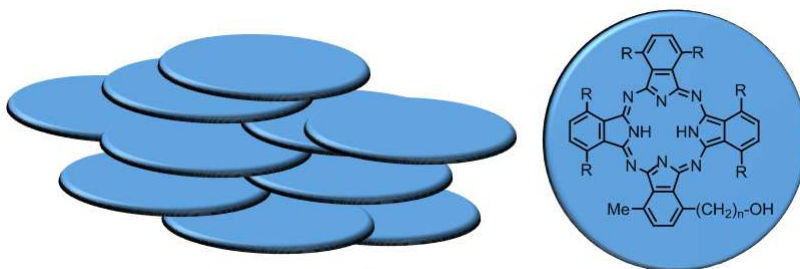# Design and synthesis of liquid crystalline phthalocyanines: combinations of substituents that promote the discotic nematic mesophase

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Graphical Abstract

Phthalocyanines forming nematic (N$_D$) mesophases

Design and synthesis of liquid crystalline phthalocyanines: combinations of substituents that promote the discotic nematic mesophase

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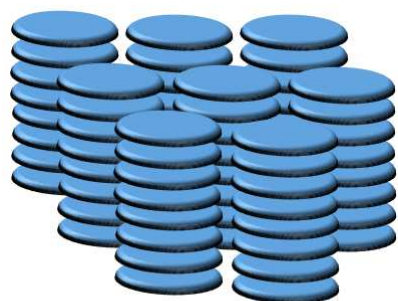
Abstract

A homologous series of fourteen metal-free 1,4,8,11,15,18-hexakis(alkyl)-22-methyl-25-hydroxyalkylphthalocyanine derivatives has been investigated to interogate the interlay of the roles of the six alkyl chains and the length of the hydroxyalkyl chain in promoting thermotropic nematic liquid crystalline behavior. All but two of the compounds form mesophases. Eight of the remaining compounds exhibit only columnar mesophases which is common among liquid crystalline phthalocyanines. However, four examples form the rare discotic nematic mesophase. A general structural feature is deduced in that this rare phase is favoured when the number of linking atoms in the hydroxyalkyl chain exceeds twice the number of carbon atoms in any one of the six common alkyl chains, disrupting the columnar packing arrangement. In addition, zinc and copper metallated examples of one of the metal-free discotic nematic compounds were prepared of which the zinc metallated compound formed a nematic phase whereas the copper containing analogue favoured columnar mesophase formation.

Keywords: Liquid Crystalline Phthalocyanines, Columnar Mesophase, Nematic Discotic Mesophase

1. Introduction

Phthalocyanines (Pcs) are highly stable man-made macrocycles. They are typically blue-green in colour and for many decades have been used as commercial dyes and pigments. The relative ease of incorporating substituents onto the macrocyclic ring and introducing a metal ion or metalloid element into the core of the macrocyclic ligand allows tuning of the properties of the system, not simply the colour but a range of interesting photophysical and semi-conducting properties. They are thus important in the area of organic materials development, building on their successfully established applications as charge carriers in photocopiers,[1] as dyes in laser/LED printing[2] and as laser light absorbers for optical data storage in certain CD-ROMs.[3] Other Pcs show promise for exploitation in organic based solar cells[4] and their photoexcited state properties, tunable by structure

variation, has provided materials suitable for optical limiting[5] and, in health care, as singlet oxygen photosensitizers for photodynamic therapy of particular cancers.[6] In a developing area, a number of Pcs that exhibit liquid crystal properties show enhanced semiconducting behaviour in the temperature range where the liquid crystal state (mesophase) occurs.[7-10]

