# The Synthesis and Glass-Forming Properties of Phthalocyanine-Containing Poly(aryl ether) Dendrimers

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**Abstract:** The synthesis, structural characterisation and properties of a number of phthalocyanine-containing dendrimers are described. Peripheral substitution of phthalocyanine (Pc) with four poly(aryl ether) dendritic wedges (1st, 2nd or 3rd generation) produces materials whose properties are dominated both by the columnar self-association of the Pc core and by the glass-forming character of the dendritic substituents. Asymmetric Pcs containing a single poly(aryl ether) dendron display a columnar mesophase, the structure of which can be frozen into an anisotropic glass at room temperature. Placing the dendritic wedges at the axial sites of silicon phthalocyanine prohibits self-association and gives materials from which can be fabricated robust, isotropic solid solutions of Pc with high glass transition temperatures. A single crystal X-ray diffraction analysis of one of these compounds illustrates the ability of the axial dendrons to prevent cofacial aggregation in the solid state.

**Keywords:** dendrimers · liquid crystals · organic glass · phthalocyanines

## Introduction

Dendrimers are well-defined macromolecules of uniform mass and contain a core, successive layers of branched repeat units and peripheral groups.[1] Over the last decade, the synthesis of novel dendrimers has been a very active area of research and one important aspect has been the incorporation of various functional units such as crown ethers,[2] chiral moieties,[3] mesogenic groups[4] and redox-active substituents based on tetrathiafulvalene,[5] anthraquinones,[6] ferrocene,[7] fullerenes[8] or transition metal complexes.[9] 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. For example, placing a porphyrin unit at the core of a dendrimer results in enhanced fluorescence due to the absence of self-quenching mechanisms and a decreased rate of interfacial electron transfer from the porphyrin core to an electrode surface.[10] Lanthanide cation cores also exhibit site isolation as demonstrated by their decreased rate of self-quenching of luminescence.[11]

Phthalocyanine (Pc) is a close relative of the porphyrin macrocycle and is the parent compound of one of the most studied class of functional organic materials.[12] Pc and its derivatives display interesting catalytic, electronic and optical properties, in addition to their widespread use as colorants.[13] Unsubstituted Pc and its metal-ion containing derivatives are characterised by strong intermolecular cohesion, which results in nonmelting, insoluble solids. Substituted derivatives of Pc are often more soluble but even these show a strong tendency to aggregate in solution and the solid phase.[14] In addition, a number of Pc derivatives form liquid crystals on heating in which the macrocycles stack in columnar arrays to maximise the interactions between the aromatic rings.[15] Such cofacial interactions have a profound, and often unwanted, effect on the optical properties of Pc and this results in exciton broadening and a bathochromic shift of the principle absorption band (the Q-band; $\lambda_{max} \approx 700$ nm) in the visible region of the spectrum.[16] In addition, the study of the optical properties of Pcs in dilute solution promises useful nonlinear optical applications (e.g. third-harmonic generation and optical limitation),[17] which are, as yet, unmatched in the solid phase. The differences between the optical properties of Pcs in solution and those in the solid phase can be attributed both to intermolecular excitonic effects and scattering at microcrystalline boundaries. Therefore, the steric isolation of the Pc ring in a noncrystalline (glassy) solid represents an interesting challenge and could lead to materials with enhanced properties.

Few examples of Pc-containing dendrimers have been reported[18] and, with the aim of producing "solid solutions" of Pc from a single component system, we decided that Pc-centred dendrimers based on Fréchet's archetypal poly(aryl

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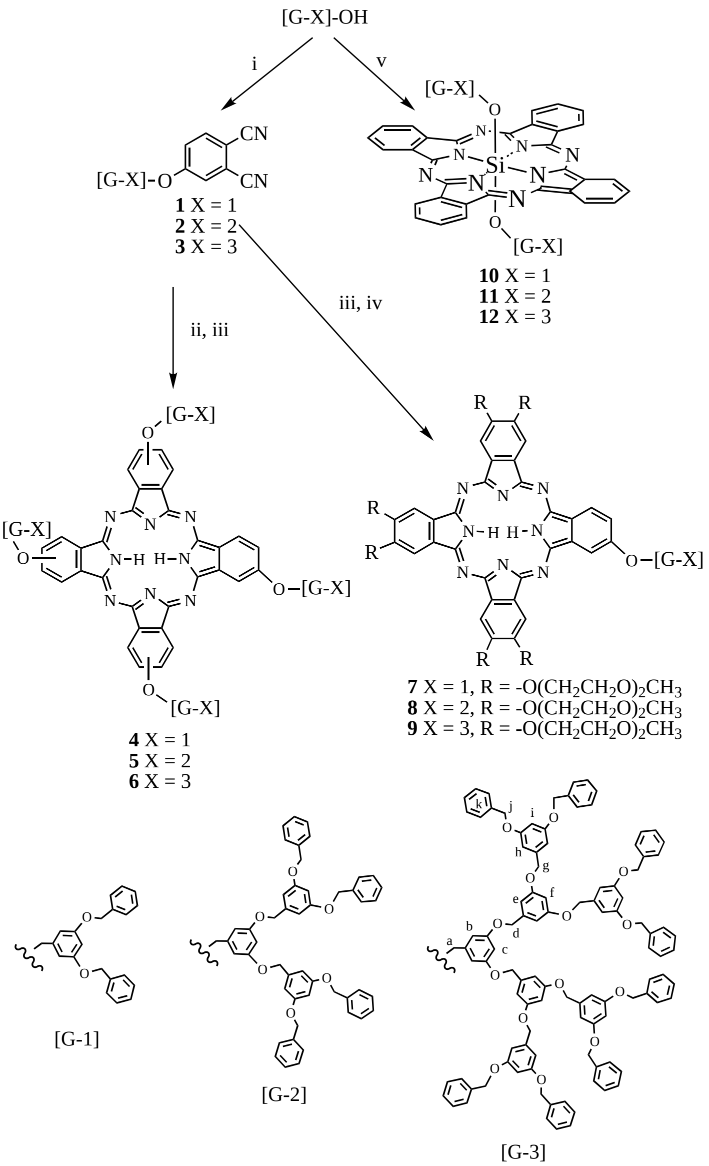
ether) system[19] would be interesting synthetic targets. Such dendrimers are known to produce glassy solids, which could be readily fabricated into nonscattering films for optical applications. In addition, the convergent route to poly(aryl ether) dendrimers provides wedge-like intermediates or *dendrons* ([G-X]–OH where X denotes the generation: 1st, 2nd or 3rd), which contain a single, synthetically versatile, benzylic alcohol group at the focal point. These dendrons can be used for the preparation of phthalonitriles **1–3**, which are ideal precursors to Pc-containing dendrimers. Initially, it was anticipated that peripheral substitution of the Pc core with poly(aryl ether) dendrons to produce Pcs **4–6** would lead to isolation of the Pc core in the solid state. Surprisingly, initial investigations found that even third generation dendritic substituents do not prevent self-association of the cores and that it was possible to prepare columnar mesogens containing a single such substituent (Pcs **7–9**).[20, 21] Therefore, the effect of placing the dendrons at the two axial sites of silicon(IV) phthalocyanine (Pcs **10–12**) was investigated.[21, 22] This paper describes the synthesis, structural characterisation and material properties of these interesting compounds.



