6 H, s), 3.60 (4 H, t), 3.79 (4 H, t), 3.89 (4 H, t), 4.02 (4 H, t), 4.16 (4 H, t), 4.40 (12 H, m), 4.53 (4 H, br t), 8.87 (2 H, br s), 8.92 (2 H, br), 8.93 (2 H, br s) and 8.97 (2 H, br s) [Found: m/z 1945. $^{13}CC_{117}H_{190}N_8O_{14}$ requires ($M^+ + H^+$), 1945]. The third fraction was collected and applied to a fresh silica column [eluent: toluene–THF (1:1) $R_f = 0.4$] and was reprecipitated from CH_2Cl_2 into ethanol to give 2,3,16,17-*tetra*(*dodecyloxy*)-7,10,23,24-*tetra*(1,4,7,10 *tetraoxaundecyl*)*phthalocyanine* **10** as a green oily solid (7.1 mg, 0.7%), t_R (HPLC) 150 s (eluent: EtOH–CH_2Cl_2, 1:9); transition temperatures: 43 °C (K-D_{ho}) and 305 °C (D_{ho}-I) (Found: C, 68.1; H, 8.9; N, 6.0. $C_{108}H_{170}N_8O_{20}$ requires C, 68.25; H, 9.02; N, 5.90%); λ_{max}(CH_2Cl_2)/nm 700, 664, 640, 604, 427 and 345; δ_H(500 MHz, solvent C_6D_6, 60 °C) -2.5 (2 H, br s), 1.05 (12 H, t), 1.38–1.72 (64 H, br m), 1.86 (8 H, pent), 2.23 (8 H, pent), 3.32 (12 H, s), 3.60 (8 H, t), 3.79 (8 H, t), 3.89 (8 H, t), 4.01 (8 H, t), 4.15 (8 H, br t), 4.44 (8 H, br t), 4.54 (8 H, br t), 8.93 (4 H, br s) and 8.95 (4 H, br s) [Found: m/z 1900, $^{13}CC_{107}H_{170}N_8O_{20}$ requires [($M^+ + H^+$), 1900]. The fourth fraction was collected and applied to a fresh silica column (eluent: toluene–THF (1:4) R_f 0.6] and was reprecipitated from CH_2Cl_2 into ethanol to give 2,3,9,10-*tetra*(*dodecyl*)-16,17,23,24-*tetra*(1,4,7,10-*tetraox-aundecyl*)*phthalocyanine* **9** as a green semi-solid (13.3 mg, 1.3%), t_R (HPLC) 250 s (eluent: EtOH–CH_2Cl_2, 1:9); transition temperatures: 39 °C (K-D_{ho}) and 306 °C (D_{ho}-I) (Found: C, 68.1; H, 9.0; N, 6.1. $C_{108}H_{170}N_8O_{20}$ requires C, 68.25; H, 9.02; N, 5.90%); λ_{max}/nm (CH_2Cl_2) 698, 664, 640, 602, 425 and 350; δ_H(500 MHz, solvent C_6D_6, 60 °C) -2.45 (2 H, br s), 1.04 (12 H, t), 1.40–1.72 (64 H, br m), 1.86 (8 H, pent), 2.22 (8 H, sept), 3.32 (12 H, s), 3.60 (8 H, t), 3.79 (8 H, t), 3.90 (8 H, t), 4.02 (8 H, t), 4.16 (4 H, t), 4.20 (4 H, t), 4.41 (4 H, br t), 4.45 (4 H, br t), 4.53 (4 H, br t), 4.60 (4 H, br t), 8.90 (4 H, br s), 8.96 (2 H, br s) and 8.98 (2 H, br s) [Found: m/z 1900. $^{13}CC_{107}H_{170}N_8O_{20}$ requires ($M^+ + H^+$), 1900]. The fourth fraction was collected and applied to a fresh silica column [eluent: toluene–THF (1:9), R_f 0.6] and was reprecipitated from CH_2Cl_2 into ethanol to give 2,3-*di*(*dodecyloxy*)-9,10,16,17,23,24-*hexa*(1,4,7,10-*tetra-oxyundecyl*)*phthalocyanine* **11** as a green oily solid (11.6 mg, 1.1%); transition temperatures 23 °C (K-D_{ho}), 295 °C (D_{ho}-I) (Found: C, 63.1; H, 8.15; N, 6.0. $C_{98}H_{150}N_8O_{26}$ requires C, 63.40; H, 8.15; N, 6.05%); λ_{max}/nm (CH_2Cl_2) 698, 664, 640, 602, 425 and 350; δ_H(500 MHz, solvent C_6D_6, 60 °C) -3.00 (2 H, br s), 1.05 (6 H, t), 1.42–1.74 (32 H, br m), 1.89 (4 H, pent), 2.26 (4 H, pent), 3.34 (18 H, s), 3.62 (12 H, t), 3.81 (12 H, t), 3.93 (12 H, t), 4.06 (12 H, t), 4.20 (4 H, t), 4.24 (8 H, t), 4.45 (4 H, br t), 4.55 (4 H, br t), 4.61 (8 H, br t), 8.79 (2 H, br s), 8.81 (2 H, br s), 8.84 (2 H, br s) and 8.87 (2 H, s) [Found: m/z 1856, ^{13}C-$C_{97}H_{150}N_8O_{26}$ requires ($M^+ + H^+$), 1856]. A sixth fraction (R_f 0.1, eluent THF) proved to be 2,3,9,10,16,17,23,24-

octa(1,4,7,10-trioxaundecyl)phthalocyanine **6** (4.1 mg, 0.4%) identical with a previously prepared sample.