Simon et al. discovered the first liquid crystalline Pcs in 1982,[11] so adding new examples to the then recently identified class of so-called 'discotic' liquid crystals. Discotic liquid crystals typically possess near planar (often aromatic) cores and bear a number of paraffinic chains. Simon's Pcs carried eight alkoxymethyl chains at the peripheral (2,3,9,10,16,17,23,24-) sites of the Pc ring.[11-14] The UEA group then reported new examples bearing eight medium length alkyl[15-18] or alkoxymethyl groups[19,20] located at the alternative non-peripheral (1,4,8,11,15,18,22,25-) positions of the macrocycle, substitution type A in Fig 1. The group then extended the range of liquid crystalline Pcs to include non-uniformly substituted compounds such as those depicted as type B in Fig 1.[21-25] All the liquid crystalline examples referred to above exhibit columnar mesophase behaviour, see Fig 2, and is discussed later. Our recent preliminary study[26] probed how a combination of particular ring substituents on the Pc core of type C metal-free compounds also promotes mesophase formation. R groups were pentyl and the hydroxyalkyl group chainlength was varied from n = 9 to 12. Pentyl groups were chosen in light of an earlier study that showed that eight pentyl groups alone in the type A structure were insufficient to promote mesophase generation.[15,16] It was found that type C compounds with six pentyl groups, a methyl group and a long hydroxyalkyl chain exhibited not merely liquid crystallinity but either columnar or the rare nematic mesophase (see Fig. 2) depending upon the length of the hydroxyalkyl chain. The present paper reports a comprehensive study into how mesophase type is indeed subtlely, but somewhat predictably, dependent upon particular substituent combinations within type C structures and also extends the investigation to two examples of metallated Pc derivatives.

A

B

C

Fig. 1. Examples of series of substituted phthalocyanines, R = alkyl, as metal-free derivatives, that exhibit liquid crystal behavior.
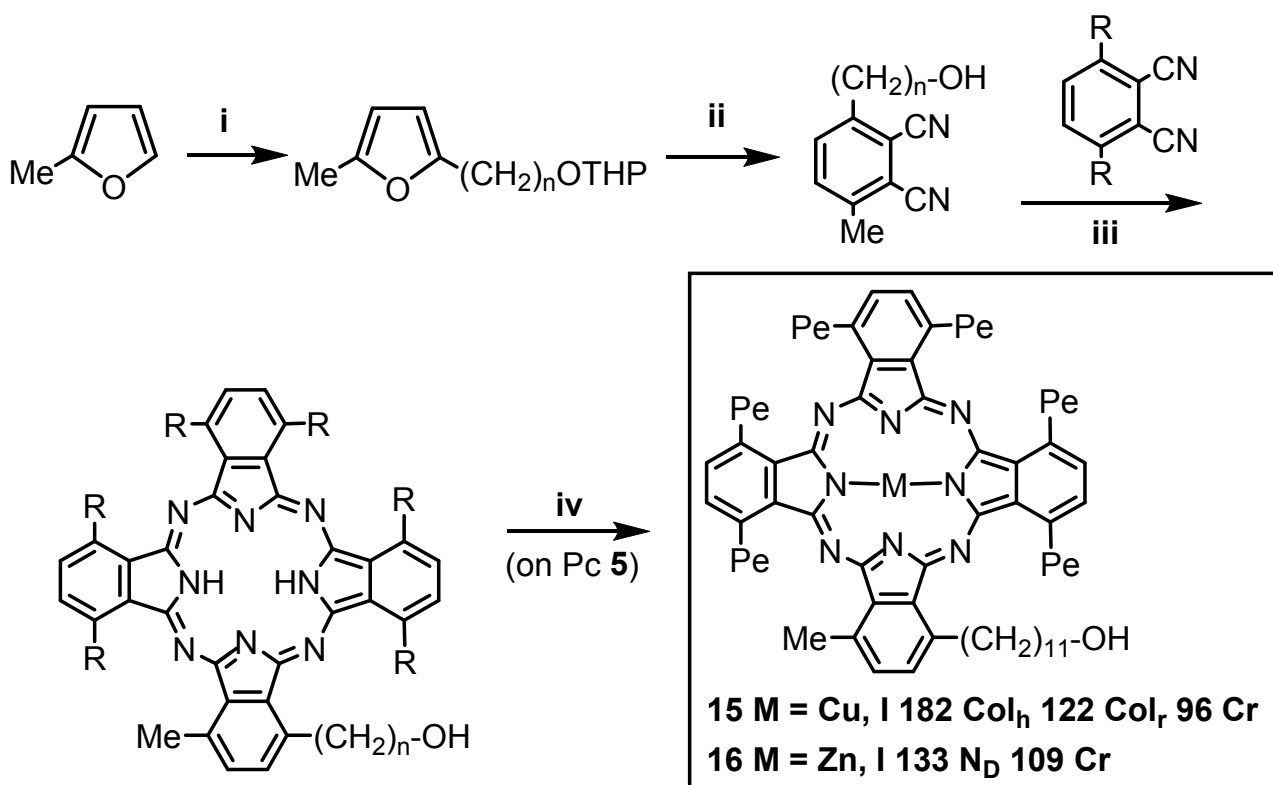

