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Synthesis and Characterization of Mesogenic Phthalocyanines Containing a Single Poly(oxyethylene) Side Chain: An Example of Steric Disturbance of the Hexagonal Columnar Mesophase

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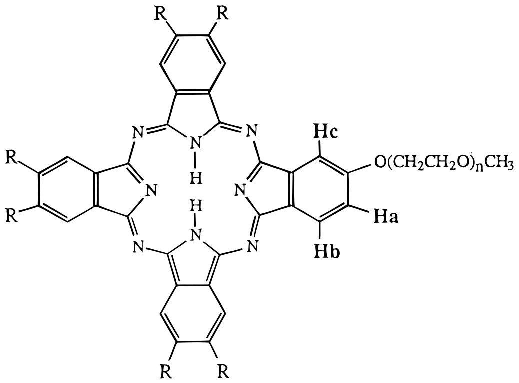
ABSTRACT: The synthesis and detailed structural characterization of phthalocyanine derivatives substituted by six dodecyloxy side chains and a single poly(oxyethylene) moiety are described. All of the materials possess columnar mesogenic properties. The phthalocyanines attached to short poly(oxyethylene)s possess an ordered hexagonal mesophase (D_{ho}) of structure similar to that obtained from octakis(dodecyloxy)phthalocyanine. However, the Pc attached to a long poly(oxyethylene) side chain displays a less ordered columnar mesophase, probably columnar nematic (N_c), due to steric disturbance of the two-dimensional hexagonal lattice by the polymeric substituent. This material also displays an interesting phase separation of the poly(oxyethylene) and alkoxy side chains in the solid state.

Columnar mesophases derived from suitably substituted triphenylene or phthalocyanine (Pc) derivatives are of great interest due to their proven anisotropic electronic conductivity[1] and photoconductivity.[2] In particular, the study of Pc-based columnar mesogens is relevant due to the widespread use of Pcs as photoconductors in xerography[3] and their high electronic conductivity when doped with oxidants.[4] In this context the untilted hexagonal ordered mesophase, designated D_{ho} (Figure 1), is of particular interest due to its greater degree of $\pi-\pi$ orbital interaction and stacking periodicity, relative to the tilted structures found in other types of columnar mesophases. It has been shown by empirical means,[5−7] and by a theoretical study,[8] that D_{ho} mesophase formation by Pcs is favored by alkoxy substitution at the peripheral (2,3,9,10,16,17,23,24) sites of the macrocycle, whereas tilted columnar phases are promoted by alkyl[6,9] or (alkyloxy)methyl[10,11] substitution at either the peripheral or nonperipheral (1,4,8,11,15,18,22,25) sites.[12,13] However, the anisotropic conductivity of the D_{ho} mesophase formed by octaalkoxy-Pcs has not been studied, to date, because its high viscosity precludes alignment by electric or magnetic fields. For measurement of the anisotropic conductivity of the relatively viscous triphenylene D_{ho} mesophase, alignment was achieved by the influence of a strong magnetic field during the formation of the mesophase from the more fluid isotropic phase.[1] However, this method is not applicable to the alignment of the D_{ho} phase of the octaalkoxy-Pcs due to their high clearing temperatures which are in excess of their decomposition temperatures (>300 °C).[5−7] Generally, for columnar mesogens, the clearing temperature can be reduced by increasing the length of the side chain;[7,12] however, octaalkoxy-Pcs with side chains containing more than 20 atoms are difficult to prepare and purify due to their low solubility in organic solvents.

This paper describes the synthesis and thermal behavior of Pc mesogens (Pcs **1**−**4**) substituted by six dodecyloxy sidechains, to promote D_{ho} mesophase formation, and a single oligo- or poly(oxyethylene) substituent. The immediate aim of this work is to use the single, flexible polymer side chain to destabilize the hexagonal structure and thus obtain a lower clearing point and a less viscous D_{ho} mesophase. In addition, it is of interest to assess whether segregation of the nonpolar alkyl and polar poly(oxyethylene) side chains occurs in the mesophase or the solid phase of these materials. This would lead to the formation of domains in analogy with the microphase separation of block copolymers.[14] Poly(oxyethylene)s are excellent media for ionic conduction and thus microphase-separated domains of a Pc-containing material may provide well-defined channels for both anisotropic ionic and electronic conductivity.[15]