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, 4,5-di(1,4,7-trioxaoctyl)phthalonitrile, $C_5H_{11}OLi$, $C_5H_{11}OH$, 135 °C; v, dichloro(phthalocyaninato)silicon, pyridine, 80 °C.

## Results and Discussion

**Synthesis**: Scheme 1 shows the synthesis of the dendritic poly(aryl ether) substituted Pcs. The phthalonitrile precursors **1–3** are prepared in high yield (75–90 %) from the aromatic nucleophilic substitution reaction between the anion of [G-X]–OH and commercially available 4-nitrophthalonitrile.[23] The assembly of dendrimers **4–6** is achieved by the formation of the Pc core using a base (lithium pentanolate) mediated cyclotetramerisation of the appropriate phthalonitrile in refluxing pentanol. Core formation represents an interesting adaptation to the conventional convergent route to dendrimer assembly, which involves attachment of the dendrons to a pre-existing core. Recently, a similar strategy for the assembly of porphyrin-centred dendrimers was reported.[10d] The metal-free Pc-centred dendrimers **4–6** are obtained, as mixtures of four inseparable isomers, by treating the crude products with acetic acid to remove the lithium ions from the central cavity of the Pc core. Similarly, asymmetric Pcs **7–9** containing a single dendritic substituent are prepared by a mixed cyclotetramerisation reaction between the appropriate dendron-substituted phthalonitrile **1–3** and a tenfold excess of 4,5-bis(1,4,7-trioxaoctyl)phthalonitrile.[24] Isolation of **7–9** from the other Pc by-products is achieved using column chromatography. Substitution of the axial chlorine ligands of dichlorophthalocyaninatosilicon by the anion of [G-X]–OH gives Pc containing dendrimers **10–12**.[25]

**Structural characterisation**: Spectroscopic analyses of **1–12** were consistent with their expected structure, although the $^1$H NMR spectra of **4–6** are each complicated by the isomeric heterogeneity and by severe broadening due to aggregation of the Pc cores (see next section). Each compound gave a satisfactory elemental analysis and all, except **6**, exhibited a parent mass ion using fast atom bombardment (FAB) mass spectrometry. Matrix-assisted laser desorption ionisation time-of-flight (MALDI-TOF) mass spectrometry successfully indicated a parent ion for **6** with a series of peaks centred at 6882 which possesses a similar appearance to that calculated from the molecular formula. In addition, analysis of **4–12** by gel permeation chromatography indicated that each material was pure and monodisperse ($M_w/M_n < 1.01$) with an estimated mass, derived from comparison with poly(styrene) standards, consistent with the calculated value.

For **11**, 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 in toluene. ORTEP-type plots of the molecular structure of Pc **11** are given in Figures 1 and 2. The asymmetric unit consists of half a molecule. The Si atom lies on a centre of symmetry and the other half of the molecule is generated by inversion. The O–Si–O bond angle is almost linear (179°) and the Pc core is

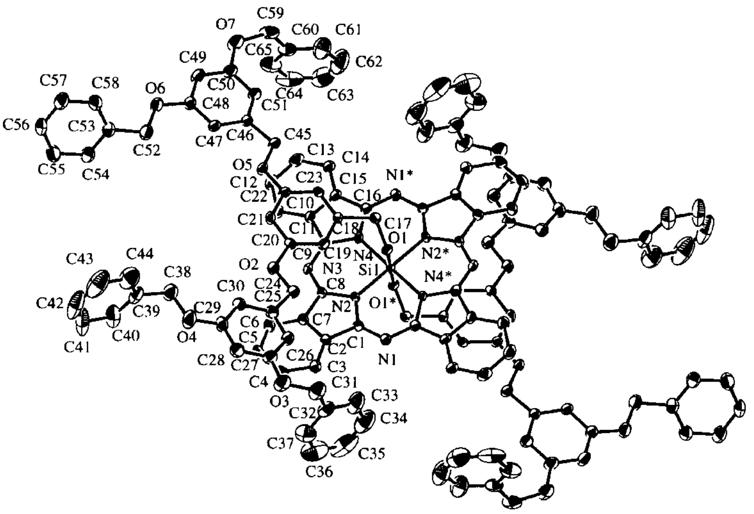


Figure 1. An ORTEP diagram of the molecular structure of **11** with crystallographic numbering scheme.