Columnar hexagonal mesophase (Col$_h$)   Discotic nematic mesophase (N$_D$)

Fig. 2. Molecular arrangements in the (discotic) columnar mesophase and nematic mesophase N$_D$.

2. Results and Discusion

2.1 Preparation of compounds

Scheme 1. Syntheses of type C compounds and summary of their liquid crystal behaviour on cooling. i *n*-Bromoalkyloxytetrahydropyran. ii Fumaronitrile then LiN(Me$_3$Si)$_2$ iii LiOH/pentanol/reflux then acetic acid workup. iv Reflux in ethanol with a copper or zinc acetate. (transition in parentheses is monotropic – the nematic mesophase is only observed on cooling; X = undefined glassy phase formed alongside partial crystallisation).

R = n	*n*-C$_4$H$_9$	*n*-C$_5$H$_{11}$	*n*-C$_6$H$_{13}$	*n*-C$_7$H$_{15}$	*n*-C$_8$H$_{17}$
9		**3** **I132Col$_h$117X**			
10		**4** **I(109N$_D$)97** **Col$_h$51Cr**	**7** **I139Col$_h$105X**	**10** **I155Col$_h$93X**	
11	**1** **mp 143**	**5** **I98N$_D$66Cr**	**8** **I130Col$_h$98X**	**11** **I134Col$_h$91X**	**13** **I147Col$_h$81X**
12	**2** **mp 115**	**6** **I98N$_D$88Cr**	**9** **I109N$_D$88Cr**	**12** **I126Col$_h$104X**	**14** **I129Col$_h$75X**

The present series of type **C** phthalocyanine derivatives investigated for liquid crystal behaviour was prepared according to the route shown in Scheme 1. The synthetic method was developed earlier by us to provide examples of homologues designed for other studies.[22-25] In the present work,

the mixed cyclisation of two phthalonitrile derivatives, i.e. a 3-methyl-6-(hydroxyalkyl) phthalonitrile and a 3,6-dialkylphthalonitrile, step iii in Scheme 1, produced the desired metal-free phthalocyanine compound. The principal side-product was the symmetrically substituted 1,4,8,11,15,18,22,25-octakis(alkyl)phthalocyanine; limited amounts of further unwanted cross-condensation products were also formed. In addition to fourteen type **C** metal-free derivatives, a zinc and a copper metalated example were also prepared by reacting metal-free derivative **5** with zinc acetate and copper acetate respectively. Yields and characterisation data for novel compounds are collected in the Experimental section.

