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Synthesis and Characterisation of some Mesogenic Mononuclear and Multinuclear Phthalocyanines

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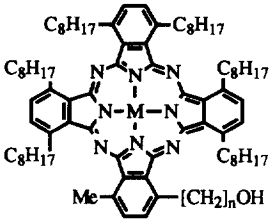
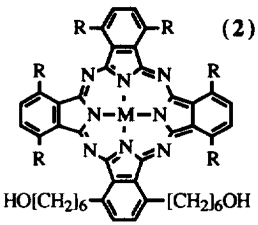
Abstract: Octa-substituted phthalocyanines carrying either one or two hydroxyalkyl chains have been synthesised and their liquid crystalline behaviour characterised by polarised light microscopy and differential scanning calorimetry. The compounds form discotic columnar mesophases with hexagonal or rectangular symmetry. Examples have been used as precursors for the synthesis of mesogenic di-nuclear and tri-nuclear phthalocyanines, ie derivatives containing two or three phthalocyanine rings. These compounds have been characterised by elemental analysis and low resolution field desorption mass spectrometry, FD-MS. ^{1}H NMR spectroscopy and gel permeation chromatography of selected examples provide supporting data. Visible region spectroscopy of dilute solutions of the multinuclear phthalocyanines in cyclohexane (down to a concentration of 5×10^{-7} mol dm^{-3} where intermolecular aggregation is expected to be minimal) suggests that the compounds exist as an equilibrium between a 'closed' conformer where the two rings are arranged cofacially (broad band centred at ca 645nm) and an open form having an absorption band similar to that of the simpler precursor phthalocyanines, λ_{max} ca. 730 nm. The closed conformer is favoured in more polar media eg 10% toluene - 90% ethanol. Examples have been deposited as spin coated films of even thickness on glass slides.

Phthalocyanines constitute a long established class of commercially important dyes and pigments. However, there is increasing interest in their redox, electrical, optoelectronic and photophysical properties for applications within a variety of devices and this has provided impetus for the design and synthesis of new derivatives showing specialised behaviour or properties.[1] Work undertaken at one of our laboratories has been concerned with the development of non-peripherally (1,4,8,11,15,18,22,25) octa-substituted phthalocyanines which can be deposited as thin films by the Langmuir-Blodgett (LB)[2] or spin coating techniques[3] and the use of these films as the chemically active component in chemical sensors.[4] It has become clear that high quality LB films containing a good degree of molecular order can be obtained when the molecules are designed for self organisation ie they bear substituents which provide amphiphilic character and confer discotic mesophase behaviour.[2] Particularly good LB films have been obtained when six of the non-peripheral sites are occupied by long alkyl chains and the remaining two by either 3-carboxypropyl groups[5] or hydroxybutyl groups.[6]

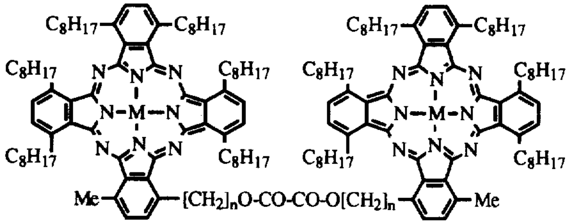
The present paper describes the preparation and synthesis of a novel series of non-uniformly octa-substituted phthalocyanines, **1**. The substituents include six octyl groups to promote liquid crystal behaviour and a single methyl group to facilitate nmr characterisation of the compounds and subsequent derivatives. Most importantly, there is a single hydroxyalkyl chain whose length is systematically varied within the series. The series is designed to explore the effect of variation in molecular geometry on discotic mesophase behaviour and on LB film forming behaviour as well as to provide building blocks for more elaborate structures using the hydroxyl functionality as a linking group. This last point is illustrated in this paper through the use of these compounds, together with three new examples of bis-hydroxyalkyl substituted derivatives, series **2**, to prepare a series of bi- and tri-nuclear phthalocyanine derivatives, **3** and **4**. To our knowledge, **3** and **4** are the first examples of this type of externally linked phthalocyanine to exhibit liquid crystal behaviour;[7] previously, Simon and co-workers demonstrated that this behaviour is shown by heavily substituted dimers in which two phthalocyanine rings share either a common benzene ring[8] or a common rare-earth metal ion as in, for example, lutetium bis-phthalocyanine sandwich compounds.[9] Lever and Leznoff's[10,11] interesting 'clamshell' dimers, where two phthalocyanine rings are attached by an external linking chain, and their more elaborate tetrameric[12] and pentameric analogues[13] lack substituent groups expected to confer liquid crystalline properties.



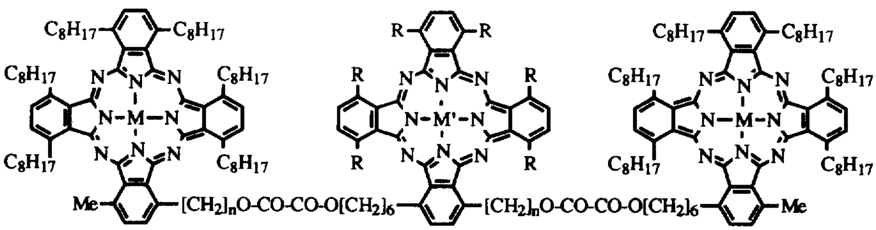
(**1**) a $M = H,H; n = 3$
b $M = H,H; n = 4$
c $M = H,H; n = 5$
d $M = H,H; n = 6$
e $M = H,H; n = 8$
f $M = Cu; n = 5$
g $M = Cu; n = 6$



(**2**) a $M = H,H; R = C_7H_{15}$
b $M = H,H; R = C_8H_{17}$
c $M = Cu; R = C_8H_{17}$



(**3**) a $M = H,H; n = 3$
b $M = H,H; n = 4$
c $M = H,H; n = 5$
d $M = H,H; n = 6$
e $M = H,H; n = 8$
f $M = Cu; n = 5$

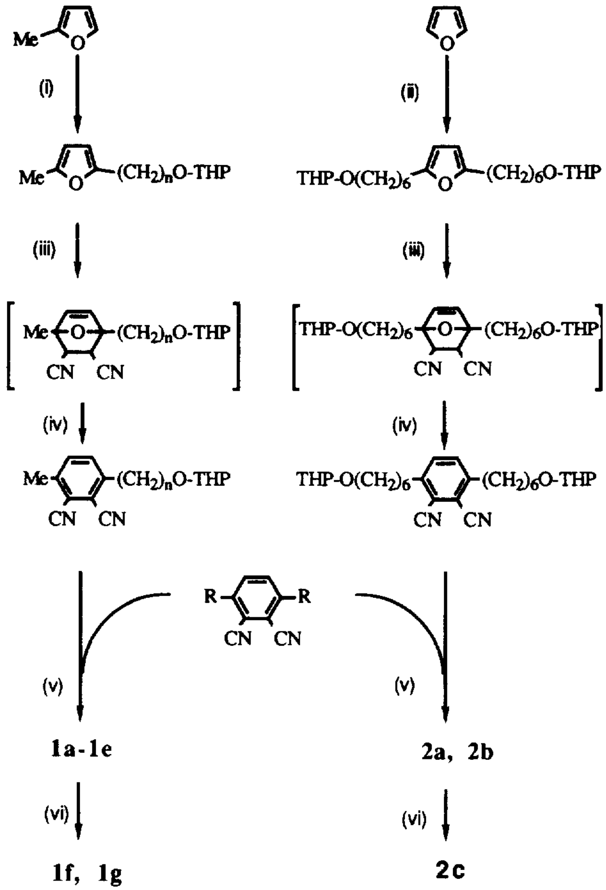


(**4**) a $M = M' = H,H; R = C_8H_{17}; n = 6$
b $M = M' = Cu; R = C_8H_{17}; n = 6$
c $M = Cu; M' = H,H; R = C_7H_{15}; n = 5$

RESULTS AND DISCUSSION

Synthesis and characterisation of mononuclear phthalocyanines 1 and 2 - The monomeric phthalocyanines were prepared by the routes depicted in scheme 1 which are adaptations of pathways devised previously in these laboratories for related compounds.[14] The immediate precursors to **1** are 3,6-dioctylphthalonitrile[14] and

the novel 3-hydroxyalkyl-6-methylphthalonitriles, prepared in a three step synthesis from 2-methylfuran, tables 1 and 2. The examples of 2 were prepared from 3,6-diheptyl or 3,6-dioctylphthalonitrile, as appropriate, and 3,6-bis(6-hydroxyhexyl)phthalonitrile, see scheme 1.