Pc **1**, **R** = $C_{12}H_{25}O$-, n = 3

Pc **2**, **R** = $C_{12}H_{25}O$-, n = 8

Pc **3**, **R** = $C_{12}H_{25}O$-, n = 10-14

Pc **4**, **R** = $C_{12}H_{25}O$-, n = ~ 50

Synthesis of Materials. Pcs **1**−**4** were prepared by the route shown in Scheme 1 which involved the lithium pentoxide catalyzed mixed cyclotetramization reactions[16] between 4,5-bis(dodecyloxy)phthalonitrile[6] and a suitable 4-[ω-methylpoly(oxyethylene)]phthalonitrile.[17] Acetic acid was used in the work-up procedure to convert the dilithium Pc to the metal-free derivative. The poly(oxyethylene)-substituted phthalonitriles containing three or eight oxyethylene units, precursors to Pcs **1** and **2**, respectively, were of uniform molecular mass whereas those with an average of 12 or 50 oxyethylene units, precursors to Pcs **3** and **4**, respectively, were composed of a broad range of molecular weights. A reactant molar ratio of 9:1 in favor of the

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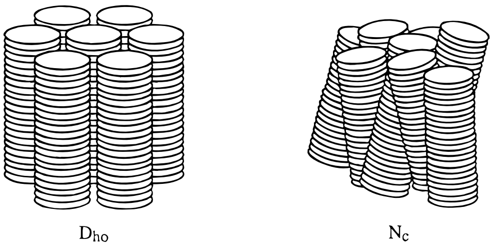


Figure 1. Diagrammatic representation of the D_{ho} columnar and N_c mesophases.

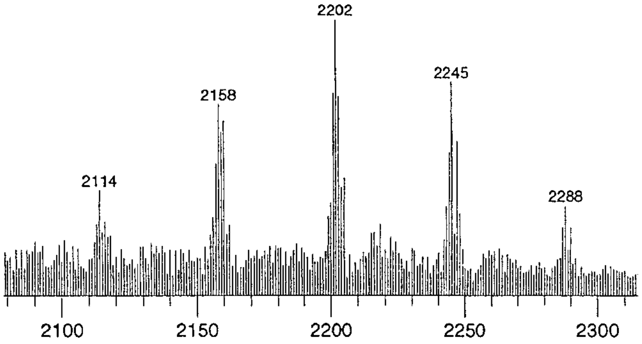
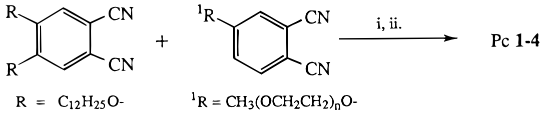


Figure 2. FAB mass spectrograph of the molecular ion region for Pc **3** showing the distribution of molecular mass. Peaks correspond to a general molecular structure with the number of ethyleneoxy units (n) = 10, 11, 12, 13, and 14.

Scheme 1[a]



[a] Reagents and conditions: (i) $LiOC_5H_{11}-C_5H_{11}OH$, 135 °C; (ii) AcOH.

4,5-bis(dodecyloxy)phthalonitrile ensured that the two major Pc products were the symmetrical 2,3,9,10,16,17,23,24-octakis(dodecyloxy)phthalocyanine and the desired nonuniformly substituted Pcs **1**−**4** with a single poly(oxyethylene) attached. In each case, these two Pcs could be separated easily by column chromatography both from each other and from the small amount of Pc products with more than one poly(oxyethylene) side chain attached. We have previously demonstrated the excellent chromatographic separation that can be achieved for complex Pc mixtures which possess different degrees of oligo(oxyethylene) and alkyl substitution due to the dissimilar polarities of these two types of side chains.[18,19] Pcs **1**−**4** were obtained pure by a second elution through a silica column followed by recrystallization from a toluene/hexane solvent system. Purity of the samples was confirmed by TLC, NMR spectroscopy, and elemental analysis.

