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The Self-Ordering Properties of Novel Phthalocyanines with Out-of-Plane Alkyl Substituents

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Abstract: Two novel homologous series of phthalocyanines were prepared from 2,2-dialkylindane and 2,2-dialkyl-1,3-benzodioxole precursors. It was anticipated that attaching alkyl chains to five-membered rings, fused to the peripheral sites of the phthalocyanine ring, would result in the adoption of an out-of-plane configuration and thereby discourage cofacial aggregation, to provide an analogy with picket-fence porphyrins. This strategy proved partially successful. Some members of the series of phthalocyanines derived from 2,2-dialkyl-1,3-benzodioxoles, in which the alkyl chains are linked to the phthalocyanine via a cyclic ketal, form spin-coated thin films in which the phthalocyanine cores are perfectly isolated. This behaviour is associated with the formation of a disordered crystal that appears as a mesophase in the thermal profile of these materials. However, the phthalocyanines derived from 2,2-dialkylindanes display a columnar mesophase over a wide temperature range, with some liquid crystalline derivatives at ambient temperature. A single-crystal X-ray diffraction structure of the octahexyl derivative of this series shows how the columnar assembly accommodates the out-of-plane alkyl chains by tilting the macrocyclic plane of the phthalocyanine components with respect to the axis of the column. This study helps to emphasise the importance of both the steric and electronic effects of substituents on the packing behaviour of phthalocyanines in the condensed phase, and especially the role of electron-donating oxygen atoms directly attached to the ring.

Keywords: dyes/pigments · liquid crystals · phthalocyanines · self-assembly · thin films

Introduction

Phthalocyanine (Pc) and its derivatives constitute one of the most studied classes of organic functional materials.[1] In addition to their widespread use as blue and green colourants, phthalocyanines are of increasing interest for applications in nonlinear optics (including optical limitation),[2] xerography (as photoconductors),[3] liquid-crystalline electronic charge carriers[4] and exciton-transport materials,[5] optical data storage (as the laser absorption layer within recordable discs),[6] photodynamic cancer therapy,[7] solar energy conversion,[8] catalysis[9] and as the active component of gas sensors.[10] For most of these applications, not only are the molecular properties of importance (e.g., λ_{max}) but also the way in which these properties are influenced by intermolecular interactions. Hence, the packing of the disc-shaped macrocycles in the condensed state needs to be understood and controlled.

By placing long alkyl (Pc series **1**)[11,12] or alkoxy (Pc series **2**)[11,13] side chains on the peripheral positions (2,3,9,10,16,17,23,24) of the phthalocyanine ring the solubility is enhanced and leads to liquid-crystalline behaviour in which the aromatic rings assemble into columnar stacks. Derivatives with long alkyl side chains attached to the nonperipheral sites (1,4,8,11,15,18,22,25) also form columnar liquid crystals (Pc series **3**).[14,15] However, nonperipheral substitution with alkoxy side chains (Pc series **4**)[16] does not result in mesogenic phthalocyanines and aggregation of the aromatic cores is suppressed in the solid state.[17] Placing alkoxy groups at the nonperipheral sites also results in a shift of the main absorption band in the visible spectrum

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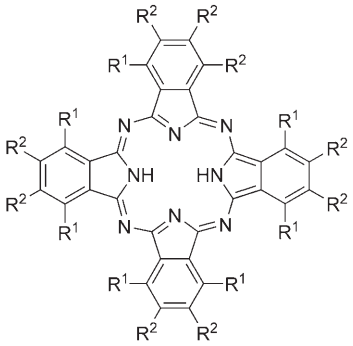
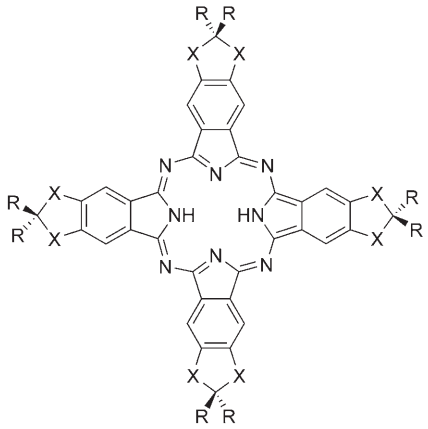


1: R^1 = H, R^2 = C_nH_{n+1}
2: R^1 = H, R^2 = OC_nH_{n+1}
3: R^1 = C_nH_{n+1}, R^2 = H
4: R^1 = OC_nH_{n+1}, R^2 = H