Scheme 1. (i) BuLi/THP-O(CH$_2$)$_n$Br; (ii) 2 x BuLi/THP-O(CH$_2$)$_6$Br; (iii) *E*-NC.CH=CH.CN; (iv) LiN(SiMe$_3$)$_2$; (v) LiOPe/PeOH,AcOH; (vi) Cu(OAc)$_2$

Table 1. Yields and ^{1}H NMR characterisation for 2-(2-tetrahydropyranyloxyalkyl)-5-methylfurans

Compound (2-substituent)	*yield (%)*[a]	δ_H *(60MHz; CDCl$_3$)*
$(CH_2)_3$-OTHP	94	1.6 (m, 8H), 2.24 (s, 3H), 2.6 (t, 2H), 3.2-4.1 (m, 4H), 4.6 (br s, 1H), 5.8 (s, 2H)
$(CH_2)_4$-OTHP	87	1.4-1.8 (m, 10H), 2.2 (s, 3H), 2.6 (t, 2H), 3.2-4.0 (m, 4H), 4.6 (br s, 1H), 5.85 (s, 2H)
$(CH_2)_5$-OTHP	90	1.2-2.0 (m, 12H), 2.2 (s, 3H), 2.6 (t, 2H), 3.2-4.0 (m, 4H), 4.6 (br s, 1H), 5.8 (s, 2H)
$(CH_2)_6$-OTHP	97	1.2-2.0 (m, 14H), 2.2 (s, 3H), 2.6 (t, 2H), 3.2-4.0(m, 4H), 4.58 (br s, 1H), 5.8 (s, 2H)
$(CH_2)_8$-OTHP	99	1.2-2.0 (m, 18H), 2.2 (s, 3H), 2.6 (t, 2H), 3.2-4.0 (m, 4H), 4.6 (br s, 1H), 5.8 (s, 2H)

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[a] Yields have not been optimised and refer to isolated material estimated to be >95% pure by NMR spectroscopy. The compounds, which are novel, were used without further purification in the next step of the synthesis.

Table 2. Preparation and characterisation data for 3-hydroxyalkyl-6-methylphthalonitriles.[a]

Compound (3-subst)	*Mp (C°)*	*Yield %*[b]	*Mol. formula*	*Found C, H, N (required)*			*m/z (required)*	*δ_H (60MHz; $CDCl_3$)*
$HO(CH_2)_3$	82	22	$C_{12}H_{12}N_2O$	72.1 (72.0	6.1 6.0	13.8 14.0)	200 (200)	1.9 (m, 3H), 2.6(s, 3H), 2.95 (t, 2H), 3.7 (t, 2H), 7.5 (s, 2H)
$HO(CH_2)_4$	58	13	$C_{13}H_{14}N_2O$	72.8 (72.9	6.6 6.6	12.9 13.1)	214 (214)	1.7 (m, 5H), 2.6 (s, 3H), 2.95(t, 2H), 3.7 (t, 2H), 7.5 (s, 2H)
$HO(CH_2)_5$	c	18	$C_{14}H_{16}N_2O$		c			1.5-1.8 (m, 7H), 2.6 (s, 3H), 2.95 (t, 2H), 3.7 (t, 2H), 7.5 (s, 2H)
$HO(CH_2)_6$	55	23	$C_{15}H_{18}N_2O$	74.1 (74.4	7.6 7.5	11.3 11.6)	242 (242)	1.5 (m, 9H), 2.6 (s, 3H), 2.9 (t, 2H), 3.65 (t, 2H), 7.5 (s, 2H)
$HO(CH_2)_8$	56	25	$C_{17}H_{22}N_2O$	75.7 (75.5	8.3 8.2	10.2 10.4)	270 (270)	1.5-1.8 (m, 13H), 2.6 (s, 3H), 2.95 (t, 2H), 3.7 (t, 2H), 7.5 (s, 2H)

[a] All compounds are novel. [b] Yields have not been optimised and refer to isolated phthalonitrile (without accounting for recovered dialkylated furan). [c] Obtained as a waxy solid, used without further puification

The two sets of precursor phthalonitriles, with the dialkylphthalonitrile in excess, were cyclised using lithium pentyloxide, scheme 1. Appropriate work-up afforded members of series **1** and **2** in 15 - 25% yield. These were readily separated from side products, of which the corresponding octa-heptyl or octa-octylphthalocyanine is predominant. Derivatives of the two series, metallated with copper, i.e. compounds **1f**, **1g** and **2c**, were obtained by reaction of metal-free compounds with copper acetate. Each compound of series **1** and **2** gave a satisfactory elemental analysis and mass spectrum, table 3. Of the various mass spectrometry methods available we investigated the effectiveness of low resolution field-desorption mass spectrometry, FD-MS. This is a 'soft' technique and led to minimal fragmentation of the charged compound. Data are collected in table 3 together with the monoisotopic masses for comparison. Metal-free derivatives were further characterised by NMR spectroscopy, table 3. ^1H NMR spectra were recorded at 400 MHz of solutions in benzene-d_6 and showed no evidence of peak broadening, a manifestation of aggregation effects common among some phthalocyanine derivatives.[15] Spectra of the compounds of series **1** were the more complex, as expected, because of the lower symmetry of the substitution pattern. Significant features observed in the spectra of the series are the singlet for the aryl-CH_3 group ca. δ 3.5, the series of overlapping triplets for the seven benzylic CH_2 groups in the region ca. δ 4.1 - 4.7, the separation of the aromatic proton resonances, ca. δ 7.38 - 7.85, and the signal for the methylene protons of the CH_2OH group which shifts upfield as the length of the hydroxyalkyl chain is increased. In the shortest chained compound, the hydroxypropyl derivative **1a**, the signal appears at δ 3.63, *cf* δ 3.28 for the signal for the hydroxyoctyl derivative, **1e**. The spectra of **2a** and **2b** show the benzylic protons as overlapping triplets centred at ca. δ 4.6, the aromatic protons as three singlets in the expected ratio 4:2:2 , and the CH_2OH methylene protons as a triplet at ca. δ 3.3.

