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Phthalocyanine-centred and naphthalocyanine-centred aryl ether dendrimers with oligo(ethyleneoxy) surface groups

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Abstract—The synthesis of the 1st, 2nd and 3rd generation phthalocyanine-centred and naphthalocyanine-centred poly(aryl ether) dendrimers possessing oligo(ethyleneoxy) surface groups is described. These materials are soluble in polar protic solvents. For both types of macrocycle, the tendency of the non-polar phthalocyanine core towards intermolecular cofacial aggregation is not reduced by peripheral dendritic substitution. However, the prohibition of cofacial aggregation can be achieved by placing the dendritic substituents at the axial sites of the silicon-containing macrocycle. A single crystal X-ray diffraction analysis of one of these compounds beautifully illustrates this concept.

1. Introduction

Dendrimers are well-defined macromolecules of uniform mass that contain a core, successive layers of branched repeat units and surface groups.[1] Over the last decade or more, the synthesis of novel dendrimers has been a very active area of research and one important aspect has been the incorporation of functional units such as crown ethers,[2] mesogenic groups[3] and various redox-active substituents based on tetrathiafulvalene,[4] anthraquinones,[5] ferrocene,[6] fullerenes,[7] or transition metal complexes.[8] An interesting consequence of placing a functional unit at the core of a dendrimer is steric isolation which can prevent unwanted interference of the functionality.[9] For example, lanthanide metal cations placed at the core of a dendrimer core exhibit site isolation as demonstrated by their decreased rate of self-quenching of luminescence.[10] Site isolation may have profound implications for the practical applications of functional organic materials within devices such as electro-luminescent displays.[11] The concept of using dendrimers to enforce site isolation of porphyrin cores has been extensively studied and is found to enhance fluorescence, provide greater catalytic selectivity and decrease the rate of interfacial electron transfer from the core to an electrode surface.[12–25] The redox potentials of the porphyrin core can also be affected by the environment provided by the dendritic substituents.[26]

Phthalocyanine (Pc), a close relative of the porphyrin macrocycle, is the parent compound of one of the most studied class of functional organic materials.[27,28] Pcs exhibit interesting catalytic, electronic and optical properties, in addition to being well-established industrial colorants and useful components of functional polymers.[29] Presently, Pc derivatives substituted with hydrophilic groups are good candidates for use as photosensitisers in the photodynamic therapy (PDT) of cancer.[30–32] However, Pcs are notable for their strong tendency to aggregate in solution, especially in polar protic solvents (e.g. water or ethanol) due to the hydrophobic nature of the Pc ring. Self-association results in the quenching of the photochemically excited state of Pc and thus prevents both fluorescence and singlet oxygen formation-which is its primary role in PDT. Previously, we have described Pc-containing poly(aryl ether) dendrimers based upon Fréchet's well established convergent route for dendrimer synthesis.[33–37] These materials possess benzyl-oxy terminal groups (T) and are soluble in a wide range of non-polar organic solvents. It was hoped that analogous Pc-centred dendrimers substituted with hydrophilic oligo-(oxyethylene) terminal groups, (i.e. $T{=}O(CH_2CH_2O)_3CH_3$) would be soluble in polar protic solvents and that the large dendritic substituents would prohibit aggregation of the Pc cores. A recent communication described, in brief, the synthesis of these phthalocyanines with first, second and third generation poly (aryl ether) dendrons placed either in the peripheral positions, $[G1]_4Pc$, $[G2]_4Pc$ and $[G2]_4Pc$, or on the axial site of silicon phthalocyanine, $[G1]_2SiPc$, $[G2]_2SiPc$ and $[G3]_2SiPc$ (Scheme 1).[38] The present paper give further details about these dendrimers and also describes the analogous materials ($[G1]_4Nc$, $[G2]_4Nc$, $[G2]_4Nc$, $[G1]_2SiNc$, $[G2]_2SiNc$ and $[G3]_2SiNc$) that possess naphthalocyanine (Nc) macrocycles, rather than phthalocyanines as cores (Scheme 2).[39] The extension of the Pc macrocycle by benzoannulation causes a significant

Keywords: macromolecules; dendrimers; aryl ether; phthalocyanine.

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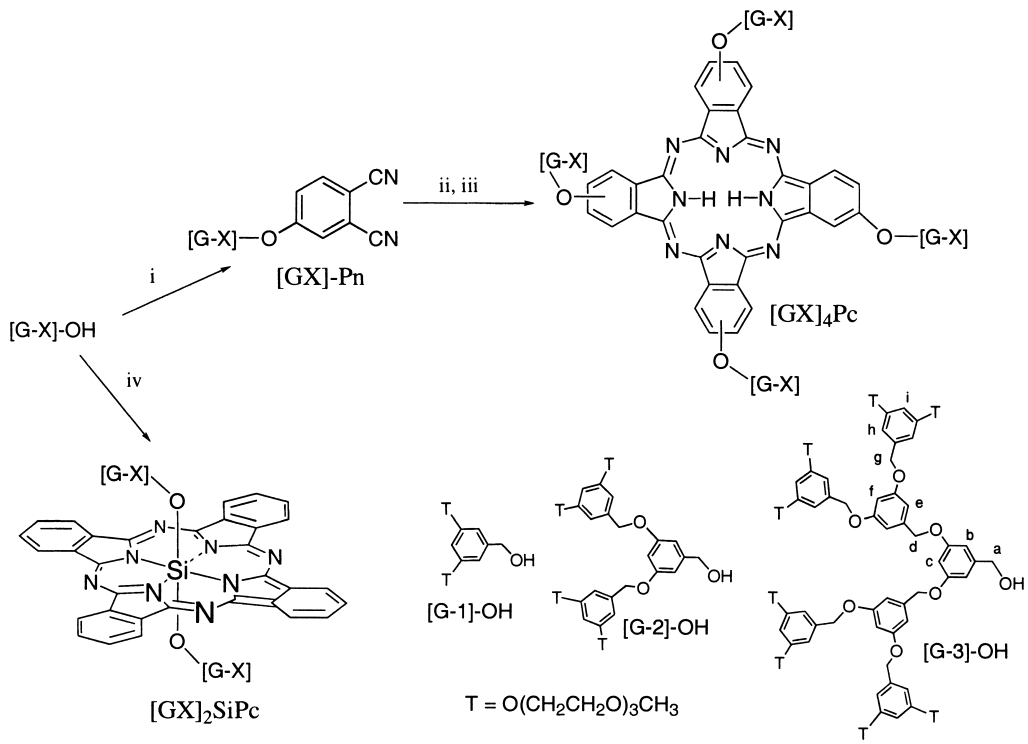


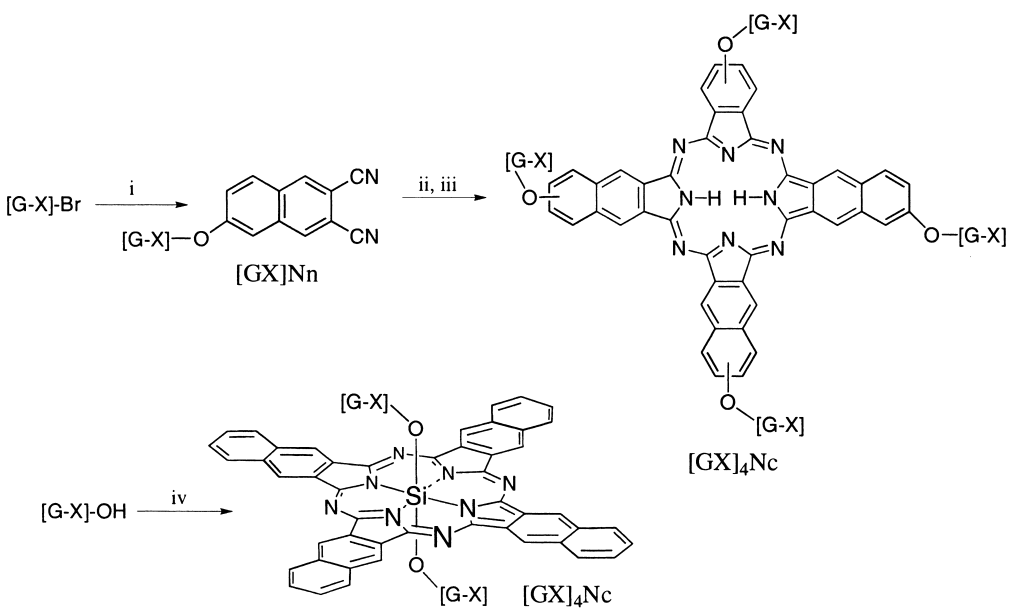
Scheme 1. *Reagents and conditions*: (i) 4-nitrophthalonitrile, anhydrous K_2CO_3, DMF, 50°C; (ii) $C_5H_{11}OLi$, $C_5H_{11}OH$, 135°C; (iii) acetic acid; (iv) dichlorophthalocyaninatosilicon, NaH, toluene, 80°C.