5(C_n): X = CH_2, R = C_nH_{n+1}
6(C_n): X = O, R = C_nH_{n+1}

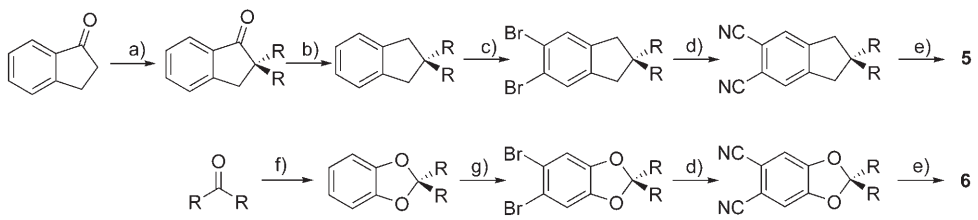
(the Q-band) into the near-IR region so that the phthalocyanines do not display their characteristic strong blue or green colour. In contrast, self-assembly into columnar aggregates broadens and blueshifts the Q-band as a result of exciton interactions.[18,19] Therefore, in order to obtain solid phthalocyanines that demonstrate similar light absorption characteristics to those of their dilute solutions, it was an attractive objective to place alkyl side chains on the macrocycle in such a way as to strongly disfavour aggregation but without perturbing the basic phthalocyanine chromophore.[20,21] The chosen strategy was to attach the alkyl chains to five-membered rings fused to the peripheral sites of the phthalocyanine so that the chains would project out of the molecular plane of the macrocycle and enforce separation through mutual steric interference. It was anticipated that the target phthalocyanines, derived from 2,2-dialkylindanes (Pc series **5**) and cyclic ketals (Pc series **6**), would possess similar characteristics to the well-known picket-fence porphyrins in which substituents prohibit aggregation of the macrocycle and protect functionality.[22]

Results

Synthesis: The synthetic route to the 2,2-dialkylindanes required for Pc series **5** proved to be challenging. Base-catalysed dialkylation of 1-indanone was achieved in moderate yield by following a literature method.[23] However, the reduction of the 2,2-dialkyl-1-indanone was sluggish under a variety of conditions (Wolf–Kishner, palladium-catalysed hydrogenation), presumably owing to steric hindrance at the crowded ketone. Ultimately, the best results were obtained from ionic reduction using triethylsilane dissolved in trifluoroacetic acid (TFA).[24] In contrast, owing to the commercial availability of dialkylketones, the 2,2-dialkyl-1,3-benzodioxole precursors to Pc series **6** were prepared much more readily by the simple ketalisation of catechol.[25]

On a laboratory scale, the synthesis of metal-free phthalocyanines is best achieved by the cyclotetramerisation of a phthalonitrile precursor by using, for example, a refluxing mixture of lithium pentyloxide in *n*-pentanol.[26] The required phthalonitrile precursors to Pc series **5** and **6** were prepared from the 2,2-dialkylindane and 2,2-dialkyl-1,3-benzodioxole intermediates, respectively, by bromination followed by substitution of the bromide by nitrile by using the Rosenmund–von Braun reaction (Scheme 1).[11] Bromination of the 2,2-dialkyl-1,3-benzodioxoles using *N*-bromosuccinimide (NBS) in DMF[27] was successfully achieved without cleavage of the cyclic ketal, which accompanied the attempted reaction with molecular bromine. Generally, members of Pc series **6** were isolated in greater yields (10–25%) than those of **5** (3–10%) from the phthalocyanine-forming reaction as a result of their greater tendency to recrystallise (from acetone), which facilitated efficient purification.

Molecular properties: All of the phthalocyanines in series **5** and **6** are highly soluble in common organic solvents (e.g., hexane, toluene, dichloromethane, THF) at room temperature, whereas the phthalocyanines of series **1** and **2**, in which the alkyl chains are directly linked to the peripheral sites, are only sparingly soluble in the same solvents at room temperature. This enhanced solubility is similar to that displayed by the members of Pc series **3** and **4**. Also, in con-



Scheme 1. The synthesis of phthalocyanine series **5** and **6**. Reagents and conditions: a) RBr, *t*BuOK, toluene, 80°C, 4 h; b) Et_3SiH, TFA, 80°C, 48 h; c) Br_2, Fe, I_2, CH_2Cl_2, 20°C, 2 h; d) CuCN, DMF, 140°C, 18 h; e) Li, 1-pentanol, reflux, 10 h; f) catechol, *p*-TSA, toluene, reflux, 48 h; g) NBS, DMF, 20°C, 48 h.

trast to Pc series **1** and **2**, the effects of aggregation (i.e., spectral peak broadening and shifts) are not observed from ^{1}H NMR and UV-visible absorption spectra for solutions of up to 1×10^{-4} mol mL^{-3} concentrations. The UV-visible absorption spectra of Pc series **5** and **6** are very similar to those of Pc series **1** and **2**, respectively, with the colour (blue for Pc series **1** and **5**, green for **2** and **6**) being determined by the element (O or C) attached directly to the peripheral site. The green colour of Pc series **1** and **5** is a result of the strong absorption bands in both the red ($\lambda=690$, 650 nm) and blue ($\lambda=430$ nm) regions of the spectrum.