Structural Characterization. Visible region absorption spectra of dilute solutions of Pcs **1**−**4** in toluene display the characteristic split Q-band absorption of nonaggregated metal-free Pcs at λ_{max} 702 and 664 nm. Pc **4** is partially soluble in ethanol and methanol but in these protic solvents only a broad band centered at 640 nm is exhibited in the visible region. This effect is characteristic of cofacial intermolecular aggregation.[4]

Pcs **1** and **2** gave fast atom bombardment mass spectrometry (FABMS) molecular ion peaks consistent with the proposed structures. Pc **3** gave five distinct peaks corresponding to the molecular ion peaks for the Pc derivatives with side chains containing 10, 11, 12, 13, and 14 oxyethylene subunits (Figure 2). Unfortunately, no FABMS spectrum could be obtained from Pc **4**, presumably due to its large and nonuniform molecular mass.

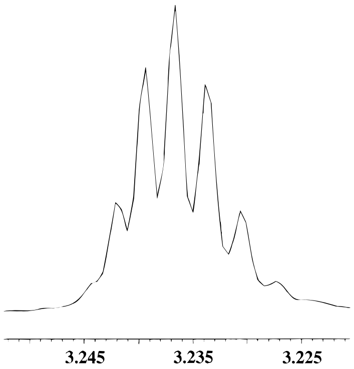


Figure 3. ^{1}H NMR (500 MHz) of the region associated with the poly(oxyethylene) terminal methyl group of Pc **3**. See text for discussion.

Excellent quality NMR spectra, with no evidence of broadening due to intermolecular aggregation, could be obtained for each Pc product from a dilute solution (1 mg/mL, in benzene-d_b), at elevated temperature (60 °C), using a high-resolution spectrometer (500 MHz). These spectra were used to confirm that the average number of oxyethylene subunits in the side chain attached to Pcs **3** and **4** were 12 and 50, respectively, by comparison of the total intensity of the signals due to the six alkoxy side chains relative to that due to the combined poly(oxyethylene) signals. The validity of this methodology was confirmed by performing the same calculations for Pcs **1** and **2** for which the oligo(oxyethylene) side chain lengths are known. The calculated average polymer side chain lengths for Pcs **3** and **4** were consistent with the elemental analyses obtained for these materials and, in the case of Pc **3**, with the FABMS.

One surprising feature of the NMR of Pc **3** is the multiplet obtained for the terminal methyl group of the poly(oxyethylene) side chain (Figure 3). This is in contrast to the sharp singlet obtained for the analogous methyl group on Pcs **1** and **2** that have oxyethylene side chains of a uniform length. We believe that this splitting is due to the influence of the strong Pc ring current producing slight differences in the chemical shift of the methyl end group because of the range of poly(oxyethylene) chain lengths (n = 10−14) which are present in Pc **3**. It is interesting to note the similarity in appearance of the terminal methyl NMR resonances with the distribution of molecular ion peaks obtained by FABMS (Figure 2). However, it is remarkable that the ring current should exert even a small influence over a distance of more than 30 atoms length. A similar effect is seen for the NMR peak of the methylene subunit neighboring the terminal methoxy group (δ = 3.45 ppm) which is a clear triplet for Pcs **1** and **2** but a complex multiplet for Pc **3**. No similar effects can be observed for Pc **4**, which also carries a side chain with a size distribution, presumably because in this case the terminal methyl group of the poly(oxyethylene) is too far from the Pc core to be affected by the ring current. The strongly shielding effect of the Pc ring current on the two internal protons is also apparent from their chemical shift (−2 to −3.5 ppm).

The aromatic region of the NMR spectra gave, in each case, signals which are consistent with the unsymmetrical hepta substitution of the Pc macrocycle. A COSY analysis (Figure 4) of Pc **2** helped to assign the protons attached to the same benzo subunit (see general