red-shift of the primary adsorption band (the Q-band) in the UV/visible spectrum to ~760 nm for Nc relative to ~680 nm for Pc. Ncs are also of interest as PDT photosensitisers due to the enhanced lifetimes of their singlet excited state, which is beneficial for singlet oxygen formation, and also due to the greater transparency of physiological tissue to light in the near-IR region of the spectrum.[31,40,41]

2. Results and discussions

2.1. Synthesis

For the main part, simple modifications to Fréchet's convergent synthetic route to poly(aryl ether) dendrimers[42,43] allows the introduction of oligo(ethyleneoxy) rather than benzyloxy terminal groups. Thus, the aryl ether



Scheme 2. *Reagents and conditions*: (i) 6-hydroxynaphthalonitrile, anhydrous K_2CO_3, DMF, 60°C; (ii) $C_5H_{11}OLi$, $C_5H_{11}OH$, 135°C; (iii) acetic acid; (iv) dichloronaphthalocyaninatosilicon, NaH, toluene, 80°C.

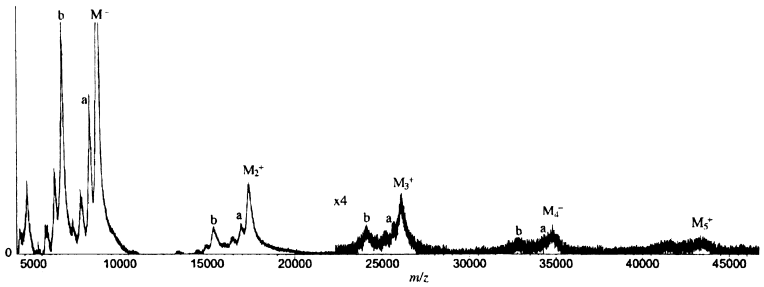


Figure 1. The MALDI mass spectrum of $[G3]_4Pc$ showing the presence of peaks due to oligomeric aggregates. Peaks labelled a and b are due to the cleavage of benzylic CH_2-O bonds.

forming reaction between methyl 3,5-dihydroxybenzoate and the tosylate of triethylene glycol monomethyl ether, followed by reduction with lithium aluminium hydride, gives the first generation dendron, [G1]-OH. The second and third oligo(ethyleneoxy) terminated dendrons, [G2]-OH and [G3]-OH, are assembled from [G1]-OH by successive bromination and aryl ether formation reactions. However, the bromination of [G1]-OH proved problematic using the conventional method, involving carbon tetrabromide and triphenylphosphine, due to the inseparability of the required product ([G1]-Br) and triphenylphosphine oxide by chromatography. Therefore, a brominating mixture of chlorodiphenylphosphine, bromine and imidazole was employed for this step.[44]

The aromatic nucleophilic substitution reaction (S_NAr) between the [GX]-OH dendron and 4-nitrophthalonitrile produces the required dendron-containing phthalonitrile precursors ([GX]-Pn) in 50–80% yield (Scheme 1).[45] However, for the required naphthalonitrile precursors to the naphthalocyanine-centred dendrimers the analogous S_NAr reaction between [GX]-OH and 6-nitronaphthalonitrile (or 6-fluoronaphthalonitrile) failed.[45] Instead, the desired naphthalonitriles ([GX]-Nn) were prepared from the S_N2 reaction between 6-hydroxynaphthalonitrile (prepared in four steps from 3,4-dimethylphenol using the method of Kovshev et al.)[46] and the appropriate [GX]-Br dendron.

In each case, the Pc- or Nc-centred dendrimer is assembled by the cyclotetramerisation of the phthalonitrile [GX]-Pn or naphthalonitrile [GX]-Nn, using lithium metal dissolved in refluxing pentanol, to give the appropriate $[GX]_4Pc$ or $[GX]_4Nc$ as a mixture of four inseparable isomers in 20–35% yield. Alternatively, the reaction between the anion of the appropriate [G-X]-OH dendron and dichlorophthalocyaninatosilicon or dichloronaphthalocyaninatosilicon produces the appropriate $[GX]_2SiPc$ or $[GX]_2SiNc$ in 10–40% yield, respectively. Within these materials the two dendritic substituents are placed in the axial positions relative to the plane of the Pc or Nc ring.

All Pc- and Nc-containing dendrimers gave satisfactory elemental analyses and spectroscopic data consistent with their expected structures (see below). In addition, analysis using gel permeation chromatography (GPC; solvent=THF) indicated that each material was obtained pure and monodisperse ($M_w/M_n<1.01$). The dendrimers are freely soluble in toluene, DCM, chloroform and THF. They are also soluble in MeOH, EtOH, and aq. EtOH (~50% v/v) but insoluble in pure water or diethyl ether.

2.2. Mass spectrometry

Analysis of each of the dendrimers using either fast atom bombardment (FAB) or matrix-assisted laser desorption ionisation (MALDI) mass spectrometry gave a cluster of peaks consistent in appearance with that calculated from its molecular formula. For each of the $[GX]_4Pc$ and $[GX]_4Nc$ dendrimers, clusters of intensity approximately 50% that of the M^+ cluster are observed due to fragmentation of the benzylic bond (CH_2-O) closest to the macrocycle (labelled b in Figure 1). In addition, smaller peaks are observed relating to cleavage at the remote benzylic sites (labelled a in Figure 1). For $[GX]_2SiPc$ and $[GX]_2SiNc$, the most intense peaks (~four times as intense as the M^+ cluster) are associated with the cleavage of the chemically labile O–Si bond. For MALDI, the major fragmentation processes may be assisted by the absorption of laser light by the macrocyclic core during ionisation. An interesting aspect of the mass spectra of the $[GX]_4Pc$ and $[GX]_4Nc$ dendrimers are peaks corresponding to oligomeric aggregates, $(M^+)_2$, $(M^+)_3$, $(M^+)_4$, and $(M^+)_5$, containing up to five dendrimer molecules (Fig. 1). These oligomer peaks have an associated peak corresponding to the loss of a single dendritic substituent of similar relative intensity in each case-confirming that they arise from fragmentation rather than a defect in the dendrimer.

2.3. ^{1}H NMR spectroscopy

The ^{1}H NMR spectra are consistent with the structures of each of the dendrimers, although for members of the series $[GX]_4Pc$ or $[GX]_4Nc$, the spectra are complicated by the presence of four regioisomers and broadening due to

Table 1. A comparison between the chemical shifts of hydrogens on the axial dendritic substituents of $[G3]_2SiPc$ and $[G3]_2SiNc$ showing the greater effect of the ring current of the Pc core on hydrogens closer to the macrocycle (e.g. those attached to carbons a and b as labelled in Scheme 1), whereas the Nc core has a greater effect on more distant hydrogens (e.g. d and e)

	$[G3]_2SiPc$	$[G3]_2SiNc$	$\Delta(\delta[G3]_2SiPc-\delta[G3]_2SiNc)$
a	−0.73	0.00	−0.73
b	3.40	3.85	−0.45
c	5.60	5.54	0.06
d	3.97	3.88	0.09
e	6.26	6.06	0.2
f	6.40	6.46	−0.06
g	4.90	4.85	−0.05
h	6.54	6.55	−0.01
i	6.44	6.41	−0.03

Table 2. The position of the primary absorption band (Q-band) of the dendrimers in CH_2Cl_2 solution compared with that in EtOH solution. All concentrations were approximately equal (1x10-6 mol dm^{-3})