One remarkable characteristic of the members of Pc series **6** is the resistance of their ketal groups towards hydrolysis. Generally, cyclic ketals are hydrolysed in dilute aqueous acid. However, even the application of strongly acidic conditions over prolonged periods does not result in removal of the cyclic ketals. Indeed, the hydrolytic destruction of the phthalocyanine core takes place prior to ketal removal. This behaviour is related to the well-documented basicity of the phthalocyanine ring, which is protonated in preference to the ketal oxygen atoms. Similar hydrolysis-resistant ketals that contain basic functional groups are known.[28]

Condensed-state properties: Pc series **5** and **6** display very different condensed-phase properties. Thermal analysis of Pc series **5**(C_6–C_{12}) by using polarising optical microscopy (POM) and differential scanning calorimetry (DSC) revealed that each derivative forms a birefringent mesophase over a very large temperature range and that the longer-chained derivatives (C_9–C_{12}) are liquid crystals at room temperature (Table 1). The observed focal conic optical texture can be unambiguously assigned to the hexagonal columnar mesophase that is commonly encountered in the thermal behaviour of alkylated phthalocyanines (e.g., Pc series **1**–**3**).[1,11–15,17,29] The UV-visible absorption spectrum of a spin-coated film of Pc **5**(C_9) displays a λ_{max} of 620 nm (Figure 1), which is consistent with a blueshifted Q-band owing to the formation of an extended cofacial stack of phthalocyanine molecules, as would be expected for a columnar mesophase.[19,21] In the context of the objectives of the molecular design, it is perhaps surprising that columnar self-assembly is demonstrated for these derivatives, as the arrangement of the alkyl chains was expected to hinder cofacial self-association. A single-crystal X-ray diffraction (XRD) study of Pc **5**(C_6) gave a clear insight into the columnar molecular arrangement formed by this series (Figure 2). Of the eight hexyl chains, five are oriented out of the plane of the phthalocyanine core, as intended. However, the out-of-plane chains do not disrupt the columnar self-association of the phthalocyanine cores owing to the severe tilt (45°) of the macrocyclic plane of the molecules relative to the stacking direction and the 30° twist of each molecule relative to its neighbour, so that there is a repeat unit of three phthalocyanines along the stack. Similar tilted stacks are inferred from the results of powder XRD studies of the hexagonal columnar mesophase displayed by members of Pc series **1**.[30]

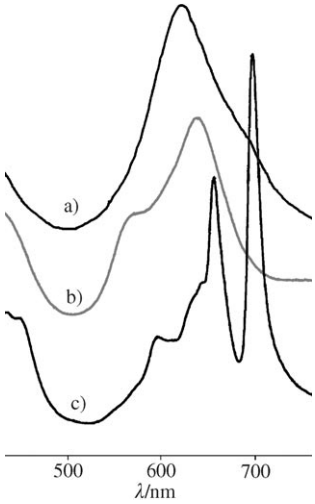


Figure 1. UV-visible absorption spectra of spin-coated films of a) Pc **5**(C_9), b) Pc **6**(C_{12}) and c) Pc **6**(C_9) after annealing at 150 °C.

As expected, short-chained Pc **6**(C_2) forms a microcrystalline solid, which does not undergo any thermal phase transition below its decomposition temperature ($\approx$350 °C). POM and DSC analyses show that long-chained Pcs **6**(C_{11} and C_{12}) melt from waxy malleable solids into fluid isotropic liquids at 87 and 49 °C, respectively. The medium-length Pcs **6**(C_5–C_{10}) are highly unusual in that they form large, square crystals (up to $5\times5\times0.1$ mm), which on heating, melt firstly into a highly viscous mesophase and then undergo a second transition to the fluid isotropic liquid (Table 1). Neither the solid crystals nor the mesophase appear birefringent but, on cooling the isotropic phase below the clearing point, air bubbles trapped within the thin film of the melt become polygonal. Despite the size and apparent quality of the large square crystals, and many attempts, X-ray crystallographic analysis failed as a consequence of poor diffraction as-

Table 1. The thermal transition temperatures (in °C) for members of phthalocyanine series **1**–**6** as measured by using polarising microscopy and differential thermal calorimetry.[a,b]

	Series **1**[12]		Series **2**[13]		Series **3**[14]		Series **4**[16]	Series **5**		Series **6**	
	K–Col_h	Col_h–I	K–Col_h	Col_h–I	K–Col_h	Col_h–I	K–I	K–Col_h	Col_h–I	K–M_x	M_x–I
C_6	250	363	119	>350	161	171	86	240	>350	177	325
C_7	–	–	104	>350	113	163	77	160	>350	150	240
C_8	186	325	94	>350	85	152	66	75	350	145	199
C_9	–	–	101	>350	103	142	50	<0	310	139	172
C_{10}	163	283	94	345	78	133	51	<0	280	109	123
C_{11}	–	–	83	334	–	–	–	<0	240	K-I	87
C_{12}	120	253	83	309	–	–	53	<0	185	K-I	49

[a] K = crystal; Col_h = hexagonal columnar liquid crystal; I = isotropic liquid; M_x = unknown mesophase—probably a disordered crystal. [b] Thermal degradation occurs above 350 °C. Thermal transitions were not measured below 0 °C.