The metal-free phthalocyanines of series **1** and **2**, as solutions in cyclohexane, show the characteristic split Q band absorption in the visible region with λ_{max} ca. 692 - 694 (Q_y) and 727- 729 (Q_x) nm. These are closely similar to those of the simpler octaalkylphthalocyanines reported earlier.[14] At concentrations between 10^{-5} and 10^{-7} mol dm^{-3} the shape of the absorption envelope is the same and the Beer-Lambert law is obeyed. Thus it can be deduced that there is no significant intermolecular aggregation at this degree of dilution. Extinction coefficients of the Q bands are of the order of 1.2×10^5 (727 nm) and 1×10^5 cm^{-1} mol^{-1}

Table 3. Preparation and characterisation data for phthalocyanines **1a** - **1g** and **2a** - **2c**

No.	*Yield (%)*	*Mol. formula*	*Found: C,*	*H,*	*N.* *(required)*	*m/z (req.)*	λ_{max} (ε x 10^5)	δ_H(400MHz: C_6D_6) . *OH protons were not detected.*
1a	16	$C_{84}H_{122}N_8O$	80.1 (80.1	10.0 9.8	8.7 8.9)	1259 (1259)	727(1.3) 694(1.1)	-0.8 (s, 2H), 0.85 (t, 18H), 1.15-1.55 (m, 60H), 2-2.5 (m, 14H), 3.46 (s, 3H), 3.63 (t, 2H), 4.07 (t, 2H), 4.41 (t, 2H), 4.43 (t, 2H), 4.48 (t, 2H), 4.53 (t, 2H), 4.66 (t, 2H), 4.68 (t, 2H), 7.38 (d, 1H), 7.52 (d, 2H), 7.61 (d, 1H), 7.82-7.85 (m, 4H).
1b	20	$C_{85}H_{124}N_8O$	80.2 (80.1	10.1 9.8	8.8 8.8)	1273 (1273)	727(1.11) 694(1.02)	-0.78 (s, 2H), 0.85 (t, 18H), 1.24-1.8 (m, 62H), 2-2.4 (m, 14H), 3.44 (t, 2H), 3.53 (s, 3H), 4.17 (t, 2H), 4.42 (t, 2H), 4.48 (t, 2H), 4.53 (t, 2H), 4.57 (t, 2H) ,4.70 (t, 4H), 7.44 (d, 1H), 7.54 (d, 1H), 7.60 (d, 1H), 7.66 (d, 1H), 7.85 (m, 4H).
1c	15	$C_{86}H_{126}N_8O$	80.3 (80.2	10.0 9.9	8.45 8.7)	1287 (1287)	728(1.4) 694(1.14)	-0.8 (s, 2H), 0.87 (t, 18H), 1.2-1.85 (m, 64H), 2-2.4 (m, 14H), 3.37 (t, 2H), 3.52 (s, 3H), 4.15 (t, 2H), 4.42 (t, 2H), 4.48 (t, 2H), 4.56 (t, 2H), 4.59 (t, 2H), 4.70 (t, 4H), 7.43 (d, 1H), 7.54 (d, 1H), 7.57 (d, 1H), 7.64 (d, 1H), 7.85 (m, 4H).
1d	25	$C_{87}H_{128}N_8O$	80.0 (80.3	10.1 9.9	8.5 8.6)	1301 (1301)	727(1.22) 691(1.01)	-0.9 (s, 2H), 0.85 (t, 18H), 1.23-1.82 (m, 66H), 2-2.33 (m, 14H), 3.32 (t, 2H), 3.47 (s, 3H), 4.09 (t, 2H), 4.38 (t, 2H), 4.43 (t, 2H), 4.53 (t, 2H), 4.55 (t, 2H), 4.68 (t, 4H), 7.41 (d, 1H), 7.53 (d, 2H), 7.61 (d, 1H), 7.82-7.86 (m, 4H).
1e	22	$C_{89}H_{132}N_8O$	80.4 (80.4	9.9 10.0	8.2 8.4)	-	727(1.28) 692(1.06)	-0.8 (s, 2H), 0.85 (t, 18H), 1.2-1.85 (m, 70H), 2-2.4 (m, 14H), 3.28 (t, 2H), 3.52 (s, 3H), 4.15 (t, 2H), 4.43 (t, 2H), 4.47 (t, 2H), 4.58 (t, 2H), 4.59 (t, 2H), 4.7 (t, 4H), 7.45 (d, 1H), 7.58 (d, 2H), 7.65 (d, 1H), 7.86 (m, 4H).
1f	90	$C_{86}H_{124}CuN_8O$	76.4 (76.5	9.3 9.3	8.2 8.3)	1348 (1348)	704 635	
1g	86	$C_{87}H_{126}CuN_8O$	76.3 (76.6	9.4 9.3	8.1 8.2)	1363 (1362)	704(1.8) 634(0.4)	
2a	23	$C_{86}H_{126}N_8O_2$	79.4 (79.2	9.95 9.7	8.4 8.6)	1305 (1303)	727(1.13) 694(1.00)	-0.37 (s, 2H), 0.82 (t, 18H), 1.23-1.43 (m, 44H), 1.64-1.77 (m, 1 2.25-2.29 (m, 16H), 3.26 (t, 4H), 4.62-4.68 (m, 16H), 7.79 (s, 2 7.82 (s, 2H), 7.84 (s, 4H).
2b	25	$C_{92}H_{138}N_8O_2$	79.4 (79.6	10.3 10.0	7.7 8.1)	1388 (1387)	727(1.21) 694(1.09)	-0.33 (s, 2H), 0.82 (t, 18H), 1.2-1.44 (m, 56H), 1.73-1.77 (m, 16 2.22-2.34 (m, 16H), 3.26 (t, 4H), 4.63-4.70 (m, 16H), 7.81 (s, 2 7.84 (s, 2H), 7.85 (s, 4H).
2c	92	$C_{92}H_{136}CuN_8O_2$	76.1 (76.2	9.7 9.5	7.6 7.7)	1449 (1448)	705(1.7) 635(0.4)	

dm^3 (694nm). The metallated compounds show the expected single Q band absorption and this appears at 705 nm.

Table 4. Transition temperatures and thermodynamic data^a for mesophase transitions^b observed for series **1** and **2**.

Compound		*Transition temperatures/^oC, ΔH/ kcal mol^{-1}, ΔS / cal mol^{-1} K^{-1}*							
		K ->D_1	*K ->D_2*	*D_2->D_1*	*D_1->I*	*I->D_1*	*D_1->D_2*	*D_2->K*	*D_1->K*
1a	T	111			121	119			82
	ΔH	11.1			0.57	0.51			9.06
	ΔS	28.9			1.45	1.31			25.53
1b	T		95	111	146	144	110	80	
	ΔH		4.48	0.04	1.00	1.06	0.04	4.24	
	ΔS		12.17	0.1	2.4	2.54	0.1	12.03	
1c	T		55	115	160	159	114	50	
	ΔH		0.33	0.06	1.42	1.59	0.05	0.27	
	ΔS		1.0	0.15	3.28	3.68	0.14	0.84	
1d	T		58	103	165	161	101	<0	
	ΔH		0.48	0.05	1.18	1.27	0.03	-	
	ΔS		1.45	0.13	2.69	2.93	0.08	-	
1e	T		56	62	170	166	60	43	
	ΔH		0.84	c	1.57	1.55	c	0.82	
	ΔS		2.71	c	3,55	3.53	c	2.59	
1f	T		80	134	237	235	133	76	
	ΔH		0.35	0.05	2.15	1.75	0.05	0.16	
	ΔS		1.0	0.12	4.22	3.44	0.12	0.46	
1g	T		88	130	244	242	128	76	
	ΔH		0.33	0.05	2.51	2.22	0.05	0.5	
	ΔS		0.9	0.13	4.85	4.3	0.13	1.5	
2a	T	122			160	155			94
	ΔH	9.69			3.65	3.21			3.86
	ΔS	24.53			8.43	7.50			10.52
2b	T		110	132	146	142	126	91	
	ΔH		2.65	12.1	2.72	2.64	0.2	10.98	
	ΔS		6.92	29.98	6.49	6.36	0.5	30.2	
2c	T		144	172	216	214	171	113	
	ΔH		12.96	0.17	4.26	4.09	0.17	11.64	
	ΔS		31.08	0.38	8.71	8.40	0.38	30.16	