	$[G1]_4Pc$	$[G2]_4Pc$	$[G3]_4Pc$	$[G1]_2SiPc$	$[G2]_2SiPc$	$[G3]_2SiPc$	$[G1]_4Nc$	$[G2]_4Nc$	$[G3]_4Nc$	$[G1]_2SiNc$	$[G2]_2SiNc$	$[G3]_2SiNc$
λ_{max} (DCM)	705[a], 670	705[a], 670	705[a], 670	678	679	680	785	786	786	789	793	793
λ_{max} (EtOH)	610	625	635	677	679	680	678	696	705	787	790	794

[a] Non-aggregated metal-free Pcs exhibit a split Q-band.

aggregation. However, well-defined spectra were obtained for members of the series $[GX]_2SiPc$ and $[GX]_2SiNc$. For these dendrimers, the ring current of the macrocycle strongly influences the chemical shifts of the peaks associated with each type of hydrogen within the axial dendritic substituents (Table 1). These materials allow a direct comparison to be made regarding the relative intensity of the shielding effect originating from the ring current of the Pc and Nc macrocycles. It is clear that the ring current of the Pc core has a greater shielding effect on hydrogens that are closer to the macrocycle (e.g. those attached to carbons labelled a and b in Scheme 1), whereas the Nc core has a greater shielding effect on more distant hydrogens (e.g. those attached to carbons d and e). This difference has been noted previously for analogous macrocycles with alkyloxy axial substituents.[47,48]

2.4. UV/visible absorption spectroscopy

As expected for all of the dendrimers, their UV/vis absorption spectra from DCM solutions (1×10^{-6} mol dm^{-3}) are consistent with non-aggregated macrocyclic cores with the primary absorption band in the visible region (Q-band) centred at ~685 nm for Pc-centred dendrimers and ~790 for the Nc-centred dendrimers (Table 2). In contrast, large bathochromic shifts (up to 90 nm) of the Q-band are observed from EtOH solutions of each of the materials in which the dendritic substituents are attached at peripheral sites ($[GX]_4Pc$ and $[GX]_4Nc$)-indicating significant aggregation of the cores.[49,50] The magnitude of the bathochromic shift in EtOH solution is greatest for $[G1]_4Pc$ and $[G1]_4Nc$ with the appearance and position of the Q-band being consistent with the formation of cofacial (columnar) aggregates of significant size, whereas, the position and shape of the Q-band from solutions of $[G2]_4Pc$, $[G3]_4Pc$, $[G2]_4Nc$ and $[G3]_4Nc$ suggests that small oligomeric molecular aggregates (i.e. dimers and trimers) are the major species but that only a small fraction of the Pc cores are isolated (Fig. 2).

In contrast to the behaviour of $[GX]_4Pc$ and $[GX]_4Nc$, UV/visible spectroscopic analysis of $[GX]_2SiPc$ and $[GX]_2SiNc$ shows that by placing the dendritic substituents in axial sites relative to the macrocycle cofacial aggregation in EtOH is prevented (Table 2). For all examples within these two series, an unperturbed Q-band was observed. In addition, preliminary fluorescence studies of EtOH solutions of series $[GX]_2SiPc$ reveal that excitation at 420 nm results in strong fluorescence at 688 nm, whereas, for series $[GX]_4Pc$ no significant fluorescence was observed due to self-quenching.

2.5. Material properties

Only $[G1]_2SiPc$ is a solid under ambient conditions, $[G1]_4Pc$, $[G1]_4Nc$ and $[G1]_2SiNc$ are highly viscous tar-like oils and the remaining dendrimers are free-flowing oils. For $[G1]_2SiPc$, it was possible to grow crystals of sufficient size and quality for a single crystal X-ray analysis by the slow diffusion of diethyl ether into a concentrated solution of the material in DCM. An ORTEP-type plot of the crystallographic packing of $[G1]_2SiPc$ is shown in Figure 3 which shows a remarkable lamellar arrangement of the Pc rings with the axial [G-1] substituents acting as spacers between the 2-dimensional arrays. This arrangement is similar to that obtained for the $[G2]_2SiPc$ dendrimer with benzyloxy terminal groups.[34,35]

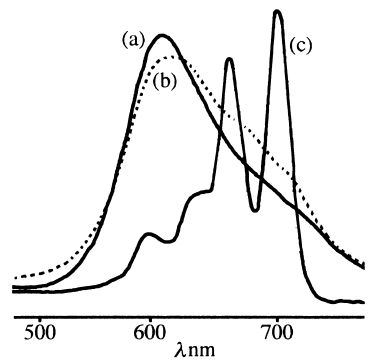


Figure 2. The Q-band absorption for (a) $[G1]_4Pc$ in EtOH, (b, - - -) $[G3]_4Pc$ in EtOH and (c) $[G1]_4Pc$ in DCM.

Previously, oligo(ethyleneoxy) substituted phthalocyanine have been shown to possess both thermotropic and lyotropic liquid crystallinity[51,52] and thus the dendrimers were examined using polarising microscopy. Both $[G1]_4Pc$ and $[G1]_4Nc$ display columnar liquid crystallinity even at room temperature with the thermal range of the mesophase extending to 260°C for $[G1]_4Pc$ and 290°C for $[G1]_4Nc$. The fan-like optical texture of the materials is consistent with a columnar mesophase of hexagonal symmetry.[53,54] Examination of concentrated ethanol solutions (~20–40% by mass) using polarising optical microscopy shows that these two materials behave as discotic amphiphiles forming a distinct lyotropic liquid crystal. The classic *schlieren* appearance of the optical texture indicates that it is a columnar nematic phase.[51,54] No other dendrimers are mesogenic.

3. Conclusion

It is apparent that placing a phthalocyanine or naphthalocyanine at the core of a poly(aryl ether) dendrimer is not a good strategy for ensuring steric isolation of the macrocycle in polar protic solvents—unless the dendritic substituents are placed at the axial sites of the macrocycle. Similar conclusions have been obtained by other researchers using dendritic substituents that possess ionic solubilising groups,