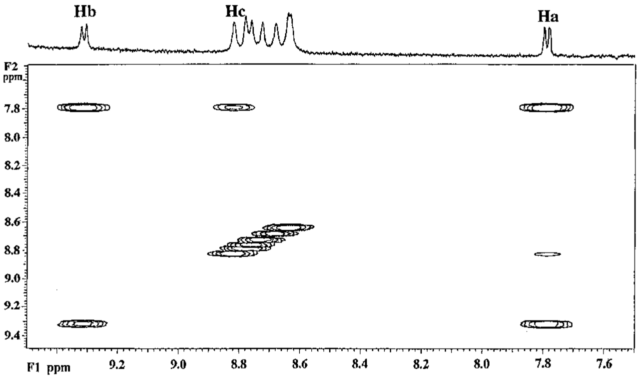


Figure 4. COSY ^{1}H NMR (500 MHz) spectrum of the aromatic region for Pc **2**. The assignments, labeled Ha−Hc, refer to the general structure of Pcs **1**−**4**. The ortho coupling between Ha and Hb and the meta coupling between Ha and Hc are clearly discernible; see text.

Table 1. Transition Temperatures[a] (°C) (Δ*H*, J/g)

Pc	K → D_{ho}	K → N_c	D_{ho} → I	N_c → I
1	72 (65)		325[b]	
2	71 (53)		289 (60)	
3	70 (46)		234−239 (3)	
4		74 (19)[c]		195−210 (2)

[a] Transition temperatures quoted are for the heating cycle. Significant supercooling is observed for solid to mesophase transitions, on cooling, but only a small amount (<5 °C) occurs for the clearing transition. [b] Transition accompanied by decomposition. [c] Second melting transition. First melting transition, associated with poly(oxyethylene) domains, at 31 °C (Δ*H* = 66 J/g).

molecular structure) as the poly(oxyethylene) side chain due to the clear ortho and meta coupling of these protons. Proton Ha (δ = 7.79 ppm) is relatively shielded because of its peripheral location,[20] and proton Hb (δ = 9.32 ppm) is relatively deshielded because it does not possess an adjacent electron-donating dodecyloxy group. The ortho coupling (J_{Ha-Hb} = 10 Hz) between these two protons is clear from the COSY spectra, as is the meta coupling (J_{Ha-Hc} = 2 Hz) between protons Ha and Hc. The six other benzo protons give rise to five peaks, one of which (at δ = 8.65 ppm) is broader and more intense than the others. The distinct appearance of the aromatic region of the NMR for Pcs **1**−**4** was used, in conjunction with FABMS (where appropriate), elemental analysis, and TLC, to confirm the lack of contamination with Pcs substituted by two or more poly(oxyethylene)s, formed during the mixed phthalonitrile cyclotetramizations. In order to obtain NMR spectra for comparison, small amounts of Pcs with two poly(oxyethylene) substituents were isolated by column chromatography from the reaction mixtures. These materials proved to have highly complex NMR spectra in the aromatic region consistent with the expected formation of five distinct regioisomers.

Mesophase Properties. As characterized by polarized optical microscopy, powder X-ray diffraction (XRD), and differential scanning calorimetry (DSC), all of the Pcs **1**−**4** possess a mesophase stable over a broad temperature range (see Table 1). There is a clear relationship between the length of the single oxyethylene side chain and the thermal stability of the mesophase. For Pc **1** (*n* = 3), the formation of the isotropic phase at 325 °C is accompanied by decoloration due to degradation of the sample. For Pcs **2**−**4**, the DSC thermograms (Figure 5) show clearly the concomitant decrease in the clearing point due to the increase in length of the poly(oxyethylene) side chain. Thus, Pcs with longer, polymeric substituents (Pcs **3** and **4**) possess a mesophase to isotropic transition well below temperatures at which they decompose. The clearing point is a sharp, well-defined transition for Pc **2** but occurs over much wider temperature ranges for both Pcs **3** and **4**, consistent with the broad distribution of poly(oxyethylene) chain lengths in these materials.

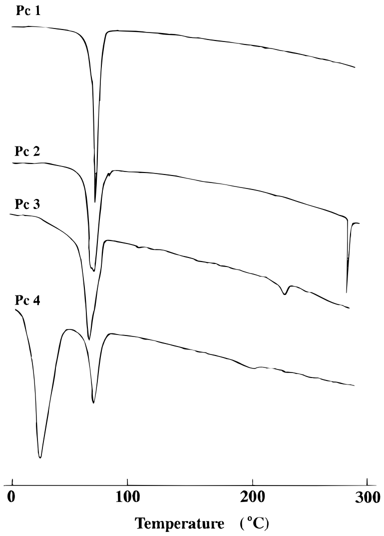


Figure 5. DSC thermograms of Pcs **1**−**4** on heating at a rate of 10 °C/min.