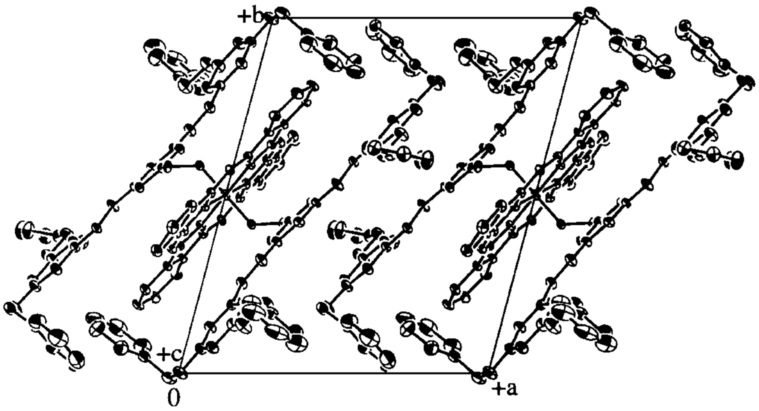


Figure 2. The crystallographic packing of **11** viewed along the *c* axis. The cofacial distance between Pc cores is 14 Å.

essentially planar. The benzyloxy group directly attached to the silicon atom forms an angle of 15.6° to the Pc core, with which it appears to interact strongly as indicated by short intramolecular contacts (e.g. N4 to C18 = 3.177(7) Å). The utility of the axial substituents to prohibit cofacial self-association is confirmed by the 14 Å distance between the planes of neighbouring Pc subunits along the *a* axis of the crystal (Figure 3). This distance is too great for significant exciton coupling. However, there are short edge-to-edge contacts between adjacent Pc cores (e.g. C5 and C21 = 3.348(9) Å).

The $^1$H NMR spectra of **7**–**12** are particularly informative as the strong ring current of the Pc macrocycle helps to differentiate protons of similar type. The chemical shifts of each type of hydrogen within the G-3 substituents of **9** (peripheral substitution) and **12** (axial substitution) are given in Table 1 alongside those of [G-3]−OH for comparison. As expected, the strong ring current of the Pc ring results in the presence of most of the hydrogens on the peripheral G-3 unit of **9**, especially those closer to the core (e.g. those attached to carbons denoted a and b), at significantly higher values of $\delta$. However, the hydrogens associated with the terminal benzyl groups (j and k) resonate at slightly lower values of $\delta$, as compared with [G-3]−OH. It is possible that these distant groups are, on average, affected more by the shielding regions of influence of the ring current that lie above and below the plane of the Pc ring. This shielding region is responsible for the high-field positions of the resonances associated with the hydrogens attached to carbons a and b of the axial G-3 units in **12**.[26] Interestingly, hydrogens at a greater distance from the Pc ring in **12** such as those attached to carbons h and i are slightly deshielded relative to the analogous hydrogens on [G-3]−OH. If the axial dendrons in **12** adopt a similar conformation in solution to that displayed

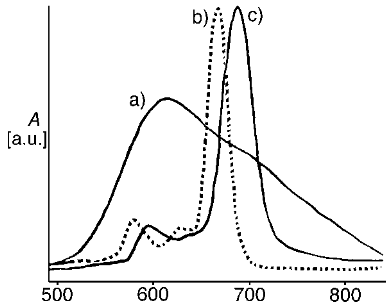


Figure 3. The Q-band absorptions in the visible spectra from spin-coated films derived from **6** (a) and **12** (c). The solution spectra of **12** (b) is given for comparison.

Table 1. The chemical shifts ($\delta$) for hydrogens on the [G-3] dendritic substituent of **9** and **12** relative to the analogous hydrogens on dendron [G-3]−OH. The position of the hydrogens on the substituent is given in the structure of [G-3] in Scheme 1.

| | $\delta$([G-3]−OH) | $\delta$ **9** ($\delta$**9** − $\delta$[G-3]−OH) | $\delta$ **12** ($\delta$**12** − $\delta$[G-3]−OH) |
|---|---|---|---|
| a | 4.57 | 5.50 (0.93) | −0.71 (−5.28) |
| b | 6.42 | 7.00 (0.58) | 3.50 (−2.92) |
| c | 6.36 | 6.49 (0.13) | 5.65 (−0.71) |
| d | 4.94 | 5.06 (0.12) | 3.97 (−0.97) |
| e | 6.48 | 6.72 (0.24) | 6.30 (−0.18) |
| f | 6.36 | 6.48 (0.12) | 6.44 (0.08) |
| g | 4.94 | 4.98 (0.04) | 4.88 (−0.06) |
| h | 6.50 | 6.69 (0.19) | 6.65 (0.15) |
| i | 6.39 | 6.52 (0.13) | 6.54 (0.15) |
| j | 5.00 | 4.88 (−0.12) | 4.99 (−0.01) |
| k | 7.27–7.41 | 7.15–7.35 (−0.09) | 7.24–7.40 (−0.02) |

by **11** in the crystalline state, so that the first benzene ring lies at a shallow angle (15.6°) relative to the Pc ring, it is likely that the more distant portions of the [G-3] units of **12** would lie, on average, within the deshielding region of influence of the ring current.

**Aggregation in solution**: Dendrimers **4–12** are all soluble in common aprotic solvents such as THF, toluene and $CHCl_3$ (although **10** is only sparingly so), but not in diethyl ether or hexane. Surprisingly, **4–6** show spectroscopic evidence of Pc core self-association even in dilute solution in $CHCl_3$ ($1-10 \times 10^{-5}$ mol dm$^{-3}$) from the presence of a broad peak in their UV/Vis absorption spectra at $\lambda_{\max} = 630$ nm in addition to the familiar split Q-band, which originates from nonaggregated metal-free Pc ($\lambda = 715$, 680 nm). Self-association of these compounds is even more marked in solution in toluene or THF. Aggregation of **4–6** is also apparent from the considerable broadening of the $^1$H NMR signals that originate from the twelve hydrogens attached directly to the periphery of the Pc core, the two internal protons and from those hydrogens of the dendritic substituents closest to the core. Remarkably, the tendency of **5** and **6** to aggregate in $CDCl_3$ is stronger than that of **4** and many other substituted Pcs, such as the much-studied tetra-*tert*-butylphthalocyanine, at similar concentrations ($5 \times 10^{-3}$ mol dm$^{-3}$, 50 °C) despite the far greater steric bulk of the dendritic substituents. The solution behaviour of **5** and **6** is analogous to that of 1,3,4-oxadiazole-based dendrimers, which were specifically designed to produce columnar supramolecular structures.[27] A very recent report describes novel dendrimers with analogous structures to **4–6**, except that they possess carboxylate terminal groups instead of benzyl groups.[28] These materials are water soluble and display a reduced tendency for aggregation in solution. The electrostatic repulsion between molecules containing multiple anionic units presumably discourages their self-association. Aggregation is less evident in the UV/Vis absorption and $^1$H NMR spectra of **7–9** at similar concentrations and there is no evidence of self-association of **10–12** in solution.