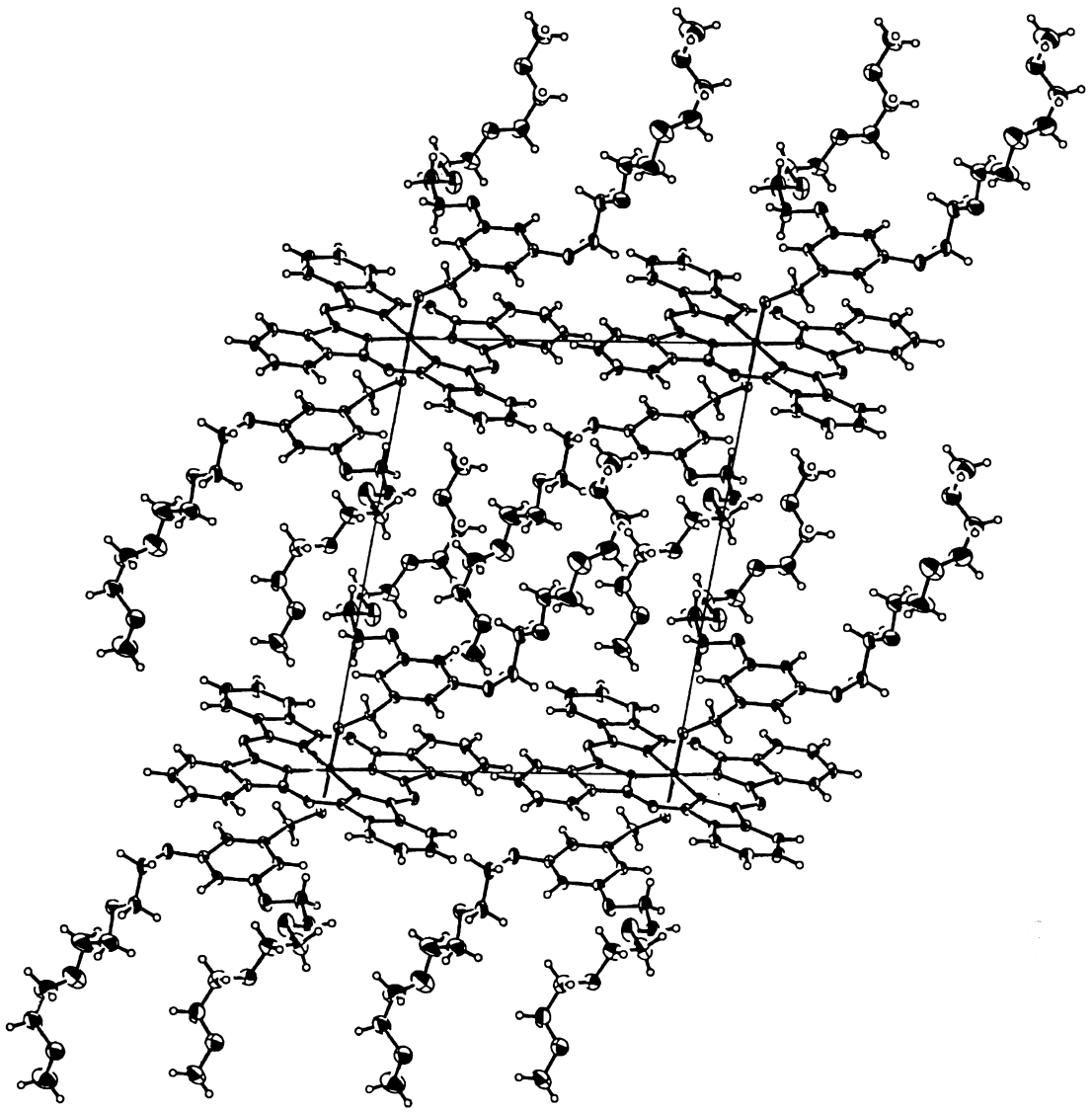


Figure 3. The crystal structure of $[G1]_2SiPc$ showing the sheet arrangement of the Pc units.

although for these materials aggregation is reduced to a greater extent for the higher generation substituents as a result of electrostatic repulsions. Molecular modelling suggests that there is sufficient space surrounding a phthalocyanine columnar aggregate to accommodate the steric bulk of the wedge-shaped dendritic substituents. An efficient method of reducing cofacial self-association in thin films is by the use of hexadeca-substituted Pcs,[55,56] and the use of a greater number of smaller polar substituents may be more successful for obtaining non-aggregating water-soluble phthalocyanines.

4. Experimental

4.1. Materials and methods

Routine ^1H NMR spectra were measured at 300 MHz using a Inova 300 spectrometer. High-resolution (500 MHz) ^1H NMR spectra were recorded using a Varian Unity 500 spectrometer. UV-visible spectra were recorded on a Shimadzu UV-260 spectrophotometer using cells of path length 10 mm. IR spectra were recorded on an ATI Mattson Genesis Series FTIR (KBr/Germanium beam splitter). Elemental analyses were obtained using a Carlo Erba Instruments CHNS-O EA 108 Elemental Analyser. Routine low-resolution electron ionisation (EI) mass spectrometry was obtained using a Fisons Instruments Trio 2000. Fast atom bombardment (FAB) mass spectra were recorded on a Kratos Concept spectrometer and MALDI mass spectra were recorded on a Micromas Tof Spec 2E instrument using a dithranol matrix. GPC analysis was carried out using a Polymer Laboratories Mixed-E (×4) column with a Polymer Laboratories LC1200 UV detector and a Gibson 307 pump. Silica gel (60 Merck 9385) was used in the separation and purification of compounds by column chromatography. All materials were heated at 120–150°C under vacuum for 18 h as the final step of purification. Differential scanning calorimetry measurements were made on a Seiko DSC 220C machine and calibrated using an indium standard. Optical microscopy observations were made on a Nikon Optiphot-2 microscope with a Mettler FP80 HT Hot Stage.

4.2. Synthesis of the oligo(ethyleneoxy) terminated dendrons

4.2.1. Methyl 3,5-di-[1′,4′,7′,10′-tetraoxaundecyl])benzoate. Methyl-3,5-dihydroxybenzoate (40 g, 0.24 mol), 1,4,7,10-tetraoxaundecyl tosylate (151 g, 0.48 mol) and potassium carbonate (51.3 g), were stirred in anhydrous acetone (1 l) at reflux for 72 h. The reaction mixture was cooled, the salts filtered off, and the solvent removed under reduced pressure. The resulting solid was dissolved in ethyl acetate and washed with aq. NaOH (1 M, 3×500 ml). On removal of the solvent under reduced pressure, methyl 3,5-di-[1′,4′,7′,10′-tetraoxaundecyl])benzoate was obtained as a pale-yellow oil (102 g, 93% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.17 (d, J=2 Hz, 2H), 6.67 (t, J=2 Hz, 1H), 4.10 (t, J=6 Hz, 4H), 3.87 (s, 3H), 3.80–3.50 (m, 20H), 3.56 (s, 6H). CIMS: m/z=478 ($M+NH_4^+$), 460 (M^+). Anal. calcd for $C_{22}H_{36}O_{10}$: C 57.38, H 7.88. Found C 57.50; H 8.10.

4.2.2. 3,5-Di-[1′,4′,7′,10′-tetraoxaundecyl])benzyl alcohol ([G1]-OH). To a stirred solution of methyl 3,5-di-[1′,4′,7′,10′-tetraoxaundecyl])benzoate (61.9 g, 0.13 mol) in anhydrous THF (45 ml) was added $LiAlH_4$ (1.71 g 45 mmol). The reaction mixture was stirred for 24 h. On cooling, water (0.2 ml) and then NaOH (1 M, 1 ml) was added. The solution was dried ($MgSO_4$), filtered and the solvent removed under reduced pressure to give [G1]-OH as a colourless oil (57.2 g, 99% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 6.63 (d, J=2 Hz, 2H), 6.40 (t, J=2 Hz, 2H), 4.59 (s, 2H), 4.10 (t, J=6 Hz, 4H), 3.80–3.50 (m, 20H), 3.36 (s, 6H). CIMS: m/z=450 ($M+NH_4^+$), 432 (M^+). Anal. calcd for $C_{21}H_{36}O_9$: C 58.32, H 8.39. Found C 58.37; H 8.69.

4.2.3. 3,5-Di-[1′,4′,7′,10′-tetraoxaundecyl])benzyl bromide ([G1]-Br). Following the method of Classon,[44] to a stirred solution of [G1]-OH (3.0 g, 6.9 mmol) chlorodiphenylphosphine (2.0 g, 10 mmol) and imidazole (1.04 g, 15 mmol) in anhydrous toluene (50 ml) was added bromine (0.72 g 9 mmol). The reaction mixture was stirred for 24 h. Then NaOH (1 M, 40 ml) was added and the solution stirred during the dropwise addition of iodine (1.14 g, 9 mmol). Aqueous sodium thiosulfate was added until the solution became colourless. The solution was washed with water, dried ($MgSO_4$) and the solvent removed under reduced pressure to give [G1]-Br as a light-brown oil (2.21 g, 64% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 6.49 (d, J=2 Hz, 2H), 6.38 (t, J=2 Hz, 2H), 4.34 (s, 2H), 4.05 (t, J=6 Hz, 4H), 3.80–3.50 (m, 20H), 3.30 (s, 6H). CIMS: m/z=516 ($M+NH_4^+$+2), 514 ($M+NH_4^+$), 498 (M^+2), 496 (M^+). Anal. calcd for $C_{21}H_{35}BrO_8$: C 50.91, H 7.19, Br 16.13. Found C 50.37; H 8.07, Br 16.00.

4.2.4. 3,5-Di-(3′,5′-di-[1″,4″,7″,10″-tetraoxaundecyl])benzyloxy)benzyl alcohol ([G2]-OH). [G1]-Br (20 g, 40 mmol), 3,5-dihydroxybenzyl alcohol (2.26 g, 16 mmol), 18-crown-6 (850 mg), sodium iodide (100 mg) and potassium carbonate (6.69 g), were stirred in anhydrous acetone (250 ml) at reflux for 5 days. The reaction mixture was cooled, the salts filtered off, and the solvent removed under reduced pressure. The resulting oil was purified by column chromatography (ethyl acetate with increasing amount of acetone) to give [G2]-OH as a pale-yellow oil (15.5 g, 52% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 6.58–6.54 (m, 6H), 6.47 (d, J=2 Hz, H), 6.41 (t, J=2 Hz, 2H), 4.95 (s, 4H), 4.58 (s, 2H), 4.09 (t, J=7 Hz, 8H), 3.88–3.50 (m, 40H), 3.36 (s, 12H). CIMS: m/z=986 ($M+NH_4^+$), 968 (M^+). Anal. calcd for $C_{49}H_{76}O_{19}$: C 60.37, H 7.90. Found C 60.27; H 7.45.