2.2 Mesophase behaviour

Typically, discotic liquid crystalline compounds exhibit the so-called columnar mesophase structure and, beyond phthalocyanines, much research has focussed in particular on triphenylenes and hexabenzocoronenes bearing flexible substituent chains. As the term implies, columnar mesophase formation involves a stacking of the cores of the molecules, providing a degree of order, with the stacks separated by the substituent chains. Thus, as temperature is raised above the melting point of the crystalline material, stacking is largely maintained while the mobility of the chains increases leading to disorder between the stacks. In short, the molecules display a positional short range order and an orientational long range order. An alternative packing arises in the much less common discotic nematic mesophase denoted as N_D.[27,28] Here the columnar stacking is destabilised leading to translational and rotational freedom of the molecules about the axis perpendicular to the plane of the core. However, the cores remain broadly aligned parallel to each other, see Fig 2. Among liquid crystalline phthalocyanines there have been no definitive reports of nematic mesophase formation prior to the present research program.[26]
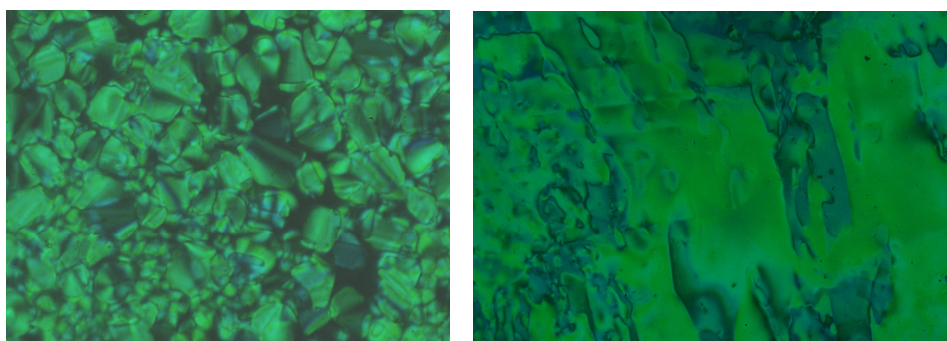

Fig 3. Polarising optical microscopic textures for Columnar hexagonal (left) and nematic (right) mesophases.

Mesophase behaviour of the Pc derivatives has been investigated using polarising optical microscopy (POM) and differential scanning calorimetry (DSC), and the results are summarized

within Scheme 1. POM in particular provides a reliable and simple method for identifying the discotic mesophases and two representative images from the present work are shown in Fig 3 for the columnar hexagonal phase and the discotic nematic phase (Schlieren texture). The nematic mesophase is further characterized by its low viscosity compared to its columnar counterpart. The table within Scheme 1 illustrates how structural features of the Pcs, i.e. chain length of the six alkyl chains (R in structure C) and the length of the hydroxyalkyl chain, govern mesophase formation and the type of mesophase that is generated. Thus two examples bearing six butyl groups are non-liquid crystalline indicating that chains longer than these are essential for liquid crystallinity within the series. The liquid crystalline Pcs fall into two categories. On cooling from the isotropic liquid the majority follow the normal trend for Pcs in that they form columnar mesophases. Columnar hexagonal, Col_h, are solely formed for all such metal-free derivatives. Characteristic textures are formed (Fig 3) that persist until a second transition occurs at lower temperatures. In some samples crystallization is clear, while others form a glassy phase where the viscosity of the system leads to partial crystallization and glass formation (denoted as X). The second category comprises a smaller subset of derivatives that display nematic mesophase behaviour on cooling. Again the nature of this low-viscosity phase is easily identified from POM. To the best of our knowledge this set of derivatives are the only Pcs known to form nematic phases and it is clear that the structural features leading to their formation are subtle and balanced. The hydrophilic end group of the hydroxyalkyl substituent is important for promoting formation of the nematic mesophase within this series of compounds. A related derivative where a $C_{12}H_{25}$ group replaces the $(CH_2)_{11}OH$ chain of compound **6** forms exclusively columnar mesophases.[26] Thus the presence of the terminal hydroxyl group is essential for promoting the nematic mesophase but it is only observed in a select subset of examples. Evidently, the relative lengths of the R chains and the hydroxyalkyl chain play a role in governing the type of mesophase that is formed. In those Pcs where the core-core separation in the columnar (Col) arrangement (ca. 2 x length of the R chains) is as long as, or longer than, the hydroxyalkyl chain, then the latter can be accommodated within the columnar assembly and may even allow for the OH group in a fully extended chain to hydrogen bond to the aza-bridge of a Pc molecule in an adjacent column. However, lengthening the link to the hydroxyl group disturbs this arrangement, potentially forcing a buckling of the chain or forcing the hydroxyl group into the hydrophobic interstitial region of the columnar stack. In such a situation the columnar arrangement will no longer favoured and formation of a nematic mesophase can be rationalised. Data for the copper and zinc metallated compounds, **15** and **16** respectively, are also instructive. The zinc centre in **16** provides a further option for interation with the OH function and is found to raise both the Cr – N_D and N_D – I transition temperatures relative to the metal-free analogue **5**. Copper at the centre of the core of the Pc is more interesting. It is known to stabilise very significantly columnar

mesophase assemblies of octaalkyl substituted Pcs, i.e extend the mesophase temperature range, through what are presumed to be interactions with the ring nitrogen atoms. Thus, unlike compounds **5** and **16**, the copper metallated analogue **15** forms exclusively columnar mesophases.