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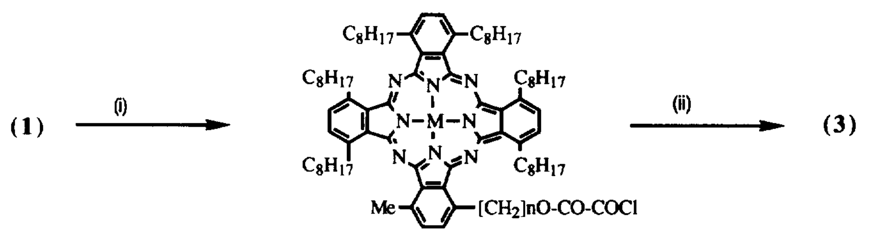
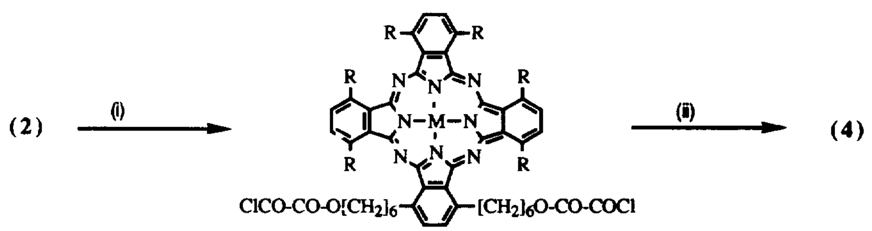
[a] Transition temperatures and ΔH values measured by DSC (rate 10°C/min) on the cooling cycle and second heating cycle. [b] K represents the highest temperature crystal state for each particular derivative. D_1 is the higher temperature mesophase, D_{hd}. D_2 is the lower temperature mesophase and is assigned as D_{rd} for series 1 and D_{hd} for series 2, see text. [c] Too low enthalpy to be identified

Mesophase behaviour, series 1 and 2 - Liquid crystal behaviour of the compounds was identified by polarised light microscopy and examined further by differential scanning calorimetry. Mesophase ranges and the enthalpies of transitions are reported in table 4. The birefringence textures observed by microscopy were best observed on cooling from the melt. The highest temperature mesophase exhibited by each compound in the series **1** and **2** gave rise to a fan texture typical of that expected for a discotic columnar (disordered) mesophase with hexagonal symmetry,[16,17] denoted as D_{hd}. This is characteristic of other octa-alkylphthalocyanines investigated earlier.[16] On further cooling, **1a** underwent transition to the crystalline state, K, with supercooling. The remaining compounds of series **1** cool into a second mesophase which appears as very fine needles which overlay the fan texture of the D_{hd} phase. This new mesophase has been investigated by Haslam and Richardson using x-ray techniques and has proved to be a disordered columnar mesophase of rectangular symmetry, D_{rd}.[18] Compounds of series **2** also underwent transition into a second mesophase on cooling and this was characterised by a needle texture which grew out of the fans. It is quite different from the needle texture of the D_{rd} mesophase in that the needles are much larger and develop zig-zag patterns. This is characteristic of the second D_{hd} mesophase exhibited by certain octa-alkyl phthalocyanines[16] and was confirmed as such by x-ray analysis.[18] Inspection of the data in table 4 for the series **1** metal-free compounds shows that the transition temperatures are highly sensitive to the length of the hydroxyalkyl chain. The highest D -> I transition temperatures (I = isotropic liquid) and the most extended mesophase temperature ranges are exhibited by compounds **1d** and **1e**. The lengths of their hydroxyalkyl chains are close to those of the six octyl chains elsewhere in the molecules. This should lead to the least distortion of the disc shape and, as such, minimise disruption of the columnar stacking in the mesophase. Introduction of copper into the macrocycle, compounds **1f** and **1g**, raises the clearing point temperature and the mesophase range further.

Synthesis and characterisation of bi-nuclear and tri-nuclear phthalocyanines, series 3 - 4: - Compounds of series **1** and **2** were converted into examples of **3** and **4** according to schemes 2 and 3 respectively. The routes allow unambiguous modifications of the structures. The di-nuclear derivatives, **3a - f**, were obtained by first esterifying a compound from series **1**, a mono-hydroxyalkyl phthalocyanine, with excess oxalyl chloride solution to create a terminal acid chloride function. Solvent and excess oxalyl chloride were removed under high vacuum and a solution containing a further equivalent of the series **1** derivative added.



Scheme 2 (i) ClCOCOCl. (ii) compound of series (1)



Scheme 3 (i) ClCOCOCl. (ii) compound of series (1)

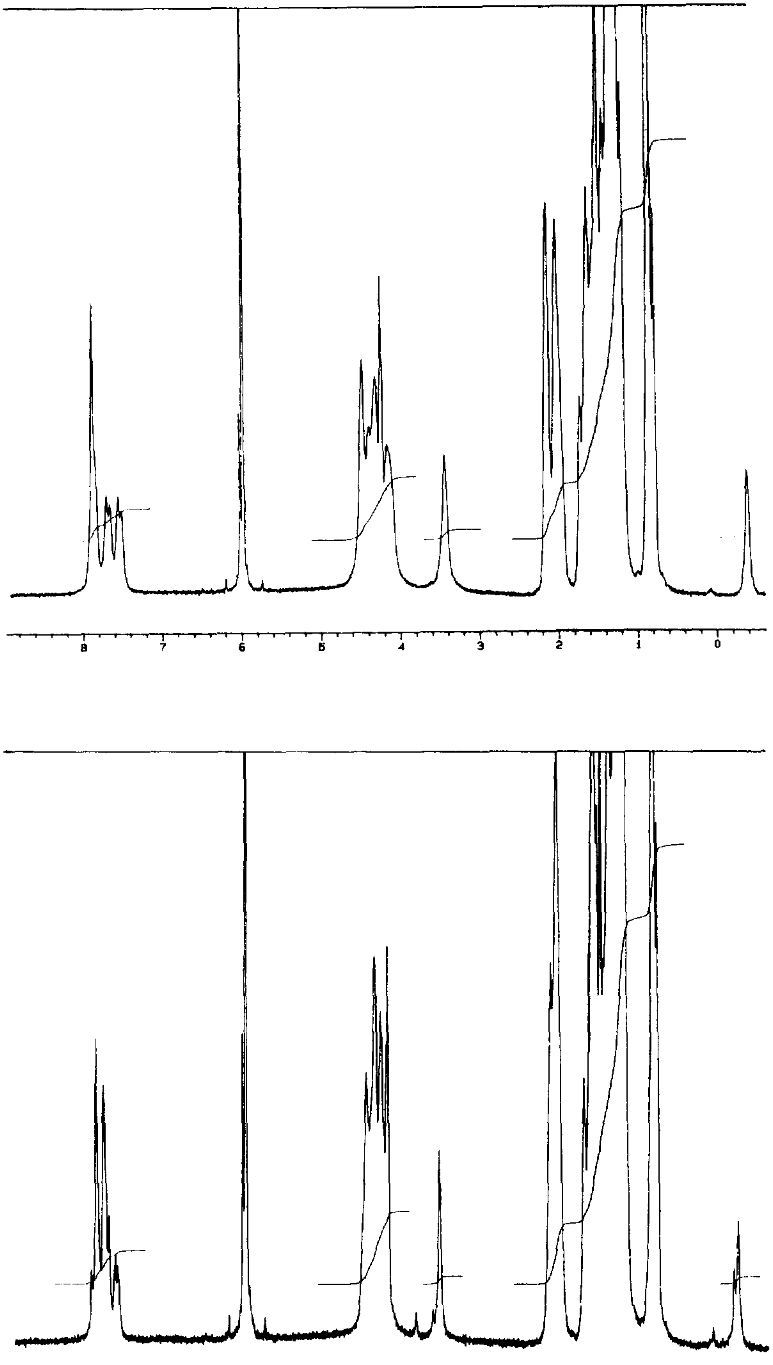


Figure 1. ^{1}H NMR spectra run at 400 MHz of solutions ([$^{2}H_{2}$]-1,1,2,2-tetrachloroethane at 80°) for, top, compound **3d** and, bottom, compound **4a**.