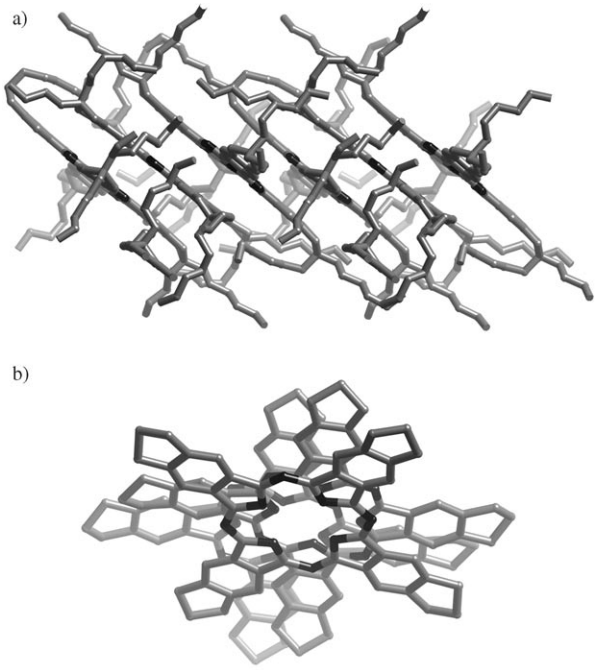


Figure 2. XRD structure from a single crystal of Pc **5**(C_6): a) the tilted arrangement of phthalocyanines relative to the axis of the columnar stack (*x* axis of crystal) that facilitates the accommodation of the out-of-plane alkyl chains; b) a view down the axis of the columnar stack, with alkyl chains removed for clarity, showing the trimeric repeat unit that forms the stacks.

sociated with the thin axis of the crystal. However, some information on packing within the crystal of the Pc series **6**-(C_5–C_{10}) is obtained from analysis of the diagnostic Q-band of the UV-visible absorption spectra obtained from spin-coated films (Figure 1). Spectra derived from as-deposited films indicate that the film contains a mixture of isolated molecules (λ_{max} = 690 and 655 nm) together with cofacial dimers (λ_{max} = 635 nm). However, films heated above the initial melting point of the phthalocyanine display spectra that are identical to those of isolated molecules obtained from a dilute solution (λ_{max} = 690 and 655 nm). Therefore, it appears that the phthalocyanines adopt an isolated arrangement in the crystal form of these materials. Similar analysis of the low-melting, long-chained members of series Pc **6**(C_{11} and C_{12}) give spectra characteristic for discrete cofacial dimers (λ_{max} = 635 nm). Therefore, the isolated solid form of Pc series **6**(C_5–C_{10}) appears to be intrinsically related to the manifestation of the mesophase.

Discussion

This work confirms that the occurrence and stability of columnar self-assembled alkyl-substituted phthalocyanines is influenced strongly by the manner in which the alkyl chains are connected to the macrocycle. Molecular modelling calculations suggest that the mutual steric interactions of the adjacent methylene linking groups of Pc series **1** encourage the peripheral alkyl chains to lie out of the plane of the Pc ring, whereas the relatively small alkoxy linking groups of Pc Series **2** allows the side chains to sit comfortably in the plane of the macrocycle.[13] This conformational difference is consistent with the lower clearing temperatures (> 50 °C) for Pc series **1** relative to those of series **2** (Table 1 and Figure 3) and has been held responsible for the tilted arrangement of the phthalocyanines within the columnar stack of the mesophases formed by Pc series **1**.

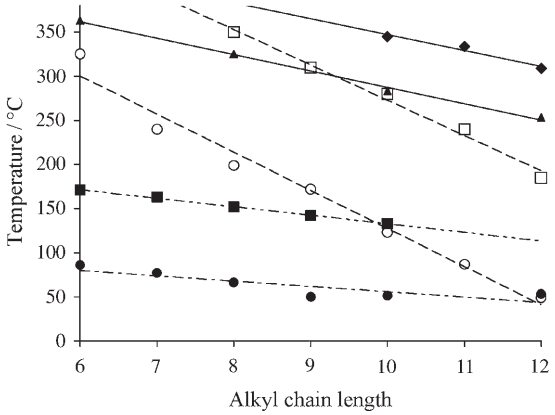


Figure 3. The transition temperatures at which the isotropic liquid is formed on heating Pc series **1**–**6** (i.e., clearing temperatures for Pc series **1**–**3**, **5** and Pc **6**(C_6–C_{10}) and melting points for Pc series **4** and Pc **6**(C_{11} and C_{12})). Pc series: **1** (▲); **2** (◆); **3** (■); **4** (●); **5** (□); **6** (○).