3. Conclusion

The study has demonstrated how a particular set of substituents on the phthalocyanine nucleus can promote formation of the rare discotic nematic mesophase N_D. Mesophase behaviour is induced by introduction of a relatively long hydroxyalkyl substituent at one of the non-peripheral sites along with six shorter alkyl chains and a methyl group at the remaining seven non-peripheral positions. Most examples of the fourteen metal-free phthalocyanine derivatives exhibit the more familiar columnar mesophases. However, it has been demonstrated that the nematic mesophase is formed when the hydroxyalkyl chain is longer than the natural separation between cores in the columnar arrangement, a separation that is governed by the length of the six common alkyl chains. Two metallated derivatives of a metal-free derivative that exhibits the N_D mesophase have also been investigated. The zinc metallated analogue provides a further example of a nematic discotic liquid crystal. However, the corresponding copper metallated derivative forms exclusively columnar mesophases. Factors such as molecular packing and local interactions drive self-assembly in discotic systems and it is apparent that subtle balance within narrow parameters is required to favour nematic assembly over the more frequently encountered columnar mesophase formation.

4. Experimental

4.1 General Equipment

Melting points were recorded using an Olympus BH-2 polarising microscope in conjunction with a Linkham TMS 92 thermal analyser with a Linkham THM 600 cell, and were not corrected. Infra-red spectra were recorded on a Perkin-Elmer 597 spectrophotometer. UV-visible spectra were measured using a Hitachi U-3000 spectrophotometer fitted with a red sensitive detector. NMR spectra were recorded on a Jeol EX-270 spectrometer (270 MHz). Routine mass spectra were obtained using a Kratos MS 25 mass spectrometer. MALDI-MS were obtained using 2,5-dihydroxybenzoic acid as a matrix and measured on a Kratos KOMPACT MALDI III spectrometer.

4.2 Synthesis

The synthesis of 3,6-bis(alkyl)phthalonitriles has been described elsewhere.[17,29]

The synthesis of unsymmetrically substituted phthalocyanines **3-6** has been recently communicated[26] and further 1,4,8,11,15,18-hexakis(alkyl)-22-methyl-25-(n-hydroxyalkyl)

phthalocyanines were similarly obtained. In a typical procedure, the individual 3-methyl-6-hydroxyalkylphthalonitriles above (1 mmol) were separately reacted with 3,6-bis(alkyl)phthalonitrile, (9 mmol) in a solution of 1-pentanol (25 ml) heated under reflux to which was slowly added lithium metal (0.30 g, 9 mmol). The reaction mixture was heated under reflux for 18 h and protected from atmospheric moisture by a $CaCl_2$ drying tube. The reaction was cooled to rt and glacial acetic acid added. The solution was stirred for 30 min. The solvents were removed by distillation under reduced pressure and the product chromatographed twice over silica. The first partial separation was achieved by elution first with petrol and then THF. The green components were then collected and chromatographed again (eluent cyclohexane, followed by cyclohexane/THF 2:1 by volume) which achieved separation of the 1,4,8,11,15,18-hexakis(alkyl)-22-methyl-25-(hydroxyalkyl)phthalocyanine from 1,4,8,11,15,18,22,25-octakis(alkyl) phthalocyanine and other minor products. ^{1}H NMR spectra were concentration and temperature dependent due to aggregation which also prevented acquisition of useful 13C NMR data. The protocol provided the following derivatives:

1,4,8,11,15,18-Hexakis(butyl)-22-methyl-25-(11-hydroxyundecyl)phthalocyanine (**1**)
[Yield 38%. Found C, 78.84; H, 8.68; N, 10.58%. $C_{68}H_{90}N_8O$ requires: C, 78.87; H, 8.76; N, 10.82%. IR (cm^{-1}) 760, 1024, 2854, 2924, 3293. ^{1}H NMR (270 MHz, C_6D_6, 2.0 mM, 23°C): δ, ppm -0.58 (2H, s), 0.96–2.32 (60H, m), 3.26 (2H, t, J 6Hz), 3.63 (3H, s), 4.35 (2H, t, J 8Hz), 4.49-4.69 (12H, m), 7.53 (1H, d), 7.64–7.73 (3H, m), 7.81 (4H, s). UV-vis (cyclohexane): λ, nm (log ε) 727 (5.1), 691 (5.02), 663 (4.6), 629 (4.41), 358 (4.72), 310 (4.61)].

1,4,8,11,15,18-Hexakis(butyl)-22-methyl-25-(12-hydroxydodecyl)phthalocyanine (**2**)
[Yield 11%. Found C, 79.01; H, 8.94; N, 10.40%. $C_{69}H_{92}N_8O$ requires: C, 78.96; H, 8.84; N, 10.68%. IR (cm^{-1}) 760, 1024, 2852, 2924, 3293. ^{1}H NMR (270 MHz, C_6D_6, 2.0 mM, 23°C): δ, ppm -0.59 (2H, s), 0.96–1.79 (48H, m), 2.06-2.32 (14H, m), 3.26-3.30 (2H, m), 3.55 (1H, s), 3.63 (3H, s), 4.34 (2H, t, J 7Hz), 4.49-4.69 (12H, m), 7.52 (1H, d), 7.64–7.73 (3H, m), 7.82 (4H, s). UV-vis (cyclohexane): λ, nm (log ε) 727 (5.08), 691 (5.0), 664 (4.57), 629 (4.38), 356 (4.69), 310 (4.59)].

1,4,8,11,15,18-Hexakis(hexyl)-22-methyl-25-(10-hydroxydecyl)phthalocyanine (**7**)
[Yield 30%. Found C, 79.86; H, 9.61; N, 9.24%. $C_{79}H_{112}N_8O$ requires: C, 79.75; H, 9.49; N, 9.42%. IR (cm^{-1}) 760, 1022, 2855, 2924, 3297. ^{1}H NMR (270 MHz, C_6D_6, 2.0 mM, 23°C): δ, ppm -0.69 (2H, s), 0.83–0.95 (18H, m), 1.11-1.83 (50H, m), 2.06-2.36 (14H, m), 3.23-3.29 (2H, m), 3.60 (3H,

s), 4.27 (2H, t, J 8Hz), 4.49-4.72 (12H, m), 7.51 (1H, d), 7.62–7.71 (3H, m), 7.84 (4H, s). UV-vis (cyclohexane): λ, nm (log ε) 728 (5.11), 692 (5.03), 664 (sh), 629 (4.43), 357 (4.73), 310 (4.63)].

1,4,8,11,15,18-Hexakis(hexyl)-22-methyl-25-(11-hydroxyundecyl)phthalocyanine (**8**)
[Yield 17%. Found C, 79.81; H, 9.52; N, 9.12%. $C_{80}H_{114}N_8O$ requires: C, 79.82; H, 9.54; N, 9.31%. IR (cm^{-1}) 760, 1020, 2853, 2924, 3295. ^{1}H NMR (270 MHz, C_6D_6, 2.0 mM, 23°C): δ, ppm -0.79 (2H, s), 0.84–0.95 (18H, m), 1.14-1.81 (52H, m), 2.03-2.35 (14H, m), 3.25-3.30 (2H, m), 3.52 (3H, s), 4.18 (2H, t, J 7Hz), 4.42-4.70 (12H, m), 7.44 (1H, d), 7.57–7.67 (3H, m), 7.83-7.84 (4H, m). UV-vis (cyclohexane): λ, nm (log ε) 728 (5.11), 692 (5.03), 664 (4.6), 629 (4.41), 356 (4.72), 310 (4.61). m/z 1204 [M$^+$]].