Tri-nuclear phthalocyanines, series **4**, were synthesised similarly. A bis-hydroxyalkyl compound, **2**, was esterified with excess oxalyl chloride to afford a phthalocyanine functionalised with two acid chloride groups. This was then reacted with an excess of a series **1** compound to yield the required compound of series **4**. The experimental procedure requires the thorough removal of the excess oxalyl chloride after the initial esterification in order to avoid subsequent esterification of the series **1** compound. Three compounds of type **4** were synthesised. Two contained symmetrical linking chains and the same alkyl groups on all three rings; in one compound, **4a**, all three rings were metal-free, in the second, **4b**, all three were metallated with copper ions. The third example, **4c**, was prepared with alkyl chains on the central ring different from those on the outer rings, with unsymmetrical linking chains, and with copper ions incorporated in the outer rings only.

Table 5 summarises characterisation data. Confirmation of molecular structure followed from satisfactory elemental analyses and FD-MS data. Each compound showed $\nu_{C=O}$ at 1770 ± 2 and at 1744 ± 1 cm^{-1}. The mass spectra showed unresolved clusters of high abundance corresponding to the molecular ion and/or $M^{+}+1$ and to multiply charged ions. Thus, compounds of series **3** showed signals for M^{+} and M^{2+} ions and, in some instances, a weak signal corresponding to M^{3+}. The FD-MS spectra for series **4** showed peaks corresponding to M^{+}, M^{2+} and M^{3+} molecular ions with the M^{3+} peak the largest, presumably corresponding to a charged ion on each phthalocyanine ring.

An example of an unmetallated bi-nuclear compound, **3d**, and an unmetallated tri-nuclear derivative, **4a**, i.e. compounds having the same length alkyl substituents and linking groups, were further characterised by NMR and gel permeation chromatography (GPC). ^{1}H NMR spectra were recorded of solutions in deuterated 1,1,2,2-tetrachloroethane at 80°, under which conditions line broadening appeared to be minimal. The ^{1}H NMR spectra for both **3d** and **4a**, figure 1, show the aromatic protons between δ 7.4 - 8. The next group of signals, centred at ca. δ 4.4, are a series of near superimposed triplets assigned to the Ar-CH_2 protons and the -CH_2-O- protons. The Ar-CH_3 protons reveal themselves as a singlet at ca. 3.4 ppm, separated from all other proton signals. Further signals above δ 0.0 are associated with the remaining methylene and methyl protons of the aliphatic side chains and the spacer group. These are observed between 0.9 - 2.2 ppm. The inner protons attached to the nitrogen atoms within the central aromatic ring have chemical shifts below δ 0.0. For **3d** they appear as a singlet and for **4a** they appear as two singlets, ratio 2:1.

GPC traces for **3d** and **4a** are compared with that for the mononuclear phthalocyanine **2b** in figure 2. The plots were obtained separately but are shown superimposed. The molecular weights for **3d** (Mw 2420; Mn 2270) and **4a** (Mw 3360; Mn 3110), derived by comparison with a polystyrene standard, are lower than the calculated molecular masses (**3d** 2658; **4a** 4101). This is presumably a reflection of the very different molecular geometries of the compounds compared to the standard.

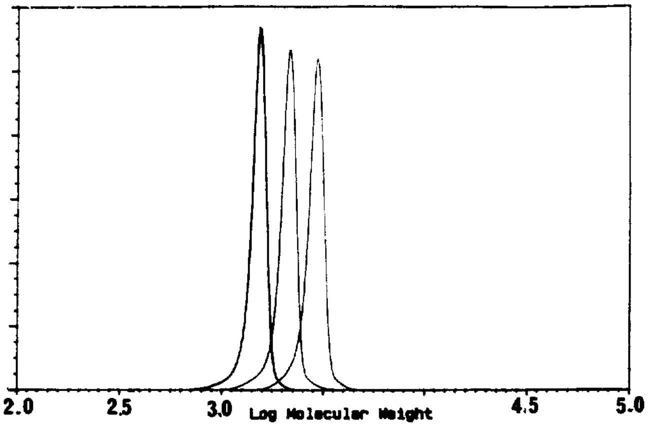


Figure 2. GPC traces, obtained separately but superimposed, for, left to right, compounds **2b**, **3d** and **4a** chromatographed over PL-gel.

Table 5. Characterisation data for di-nuclear and tri-nuclear phthalocyanines, series 3 and 4

No	Transition Temp.[b] (°C)	Mol. Formula	Found: C, H, N (required)			FD-MS signals[a] (required)	Q-band data (nm)	
			C	H	N		λ_{max} [c]	λ_{max} film[d]
3a	m.p. 160	$C_{170}H_{242}N_{16}O_4$	79.0 (79.3	9.4 9.5	8.7 8.7)	1286, 2573 (2572)	727, 696	
3b	D ->I 163 D ->D 144	$C_{172}H_{246}N_{16}O_4$	79.3 (79.4	9.7 9.5	8.5 8.6)	301, 2601 (2600)	727 (1.35), 696 (1.45)	702, 659
3c	D ->I 180 D ->D 135	$C_{174}H_{250}N_{16}O_4$	79.4 (79.5	9.75 9.6	8.4 8.5)	1288, 1317, 2629 (2628)	728, 695	
3d	D ->I 188 D ->D 123	$C_{176}H_{254}N_{16}O_4$	79.2 (79.5	9.6 9.6	8.3 8.4)	886, 1330, 2660 (2656)	727 (1.26), 696 (1.39)	730 (sh), 703, 653
3e	D ->I 175 [e]	$C_{180}H_{262}N_{16}O_4$	79.5 (79.7	9.8 9.7	8.15 8.3)	357, 2713 (2712)	727 (1.44), 696 (1.57)	
3f	D ->I 254 D ->D 161	$C_{174}H_{246}N_{16}O_4Cu_2$	75.6 (75.9	8.85 9.0	7.9 8.1)	1377, 2756 (2750)	705, 646	711, 648
4a	D ->I 177	$C_{270}H_{390}N_{24}O_8$	79.0 (79.1	9.6 9.6	8.1 8.2)	1367, 2051, 4101 (4101)	728 (1.85), 695 (2.03)	730 (sh) 706, 664
4b	D ->I 252	$C_{270}H_{384}N_{24}O_8Cu_3$	75.8 (75.7	9.1 9.0	7.7 7.85)	1430, 2143, 4286 (4285)	705 (2.2), 646 (1.54)	711, 648
4c	D ->I 222 D ->D? 125	$C_{262}H_{370}N_{24}O_8Cu_2$	76.3 (76.6	9.2 9.1	8.0 8.2)	1370, 2055, 4106 (4111)	700, 651	708, 645

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[a] Field desorption mass spectral data (centre of the clusters for the M^{3+}, M^{2+} and M^{+} ions). Number in parentheses refers to the calculated monoisotopic mass. Apparent discrepancies for **3f** and **4c** may arise from a poor calibration. [b] Data (from Ref. 7) correspond to the second heating cycle. [c] Data in parentheses refer to ε x 10^5. [d] Data for spin coated films. [e] A second transition is apparent over the range 72 - 86°.