4.2.5. 3,5-Di-(3′,5′-di-(3″,5″-di-[1‴,4‴,7‴,10‴-tetraoxaundecyl])benzyloxy)-benzyloxy)benzyl alcohol ([G3]-OH). Prepared from [G2]-Br as above and purified by column chromatography (ethyl acetate with increasing amount of acetone) (25% yield) as a colourless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 6.65 (d, J=2 Hz, 4H), 6.58 (d, J=2 Hz, 2H), 6.53 (d, J=2 Hz, 8H), 6.52 (t, J=2 Hz, 2H), 6.41–6.44 (m, 5H), 4.97 (s, 8H), 4.92 (s, 4H), 4.58 (s, 2H), 4.11 (t, J=7 Hz, 16H), 3.88–3.50 (m, 80H), 3.35 (s, 24H). FABMS: m/z=cluster centred at 2064 ($M+Na^+$). Anal. calcd for $C_{105}H_{156}O_{39}$: C 61.75, H 7.70. Found C 60.80; H 7.55.

4.2.6. 3,5-Di-(3′,5′-di-[1″,4″,7″,10″-tetraoxaundecyl])benzyloxy)benzyl bromide ([G2]-Br). A solution of triphenylphosphine (2.5 g, 9.5 mmol) in DCM (50 ml) was added dropwise to a cooled stirred solution of [G2]-OH (7.38 g, 7.6 mmol) and carbon tetrabromide (3.16 g, 8.5 mmol). The reaction mixture was stirred for 24 h. The solvent was removed under reduced pressure and water (50 ml) added. The product was extracted with DCM (3×50 ml) and purified by column chromatography (ethyl acetate with increasing amount of acetone) to give [G2]-Br as a pale-brown oil (6.6 g, 85% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 6.60 (d, J=2 Hz, 2H), 6.56 (d, J=2 Hz, 4H), 6.50 (d, J=2 Hz, 1H), 6.44 (t, J=2 Hz, 2H), 4.93 (s, 4H), 4.39 (s, 2H), 4.10 (t, J=7 Hz, 8H), 3.88–3.50 (m, 40H), 3.40 (s, 12H). CIMS: m/z=1050 (M^++NH_4^++2), 1048 (M^++NH_4^+), 1032 (M^+ +2), 1030 (M^+). Anal. calcd for $C_{49}H_{75}BrO_{18}$: C 57.03, H 7.33, Br 7.74. Found C 56.70; H 7.45, Br 7.48.

4.2.7. 3,5-Di-(3′,5′-di-(3″,5″-di-[1‴,4‴,7‴,10‴-tetraoxaundecyl])benzyloxy)-benzyloxy)benzyl bromide ([G3]-Br). Prepared from [G3]-OH as above and purified by column chromatography (ethyl acetate with increasing amount of acetone) (25% yield) as a pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 6.63 (d, J=2 Hz, 4H), 6.61 (d, J=2 Hz, 2H), 6.56 (d, J=2 Hz, 8H), 6.52 (t, J=2 Hz, 2H), 6.41–6.44 (m, 5H), 4.94 (s, 8H), 4.92 (s, 4H), 4.39 (s, 2H), 4.09 (t, J=7 Hz, 16H), 3.88–3.50 (m, 80H), 3.35 (s, 24H). FABMS: m/z=cluster centred at 2127 ($M+Na^+$). Anal. calcd for $C_{105}H_{155}BrO_{38}$: C 59.90, H 7.47, Br 3.80. Found C 59.80; H 7.35; Br 3.45.

4.3. The synthesis of [GX]-Pn precursors

4.3.1. 4-(3′,5′-Di-[1″,4″,7″,10″-tetraoxaundecyl])benzyloxyphthalonitrile ([G1-Pn). Potassium carbonate (1.12 g, 8.1 mmol), 4-(3′,5′-di-[1″,4″,7″,10″-tetraoxaundecyl])-benzyl alcohol ([G-1]-OH, 2.29 g, 5.30 mmol) and 4-nitrophthalonitrile (1.19 g, 6.70 mmol), were stirred in anhydrous DMSO (8 ml) at 25°C for 72 h. The reaction mixture was cooled and poured into water (25 ml). The solution was extracted with DCM (3×50 ml), dried over magnesium sulfate and filtered. The organic layer was evaporated to dryness, leaving a green oil. Purification was

achieved by column chromatography (ethyl acetate with increasing amount of acetone). Removal of the solvent under reduced pressure gave ([G1-Pn) (2.0 g, 68% yield) as a pale green oil; IR (KBr, cm^{-1}): ν_{CN}=2220. ^1H NMR (500 MHz, $CDCl_3$) δ ppm 7.68 (d, J=8 Hz, 1H), 7.29 (d, J=2 Hz, 1H), 7.22 (dd, J=8, 2 Hz, 1H), 6.51 (d, J=2 Hz, 2H), 6.45 (t, J=2 Hz, H), 5.10 (s, 2H), 4.12–3.50 (m, 24H), 3.35 (s, 6H). CIMS: m/z=576 ($M+NH_4^+$). Anal. calcd for $C_{29}H_{38}N_2O_9$: C 62.35, H 6.86, N 5.01. Found C 62.27; H 6.98; N 5.07.

The following phthalonitriles were prepared from the appropriate [GX]-OH dendron using similar methodology.

4.3.2. 4-(3′,5′-Di-(3″,5″-di-[1‴,4‴,7‴,10‴- tetraoxaundecyl])benzyloxy)-benzyloxyphthalonitrile ([G2]-Pn). Purification was achieved by column chromatography (THF with increasing amount of acetone) to give ([G2]-Pn) (84% yield) as a pale green oil; IR (KBr, cm^{-1}): ν_{CN}=2220. ^1H NMR (500 MHz, $CDCl_3$) δ ppm 7.69 (d, J=8 Hz, 1H), 7.27 (d, J=2 Hz, 1H), 7.18 (dd, J=8, 2 Hz, 1H), 6.58–6.50 (m, 7H), 6.43 (t, J=2 Hz, 2H), 5.08 (s, 2H), 4.95 (s, 4H), 4.09 (t, J=7 Hz, 8H), 3.88–3.50 (m, 40H), 3.36 (s, 12H). CIMS: m/z=1112 ($M+NH_4^+$). Anal. calcd for $C_{57}H_{78}N_2O_{19}$: C 62.51, H 7.18, N 2.56. Found C 62.27; H 7.43; N 2.42.

4.3.3. 4-(3′,5′-Di-(3″,5″-di-(3‴,5‴-di-[1⁗,4⁗,7⁗,10⁗-tetraoxaundecyl])benzyloxy)benzyloxy)benzyloxyphthalonitrile ([G3]-Pn). Purification was achieved by column chromatography (ethyl acetate with increasing amount of acetone) to give ([G3]-Pn) (42% yield) as a pale green oil; IR (KBr, cm^{-1}) ν_{CN}=2220. ^1H NMR (500 MHz, $CDCl_3$) δ ppm 7.67 (d, J=8 Hz, 1H), 7.29 (d, J=2 Hz, 1H), 7.20 (dd, J=8, 2 Hz, 1H), 6.64–6.53 (m, 17H), 6.43 (t, J=2 Hz, 4H), 5.06 (s, 2H), 4.99 (s, 4H), 4.93 (s, 8H), 4.10 (t, J=7 Hz, 16H), 3.88–3.50 (m, 80H), 3.36 (s, 24H). FABMS: m/z=2192 ($M+Na^+$). Anal. calcd for $C_{113}H_{158}N_2O_{39}$: C 62.60, H 7.34, N 1.30. Found C 62.80; H 7.35; N 1.20.