(iii) Cyclotetramisation of 4-dodecyloxy-5-(1,4,7,10-tetra-oxaundecyl)phthalonitrile (19). *Phthalocyanines* **12–15.**— Dry ammonia gas was bubbled through a stirred solution of 4-dodecyloxy-5-(1,4,7,10-tetraoxaundecyl) phthalonitrile (300 mg, 0.63 mmol) and sodium methoxide (5 mg) in dry 2-dimethylaminoethanol (5 cm³), at 60 °C, for 2 h. The temperature of the reaction mixture was then raised to 130 °C for 24 h. On cooling, the product mixture was placed on a column of silica and washed with ethanol (100 cm³), ethanol–water (1:1; 100 cm³) and finally ethanol (100 cm³); the green products were eluted with dichloromethane–ethanol (1:1), collected and applied to a fresh silica column. The first fraction (eluent: toluene–THF, 4:1) was reprecipitated from CH_2Cl_2 into ethanol to give 2,9,16,23-*tetradodecyloxy*-3,10,17,24-*tetra*(1,4,7,10 *tetraoxaundecyl*)*phthalocyanine* **12** as a green oil (11 mg, 3.6%), t_R(HPLC) 90 s (eluent: MeOH–ethyl acetate, 1:30); transition temperatures 306 °C (D_{ho}-I) (Found: C, 68.1; H, 8.9; N, 6.3. $C_{168}H_{170}N_8O_{20}$ requires C, 68.25; H, 9.02; N, 5.90%) λ_{max}/nm (CH_2Cl_2) 700, 664, 640, 600, 425 and 345; δ_H(500 MHz, solvent C_6D_6, 60 °C) −2.80 (2 H, br s), 1.05 (12 H, t), 1.40–1.70 (64 H, m), 1.84 (8 H, pent), 2.24 (8 H, pent), 3.33 (12 H, s), 3.61 (8 H, t), 3.80 (8 H, t), 3.91 (8 H, t), 4.05 (8 H, t), 4.19 (8 H, t), 4.45 (8 H, br t), 4.54 (8 H, br t), 8.88 (4 H, br s) and 8.90 (4 H, br s) [Found: m/z, 1900. $^{13}CC_{107}H_{170}N_8O_{20}$ requires ($M^+ + H^+$), 1900]. The second fraction (eluent: toluene–THF, 3:1) was reprecipitated from CH_2Cl_2 into MeOH to give an inseparable mixture of 2,9,17,23-tetradodecyloxy-3,10,16,24-tetra(1,4,7,10-tetraoxaundecyl)-phthalocyanine **13** and 2,10,17,23-tetradodecyloxy-3,9,16,24-tetra(1,4,7,10-tetraoxaundecyl)phthalocyanine **14** as an oily solid (59 mg, 20%), t_R(HPLC) 119 s (eluent: MeOH–ethyl acetate, 1:30); transition temperatures: 12 °C (K-D_{ho}) and 307 °C (D_{ho}-I) (Found: C, 68.1; H, 8.7; N, 5.8. C_{108}-$H_{170}N_8O_{20}$ requires C, 68.25; H, 9.02; N, 5.90%); λ_{max}(CH_2-Cl_2)/nm 700, 664, 642, 602, 425 and 345; δ_H(500 MHz, solvent C_6D_6, 60 °C) −2.67 (2 H, br s), 1.05 (12 H, t), 1.40–1.70 (64 H, br m), 1.84 (8 H, pentet), 2.24 (8 H, m), 3.33 (12 H, s), 3.61 (8 H, t), 3.80 (8 H, t), 3.90 (8 H, t), 4.05 (8 H, t), 4.18 (4 H, t), 4.22 (4 H, t), 4.38 (4 H, br t), 4.45 (4 H, br t), 4.53 (4 H, br t), 4.63 (4 H, br t) and 8.88 (8 H, br s) [Found: m/z, 1900, $^{13}CC_{107}H_{170}N_8O_{20}$ requires ($M^+ + H^+$), 1900]. The third fraction (eluent: toluene–THF, 1:1) was reprecipitated from CH_2Cl_2 into MeOH to give 2,10,16,24-*tetra*(*dodecyloxy*)-3,9,17,23-*tetra*(1,4,7,10-*tetraoxaundecyl*)*phthalocyanine* **15** as a green solid (13 mg, 4.3%), t_R(HPLC) 165 s (eluent: MeOH–ethyl acetate, 1:30); transition temperatures 80 °C (K-D_{ho}) and 304 °C (D_{ho}-I) (Found: C, 68.4; H, 9.4; N, 5.4. $C_{108}H_{170}N_8O_{20}$ requires C, 68.25; H, 9.02; N, 5.90%); λ_{max}(CH_2Cl_2)/nm 700, 664, 642, 600. 425 and 345; δ_H(500 MHz, solvent C_6D_6, 60 °C) −2.90 (2 H, br s), 1.05 (12 H, t), 1.42–1.72 (64 H, m), 1.85 (8 H, pent), 2.23 (8 H, pent), 3.33 (12 H, s), 3.62 (8 H, t), 3.81 (8 H, t), 3.91 (8 H, t), 4.06 (8 H, t), 4.24 (8 H, t), 4.37 (8 H, br t), 4.63 (8 H, br t), 8.82 (4 H, br s) and 8.84 (4 H, br s) [Found: m/z, 1900. $^{13}CC_{107}H_{170}N_8O_{20}$ requires ($M^+ + H^+$), 1900.

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