**Thermal behaviour**: The thermal behaviour of **4–12**, as measured by optical polarising microscopy and differential scanning calorimetry (DSC), is reported in Table 2. On cooling from the isotropic melt, **4**, **7**, **8** and **9** display a focal-conic optical texture, which is characteristic of a columnar mesophase within which the molecular columns form a close-packed, two-dimensional hexagonal array. The initially observed "sandy texture" exhibited by **9** requires annealing at 105 °C for several hours in order to obtain a recognisable focal-conic texture. The hexagonal columnar mesophase is commonly encountered in Pc derivatives.[15] However it is remarkable that the presence of the large [G-3] dendritic substituent on Pc **9** does not prohibit columnar mesophase formation but merely limits the thermal range over which the mesophase is stable. A small-angle X-ray diffraction analysis (powder) of the mesophase of **4** and **7–9** reveals a single strong, sharp band, which we believe originates from the (1, 0) plane of the hexagonal lattice. Based on this assumption, the calculated intercolumnar spacings for these compounds are given in Table 2. In each case, a weaker band corresponding to a repeat distance of 3.5 Å is observed which can be attributed to the cofacial distance between neighbouring Pc units along the axis of the column.

Table 2. The physical properties of the Pc-containing dendrimers **4–12**. I = isotropic liquid, $\varphi_h$ = hexagonal columnar mesophase, $d$ = intercolumnar distance within mesophase calculated from 1,0 diffraction ring.

| | $\lambda_{\max}$[a] [nm] | $\lambda_{\max}$[b] [nm] | Glass → I | Glass → $\varphi_h$ | $\varphi_h$ → I | $d$ [Å] |
|---|---|---|---|---|---|---|
| **4** | 718, 682 | 620 | – | 115[c] | 270[c] | 31.2 |
| **5** | 716, 680 | 620 | 112 | – | – | – |
| **6** | 715, 680 | 627 | 71 | – | – | – |
| **7** | 700, 664 | 622 | – | < –20[c] | > 320[c] | 28.9 |
| **8** | 700, 664 | 622 | – | 115 | 250–255 | 30.0 |
| **9** | 702, 664 | 622 | – | 94 | 108–112 | 35.0 |
| **10** | 678 | 704 | 139 (253)[d] | – | – | – |
| **11** | 680 | 692 | 124 (168)[d] | – | – | – |
| **12** | 680 | 688 | 110 | – | – | – |

[a] In toluene solution. [b] From a spin-coated film. [c] Transition not observed by DSC. [d] Value in parenthesis is the melting point of the crystalline substance obtained from solution.

Organic glass-forming materials, especially those which incorporate useful optical or opto-electronic functionality (e.g. electroluminescence,[29] photorefraction[30] and nonlinear optical behaviour[31]) are of rapidly increasing technological importance as a result of their ability to form homogeneous and optically clear films by vacuum sublimation or spin coating. With the exception of **7**, which remains liquid crystalline at room temperature, DSC investigation shows that the Pc-containing dendrimers have the tendency to form glassy rather than crystalline solids, as indicated by distinct second-order glass transitions both on heating and cooling.[32] Crystalline samples of **10** and **11**, formed from solution, show this behaviour after initially melting at 253 and 168 °C, respectively. The mesogenic materials **4**, **8** and **9** show no change in their microscopic optical texture on cooling from their columnar liquid crystal phase to below their glass transition temperatures. X-ray diffraction confirms in each case that the structure of the hexagonal columnar mesophase is frozen into the solid phase and this results in an anisotropic glass, although with a slight reduction (≈1 Å) in the intercolumnar spacings. Pc-based materials which display both an alignable liquid crystal phase at elevated temperature and a robust glassy phase at room temperature are rare.[33] These materials could be used to fabricate solid monodomainal films with interesting optical or electronic properties based on the proven anisotropic transportation of charge[34] and excitons[35] within Pc columnar mesogens.

**Film formation**: Spin-coated films derived from each of the [G-X] substituted Pcs were deposited onto glass substrates from solution in chloroform. Table 2 shows the position of the Q-band in the visible absorption spectra of these films. The nonmesogenic dendrimers **5** and **6** produce clear, crack-free solid films, in which the position of the Q-band ($\lambda_{\max}$ = 620 nm) indicates strong cofacial interactions of the Pc cores (Figure 3), as expected from their solution behaviour. It is conceivable that the substitution of higher generation dendritic wedges (e.g. [G-4] or [G-5]) at the periphery of the Pc core would eventually result in core isolation and the attainment of a solid solution as observed for poly(aryl ether) dendrimers with porphyrin cores.[10d] However, this would be at the expense of further, laborious synthetic effort and a considerable dilution of the Pc functionality within the resultant material.