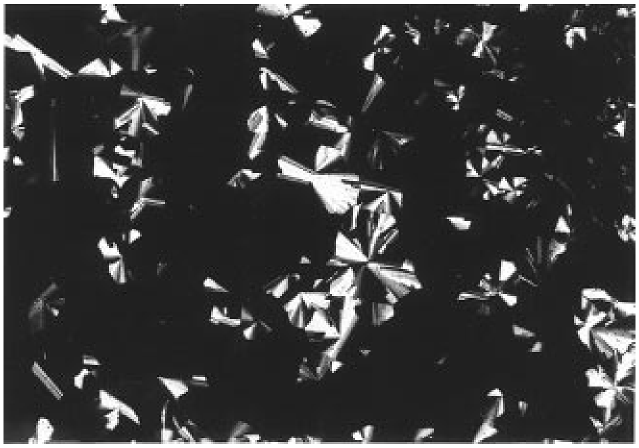


Figure 6. Optical texture of the D_{ho} mesophase of Pc **3** (220 °C, 200× magnification, crossed polarisers) formed on cooling from the isotropic phase. (The original figure was reduced to 42% for publication.)

The related symmetrical octakis(dodecyloxy)phthalocyanine has previously been shown, by an X-ray diffraction study, to possess a D_{ho} mesophase.[5−7] Although the Pcs **1**−**3** have a less symmetrical substitution pattern, they display a mesophase of an identical optical texture which is characterized by large homeotropic domains with *fanlike* birefringent defects (Figure 6) when viewed by optical microscopy with crossed polarizers. In particular, the hexagonal symmetry of this mesophase is evident by the formation of digitate stars (best observed with parallel polarizers) on slow cooling from the isotropic phase.[7] A powder XRD analysis of the mesophase of Pcs **2** and **3** gave diffraction patterns which in each case confirm the D_{ho} structural assignment (Table 2).

On examination by optical microscopy, Pc **4** gave a mesophase with a different optical texture, composed of a smaller domain size, which is similar to the *marbled* texture (Figure 7) often observed for nematic liquid

Table 2. Mesophase Powder X-ray Diffraction Data

Bragg spacing (d)	intensity	hexagonal lattice assignment (h,k)
Pc **2** (D_{ho}, 150 °C), Intercolumnar Distance[a] (D) = 35.1 Å		
30.4	strong	1,0
17.2	medium	1,1
14.8	weak	2,0
4.7	broad	paraffinic chains
3.4	sharp	intracolumnar periodicity
Pc **3** (D_{ho}, 150 °C), Intercolumnar Distance[a] (D) = 35.6 Å		
30.8	strong	1,0
17.7	weak	1,1
4.6	broad	paraffinic chains
3.4	sharp	intracolumnar periodicity
Pc **4** (N_c, 150 °C)		
32.2	broad	column diameter
4.6	broad	paraffinic chains
3.4	sharp	intracolumnar periodicity

[a] Calculated from (1,0) d spacing.

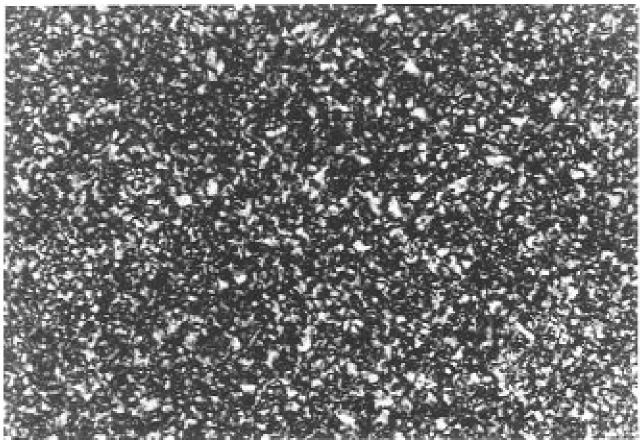


Figure 7. Optical texture of the N_c mesophase of Pc **4** (185 °C, 200× magnification, crossed polarisers) formed on cooling from the isotropic phase. (The original figure was reduced to 42% for publication.)