For Pc series **3** and **4**, the strongest steric interactions involving the nonperipheral side chains are between the chains on neighbouring benzo moieties. These interactions result in the displacement of the side chains from the plane of the Pc ring. This effect is clearly evident in the crystal structures of members of these series[31] and explains the much lower clearing temperatures (>150 °C) of Pc series **3** relative to those of series **1** (Figure 3). The members of Pc series **4** melt directly from the crystal to the isotropic liquid at low temperatures (45–85 °C) without the formation of a columnar mesophase.[16] This behaviour has been ascribed to the combined effect of the mutual steric interference of the nonperipheral side chain and the modulation of the attractive π--π intermolecular interactions as a result of the electron-donating effect of the eight oxygen atoms directly attached to the macrocycle.[1,17,21,32]

Based on the clearing temperatures of the hexagonal columnar mesophase of the members of series **1**, **3** and **5** (Figure 3), it can be concluded that the strategy of reducing phthalocyanine cofacial association by attaching alkyl chains to a five-membered carbon ring fused to the periphery of the macrocycle (series **5**) is no more efficient than the direct attachment of the chains at the peripheral sites (series **1**). Indeed, by placing the alkyl chains at the nonperipheral sites (series **3**), a much greater destabilising effect on the thermal stability of the columnar mesophase appears to be induced. However, crystallisation of the mesophase is suppressed in Pc series **5** so that longer-chained members dis-

play a stable columnar mesophase at room temperature, which may be a useful property (Table 1).

A similar comparison of the phthalocyanines with oxygen atoms directly attached to the ring (Pc series **2**, **4** and **6**) shows that members of novel Pc series **6** do not form columnar assemblies, which is in stark contrast to the behaviour of series **2** but mirrors the behaviour of series **4**. For both series **4** and **6**, the out-of-plane configuration of the alkyl chains must combine with the electronic effect of the oxygen atoms, linked directly to the macrocycle, to discourage cofacial association. The unexpected thermal behaviour of series **6**(C_6–C_{10}) appears to be related to the ease of formation of a disordered crystal in which the out-of-plane alkyl chains act as efficient spacers between the neighbouring macrocycles. Based upon the distinct square-shaped crystals formed by these compounds, it is tempting to suggest a planar tetragonal arrangement of the phthalocyanines separated by a layer of disordered alkyl chains with only loose structural correlation between the planar arrays. The difference between the crystalline and mesophase state of these phthalocyanines may be related only to the mobility of the alkyl chains (i.e., the mesophase is a disordered crystal). It is notable that the change in enthalpy for the transition from crystal to mesophase is only a few $kJ\,mol^{-1}$ for Pc series **6**, whereas for Pc series **2** the crystal to columnar mesophase transition is associated with a much larger enthalpy change (70–100 $kJ\,mol^{-1}$) consistent with the melting of highly ordered alkyl chains.[13] Further structural characterisation of the highly disordered crystals formed by Pc series **6** is required.

An interesting observation can be made regarding the transition temperature at which each phthalocyanine forms an isotropic melt (Figure 3). For each pair of series in which the alkyl side chains are attached to the phthalocyanine at the same sites (i.e., series **1** and **2**, series **3** and **4**, series **5** and **6**) and which, therefore, differ only in the group directly attached to the ring (i.e., O or CH_2), the transition temperature trend lines are parallel. Each additional methylene unit on the alkyl chains causes an average reduction in the transition temperature of 18 °C for peripheral substitution (series **1** and **2**), 9 °C for nonperipheral substitution (series **3** and **4**) and 42 °C for linking the alkyl chain to the phthalocyanine via a fused ring (series **5** and **6**). The much greater destabilising effect on phthalocyanine self-assembly per additional methylene unit for series **5** and **6** is consistent with an out-of-plane conformation of the alkyl chains.

Conclusion

The strategy to discourage cofacial aggregation of the phthalocyanine macrocycle by attaching alkyl side chains to a five-membered ring fused to the peripheral sites of the macrocycle proved partially successful. Pc series **6**(C_6–C_{10}), where the alkyl chains are linked to the phthalocyanine via a cyclic ketal, form thin-films in which the phthalocyanine cores are perfectly isolated. This behaviour is associated with the formation of a disordered crystal that appears as a mesophase in the thermal profile of these materials. However, similar phthalocyanines derived from 2,3-dialkylindanes (Pc series **5**) form columnar liquid crystals of similar thermal stability to derivatives in which the alkyl chains are linked directly to the peripheral sites of the ring. A single-crystal XRD structure shows how the columnar assembly formed by these derivatives accommodates the alkyl chains by drastically tilting the macrocyclic plane of the phthalocyanine components with respect to the axis of the column. This study helps to emphasise the importance of both steric and electronic effects of substituents on the packing behaviour of phthalocyanines in the condensed phase.