As expected, the axial substitution of poly(aryl ether) wedges onto silicon phthalocyanine efficiently suppresses cofacial interactions in the solid state as illustrated by the X-ray structure of **11** (Figures 1 and 2). However, edge-to-edge excitionic interactions between neighbouring Pc units are apparent from the broadened and red-shifted (26 nm) Q-band exhibited by the grainy, microcrystalline films derived from **10**. Only weak edge-to-edge exciton interactions occur in the glassy, homogeneous spin-coated films of **11** and **12**, as indicated by the relatively small red-shift of the Q-band (Figure 3) compared with the Q-band position in their solution absorption spectra. Broadening of the Q-band due to excitonic effects is also small (12 and 5 nm for the Q-band at half height in **11** and **12**, respectively). In each case, glassy thin films formed by cooling from the melt display very similar UV/Vis absorption spectra to those prepared by spin coating. Thus, films from **11** and **12** produced by both methods of fabrication are optically clear, defect-free, nonbirefringent and approximate to true solid solutions.

## Conclusion

To summarise, Pc-containing dendrimers possess the ability to form clear, robust glassy solids, which appear indefinitely stable towards crystallisation and which contain a high concentration of Pc functionality. The structure within the glass is controlled by the size, number and position of the dendritic wedges attached to the Pc macrocycle. It is clear from the solution and materials properties of **4**–**9** that the peripheral substitution of the dendritic wedges does not result in steric isolation of the Pc ring as intended. In fact, the properties of these materials are dominated by the intermolecular association of the Pc cores which produces columnar aggregates in concentrated solution and the solid state. Thus, **5** and **6** are amorphous glasses in which the Pc cores are cofacially aggregated, whereas **4**, **8** and **9** form anisotropic glasses, in which the structure of the columnar mesophase, observed above their glass transitions, is frozen at room temperature. In contrast, placing even [G-1] dendritic substituents at the two axial sites of silicon Pc does enforce cofacial isolation, but higher generations are required to obtain site isolation by the reduction of edge-to-edge interactions. Thus, **10** forms a microcrystalline spin-coated film or a glass, on cooling from the melt, which displays significant edge-to-edge exciton effects, whereas **11** and **12** form glassy films, which approximate to true solid solutions. Studies to examine the optical properties of these materials are in progress.

## Experimental Section

**Materials and methods**: Routine $^1$H NMR spectra were measured at 300 MHz using a Inova 300 spectrometer. High-resolution (500 MHz) $^1$H NMR spectra were recorded using a Varian Unity 500 spectrometer. UV/Visible spectra were recorded on a Shimadzu UV 260 spectrophotometer using cells of pathlength 10 mm. IR spectra were recorded on a 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 spectra were 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 Micromass 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. All solvents were dried and purified as described in Perrin and Armarego.[36] 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 hours as the final step of purification.

**4-(3′,5′-Dibenzyloxy)benzyloxyphthalonitrile (1)**: Potassium carbonate (1.12 g, 8.1 mmoles), 4-(3′,5′-dibenzyloxy)benzyl alcohol ([G-1]–OH, 2.0 g, 6.25 mmoles) and 4-nitrophthalonitrile (1.41 g, 8.15 mmoles) were stirred in DMF (5 mL) at 60 °C for 48 hours. The reaction mixture was cooled and poured into water (100 mL). The aqueous layer was extracted with DCM (3 × 50 mL), dried over magnesium sulfate and filtered. The organic layer was evaporated to dryness and this left a green oil. Purification was achieved by column chromatography (toluene/ethyl acetate, 9:1). Removal of the solvent under reduced pressure gave **1** (2.5 g, 90 % yield) as a white solid. M.p. 114–116 °C; $^1$H NMR (500 MHz, $CDCl_3$, 20 °C): $\delta = 5.05$ (s, 4H), 5.10 (s, 2H), 6.58 (t, $J = 1$ Hz, 1H), 6.60 (d, $J = 1$ Hz, 2H), 7.15 (dd, $J = 9$ and 2 Hz, 1H), 7.25 (d, $J = 2$ Hz, 1H), 7.29–7.45 (m, 10H), 7.65 (d, $J = 9$ Hz, 1H); IR (KBr): $\tilde{\nu} = 2229$ cm$^{-1}$ (CN); MS (EI): $m/z$: 446 [$M^+$]; elemental analysis calcd (%) for $C_{29}H_{22}O_3N_2$: C 78.01, H 4.97, N 6.27; found C 77.9, H 5.03, N 6.4.

The following phthalonitriles were prepared using the same methodology.

**4-(3′,5′-Di(3″,5″-dibenzyloxy)benzyloxy)benzyloxyphthalonitrile (2)**: This compound was prepared as a glassy solid (85 % yield). $^1$H NMR (500 MHz, $CDCl_3$, 20 °C): $\delta = 4.97$ (s, 4H), 5.02 (s, 8H), 5.08 (s, 2H), 6.52 (t, $J = 1$ Hz, 1H), 6.57 (t, $J = 1$ Hz, 2H), 6.59 (d, $J = 1$ Hz, 2H), 6.67 (d, $J = 1$ Hz, 4H), 7.14 (dd, $J = 9$ and 2 Hz, 1H), 7.23 (d, $J = 2$ Hz, 1H), 7.29–7.42 (m, 20H), 7.65 (d, $J = 9$ Hz, 1H); IR (thin film on KBr): $\tilde{\nu} = 2230$ cm$^{-1}$ (CN); MS (EI): $m/z$: 871 [$M^+$]; elemental analysis calcd (%) for $C_{57}H_{46}O_7N_2$: C 78.60, H 5.32, N 3.22; found C 78.12, H 5.82, N 2.89.