4.4. The synthesis of [GX]-Nn precursors

4.4.1. 6-(3′,5′-Di-[1″,4″,7″,10″-tetraoxaundecyl])benzyloxynaphthalonitrile ([G1-Nn). Potassium carbonate (744 mg, 5.4 mmol), 4-(3′,5′-di-[1″,4″,7″,10″-tetraoxaundecyl])benzyl bromide ([G-1]-Br, 1.78 g, 3.58 mmol) and 6-hydroxynaphthalonitrile (837 g, 4.29 mmol), were stirred in anhydrous DMF (4 ml) at 60°C for 72 h. The reaction mixture was cooled and poured into water (25 ml). The solution was extracted with DCM (3×50 ml), dried over magnesium sulphate and filtered. The organic layer was evaporated to dryness, leaving a yellow oil. Purification was achieved by column chromatography (petroleum with increasing amount of ethyl acetate). Removal of the solvent under reduced pressure gave ([G1-Nn) (1.32 g, 60% yield) as a colourless powder; Mp 61°C. IR (KBr, cm^{-1}): ν_{CN}=2231. ^1H NMR (500 MHz, $CDCl_3$) δ ppm 8.25 (s, 1H), 8.19 (s, 1H), 7.88 (d, J=8 Hz, 1H), 7.48 (dd, J=8, 2 Hz, 1H), 7.25 (d, J=2 Hz, 1H), 6.51 (d, J=2 Hz, 2H), 6.47 (t, J=2 Hz, H), 5.16 (s, 2H), 4.12 (t, J=2 Hz, 4H), 3.85 (t, J=7 Hz, 4H), 3.75–3.53 (m, 16H), 3.38 (s, 6H). FABMS: m/z=632 ($M+Na^+$). Anal. calcd for $C_{33}H_{38}N_2O_9$: C 65.12, H 6.62, N 4.60. Found C 64.80; H 6.33; N 4.57.

The following naphthalonitriles were prepared from the appropriate [GX']-Br dendron using similar methodology.

4.4.2. 4-(3′,5′-Di-(3″,5″-di-[1‴,4‴,7‴,10‴-tetraoxaundecyl])benzyloxy)-benzyloxynaphthalonitrile ([G2]-Nn). Purification was achieved by column chromatography (ethyl acetate with increasing amount of acetone) to give ([G2]-Nn) (68% yield) as a pale yellow oil; IR (KBr, cm^{-1}): ν_{CN}=2230. ^1H NMR (500 MHz, $CDCl_3$) δ ppm 8.26 (s, 1H), 8.17 (s, 1H), 7.89 (d, J=8 Hz, 1H), 7.47 (dd, J=8, 2 Hz, 1H), 7.22 (d, J=2 Hz, 1H), 6.62 (t, J=2 Hz, 2H), 6.57–6.52 (m, 5H), 6.41 (t, J=2 Hz, 2H), 5.16 (s, 2H), 4.96 (s, 4H), 4.10 (t, J=7 Hz, 8H), 3.88–3.50 (m, 40H), 3.36 (s, 12H). FABMS: m/z=1168 ($M+Na^+$). Anal. calcd for $C_{117}H_{160}N_2O_{39}$: C 63.97, H 7.00, N 2.45. Found C 64.10; H 7.20; N 2.35.

4.4.3. 4-(3′,5′-Di-(3″,5″-di-(3‴,5‴-di-[1⁗,4⁗,7⁗,10⁗-tetraoxaundecyl])benzyloxy)benzyloxy)benzyloxynaphthalonitrile ([G3]-Nn). Purification was achieved by column chromatography (ethyl acetate with increasing amount of acetone) to give ([G3]-Nn) (58% yield) as a pale brown oil; IR (KBr, cm^{-1}): ν_{CN}=2230. ^1H NMR (500 MHz, $CDCl_3$) δ ppm 8.22 (s, 1H), 8.15 (s, 1H), 7.85 (d, J=8 Hz, 1H), 7.45 (dd, J=8, 2 Hz, 1H), 7.22 (d, J=2 Hz, 1H), 6.67–6.54 (m, 17H), 6.43 (t, J=2 Hz, 4H), 5.16 (s, 2H), 4.99 (s, 4H), 4.93 (s, 8H), 4.10 (t, J=7 Hz, 16H), 3.88–3.50 (m, 80H), 3.37 (s, 24H). FABMS: m/z=2232 ($M^+ + Na^+$). Anal. calcd for $C_{113}H_{158}N_2O_{39}$: C 63.34, H 7.27, N 1.26. Found C 63.47, H 7.53, N 1.23.

4.5. The synthesis of $[GX]_4Pc$ and $[GX]_4Nc$

4.5.1. 9(10),16(17),23(24)-Tetra(3′,5′-di-[1″,4″,7″,10″-tetraoxaundecyl])-benzyloxy)phthalocyanine ($[G\text{-}1]_4Pc$). Excess lithium metal was added to a rapidly stirred solution of [G1]-Pn (209 mg, 0.37 mmol) in refluxing pentanol (1 ml). The reaction mixture was heated at reflux for 24 h. The reaction was cooled and acetic acid (0.1 M, 0.2 ml) added. The solvent was removed under reduced pressure. The crude product was purified by column chromatography (DCM/ethanol) to give $[G\text{-}1]_4Pc$ (74 mg, 35% yield) as a dark blue viscous oil; UV/vis (CH_2Cl_2, nm): 705 (1.2×10^5), 670 (1.0×10^5), 655 (3.2×10^4), 620 (1.4×10^4), 422 (3.2×10^4), 346 (8.0×10^4). IR (KBr, cm^{-1}): ν_{NH}=3275. ^1H NMR (500 MHz, $CDCl_3$) δ ppm 9.10–9.06 (br m, 4H), 8.72–8.64 (br m, 4H), 7.73–7.66 (br m, 4H), 6.91 (br s, 8H), 6.57 (br s, 4H), 5.45 (br s, 8H), 4.23–4.28 (m, 16H), 3.90–3.80 (m, 16H), 3.75–3.60 (m, 48H), 3.53–3.49 (m, 16H), 3.35–3.30 (m, 24H), −1.5 (br s, 2H). MALD-MS: m/z=2237 ($M+H^+$). GPC (vs polystyrene standards): 3300. Anal. calcd for $C_{116}H_{154}N_8O_{36}$: C 62.30, H 6.94, N 5.01. Found C 62.07, H 6.91, N 4.87.

The following phthalocyanines and naphthalocyanines were prepared using the same methodology.

4.5.2. 2,9(10),16(17),23(24)-Tetra(3′,5′-di-(3″,5″-di-[1‴,4‴,7‴,10‴-tetraoxaundecyl])benzyloxy)benzyloxyphthalocyanine ($[G2]_4Pc$). The crude product was purified by preparative TLC (DCM with increasing amount of ethanol) to give $[G\text{-}2]_4Pc$ (22% yield) as a dark green viscous oil; UV/vis (CH_2Cl_2, nm): 705 (1.0×10^5), 670

(0.8×10^5), 655 (2.2×10^4), 620 (1.0×10^4), 422 (2.2×10^4), 346 (7.0×10^4). IR (KBr, cm^{-1}) ν_{NH}=3275. ^1H NMR (500 MHz, $CDCl_3$) δ ppm 9.41–9.31 (br m, 4H), 9.03–8.94 (br m, 4H), 7.85–7.76 (br m, 4H), 6.95 (br s, 8H), 6.64–6.52 (m, 20H), 6.45–6.41 (m, 8H), 5.55 (br s, 8H), 5.06–5.00 (m, 16H), 4.12–4.06 (m, 32H), 3.82–3.47 (m, 160H), 3.36–3.31 (m, 48H), −0.5 (br s, 2H). MALDI-MS *m*/*z*=4384 (M^++H^+). GPC (vs polystyrene standards): 6200. Anal. calcd for $C_{228}H_{314}N_8O_{76}$: C 62.48, H 7.22, N 2.56. Found C 62.37, H 6.98, N 2.47.