Experimental Section

^{1}H NMR spectra (300 MHz) were recorded by using an Inovo 300 spectrometer. IR spectra were recorded on an ATI Mattson Genesis Series FTIR instrument (KBr/Germanium beam splitter). Elemental analyses were obtained by using a Carlo Erba Instruments CHNS-O EA 108 Elemental Analyser. MALDI mass spectra were obtained by using a Micro-Mass Tofspec 2E spectrometer. UV-visible spectra were recorded on a Shimadzu UV-260 spectrometer. All solvents were dried and purified as described in ref. [33]. All materials were placed under vacuum at 100 °C for 18 h as the final step of purification. Intermediates that gave viscous oils were used in the next step without purification—details of their synthesis are given in the Supporting Information.

Pc 5(C_{12}): Lithium metal (0.02 g, 7 mmol) was added to a stirred solution of 5,6-dicyano-2,2-dodecylindane (0.5 mg, 0.1 mmol) in 1-pentanol (2 mL) at 120 °C under nitrogen. The mixture was stirred at reflux for 10 h. On cooling, acetic acid (2 mL) was added and the reaction was stirred at room temperature for 1 h. Methanol (20 mL) was added, the mixture was stirred for a further 30 min and the solid material was collected by filtration. The product was purified by means of column chromatography using a silica gel column with CH_2Cl_2/hexane as eluent and by recrystallisation from acetone to give a blue waxy solid (35 mg, 7 %). M.p (mesophase–isotropic) 185 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 60 °C): $\delta = -2.05$ (brs, 2H), 0.93 (t, 24H), 1.17–1.60 (m, 160H), 1.75 (brm, 16H), 3.30 (brs, 16H), 8.60 ppm (s, 8H); UV/Vis (CH_2Cl_2): $\lambda_{max} = 700$, 660, 638, 580, 340, 285 nm; MALDI MS: m/z: 2023 [$M^+ + H^+$]; elemental analysis calcd (%) for $C_{140}H_{226}N_8$: C 83.19, H 11.27, N 5.54; found: C 83.11, H 11.90, N 5.47.

The following phthalocyanines were prepared from the appropriate 5,6-dicyano-2,2-dialkylindanes by using a similar procedure.

Pc 5(C_6): 4 % yield; m.p (crystal–mesophase) 250 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 60 °C): $\delta = 0.93$ (t, 24H), 1.0–1.50 (m, 64H), 1.75 (brm, 16H), 3.30 (brs, 16H), 8.60 ppm (s, 8H); UV/Vis (CH_2Cl_2): $\lambda_{max} = 700$, 660, 638, 580, 340, 285 nm; MALDI MS: m/z: 1349 [$M^+ + H^+$]; elemental analysis calcd (%) for $C_{98}H_{130}N_8$: C 81.87, H 9.72, N 8.31; found: C 81.00, H 9.94, N 7.71.

*Crystal data for Pc **5**(C_6)*: Data were collected at 150 K using synchrotron radiation at Daresbury SRS, UK (Station 9.8), on a Siemens SMART CCD diffractometer ($\lambda = 0.6934$ Å) and the structure was solved by direct methods. All calculations were carried out by using the SHELXTL package.[34] Crystal size $0.42 \times 0.12 \times 0.01$ mm; triclinic; space group $P\bar{1}$, $a = 1.57306(16)$, $b = 2.0621(3)$, $c = 2.1527(4)$ nm; $\alpha = 62.462(10)$, $\beta = 82.358(17)$, $\gamma = 86.470(13)$°; $V = 6.1367(15)$ nm^3; $Z = 3$; $\mu(0.6934) = 0.063$ mm^{-1}; 44819 reflections measured; 21369 unique reflections ($R_{int} = 0.0817$); 12988 reflections with $I > 2\sigma(I)$; $R = 0.1194$ and $wR2 = 0.3071$ (observed data); $R = 0.1911$ and $wR2 = 0.3353$ (all data). The asymmetric unit consists of one whole molecule, together with a half molecule from which the complete molecule is generated by inversion. There is disorder in some of the hexyl chains, such that some atoms are disordered over

two sites with occupancies constrained to sum to unity. Non-hydrogen atoms were refined anisotropically, with restraints on the thermal motion of the carbon atoms, except those that were disordered. Hydrogen atoms were included in calculated positions. CCDC-607387 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Pc 5(C_7): 4% yield; m.p (crystal–mesophase) 160°C; ^{1}H NMR (500 MHz, $CDCl_3$, 60°C): δ=0.93 (t, 24H), 1.0–1.55 (m, 80H), 1.75 (brm, 16H), 3.30 (brs, 16H), 8.60 ppm (s, 8H); UV/Vis (CH_2Cl_2): λ_{max}=700, 660, 638, 580, 340, 285 nm; MALDI MS: *m/z*: 1461 [M^++H$^+$]; elemental analysis calcd (%) for $C_{100}H_{146}N_8$: C 82.25, H 10.08, N 7.67; found: C 81.93, H 9.91, N 7.22.