**4-(3′,5′-Di(3″,5″-di(3‴,5‴dibenzyloxy)benzyloxy)benzyloxy)benzyloxyphthalonitrile (3)**: This compound was prepared as a glassy solid (79 % yield). $^1$H NMR (500 MHz, $CDCl_3$, 20 °C): $\delta = 4.97$ (s, 4H), 5.00 (s, 16H), 5.03 (s, 8H), 5.08 (s, 2H), 6.50–6.63 (m, 7H), 6.69–6.74 (m, 14H), 7.10 (dd, $J = 9$ and 2 Hz, 1H), 7.23 (d, $J = 2$ Hz, 1H), 7.29–7.46 (m, 40H), 7.64 (d, $J = 9$ Hz, 1H); IR (thin film on KBr): $\tilde{\nu} = 2230$ cm$^{-1}$ (CN); MS (FAB): $m/z$: 1720 [$M^+$] $^{13}C_2C_{111}H_{94}O_{15}N_2$ requires 1720; elemental analysis calcd (%) for $C_{113}H_{94}O_{15}N_2$: C 78.91, H 5.51, N 1.63; found C 79.08, H 5.38, N 1.46.

**2,9(10),16(17),23(24)-Tetra((3′,5′-dibenzyloxy)benzyloxy)phthalocyanine (4)**: Excess lithium metal was added to a rapidly stirred solution of **1** (0.2 g, 0.45 mmoles) in refluxing pentanol (2 mL). The reaction mixture was heated at 120 °C for 24 hours. The reaction was cooled and acetic acid (0.1 M, 0.5 mL) added. The solvent was removed under reduced pressure. The crude product was purified by column chromatography (toluene, ethyl acetate) and by repeated reprecipitations from solution (in DCM) in MeOH to give **4** (0.143 g, 18.0 % yield) as a dark blue solid. $^1$H NMR (500 MHz, $CDCl_3$, 50 °C): $\delta = -3.2$ (s, 2H), 5.04 (br s, 16H), 5.26 (br s, 8H), 6.40–6.90 (br s, 12H), 7.29–7.45 (m, 40H), 7.7–9.1 (br m, 12H); IR (KBr): $\tilde{\nu} = 3275$ cm$^{-1}$ (N–H); UV/Vis ($CH_2Cl_2$): $\lambda_{max} = 718$, 682, 654, 620, 422, 346 nm; MS (FAB): $m/z$: 1788 [$M^+$] $^{13}CC_{115}H_{90}O_{12}N_8$ requires 1787; elemental analysis calcd (%) for $C_{116}H_{90}O_{12}N_8$; C 77.92, H 5.07, N 6.27; found C 78.30, H 5.10, N 6.20.

The following phthalocyanines were prepared using the same methodology.

**2,9(10),16(17),23(24)-Tetra((3′,5′-di(3″,5″-dibenzyloxy)benzyloxy)benzyloxy)phthalocyanine (5)**: This compound was prepared as a glassy blue solid (22 % yield). $^1$H NMR (500 MHz, $CDCl_3$, 50 °C): $\delta = -3.5$ (s, 2H), 4.75–5.05 (br m, 48H), 5.26 (br s, 8H), 6.40–6.75 (br d, 28H), 6.90 (br s, 8H), 7.29–7.45 (m, 80H), 7.70–9.1 (br m, 12H); IR (KBr): $\tilde{\nu} = 3275$ cm$^{-1}$ (N–H); UV/Vis ($CH_2Cl_2$): $\lambda_{max} = 716$, 680, 654, 620, 422, 346 nm; MS (FAB): $m/z$: 3488 [$M^+$] $^{13}C_3C_{225}H_{186}O_{28}N_8$ requires 3485; elemental analysis calcd (%) for $C_{228}H_{186}O_{28}N_8$: C 78.55, H 5.38, N 3.21; found C 78.32, H 5.45, N 3.00.

**2,9(10),16(17),23(24)-Tetra((3′,5′-di(3″,5″-di(3‴,5‴dibenzyloxy)benzyloxy)benzyloxy)benzyloxy)phthalocyanine (6)**: This compound was prepared as a glassy blue solid (15 % yield). $^1$H NMR (500 MHz, CDCl$_3$, 50 °C): $\delta = -3.4$ (s, 2 H), 4.66–5.05 (br m, 96 H), 5.28 (br s, 8 H), 6.30–6.70 (br m, 76 H), 6.90 (br s, 8 H), 7.29–7.45 (m, 160 H), 7.7–9.1 (br m, 12 H); IR (KBr): $\tilde{\nu} = 3277$ cm$^{-1}$ (N–H); UV/Vis (CH$_2$Cl$_2$): $\lambda_{max} = 715$, 680, 654, 620, 422, 346 nm; MS (MALDI): $m/z$: 6882 [$M^+$] $^{13}C_6C_{446}H_{378}O_{60}N_8$ requires 6880; elemental analysis calcd (%) for $C_{452}H_{378}O_{60}N_8$: C 78.88, H 5.54, N 1.63; found C 78.32, H 5.55, N 3.00.

**2-(3′,5′-Dibenzyloxy)benzyloxy-9,10,16,17,23,24-hexa(1,4,7-trioxaoctyl)phthalocyanine (7)**: Lithium hydride (0.02 g, 0.54 mmoles) was added to a stirred solution of [G-1]-phthalonitrile (0.122 g, 0.027 mmoles) and 4,5-bis(1,4,7-trioxaoctyl)phthalonitrile (1 g, 0.27 mmoles) in dry refluxing pentanol (2 mL) which was maintained under a nitrogen atmosphere. After six hours, glacial acetic acid (0.25 mL) was carefully added and the reaction mixture allowed to cool. The solvents were removed under reduced pressure to give a crude mixture of Pc products. Purification was achieved by column chromatography (DCM with a steadily increasing amount of EtOH). A green band, collected at 6 % EtOH, was further purified by reprecipitation from solution (in DCM) into hexane and proved to be the desired product **7** (0.216 g, 30 % based on **1**), which was obtained as a highly viscous green oil. $^1$H NMR (500 MHz, CDCl$_3$, 50 °C): $\delta = -2.14$ (br s, 2 H), 3.47 (s, 18 H), 3.70 (t, $J = 6$ Hz, 12 H), 3.95 (t, $J = 6$ Hz, 12 H), 4.20 (t, $J = 6$ Hz, 12 H), 4.74 (t, $J = 6$ Hz, 12 H), 5.18 (s, 4 H), 5.33 (s, 2 H), 6.69 (t, $J = 1$ Hz, 1 H), 7.05 (d, $J = 1$ Hz, 2 H), 7.22–7.50 (br m, 10 H), 8.55–8.70 (br m, 8 H), 9.05 (d, $J = 9$ Hz, 1 H); IR (KBr): $\tilde{\nu} = 3433$ cm$^{-1}$ (N–H); UV/Vis (CH$_2$Cl$_2$): $\lambda_{max} = 700$, 664, 646, 398, 342 nm; MS (FAB): $m/z$: 1542 [$M^+$] $^{13}CC_{82}H_{96}O_{21}N_8$ requires 1541; elemental analysis calcd (%) for $C_{83}H_{96}O_{21}N_8$: C 64.66, H 6.23, N 7.27; found C 64.47, H 6.32, N 6.84.