4.5.3. 2,9(10),16(17),23(24)-Tetra(3′,5′-di-(3″,5″-di-(3‴,5‴-(di-[1⁗,4⁗,7⁗,10⁗-tetraoxaundecyl])benzyloxy)-benzyloxy)benzyloxy-phthalocyanine ([G3]$_4$Pc). The crude product was purified by preparative TLC (DCM with increasing amount of ethanol) to give [G-3]$_4$Pc (23% yield) as a green viscous oil; UV/vis (CH_2Cl_2, nm): 705 (1.3×10^5), 670 (1.0×10^5), 655 (3.2×10^4), 620 (1.4×10^4), 422 (3.2×10^4), 346 (8.0×10^4). IR (KBr, cm^{-1}) ν_{NH}=3275. ^1H NMR (500 MHz, $CDCl_3$) δ ppm 9.73–9.64 (br m, 4H), 9.03–8.98 (br m, 4H), 7.87–7.80 (br m, 4H), 6.98–6.93 (br m, 8H), 6.72–6.30 (m, 76H), 5.56–5.50 (m, 8H), 5.08–4.85 (m, 48H), 4.07–3.96 (m, 64H), 3.82–3.44 (m, 320H), 3.30–3.31 (m, 96H), −0.8 (br s, 2H). MALDI-MS *m*/*z*=cluster centred at 8676 (M^+). GPC (vs polystyrene standards): 10000. Anal. calcd for $C_{452}H_{634}N_8O_{156}$: C 62.57, H 7.37, N 1.29. Found C 62.14, H 6.99, N 1.09.

4.5.4. 3,12(13),21(22),30(31)-Tetra(3′,5′-di-[1″,4″,7″,10″-tetraoxaundecyl])benzyloxynaphthalocyanine ([G1]$_4$-Nc). The crude product was purified by preparative TLC (THF) and by repeated re-precipitations from DCM solution in diethyl ether to give [G-1]$_4$Nc (16% yield) as a dark green viscous oil; UV/vis (CH_2Cl_2, nm): 785 (5.0×10^4), 740 (3.0×10^4), 695 (4.0×10^4), 450 (1.2×10^4). IR (KBr, cm^{-1}) ν_{NH}=3275. ^1H NMR (500 MHz, $CDCl_3$) δ ppm 9.10–8.53 (br m, 8H), 8.28–7.84 (br m, 12H), 6.78 (br s, 4H), 6.60–6.56 (br m, 8H), 5.20–5.15 (br s, 8H), 4.12–3.53 (m, 96H), 3.34 (s, 24H), internal protons not discernable. MALDI-MS *m*/*z*=2436 (M+ H^+). GPC (vs polystyrene standards): 820. Anal. calcd for $C_{132}H_{162}N_8O_{36}$: C 65.04, H 6.70, N 4.60. Found C 64.28, H 6.78, N 4.47.

4.5.5. 3,12(13),21(22),30(31)-Tetra(3′,5′-di-(3″,5″-di-[1‴,4‴,7‴,10‴-tetraoxaundecyl])benzyloxy)benzyloxy-naphthalocyanine ([G2]$_4$Nc). The crude product was purified by preparative TLC (DCM with an increasing amount of ethanol) and by repeated re-precipitations from DCM solution in diethyl ether to give [G-2]$_4$Nc (18% yield) as a dark green viscous oil; UV/vis (CH_2Cl_2, nm): 785 (1.4×10^5), 740 (1.0×10^4), 695 (1.2×10^4), 450 (1.2×10^4). IR (KBr, cm^{-1}) ν_{NH}=3275. ^1H NMR (500 MHz, $CDCl_3$) δ ppm 9.64–9.10 (br m, 8H), 8.55–8.01 (br m, 12H), 6.91 (br s, 8H), 6.62–6.55 (br m, 20H), 6.45–6.41 (m, 8H), 5.30 (br s, 8H), 5.00–4.95 (m, 16H), 4.12–3.35 (m, 192H), 3.36–3.31 (m, 48H), −1.38 (br s, 2H). MALDI-MS *m*/*z*=4584 (M+H^+). GPC (vs polystyrene standards): 4600. Anal. calcd for $C_{244}H_{322}N_8O_{76}$: C 63.94, H 7.08, N 2.44. Found C 63.37, H 6.85, N 2.40.

4.5.6. 3,12(13),21(22),30(31)-Tetra(3′,5′-di-(3″,5″-di-(3‴,5‴-(di-[1⁗,4⁗,7⁗,10⁗-tetraoxaundecyl])benzyloxy)-benzyloxy)benzyloxy-naphthalocyanine ([G3]$_4$Nc). The crude product was purified by preparative TLC (DCM with an increasing amount of ethanol) to give [G-3]$_4$Nc (12% yield) as an olive-green oil; UV/vis (CH_2Cl_2, nm): 785 ($1.2.0\times10^5$), 740 (2.0×10^4), 695 (3.2×10^4), 450 (1.2×10^4). IR (KBr, cm^{-1}) ν_{NH}=3275. ^1H NMR (500 MHz, $CDCl_3$) δ ppm 9.85–9.70 (m, 8H), 8.53–8.49 (m, 4H), 7.99–7.89 (m, 4H), 7.60–7.55 (m, 4H), 6.94–6.88 (m, 8H), 6.72–6.35 (m, 76H), 5.38–5.32 (br m, 8H), 5.08–4.99 (m, 16H), 4.95–4.90 (m, 32 H), 4.07–4.00 (m, 64H), 3.82–3.46 (m, 320H), 3.32–3.30 (m, 96H), −1.8 (br s, 2H). MALDI-MS *m*/*z*=cluster centred at 8876 (M^+). GPC (vs polystyrene standards): 7200. Anal. calcd for $C_{468}H_{642}N_8O_{156}$: C 63.33, H 7.29, N 1.26. Found C 62.78, H 6.88, N 1.19.

4.6. The synthesis of [GX]$_2$SiPc and [GX]$_2$SiNc

4.6.1. Di-(3′,5′-di-[1″,4″,7″,10″-tetraoxaundecyl])benzyloxy)phthalocyaninato-silicon ([G-1]$_2$SiPc). Lithium hydride (8 mg, 1 mmol) was added to a rapidly stirred solution of dichlorophthalocyaninatosilicon (200 mg, 0.33 mmol) and [G1]-OH (432 mg, 1 mmol) in pyridine (1 ml). The reaction mixture was heated at 120°C for 72 h. The reaction was cooled and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (ethyl acetate/acetone) and by recrystallsation from diethyl ether to give [G-1]$_2$SiPc (200 mg, 44% yield) as dark blue prismatic crystals; Mp 85°C. UV/vis (CH_2Cl_2, nm): 678 (2.5×10^5), 650 (2.5×10^4), 610 (2×10^4), 354 (5×10^4). ^1H NMR (500 MHz, $CDCl_3$) δ ppm 9.58–9.51 (m, 8H), 8.33–8.27 (m, 8H), 5.51 (t, *J*=2 Hz, 2H), 3.59–3.56 (m, 16H), 3.65 (t, *J*=8 Hz, 8H), 3.49 (t, *J*=8 Hz, 8H), 3.40 (t, *J*=8 Hz, 8H) 3.36 (d, *J*=2 Hz, 4H), 3.33 (s, 12H), 3.10 (t, *J*=8 Hz, 8H), −0.78 (s, 4H). FAB-MS: *m*/*z*=1403 (M+H^+). GPC (vs polystyrene standards): 1720. Anal. calcd for $C_{74}H_{86}N_8O_{18}Si$: C 63.32, H 6.18, N 7.98. Found C 62.92, H 6.00, N 8.00.