Pc 5(C_8): 10% yield; m.p (crystal–mesophase) 75°C, (mesophase-isotropic) 350°C; ^{1}H NMR (500 MHz, $CDCl_3$, 60°C): δ=0.93 (t, 24H), 1.0–1.55 (m, 96H), 1.75 (brm, 16H), 3.30 (brs, 16H), 8.60 ppm (s, 8H); UV/Vis (CH_2Cl_2): λ_{max}=700, 660, 638, 580, 340, 285 nm; MALDI MS: *m/z*: 1573 [M^++H$^+$]; elemental analysis calcd (%) for $C_{108}H_{162}N_8$: C 82.49, H 10.38, N 7.13; found: C 81.99, H 10.28, N 6.92.

Pc 5(C_9): 3% yield; m.p. (mesophase-isotropic) 310°C; ^{1}H NMR (500 MHz, $CDCl_3$, 60°C): δ=0.93 (t, 24H), 1.0–1.55 (m, 112H), 1.75 (brm, 16H), 3.30 (brs, 16H), 8.60 ppm (s, 8H); UV/Vis (CH_2Cl_2): λ_{max}= 700, 660, 638, 580, 340, 285 nm; MALDI MS *m/z*: 1686 [M^++H$^+$]; elemental analysis calcd (%) for $C_{116}H_{178}N_8$: C 82.70, H 10.65, N 6.65; found: C 82.44, H 10.68, N 6.36.

Pc 5(C_{10}): 8% yield; m.p. (mesophase–isotropic) 280°C; ^{1}H NMR (500 MHz, $CDCl_3$, 60°C): δ=0.93 (t, 24H), 1.0–1.55 (m, 128H), 1.75 (brm, 16H), 3.30 (brs, 16H), 8.60 ppm (s, 8H); UV/Vis (CH_2Cl_2): λ_{max}= 700, 660, 638, 580, 340, 285 nm; MALDI MS *m/z*: 1797 [M^++H$^+$]; elemental analysis calcd (%) for $C_{124}H_{194}N_8$: C 82.98, H 10.88, N 6.24; found: C 82.39, H 10.65, N 6.65.

Pc 5(C_{11}): 4% yield; m.p. (mesophase–isotropic) 240°C; ^{1}H NMR (500 MHz, $CDCl_3$, 60°C): δ=0.93 (t, 24H), 1.0–1.55 (m, 144H), 1.75 (brm, 16H), 3.30 (brs, 16H), 8.60 ppm (s, 8H); UV/Vis (CH_2Cl_2): λ_{max}= 700, 660, 638, 580, 340, 285 nm; MALDI MS: *m/z*: 1909 [M^++H$^+$]; elemental analysis calcd (%) for $C_{132}H_{210}N_8$: C 93.03, H 10.09, N 5.87; found: C 82.34, H 11.51, N 5.70.

The following phthalocyanines were prepared from the appropriate 5,6-dicyano-2,2-dialkyl-1,3-benzodioxole by using a similar procedure.

Pc 6(C_2): 23% yield; m.p. >350°C; ^{1}H NMR (500 MHz, $CDCl_3$, 60°C): δ=−1.85 (brs, 2H), 1.25 (t, 24H), 2.25 (q, 16H), 8.65 ppm (brs, 8H); UV/Vis (toluene): λ_{max}=691, 651, 645, 590, 429, 348 nm; MALDI MS: *m/z*: 915 [M^++H$^+$]; elemental analysis calcd (%) for $C_{52}H_{50}N_8O_8$: C 68.24, H 5.51, N 12.24; found: C 68.32, H 5.55, N 12.15.

Pc 6(C_5): 14% yield; m.p. >350°C; ^{1}H NMR (500 MHz, $CDCl_3$, 60°C): δ=−1.80 (brs, 2H); 1.00 (t, 24H); 1.40–1.45 (brm, 32H), 1.82 (brs, 16H), 2.30 (brs, 16H), 8.35 ppm (s, 8H); UV/Vis (toluene): λ_{max}=690, 653, 645, 595, 430, 350 nm; MALDI MS: *m/z*: 1251 (M^++H$^+$); elemental analysis calcd (%) for $C_{76}H_{98}N_8O_8$: C 72.93, H 7.90, N 8.95; found: C 72.80, H 7.89, N 10.03.