1,4,8,11,15,18-Hexakis(hexyl)-22-methyl-25-(12-hydroxydodecyl)phthalocyanine (**9**)
[Yield 44%. Found C, 79.84; H, 9.57; N, 8.91%. $C_{81}H_{116}N_8O$ requires: C, 79.88; H, 9.60; N, 9.20%. IR (cm^{-1}) 760, 1020, 2853, 2924, 3297. ^{1}H NMR (270 MHz, C_6D_6, 2.0 mM, 23°C): δ, ppm -0.68 (2H, s), 0.83–0.94 (18H, m), 1.12-1.83 (54H, m), 2.06-2.36 (14H, m), 3.25-3.30 (2H, m), 3.61 (3H, s), 4.27 (2H, t, J 7Hz), 4.49-4.72 (12H, m), 7.50 (1H, d), 7.62–7.69 (3H, m), 7.85 (4H, s). UV-vis (cyclohexane): λ, nm (log ε) 728 (5.09), 691 (5.01), 665 (4.6), 629 (4.41), 356 (4.71), 310 (4.60)].

1,4,8,11,15,18-Hexakis(heptyl)-22-methyl-25-(10-hydroxydecyl)phthalocyanine (**10**)
[Yield 6%. Found C, 79.80; H, 9.86; N, 8.50%. $C_{85}H_{124}N_8O$ requires: C, 80.14; H, 9.81; N, 8.80%. IR (cm^{-1}) 760, 1022, 2853, 2924, 3297. ^{1}H NMR (270 MHz, C_6D_6, 2.0 mM, 23°C): δ, ppm -0.58 (2H, s), 0.8–0.9 (18H, m), 1.13-1.78 (62H, m), 2.22-2.35 (14H, m), 3.26 (2H, t, J 6Hz), 3.68 (3H, s), 4.32-4.39 (2H, m), 4.56-4.73 (12H, m), 7.57 (1H, d), 7.67–7.74 (3H, m), 7.86 (4H, s). UV-vis (cyclohexane): λ, nm (log ε) 728 (5.09), 692 (5.01), 665 (4.58), 629 (4.4), 357 (4.71), 310 (4.60)].

1,4,8,11,15,18-Hexakis(heptyl)-22-methyl-25-(11-hydroxyundecyl)phthalocyanine (**11**)
[Yield 12%. Found C, 80.24; H, 9.86; N, 8.45%. $C_{86}H_{126}N_8O$ requires: C, 80.20; H, 9.86; N, 8.70%. IR (cm^{-1}) 760, 1020, 2853, 2924, 3297. ^{1}H NMR (270 MHz, C_6D_6, 2.0 mM, 23°C): δ, ppm -0.71 (2H, s), 0.81–0.95 (18H, m), 1.15-1.80 (64H, m), 2.08-2.32 (14H, m), 3.28 (2H, t, J 7Hz), 3.60 (3H, s), 4.23-4.27 (2H, m), 4.48-4.73 (12H, m), 7.50 (1H, d), 7.62–7.71 (3H, m), 7.85 (4H, s). UV-vis (cyclohexane): λ, nm (log ε) 728 (5.09), 692 (5.01), 664 (4.59), 629 (4.41), 358 (4.71), 310 (4.61)].

1,4,8,11,15,18-Hexakis(heptyl)-22-methyl-25-(12-hydroxydodecyl)phthalocyanine (**12**)

[Yield 21%. Found C, 80.14; H, 9.86; N, 8.39%. $C_{87}H_{128}N_8O$ requires: C, 80.26; H, 9.91; N, 8.61%. IR (cm^{-1}) 760, 1020, 2853, 2922, 3297. ^{1}H NMR (270 MHz, C_6D_6, 2.0 mM, 23°C): δ, ppm -0.71 (2H, s), 0.81–0.95 (18H, m), 1.14-1.83 (66H, m), 2.09-2.36 (14H, m), 3.29 (2H, t, J 6Hz), 3.54-3.60 (4H, m), 4.23-4.28 (2H, m), 4.47-4.72 (12H, m), 7.50 (1H, d), 7.62–7.68 (3H, m), 7.85 (4H, s). UV-vis (cyclohexane): λ, nm (log ε) 728 (5.11), 692 (5.03), 665 (4.61), 629 (4.43), 357 (4.73), 310 (4.62)].