The following phthalocyanines were prepared using the same methodology.

**2-(3′,5′-Di(3″,5″-dibenzyloxy)benzyloxy)benzyloxy-9,10,16,17,23,24-hexa-(1,4,7-trioxaoctyl)phthalocyanine (8)**: This compound was obtained as a glassy green solid (32 % yield based on **2**). $^1$H NMR (500 MHz, CDCl$_3$, 50 °C): $\delta = -2.00$ (br s, 2 H), 3.46 (s, 18 H), 3.70 (t, $J = 6$ Hz, 12 H), 3.95 (t, $J = 6$ Hz, 12 H), 4.20 (t, $J = 6$ Hz, 12 H), 4.74 (t, $J = 6$ Hz, 12 H), 4.98 (s, 8 H), 5.10 (s, 4 H), 5.53 (s, 2 H), 6.52 (t, $J = 1$ Hz, 2 H), 6.65 (t, $J = 1$ Hz, 1 H), 6.73 (d, $J = 1$ Hz, 4 H), 7.03 (d, $J = 1$ Hz, 2 H), 7.18–7.32 (m, 20 H), 8.52–8.70 (br m, 8 H), 9.02 (d, $J = 9$ Hz, 1 H); IR (KBr): $\tilde{\nu} = 3422$ cm$^{-1}$ (N–H); UV/Vis (CH$_2$Cl$_2$): $\lambda_{max} = 700$, 664, 646, 398, 342 nm; MS (FAB): $m/z$: 1989 [$M^+$+Na$^+$] $^{13}C_2C_{109}H_{120}O_{25}N_8$+Na$^+$ requires 1987; elemental analysis calcd (%) for $C_{111}H_{120}O_{25}N_8$: C 67.80, H 6.15, N 5.70; found C 67.99, H 6.45, N 5.95.

**2-(3′,5′-Di(3″,5″-di(3‴,5‴-dibenzyloxy)benzyloxy)benzyloxy)benzyloxy-9,10,16,17,23,24-hexa(1,4,7-trioxaoctyl)phthalocyanine (9)**: This compound was obtained as a glassy green solid (9 % yield based on **3**). $^1$H NMR (500 MHz, CDCl$_3$, 50 °C): $\delta = -1.70$ (br s, 2 H), 3.42 (s, 18 H), 3.70 (t, $J = 6$ Hz, 12 H), 3.95 (t, $J = 6$ Hz, 12 H), 4.20 (t, $J = 6$ Hz, 12 H), 4.74 (t, $J = 6$ Hz, 12 H), 4.88 (s, 16 H), 4.98 (s, 8 H), 5.06 (s, 4 H), 5.50 (s, 2 H), 6.48 (t, $J = 1$ Hz, 2 H), 6.49 (t, $J = 1$ Hz, 1 H), 6.52 (t, $J = 1$ Hz, 4 H), 6.69 (d, $J = 1$ Hz, 8 H), 6.72 (d, $J = 1$ Hz, 4 H), 7.00 (d, $J = 1$ Hz, 2 H), 7.15–7.35 (br m, 40 H), 8.62–8.75 (br m, 8 H), 9.10 (d, $J = 9$ Hz, 1 H); IR (KBr): $\tilde{\nu} = 3429$ cm$^{-1}$ (N–H); UV/Vis (CH$_2$Cl$_2$): $\lambda_{max} = 702$, 664, 640, 400, 340 nm; MS (FAB): $m/z$: 2837 [$M^+$+Na$^+$] $^{13}C_2C_{165}H_{168}O_{33}N_8$+Na$^+$ requires 2837; elemental analysis calcd (%) for $C_{167}H_{168}O_{33}N_8$: C 71.25, H 6.02, N 3.98; found C 71.05, H 6.08, N 4.27.

**Di-((3,5-di-(3′,5′-dibenzyloxy)benzyloxy)benzyloxy)phthalocyaninatosilicon (11)**: Sodium hydride (0.055 g, 2.3 mmoles) was added to a mixture of dichlorophthalocyaninatosilicon (0.2 g, 0.33 mmoles) and 3,5-di-(3′,5′-dibenzyloxy)benzyloxy)benzyl alcohol (1.15 g, 1.32 mmoles) in dry toluene (2 mL). After heating under nitrogen at 80 °C for 96 hours, the reaction mixture was poured into water and the aqueous layer extracted with toluene (3 × 50 mL), dried over magnesium sulfate and the solvent removed under reduced pressure. Purification was achieved by column chromatography (toluene) followed by recrystallisation from a mixture of toluene and diethyl ether to give **11** as green prismatic crystals (0.310 g, 46 % yield). M.p. 168 °C; $^1$H NMR (500 MHz, CDCl$_3$, 20 °C): $\delta = -0.69$ (s, 4 H), 3.54 (d, $J = 1$ Hz, 4 H), 4.02 (s, 8 H), 4.96 (s, 16 H), 5.64 (t, $J = 1$ Hz, 2 H), 6.32 (d, $J = 1$ Hz, 8 H), 6.46 (t, $J = 1$ Hz, 4 H), 7.20–7.32 (m, 40 H), 8.12–8.14 (m, 8 H), 9.49–9.52 (m, 8 H); UV/Vis (CH$_2$Cl$_2$): $\lambda_{max} = 680$, 650, 612, 348 nm; MS (FAB): $m/z$: 2028 [$M^+$] $^{13}C_2C_{128}H_{102}O_{14}N_8Si$ requires 2028; elemental analysis calcd (%) for $C_{130}H_{102}O_{14}N_8Si$: C 76.98, H 5.07, N 5.52; found C 76.60, H 4.82, N 5.62.