crystals. This relatively fluid mesophase develops from the cooled isotropic phase as droplets. The XRD study of this mesophase shows only a single diffuse diffraction pattern at low angles (Table 2). The absence of rings due to higher order diffractions suggests that there is no long-range two-dimensional hexagonal ordering or that there is a weakening of the stacking register of the molecules with respect to the columnar axis. However, there is a wide angle diffraction corresponding to a distance of 3.4 Å, in addition to the commonly encountered diffuse diffraction corresponding to 4.4 Å, associated with the disordered paraffinic side chains, which indicates that the Pc molecules are stacked in columns. This structural analysis and the optical texture of the mesophase displayed by Pc **4** suggests it to be a columnar nematic (N_c) phase. The N_c mesophase is rarely encountered in single-component systems but is common in aqueous lyotropic phases composed of discotic amphiphiles such as oligo(oxyethylene)-substituted triphenylenes[21] or Pcs.[17] Ringsdorf et al. have reported the induction of a thermotropic N_c phase into a D_{ho} mesophase, forming a triphenylene system by the introduction of an electron-accepting trinitrofluorenone derivative substituted by long alkyl chains.[22] The occurrence of the N_c phase in the resultant charge-transfer complex was attributed to the mismatch in the chain length of the short alkyl chains attached to the triphenylene with the longer alkyl substituents of the trinitrofluorenone. This effect has been observed in other thermotropic two-component systems[23] and has been termed "steric disturbance of the hexagonal columnar mesophase". The optical texture and X-ray diffraction pattern of these mixed systems and those of the mesophase of Pc **4** are analogous and suggest that the long poly(oxyethylene) chain of Pc **4** is responsible for the disruption of long-range hexagonal order and the induction of the N_c mesophase.

It is clear, from a comparison of the DSC scan of Pc **4** as compared with those obtained for Pcs **1**−**3**, that the long poly(oxyethylene) side chain of Pc **4** also has a very strong influence on the material's initial melting behavior. Pcs **1**−**3** each have an endothermic transition between 70 and 75 °C, on heating, which is associated with the formation of the D_{ho} mesophase resulting from the melting of the six alkoxy side chains. In addition to a transition at 74 °C, Pc **4** has an endothermic transition at 31 °C which appears to be due to the melting of the long poly(oxyethylene) side chain. This conclusion is based on the XRD study of Pc **4** which shows, at room temperature, very strong diffraction rings corresponding to a distance of 3.86 and 4.70 Å, whereas at 50 °C these diffraction rings are absent although the small angle region of the X-ray diffraction pattern remains unchanged. These wide angle diffraction rings are characteristic of crystalline poly(oxyethylene),[24] and we obtained analogous intense diffraction rings from a crystalline sample of commercially available (Fluka) poly(ethylene glycol) 2000. No equivalent wide angle diffractions are obtained from solid samples of Pcs **2** and **3** at room temperature. This "double melting" behavior strongly implies that the solid form of Pc **4** is composed of separate domains of alkoxy and poly(oxyethylene). Interestingly, heating Pc **4** above 30 °C changes it from a brittle solid to a malleable, but highly viscous, birefringent material consistent with partial melting. The enthalpy associated with this transition is 66 J/g and, therefore, the enthalpy of fusion per gram of poly(oxyethylene) in Pc **4** is calculated as 116 J. Thus, the degree of crystallinity for the poly(oxyethylene) side chain can be estimated as 58%, a value similar to that of poly(oxyethylene) segments within a number of block copolymers, based upon the reported enthalpy of fusion of 200 J/g for an infinitely thick crystal of poly(oxyethylene) free from chain ends.[25]

To conclude, the incorporation of a covalently attached poly(oxyethylene) chain to a mesogenic Pc moiety causes a destabilization of the hexagonal columnar mesophase, resulting in lower clearing temperatures. This may allow greater ease of alignment which is crucial for examination of the anisotropic properties of this potentially important system. Alignment studies are in progress. If the polymer side chain is long, the shape asymmetry induces a fluid N_c phase and an interesting phase separation in the solid phase.