Pc 6(C_6): 21% yield; m.p. 177°C (crystal–mesophase), 325°C (mesophase-I); ^{1}H NMR (500 MHz, $CDCl_3$, 60°C): δ=−1.80 (brs, 2H); 1.00 (t, 24H), 1.40–1.45 (brm, 48H), 1.82 (brs, 16H), 2.30 (brs, 16H), 8.35 ppm (s, 8H); UV/Vis (toluene): λ_{max}=690, 653, 645, 595, 430, 350 nm; MALDI MS: *m/z*: 1363 [M^++H$^+$]; elemental analysis calcd (%) for $C_{84}H_{114}N_8O_8$: C 73.97, H 8.43, N 8.22; found: C 73.80, H 8.15, N 8.10.

Pc 6(C_7): 15% yield; m.p. 150°C (crystal–mesophase), 240°C (mesophase-I); ^{1}H NMR (500 MHz, $CDCl_3$, 60°C): δ=−1.80 (brs, 2H), 1.00 (t, 24H), 1.40–1.45 (brm, 64H), 1.82 (brs, 16H), 2.30 (bs, 16H), 8.35 ppm (s, 8H); UV/Vis (toluene): λ_{max}= 690, 653, 645, 595, 430, 350 nm; MALDI MS: *m/z*: 1475 [M^++H$^+$]; elemental analysis calcd (%) for $C_{92}H_{130}N_8O_8$: C 74.86, H 8.88, N 7.59; found: C 74.30, H 8.65, N 7.22.

Pc 6(C_8): 15% yield; m.p. 145°C (crystal–mesophase), 199°C (mesophase-I); ^{1}H NMR (500 MHz, $CDCl_3$, 60°C): δ=−1.80 (brs, 2H), 0.92 (t, 24H), 1.40–1.45 (brm, 80H), 1.82 (brs, 16H), 2.30 (brs, 16H), 8.35 ppm (s, 8H); UV/Vis (toluene): λ_{max}=690, 653, 645, 595, 430, 350 nm; MALDI MS: *m/z*: 1588 [M^++H$^+$]; elemental analysis calcd (%) for $C_{100}H_{146}N_8O_8$: C 75.60, H 9.28, N 7.05; found: C 75.56, H 9.26, N 7.05.

Pc 6(C_9): 22% yield; m.p. 139°C (crystal–mesophase), 172°C (mesophase-I); ^{1}H NMR (500 MHz, $CDCl_3$, 60°C): δ=−1.75 (brs, 2H), 0.90 (t, 24H), 1.40–1.45 (brm, 96H), 1.82 (brs, 16H), 2.30 (brs, 16H), 8.45 ppm (s, 8H); UV/Vis (toluene): λ_{max}=692, 651, 645, 595, 430, 350 nm; MALDI MS: *m/z* (MALDI): 1811 [M^++H$^+$]; elemental analysis calcd (%) for $C_{108}H_{162}N_8O_8$: C 76.28, H 9.60, N 6.59; found: C 76.49, H 9.71, N 6.75.

Pc 6(C_{10}): 21% yield; m.p. 109°C (crystal–mesophase), 123°C (mesophase-I); ^{1}H NMR(500 MHz, $CDCl_3$, 60°C): δ=−1.45 (brs, 2H), 0.82 (t, 24H), 1.30–1.60 (m, 112H), 2.05 (brs, 16H), 2.36 (brs, 16H), 8.65 ppm (s, 8H); UV/Vis (toluene): λ_{max}=691, 651, 645, 595, 430, 350 nm; MALDI MS: *m/z*: 1700 [M^++H$^+$]; elemental analysis calcd (%) for $C_{116}H_{178}N_8O_8$: C 76.84, H 9.91, N 6.18; found: C 76.77, H 10.00, N 6.19.

Pc 6(C_{11}): 15% yield; m.p. 87°C; ^{1}H NMR (500 MHz, $CDCl_3$, 60°C): δ= −1.45 (brs, 2H), 0.81 (t, 24H), 1.25–1.60 (m, 112H), 2.06 (brs, 16H), 2.38 (brs, 16H), 8.65 ppm (s, 8H); UV/Vis (toluene): λ_{max}=691, 651, 645, 595, 430, 350 nm; MALDI MS: *m/z*: 1825 [M^++H$^+$]; elemental analysis calcd (%) for $C_{124}H_{194}N_8O_8$: C 77.35, H 10.17, N 5.82; found: C 77.45, H 10.31, N 5.76.

Pc 6(C_{12}): 19% yield; m.p. 49°C; ^{1}H NMR (500 MHz, $CDCl_3$, 60°C): δ= −1.46 (brs, 2H), 0.80 (t, 24H), 1.17–1.57 (m, 144H), 1.79 (brs, 16H), 2.25 (brs, 16H), 8.45 ppm (s, 8H); UV/Vis (toluene): λ_{max}=692, 651, 638, 591, 428, 349 nm; MALDI MS: *m/z*: 2037 [M^++H$^+$]; elemental analysis calcd (%) for $C_{132}H_{210}N_8O_8$: C 77.80, H 10.40, N 5.50; found: C 77.45, H 10.53, N 5.64.

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