Mesophase behaviour, series 3 and 4: - The mesophase properties of these compounds have been described as part of a conference presentation and details are available elsewhere.[7] Here we note only that all the di- and tri-nuclear compounds show liquid crystal behaviour with the exception of **3a** which has the shortest linker connecting the two rings. Table 5 contains transition temperature data as part of the overall characterisation of the materials. The mesophases have very low mobility and at room temperature appear almost glass like. The di-nuclear compounds **3b** - **3f** generate the same types of mesophase as their precursors, **1b** - **1f**, i.e. the higher temperature mesophase is assigned as D_{hd} and on cooling a new mesophase of rectangular symmetry is generated. The tri-nuclear series give rise to D_{hd} mesophases only. Both series show a somewhat higher D -> I transition temperature than that for the corresponding compounds of series **1** and **2**. In series **3** the transition occurs typically 10° higher than for the series **1** analogues. Furthermore, because the compounds appear to retain the liquid crystal phase down to room temperature, they have a much wider mesophase range than their mononuclear precursors.

Visible region spectral properties of series 3 and 4: - Spectra for the compounds of series **3** and **4** as solutions in toluene and/or cyclohexane were recorded over the same range of concentrations used to study series **1** and **2**, i.e. between 10^{-5} M and 10^{-7} M. The spectra differ somewhat from those of the mono-nuclear phthalocyanines in that they show higher intensity absorption bands to the blue of the main Q-band absorptions. This is attributable to exciton coupling arising from cofacial association of two or more nuclei

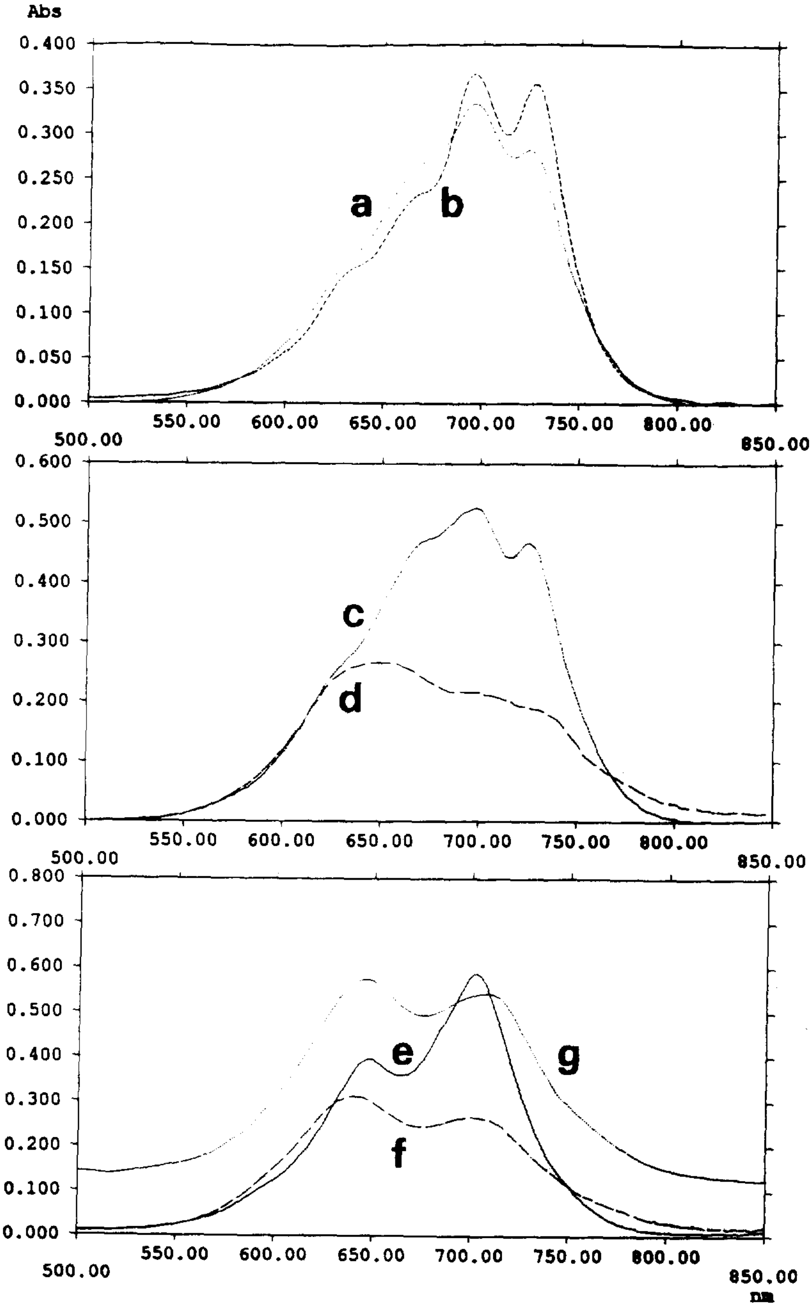

Figure 3. Top. The solution phase spectrum of 3a in toluene at room temperature (line a) and of the same solution at ca. 40° (line b). Middle. The same compound as a solution in cyclohexane (line c) and in 5% cyclohexane : 95% ethanol (line d). Bottom. The solution phase spectrum of 3f in cyclohexane (line e) and in 20% cyclohexane : 80% ethanol (line f). Line g shows the compound spread as a spin coated film on a glass slide.

and is also observed in the spectra of Leznoff and Lever's clamshell derivatives.[19] They attributed the exciton coupling to an intramolecular association within conformations where one ring lies over the second, the 'closed clam-shell' form. The spectra obtained of **3a** and **3f** are typical of the metal free and copper derivatives respectively, figure 3, the former being more complex through the lower symmetry of metal-free derivatives. They do not change in their shape over the concentration range 5 x 10^{-7} to 5 x 10^{-6} M, suggesting that the association is indeed essentially intramolecular rather than intermolecular. The observed band shapes can thus be attributed to population of both the open and closed conformations. On raising the temperature of the solution, there was a decrease in intensity of the higher energy bands, and an increase in the intensity of the 730nm Q-band, figure 3.

Further spectral measurements were recorded of solutions with different mixtures of toluene or cyclohexane with ethanol as solvent. As the polarity of the medium is increased the band shape changes; for compound **3a**, the substantial difference observed on changing from cyclohexane to 5% cyclohexane : 95% ethanol is shown in figure 3. In the more polar medium the blue shifted component assigned to the ring closed form is the major band. Solute : solvent interactions are dominant in the hydrocarbon solution but these become less important as the polarity increases and ring : ring interactions become dominant, causing the equilibrium to shift to the closed conformer. A similar effect is exhibited by other compounds of the series, see figure 3 for spectra of **3f**.

Spectra were also recorded of several compounds of series **3** and **4** formulated as spin coated films on glass slides. The films were prepared by adding a drop of a solution of known concentration of the compound in toluene or THF onto a glass slide rotating at 2000 rpm. After 20 sec the solvent had evaporated to give a very even film which, under the conditions used, had a thickness (mechanical stylus; alpha-step method) of ca. 1000Å. Visual inspection through a microscope showed no evidence for the formation of crystallites. Spectral data for the visible region are reported in table 5 and the spectrum for the film of **3f** is incorporated into figure 3. These broad band spectra show some resemblance to the solution phase spectra of the 'closed form' of the molecules.

CONCLUSION

A series of 1-(hydroxyalkyl)-4-methyl-8,11,15,18,22,25-hexaoctylphthalocyanines has been synthesised. The compounds exhibit liquid crystalline properties and the transition temperatures are sensitive to the length of the hydroxyalkyl chain. The compounds have been used as precursors for the synthesis of more complex phthalocyanine derivatives. The preparation of di- and tri-nuclear phthalocyanines linked through oxalyl ester groups has been achieved by an unambiguous stepwise route which, in principle, provides a means of having different substitution patterns and/or central ions at the various component rings. All but one of the multinuclear derivatives exhibit liquid crystal behaviour. The temperature ranges over which the mesophases exist are larger than those of the precursors. There is evidence from visible spectroscopy that the multinuclear compounds can exist in a conformational equilibrium involving 'closed' and 'open' forms. The compounds are also readily deposited as spin coated films of even thickness, with no visible evidence of crystallite formation during the evaporation process. Such films may find application within gas sensing devices.