Experimental Section

Equipment and Materials. High-resolution (500 MHz) ^1H NMR spectra were recorded using a Varian Unity 500 spectrometer. UV−visible spectra were recorded on a Shimadzu UV-260 spectrophotometer from toluene or ethanol solutions using cells of path length 10 mm. Elemental analyses were obtained using a Carlo Erba Instruments CHNS-O EA 108 elemental analyzer. 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 results are uncorrected. Determination of transition temperatures, crystal (K) to mesophase (D_{ho} or N_c) to isotropic liquid

(I), was by optical microscopy using a Nikon Optiphot-2 microscope in conjunction with a Mettler FP82HT hot stage, and values were confirmed by differential scanning calorimetry (DSC) using a Seiko DSC 220C. Variable temperature, 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 were collected on a photographic plate placed 60 mm away from the sample.

All solvents were dried and purified as described by Perrin and Armarego.[26] Silica gel (60 Merck 9385) was used in the separation and purification of Pcs by column chromatography.

Synthesis of Materials. 2,3,9,10,16,17-Hexakis(dodecyloxy)-23-(1,4,7,10,13,16,19,22,25-nonaoxahexacosyl)-phthalocyanine (Pc 2). To a stirred solution of 4-(1,4,7,10,-13,16,19,22,25-nonaoxahexacosyl)phthalonitrile (150 mg, 0.29 mmol) and 4,5-bis(dodecyloxy)phthalonitrile (1.5 g, 3.0 mmol) in refluxing pentanol was added an excess of lithium metal (0.2 g). The reaction mixture was stirred at reflux for a further 3 h and cooled and a solution of acetic acid (10 mL) in acetone (50 mL) added. The resultant green precipitate was collected by filtration and washed with acetone (3 × 50 mL). The crude product mixture was applied to a column of silica gel and the symmetrical octakis(dodecyloxy)phthalocyanine eluted with warm toluene. Further elution of the silica with a solvent mixture of toluene/THF (1:1) gave a green fraction which, on removal of solvent under reduced pressure, reapplication to a fresh silica column (eluent toluene/THF), and finally recrystallization from toluene/hexane, afforded pure 2,3,9,10,16,17-hexakis(dodecyloxy)-23-(1,4,7,10,13,16,19,22,25-nonaoxahexacosyl)phthalocyanine (200 mg, 12%). Anal. Calcd for $C_{121}H_{196}N_8O_{15}$: C, 72.56; H, 9.9; N, 5.6. Found: C, 72.4, H, 9.8; N, 5.65. λ_{max}/nm (toluene): 702, 664, 641, 604, 420, 340. δ_H (500 MH, solvent C_6H_6): −3.0 (2H, br s), 1.05 (18H, t), 1.4−1.8 (96H, m), 1.86 (10H, p), 1.94 (2H, p), 2.22 (10H, p), 2.30 (2H, p), 3.23 (3H, s), 3.46 (2H, t), 3.56 (8H, br s), 3.61 (4H, br s), 3.66 (4H, m), 3.73 (2H, t), 3.78 (2H, t), 3.86 (2H, t), 3.93 (2H, t), 4.10 (2H, t), 4.34 (10H, t), 4.40 (2H, t), 4.47 (2H, t), 4.52 (2H, t), 7.79 (1H, d of d), 8.65 (2H, s), 8.70 (1H, s), 8.74 (1H, s), 8.77 (1H, s), 8.80 (1H, s), 8.84 (1H, s), 9.32 (1H, d). $^{13}C_2C_{119}H_{196}N_8O_{15}$ $(M + H)^+$ calcd: *m*/*e* 2003. Found: *m*/*e* 2003.

The following Pcs were made by similar methods.