The following phthalocyanines were prepared using the same methodology.

**Di-((3,5-dibenzyloxy)benzyloxy)phthalocyaninatosilicon (10)**: This compound was obtained as a microcrystalline powder (14 % yield). M.p. 253 °C. $^1$H NMR (500 MHz, CDCl$_3$, 20 °C): $\delta = -0.69$ (s, 4 H), 3.58 (d, $J = 1$ Hz, 4 H), 4.11 (s, 8 H), 5.64 (t, $J = 1$ Hz, 2 H), 7.05–7.30 (m, 20 H), 8.20–8.31 (m, 8 H), 9.52–9.62 (m, 8 H); UV/Vis (CH$_2$Cl$_2$): $\lambda_{max} = 678$, 650, 610, 354 nm; MS (FAB): $m/z$: 1179 [$M^+$] $^{13}CC_{73}H_{54}O_6N_8Si$ requires 1179; elemental analysis calcd (%) for $C_{74}H_{54}O_6N_8Si$: C 75.36, H 4.61, N 9.50; found C 75.37, H 4.44, N 9.56.

**Di-((3′,5′-di(3″,5″-di(3‴,5‴-dibenzyloxy)benzyloxy)benzyloxy)benzyloxy)phthalocyaninatosilicon (12)**: This compound was obtained as a blue glassy solid (54 % yield). $T_g$ 110 °C. $^1$H NMR (500 MHz, CDCl$_3$, 20 °C): $\delta = -0.71$ (s, 4 H), 3.50 (d, $J = 1$ Hz, 4 H), 3.97 (s, 8 H), 4.88 (s, 16 H), 4.99 (s, 32 H), 5.65 (t, $J = 1$ Hz, 2 H), 6.30 (d, $J = 1$ Hz, 8 H), 6.44 (t, $J = 1$ Hz, 4 H), 6.54 (t, $J = 1$ Hz, 8 H), 6.65 (d, $J = 1$ Hz, 16 H), 7.24–7.40 (m, 80 H), 8.12–8.14 (m, 8 H), 9.49–9.52 (m, 8 H); UV/Vis (CH$_2$Cl$_2$): $\lambda_{max} = 680$, 650, 610, 354 nm; MS (FAB): $m/z$: 3726 [$M^+$] $^{13}C_3C_{239}H_{198}O_{30}N_8Si$ requires 3725; elemental analysis calcd (%) for $C_{242}H_{198}O_{30}N_8Si$: C 78.00, H 5.36, N 3.00; found C 78.06, H 5.55, N 2.93.

**Crystal structure determination of 11**: ($C_{130}H_{102}N_8O_{14}Si$): $M_r = 2028.37$; green prismatic crystal (0.07 × 0.3 × 0.4 mm); triclinic, space group $P\bar{1}$ (no. 2); $a = 14.079(3)$, $b = 16.291(5)$, $c = 12.710(3)$ Å, $\alpha = 103.62(2)$, $\beta = 109.30(2)$, $\gamma = 71.83(2)°$; $V = 2585(1)$ Å$^3$; $Z = 1$; $\rho_{calcd} = 1.303$ g cm$^{-3}$; $\mu = 0.9$ cm$^{-1}$; Rigaku AFC5R diffractometer, monchromatic Mo$_{K\alpha}$ radiation ($\lambda = 0.71069$ Å), 20 °C, $\omega - 2\theta$ scan mode; $2\theta_{max} = 50.1°$; 9709 total reflections; 9175 unique reflections ($R_{int} = 0.102$); 691 parameters refined; 4023 reflections included in the refinement. Lorentz and polarisation and absorption corrections were carried out (transmission factors = 0.9331–1.0000; $\mu = 0.9$ cm$^{-1}$). A decay correction based on a decrease in the intensity of three standard reflections of 4.5 % was also applied; structure determination by direct methods (SHELXS86) and expanded using Fourier techniques (DIRDIF94). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions but not refined. Refinement was carried out by the full-matrix least-squares methods based on 4023 observed reflections ($I > 2.50\sigma(I)$) and 691 variable parameters; $R = 0.067$; $R_w = 0.052$; maximum and minimum peaks on the final Fourier map corresponded to 0.29 and $-0.24$ e Å$^{-3}$, respectively. Crystallographic data (excluding structural factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100742. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44) 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk).

**Liquid crystal characterisation and film fabrication**: Differential scanning calorimetry measurements were made on a Seiko DSC220C machine and calibrated using an indium standard. Optical microscopy was performed on a Nikon Optiphot-2 microscope with a Mettler FP80HT Hot Stage. Low-resolution X-ray diffraction measurements from powder samples were recorded using Cu–K$_\alpha$ radiation ($\lambda = 1.54$ Å) from a Philips PW1130/00 generator with a nickel filter. The samples were each contained in a glass capillary (Hilgenberg 0.01 mm thick glass, 1.0 mm outside diameter) and placed in the beam in an aluminium heating block. The temperature was regulated by a Control Techniques Process Instruments 453 Plus Thermal Controller. The diffracted X-rays were detected with a flat-plate photographic camera using Agfa-Gevaert Osray M3 X-ray film. The system was calibrated using sodium chloride. Spin-coated films were prepared from solutions in chloroform (≈0.02 g mL$^{-1}$) and deposited onto clean silicon or glass microscope slides rotating at 5000 rpm, using a Headway Research PM80 wafer spin cleaner.

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