EXPERIMENTAL

Equipment and measurements:- IR spectra were recorded on a Perkin-Elmer 297, 298 or a FT-IR 1720 spectrophotometer as either neat liquids or as nujol mulls of solids. Routine ^{1}H-NMR spectra were measured at 60 MHz using a Jeol JNM-PMX 60. Spectra obtained at 400 MHz were obtained using a Jeol GX-400 spectrometer. Routine mass spectra were obtained using a Kratos MS 25 mass spectrometer. For the phthalocyanine derivatives, field desorption mass spectrometry (FD-MS) and gel permeation chromatography (GPC) were carried out at the ICI Wilton Research Centre, Physical Sciences Group. FD-MS spectra were measured using a low resolution VG Analytical/Fisons Instruments ZAB-2SE Field Desorption Mass Spectrometer, the samples being analysed over the mass range 100 - 50000. GPC was carried out over PL-gel

Transition temperatures for the changes from crystal to mesophase and mesophase to isotropic liquid were measured using an Olympus BH2 polarising optical microscope fitted with a Linkam hotstage and confirmed by differential scanning calorimetry (Perkin Elmer 7 Series). M.p.s. of intermediates were recorded using a Koppfler hot stage melting point apparatus and are uncorrected.

Spin coated films were prepared from solutions of a phthalocyanine in either Aristar grade toluene or THF (ca 2.5 mg in 0.1 ml) dropped onto a glass slide rotating at 2000 rpm. Spinning was continued for 20 sec. by which time the solvent had evaporated. Measurements of film thicknesses were made using mechanical stylus equipment (Alpha-step).

UV-visible spectra of solutions and films were measured using a Hitachi U3000 spectrophotometer. Variable temperature measurements on the films were made using a Mettler FP82 Hotstage adapted to fit inside the sample compartment.

Preparation of phthalonitrile precursors:- 3,6-Diheptylphthalonitrile and 3,6-dioctylphthalonitrile were prepared according to literature procedures.[14] The 3-(hydroxyalkyl)-6-methylphthalonitrile precursors also required for the preparation of series **1** were prepared in two steps using general procedures, examples of which are given as (a) and (b); 3,6-bis(6-hydroxyhexyl)phthalonitrile, a precursor for compounds of type **2** was prepared via the sequence of experiments (c), (d) and (e).

Procedure (a): 2-Methyl-5-[n-(2-tetrahydropyranyloxy)alkyl]furans: - In a typical reaction, n-BuLi [2.5 M in hexane (40 ml, 0.1 mol)] was added to a stirred solution of 2-methylfuran (8.9 g, 0.11 mol) in dry tetrahydrofuran (50 ml) at -78°C under an atmosphere of dry argon. The solution was allowed to warm to rt, stirred for 20h, cooled to -78°C and quenched with 2-(6-iodohexyloxy)tetrahydropyran (31.2 g, 0.1 mol). The mixture was allowed to warm to rt and stirred for a further 24 h, then poured onto ice (100 g) and extracted with diethylether (3x100 ml). The organic layer was then washed with water (50 ml), saturated brine (50 ml), dried ($MgSO_4$), filtered and the solvents removed under reduced pressure to afford *2-methyl-5-[6-(2-tetrahydropyranyloxy)hexyl]furan* (25.8g, 97%) which was used without further purification. δ_H (60MHz, $CDCl_3$): 1.2-2.0 (m, 14H), 2.2 (s, 3H), 2.6(t, 2H), 3.2-4.0 (m, 4H), 4.58 (br.s, 1H), 5.8 (s, 2H).

Procedure (b): 3-Methyl-6-(6-hydroxyalkyl)phthalonitriles:- In a typical experiment, fumaronitrile (1.5 g, 19 mmol) was added to 2-methyl-5-[6-(2-tetrahydropyranyloxy)hexyl]furan (4.7g, 18 mmol) in the minimum amount of dry THF. The mixture was left in the fridge (T~5°C) for 7 days, after which time ^1H NMR spectroscopy indicated ca. 55% conversion to the adduct. The mixture was added to dry THF (50 ml), pre-cooled to -78°C, and a slight excess of 1.0 M lithium bis(trimethylsilyl)amide (25 ml, 25 mmol) in THF was added slowly. Saturated aqueous ammonium chloride (50 ml) was then added and the dark solution was stirred for 1.25 h, and allowed to warm to rt. The mixture was extracted with diethylether (3x70ml), dried ($MgSO_4$), filtered and the solvents removed under reduced pressure. The resultant mixture was separated by column chromatography over silica gel using as eluent dichloromethane to afford the crude product which was treated with *p*-toluene sulphonic acid (50mg) in methanol (100ml) and stirred for 24h. The resultant mixture was separated by column chromatography over silica gel using as eluent THF/dichloromethane (1/5) and then recrystallized from ethanol/petroleum ether bp 40-60°C to afford as colourless needles *3-methyl-6-(6-hydroxyhexyl)phthalonitrile* (0.7 g, 23%), M.p. 55°C, δ_H (60MHz, $CDCl_3$): 1.5 (m, 9H), 2.6 (s, 3H), 2.9 (t, 2H), 3.65 (t, 2H),7.5 (s, 2H), m/z 242.

Procedure (c): 2-[6-(2-tetrahydropyranyloxy)hexyl]furan:- n-BuLi [2.5 M in hexane (50 ml, 0.125 mol)] was added to a solution of furan (10 g, 0.15 mol) in dry tetrahydrofuran (50 ml) at -78°C under an atmosphere of dry argon. The solution was allowed to warm to rt and stirred for 24 h, cooled to -78°C and quenched with 2-(6-iodohexyloxy)tetrahydropyran (28.1 g, 0.09 mol). The mixture was allowed to warm to rt and stirred for a further 24 h, then poured onto crushed ice (100 g) and extracted with diethylether (3x100 ml). The organic layer was then washed with water (50 ml), saturated brine (50 ml) and dried ($MgSO_4$), filtered and the solvents removed under reduced pressure to afford *2-[6-(2-tetrahydropyranyloxy)hexyl]furan* (21.5 g, 0.09 mmol, 96%), δ_H (60MHz, $CDCl_3$): 1.2-1.8 (m, 14H), 2.6 (t, 2H), 3.2-4.0 (m, 4H), 4.6 (brs, 1H), 5.95 (m, 1H), 6.1 (m, 1H), 7.2 (m, 1H).

Procedure (d): 2,5-Bis-[6-(2-tetrahydropyranoxy)hexyl]furan: - n-BuLi [2.5M in hexane (34.5 ml, 0.086 mol)] was added to a solution of 2-[6-(2-tetrahydropyranyloxy)hexyl]furan (21.5 g, 0.085 mol) in dry THF (50 ml) at -78°C under an atmosphere of dry argon. The solution was allowed to warm to rt and stirred for 24h, cooled to -78°C and quenched with 2-(6-iodohexyloxy)tetrahydropyran (27.5 g, 0.088 mol). The mixture was allowed to warm to rt and stirred for a further 24h. It was then poured onto crushed ice (100 g) and extracted with diethylether (3x100 ml). The organic layer was then washed with water (50 ml), saturated brine (50 ml), dried ($MgSO_4$), filtered and the solvents and unreacted 2-(6-iodohexyloxy)-tetrahydropyran removed under vacuum (0.1 mmHg) to afford *2,5-bis-[6-(2-tetrahydropyranoxy)hexyl]furan* (35 g, 0.8 mol., 94%) which was used in the next step without further purification, δ_H (60MHz, $CDCl_3$): 1.2-1.8 (m, 28H), 2.6 (t, 4H), 3.2-4.0 (m, 8H), 4.6 (brs, 2H), 5.8 (s, 2H).