1,4,8,11,15,18-Hexakis(octyl)-22-methyl-25-(11-hydroxyundecyl)phthalocyanine (**13**)
[Yield 24%. Found C, 80.30; H, 10.23; N, 8.02%. $C_{92}H_{138}N_8O$ requires: C, 80.53; H, 10.14; N, 8.17%. IR (cm^{-1}) 760, 1022, 2853, 2922, 3297. ^{1}H NMR (270 MHz, C_6D_6, 2.0 mM, 23°C): δ, ppm -0.70 (2H, s), 0.83–0.93 (18H, m), 1.13-1.84 (76H, m), 2.09-2.37 (14H, m), 3.28 (2H, t, J 6Hz), 3.60 (3H, s), 4.24-4.26 (2H, m), 4.48-4.73 (12H, m), 7.50 (1H, d), 7.63–7.69 (3H, m), 7.86 (4H, s). UV-vis (cyclohexane): λ, nm (log ε) 728 (5.08), 692 (5.0), 664 (sh), 629 (4.41), 357 (4.71), 310 (4.61)].

1,4,8,11,15,18-Hexakis(octyl)-22-methyl-25-(12-hydroxydodecyl)phthalocyanine (**14**)
[Yield 26%. Found C, 80.56; H, 10.01; N, 7.84%. $C_{93}H_{140}N_8O$ requires: C, 80.58; H, 10.18; N, 8.08%. IR (cm^{-1}) 760, 1020, 2853, 2922, 3297. ^{1}H NMR (270 MHz, C_6D_6, 2.0 mM, 23°C): δ, ppm -0.70 (2H, s), 0.80–0.93 (18H, m), 1.14-1.83 (78H, m), 2.10-2.36 (14H, m), 3.29 (2H, t, J 6Hz), 3.60 (3H, s), 4.22-4.28 (2H, m), 4.51-4.73 (12H, m), 7.51 (1H, d), 7.62–7.72 (3H, m), 7.86 (4H, s). UV-vis (cyclohexane): λ, nm (log ε) 728 (5.08), 692 (5.0), 664 (4.58), 628 (4.40), 357 (4.71), 310 (4.61)].

1,4,8,11,15,18-Hexakis(pentyl)-22-methyl-25-(11-hydroxyundecyl)phthalocyaninato copper (**15**)
[Yield 30%. Found C, 75.07; H, 8.65; N, 9.26%. $C_{74}H_{100}N_8OCu$ requires: C, 75.25; H, 8.53; N, 9.49%. IR (cm^{-1}) 1091, 1175, 1325, 2855, 2924. UV-vis (cyclohexane): λ, nm (log ε) 704 (5.16), 671 (sh), 636 (4.66), 344 (4.74), 309 (4.61). m/z 1181 [M$^+$]].

1,4,8,11,15,18-Hexakis(pentyl)-22-methyl-25-(11-hydroxyundecyl)phthalocyaninato zinc (**16**)
[Yield 57%. Found C, 75.17; H, 8.63; N, 9.27%. $C_{74}H_{100}N_8OZn$ requires: C, 75.13; H, 8.52; N, 9.47%. IR (cm^{-1}) 1094, 1167, 1323, 2855, 2924. ^{1}H NMR (270 MHz, C_6D_6, 2.0 mM, 23°C): δ, ppm -2.28 (1H, s), -0.58--0.45 (2H, m), -0.3--0.18 (2H, m), 0.65-1.85 (56H, m), 2.15-2.50 (14H, m), 3.74 (3H, s), 4.42 (2H, m), 4.52-4.89 (12H, m), 7.51 (1H, d), 7.61–7.72 (3H, m), 7.88-7.95 (4H, m). UV-vis (cyclohexane): λ, nm (log ε) 699 (5.22), 669 (4.43), 630 (4.45), 344 (4.62), 309 (4.52). m/z 1183 [M$^+$]].

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