1: Recrystallized from toluene hexane (yield, 16%). Anal. Calcd for $C_{111}H_{176}N_8O_{10}$: C, 74.78; H, 10.0; N, 6.3. Found: C, 74.5; H, 10.3; N, 6.4. λ_{max}/nm (toluene): 702, 664, 641, 604, 420, 340. δ_H (500 MH, solvent C_6H_6): −3.2 (2H, br s), 1.05 (18H, t), 1.4−1.8 (96H, m), 1.85 (10H, p), 1.95 (2H, p), 2.22 (10H, p), 2.31 (2H, p), 3.31 (3H, s), 3.61 (2H, t), 3.86 (2H, t), 3.93 (2H, t), 4.10 (2H, t), 4.29 (10H, t), 4.35 (2H, t), 4.44 (2H, t), 4.51 (2H, t), 7.78 (1H, d of d), 8.66 (2H, s), 8.70 (1H, s), 8.74 (1H, s), 8.77 (1H, s), 8.80 (1H, s), 8.85 (1H, s), 9.34 (1H, d). $^{13}C_2C_{109}H_{176}N_8O_{10}$ $(M + H)^+$ calcd: *m*/*e* 1783. Found: *m*/*e* 1783.

3: Reprecipitated from dichloromethane into hexane (yield, 10%). Anal. Calcd for $C_{129}H_{212}N_8O_{19}$ (average $n = 12$): C, 71.10; H, 9.81; N, 5.14. Found: C, 70.92; H, 10.15; N, 5.08. UV/vis (toluene, nm): 702, 664, 641, 604, 420, 340. δ_H (500 MHz, solvent C_6H_6): −2.6 (2H, br s), 1.05 (18H, t), 1.4−1.8 (96H, m), 1.86 (10H, p), 1.94 (2H, p), 2.22 (10H, p), 2.30 (2H, p), 3.22 (3H, m), 3.45 (2H, m), 3.55 (24H, br s), 3.59 (4H, br s), 3.66 (4H, m), 3.73 (2H, t), 3.79 (2H, t), 3.86 (2H, t), 3.93 (2H, t), 4.10 (2H, t), 4.35 (10, t), 4.40 (2H, t), 4.46 (2H, t), 4.52 (2H, t), 7.80 (1H, d of d), 8.72 (2H, s), 8.76 (1H, s), 8.80 (1H, s), 8.83 (1H, s), 8.85 (1H, s), 8.90 (1H, s), 9.36 (1H, d). $^{13}C_2C_{123}H_{204}N_8O_{17}$ $(M + Na^+)^+$ calcd: *m*/*e* 2113 ($n = 10$, 12%). Found: *m*/*e* 2114. $^{13}C_2C_{125}H_{208}N_8O_{18}$ $(M + Na^+)^+$ calcd: *m*/*e* 2159 ($n = 11$, 21%). Found: *m*/*e* 2158. $^{13}C_2C_{127}H_{212}N_8O_{19}$ $(M + Na^+)^+$ calcd: *m*/*e* 2203 ($n = 12$, 32%). Found: *m*/*e* 2202. $^{13}C_2C_{129}H_{216}N_8O_{20}$ $(M + Na^+)^+$ calcd: *m*/*e* 2245 ($n = 13$, 24%). Found: *m*/*e* 2245. $^{13}C_2C_{131}H_{220}N_8O_{21}$ $(M + Na^+)^+$ calcd: *m*/*e* 2289 ($n = 14$, 11%). Found: *m*/*e* 2288.

4: Reprecipitated from dichloromethane into hexane (yield, 15%). Anal. Calcd for $C_{205}H_{364}N_8O_{57}$ (average $n = 50$): C, 63.90; H, 9.50; N, 2.91. Found: C, 63.56; H, 9.21; N, 3.04. UV/vis (toluene, nm): 702, 664, 641, 604, 420, 340. δ_H (500 MHz, solvent C_6H_6): −2.2 (2H, br s), 1.05 (18H, t), 1.4−1.76 (96H, m), 1.84 (10H, p), 1.92 (2H, p), 2.18 (10H, p), 2.27 (2H, p), 3.26 (3H, s), 3.48 (2H, t), 3.60 (184H, br s), 3.73 (2H, t), 3.78 (2H, t), 3.84 (2H, t), 3.90 (2H, t), 4.07 (2H, t), 4.35 (10, t), 4.40 (2H, t), 4.46 (2H, t), 4.54 (2H, t), 7.80 (1H, d of d), 8.85 (2H, s), 8.91 (1H, s), 8.93 (1H, s), 8.97 (2H, s), 8.99 (1H, s), 9.43 (1H, d). No parent ions in FABMS.

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