Procedure (f): 3,6-Bis(6-hydroxyhexyl)phthalonitrile: - Fumaronitrile (3.35g, 43 mmol) was added to 2,5-bis[6-(2-tetrahydropyranyloxy)hexyl]furan (17.5g, 40 mmol) in the minimum amount of dry THF. The mixture was left in the fridge (T~5°C) for 14 days, after which time ^{1}H-nmr spectroscopy indicated a 50% conversion to the adduct. The mixture was added to dry THF (50 ml) at -78°C and lithium bis(trimethylsilyl)amide 1.0 M in THF (85 ml, 85 mmol) was added slowly. The dark solution was left stirring at -78°C for 0.5 h, then left to warm to rt. The mixture was then poured over a saturated aqueous ammonium chloride and crushed ice (100 ml), and extracted with diethylether (3x50 ml). The organic layer was then washed with water (50 ml), saturated brine (50 ml) and dried ($MgSO_4$), filtered and the solvents removed under reduced pressure. The resultant mixture was separated by column chromatography over silica gel using as eluent dichloromethane/acetone (9:1) to afford the crude product, which was treated with *p*-toluene sulfonic acid (50 mg) in methanol (100 ml) for 24h. The resultant mixture was separated by column chromatography over silica gel using as eluent CH_2Cl_2 / acetone (6/1) and then recrystallized from ethanol to afford as colourless needles *3,6-bis(6-hydroxyhexyl)phthalonitrile* 4.2 g (32%), m.p. 63-64°C, ν_{max} (nujol): 3295 (OH), 2226 (CN), δ_H (60MHz, $CDCl_3$): 1.2-1.9 (m, 16H), 1.8(s, 2H), 2.9 (t, 4H), 3.65 (t, 4H), 7.5 (s, 2H), m/z 328. (Found: C, 73.21; H, 8.74; N, 8.35. $C_{20}H_{128}N_2O_2$ requires C, 73.14; H, 8.59; N, 8.53).

Synthesis of phthalocyanines, series 1 and 2:- Members of both series were prepared by adaptation of the following method.

1,4-Bis(6-hydroxyhexyl)-8,11,15,18,22,25-hexaoctylphthalocyanine: -In a typical procedure, 3,6-dioctylphthalonitrile (10.6 g, 30 mmol) and 3,6-bis(hydroxyhexyl)phthalonitrile (1.1 g, 3.35 mmol) in dry pentan-1-ol (25 ml) were heated under reflux with stirring and lithium metal (0.1 g) was added slowly in small portions. The solution turned an intense green colour immediately and reflux was continued for 6h, the mixture was allowed to cool to rt and acetic acid (50 ml) was added and stirring continued for 0.5 h. The solvents were removed under reduced pressure and the mixture triturated with methanol (100 ml) to remove non-phthalocyanine impurities. The solution was filtered and the resultant solid dissolved in THF and filtered again. The solvent was removed under reduced pressure and the mixture separated over silica gel. The first green fraction [eluent; petroleum ether (bp 40/60°)] contained 1,4,8,11,15,18,22,25-octaoctylphthalocyanine (3.8 g, 36%). The next green fraction (eluent; THF/cyclohexane, 1:2) was further purified by chromatography over silica gel (eluent; THF/cyclohexane, 1:2) and recrystallized from acetone/THF to afford *1,4-bis(6-hydroxyhexyl)-8,11,15,18,22,25-hexaoctylphthalocyanine*, ***2b***, as dark green cubes. (1.1 g, 24% based on 3,6-bis(6-hydroxyhexyl)phthalonitrile, m.p. 110°C (K->D), 146°C (D->I), δ_H (400MHz, C_6D_6): -0.33(s, 2H), 0.82(t, 18H), 1.2-1.44(m, 56H), 1.73-1.77(m, 16H), 2.22-2.34(m, 16H), 3.26(t, 4H),4.63-4.70(t, 16H), 7.81-7.85(m, 8H), FD-MS 1388. (Found: C, 79.42; H, 10.26; N, 7.73. $C_{92}H_{138}N_8O_2$ requires C, 79.60; H, 10.02; N, 8.07).

Synthesis of metallated phthalocyanines of series 1 and 2: - The following procedure is typical.

Copper(II) 1,4-bis(6-hydroxyhexyl)-8,11,15,18,22,25-hexaoctylphthalocyaninate:- 1,4-bis(6-hydroxyhexyl)-8,11,15,18,22,25-hexaoctylphthalocyanine (50 mg) and copper(II) acetate (*ca.*50 mg) were dissolved in pentan-1-ol (20ml) and heated under reflux for 45 minutes. The pentan-1-ol was then removed under reduced pressure and the solid mixture purified using column chromatography over silica gel (eluent; cyclohexane/THF 2:1) and recrystallized from acetone/THF mixtures to afford as blue fibres *copper(II) 1,4-bis(6-hydroxyhexyl)-8,11,15,18,22,25-hexaoctylphthalocyaninate* (45 mg, 92%), M.p. 144°C (K->D), 216°C (D->I), FD-MS 1449. (Found: C, 76.06; H, 9.69; N, 7.60. $C_{92}H_{136}N_8O_2Cu$ requires C, 76.22; H, 9.46; N, 7.73).

Synthesis of multi-nuclear phthalocyanines, series 3 and 4: -

Di-nuclear phthalocyanines:- In a typical procedure oxalyl chloride (5mL of a 2.0M solution in dichloromethane) was added to **1d** (110mg, 0.085mM) and K_2CO_3 (100mg) and the mixture stirred under Argon for 3hrs. The solvent and excess oxalyl chloride were then removed under high vacuum. To the solid mixture **1d** (100mg, 0.077mM) anhydrous 1,1-dichloroethane (5mL) was then added, and the solution stirred for 24h at 50 - 60°. The solvents were removed under reduced pressure and the mixture eluted on a silica column (eluent; petrol / THF 5:1) to give the *di-nuclear phthalocyanine* **3d**, (190mg, 92%). M.p. 123°C (K->D), 188°C (D->I), FD-MS 2658, GPC 2420(M_w), 2270(M_n), ν_{max}(KBr) 3292(NH), 1743 (C=O)cm^{-1}. (Found: C, 79.24; H, 9.63; N, 8.29. $C_{176}H_{254}N_{16}O_4$ requires C, 79.53; H, 9.63; N, 8.4).

Tri-nuclear phthalocyanines:- In a typical procedure, oxalyl chloride (5mL of a 2.0M solution in dichloromethane) was added to **2b** (100mg, 0.072mM) and K_2CO_3 (100mg) and the mixture stirred under argon for 3hrs. The solvent and excess oxalyl chloride were then removed under high vacuum. To the solid mixture **1d** (200mg, 0.144mM) and anhydrous 1,1-dichloroethane (5mL) was then added, and the solution stirred for 24h at 50-60°. The solvents were removed under reduced pressure and the mixture eluted on a silica column (eluent : Petrol / THF 5:1) to give the *tri-nuclear phthalocyanine* **4a** (240mg, 80%). M.p. <25°C (K->D), 178°C (D->I), FD-MS 4101, GPC 3360(M_w), 3110(M_n), ν_{max}(KBr) 3292(NH), 1743 (C=O)cm^{-1}. (Found: C, 79.01; H, 9.58; N, 8.07. $C_{270}H_{390}N_{24}O_8$:requires C, 79.09; H, 9.59; N, 8.20).

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