Crystal data for [G1]$_2$SiPc. $C_{74}H_{86}N_8O_{18}Si$, *M*=1403.62, green needle crystal; 0.05×0.15×0.60 mm^3, *M*=1403.62, 0.05×0.15×0.60 mm^3, triclinic space group *P*1 (no. 2), *a*=13.064(4), *b*=16.318(3), *c*=8.208(2) Å, α=92.02(2), β=96.05(2), γ=79.55(2)°, *U*=1710.8(7) $Å^3$, *Z*=1, D_c=1.362 g cm^{-3}, *F*(000)=744, μ(Mo Kα)=1.14 cm^{-1}, *T*=296 K,λ=0.71069 Å, 6364 reflections measured, 6072 unique (R_{int}=0.017). The refinement (458 variables) with *R*=0.062, R_w=0.055 and GOF=2.29 using 4002 unique reflections ($I>3.0\sigma(I)$). Data was collected on a Rigaku AFC5R diffractometer with graphite monochromator, ω–2θ scan mode, 6364 reflections measured, 6072 unique reflections, R_{int}=0.017, structure solved by direct methods and all of the non-hydrogen atoms were refined using full matrix least squares (SHELXS86). Crystallographic data (excluding structure factors) for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 194209. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax;+44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

The following phthalocyanines and naphthalocyanines were prepared using the same methodology using either dichloro-

phthalocyaninatosilicon or dichloronaphthalocyaninatosilicon as precursors, respectively.

4.6.2. Di-(3′,5′-di-(3″,5″-di-[1‴,4‴,7‴,10‴-tetraoxaundecyl])benzyloxy)-benzyloxyphthalocyaninatosilicon ([G2]$_2$SiPc). The crude product was purified by column chromatography (ethyl acetate with an increasing amount of acetone) to give [G-2]$_2$SiPc (27% yield) as a dark blue viscous oil; UV/vis (CH_2Cl_2, nm): 679 (2.5×10^5), 650 (2.5×10^4), 610 (2×10^4), 354 (5×10^4). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 9.58–9.51 (m, 8H), 8.33–8.27 (m, 8H), 6.36 (t, J=2 Hz, 4H), 6.23 (d, J=2 Hz, 8H), 5.64 (t, J=2 Hz, 2H), 4.04 (t, J=8 Hz, 16H), 3.96 (s, 8H), 3.82 (t, J=8 Hz, 16H), 3.72 (t, J=8 Hz, 16H), 3.67 (t, J=8 Hz, 16H), 3.63 (t, J=8 Hz, 16H), 3.53 (t, J=8 Hz, 16H), 3.48 (d, J=2 Hz, 4H), 3.30 (s, 24H), −0.70 (s, 4H). FAB-MS m/z=2499 ($M+Na^+$). GPC (vs polystyrene standards): 3100. Anal. calcd for $C_{130}H_{166}N_8O_{38}Si$: C 63.04, H 6.74, N 4.52. Found C 63.05, H 6.79, N 4.44.

4.6.3. Di-(3′,5′-di-(3″,5″-di-(3‴,5‴-(di-[1⁗,4⁗,7⁗,10⁗-tetraoxaundecyl])-benzyloxy)benzyloxy)benzyloxyphthalocyaninatosilicon ([G3]$_2$SiPc). The crude product was purified by preparative TLC (DCM with an increasing amount of ethanol) and to give [G-3]$_2$SiPc (5% yield) as a blue oil; UV/vis (CH_2Cl_2, nm): 680 (2.5×10^5), 650 (2.5×10^4), 610 (2×10^4), 354 (5×10^4). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 9.58–9.51 (m, 8H), 8.33–8.27 (m, 8H), 6.54 (t, J=2 Hz, 16H), 6.46–6.42 (m, 12H), 6.30 (t, J=2 Hz, 8H), 5.66 (t, J=2 Hz, 2H), 4.90 (br s, 16H), 4.08 (t, J=8 Hz, 32H), 3.98 (s, 8H), 3.81 (t, J=8 Hz, 32H), 3.69 (t, J=8 Hz, 32H), 3.67–3.60 (m, 64H), 3.50–3.45 (m, 36H), 3.33 (s, 48H), −0.72 (s, 4H). MALDI-MS m/z=cluster centred at 4623 (M^+). GPC (vs polystyrene standards): 3800. Anal. calcd for $C_{242}H_{326}N_8O_{78}Si$: C 62.87, H 7.11, N 2.42. Found C 62.44, H 6.95, N 2.19.

4.6.4. Di-(3′,5′-di-[1″,4″,7″,10″-tetraoxaundecyl])benzyloxy)-naphthalocyaninatosilicon ([G-1]$_2$SiNc). The crude product was purified by preparative TLC (ethyl acetate with an increasing amount of acetone) to give [G-1]$_2$SiPc (43% yield) as a dark green wax; UV/vis (CH_2Cl_2, nm): 789 (2.5×10^5), 730 (4.0×10^4), 695 (3.5×10^4), 438 (8×10^4), 370 (1×10^5). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 10.04 (s, 8H), 8.67–8.62 (m, 8H), 7.93–7.90 (m, 8H), 5.50 (t, J=2 Hz, 2H), 3.74 (d, J=2 Hz, 4H), 3.51 (t, J=8 Hz, 8H), 3.43 (t, J=8 Hz, 8H), 3.34 (s, 12H), 3.31–3.28 (m, 16H), 2.97 (t, J=8 Hz, 8H), 2.89 (t, J=8 Hz, 8H), −0.02 (s, 4H). FAB-MS m/z=1626 ($M+Na^+$). GPC (vs polystyrene standards): 790. Anal. calcd for $C_{90}H_{94}N_8O_{18}Si$: C 67.40, H 5.91, N 6.99. Found C 67.02, H 5.54, N 6.74.

4.6.5. Di-(3′,5′-di-(3″,5″-di-[1‴,4‴,7‴,10‴-tetraoxaundecyl])benzyloxy)-benzyloxynaphthalocyaninatosilicon ([G2]$_2$SiNc). The crude product was purified by preparative TLC (DCM with an increasing amount of ethanol) to give [G-2]$_2$SiNc (16% yield) as an olive-green oil; UV/vis (CH_2Cl_2, nm): 793 (2.9×10^5), 730 (5.0×10^4), 695 (3.5×10^4), 438 (8×10^4), 370 (1×10^5). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 9.98 (s, 8H), 8.60–8.55 (m, 8H), 7.90–7.85 (m, 8H), 6.28 (t, J=2 Hz, 4H), 6.01 (d, J=2 Hz, 8H), 5.55 (t, J=2 Hz, 2H), 3.92 (t, J=8 Hz, 16H), 3.90 (s, 4H), 3.86 (s, 8H), 3.78 (t, J=8 Hz, 16H), 3.71 (t, J=8 Hz, 16H), 3.66 (t, J=8 Hz, 16H), 3.62 (t, J=8 Hz, 16H), 3.51 (t, J=8 Hz, 16H), 3.33 (s, 24H), 0.01 (s, 4H). FAB-MS m/z=2677 ($M+H^+$). GPC (vs polystyrene standards): 3300. Anal. calcd for $C_{146}H_{174}N_8O_{38}$: C 65.50, H 6.55, N 4.19. Found C 64.98, H 6.45, N 4.12.

4.6.6. Di-(3′,5′-di-(3″,5″-di-(3‴,5‴-(di-[1⁗,4⁗,7⁗,1⁗-tetraoxaundecyl])-benzyloxy)benzyloxy)benzyloxy-naphthalocyaninatosilicon ([G3]$_2$SiNc). The crude product was purified by preparative TLC (DCM/ethanol) to give [G-3]$_2$SiNc (4% yield) as an olive-green oil; UV/vis (CH_2Cl_2, nm): 793 (2.0×10^5), 730 (3.0×10^4), 695 (3.0×10^4), 438 (7×10^4), 370 (1×10^5). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 10.01 (s, 8H), 8.55–8.52 (m, 8H), 7.81–7.78 (m, 8H), 6.64 (t, J=2 Hz, 4H), 6.54 (br s, 16H), 6.41 (t, J=2 Hz, 8H), 5.58 (t, J=2 Hz, 2H), 4.85 (br s, 16H), 4.06 (t, J=8 Hz, 32H), 3.94 (t, J=2 Hz, 4H), 3.90 (s, 8H), 3.79 (t, J=8 Hz, 32H), 3.68 (t, J=8 Hz, 32H), 3.66–3.60 (m, 64H), 3.50 (t, J=8 Hz, 32H), 3.33 (s, 48H), 0.06 (s, 4H). MALDI-MS m/z=cluster centred at 4622 (M^+). GPC (vs polystyrene standards): 5600. Anal. calcd for $C_{242}H_{326}N_8O_{78}Si$: C 62.87, H 7.11, N 2.42. Found C 62.22, H 6.82, N 2.09.

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