Silicon Phthalocyanines with Axial Dendritic Substituents**

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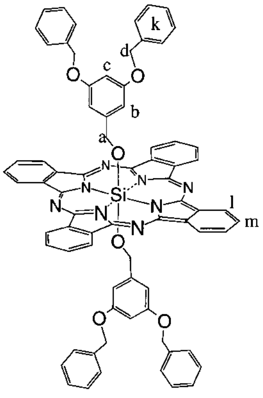
In the last few years dendrimers have attracted much attention due to their uniform hierarchical structures, which offer a wide range of potential applications.[1] Initial studies concentrated on the preparation of materials with high molecular mass, but recent emphasis has been on the functionalization of dendrimers of more modest size. For example, crown ethers,[2] chiral moieties,[3] mesogenic groups,[4] and redox-active substituents based on tetrathiafulvalene,[5] ferrocene,[6] or transition metal complexes[7] have been directly incorporated into dendrimers. In addition, the concept of employing dendritic substituents to effect steric isolation of a functional core (e.g., fullerene, porphyrin, etc.) is being actively studied by a number of groups.[8]

Our interests lie in the preparation of novel phthalocyanine (Pc) derivatives in which the structure of the bulk material is controlled by attaching suitable substituents to the Pc core.[9] Such control may help to exploit the fascinating optical and electronic properties of the Pc macrocycle.[10] For example, the studies on Pcs in solution promise useful applications in nonlinear optics (e.g., as optical limiters), which, however, have not yet been realized in the solid state.[11] The difference in optical properties between Pcs in solution and in the solid state can be attributed both to excitonic effects, especially cofacial interactions between neighboring Pc molecules, and to scattering at microcrystalline boundaries.[12] Here we describe the steric isolation of Pc molecules in the solid state by means of substituents composed of Fréchet's poly(aryl ether) dendrons.[13] Such dendrons produce transparent, glassy solids, and this would be an attractive property for the fabrication of readily processable, nonscattering Pc-containing films for optical applications.[14, 15]

The Pcs **1**–**3** were prepared by the substitution of the axial chloro ligands of dichloro(phthalocyaninato)silicon by the benzyl alcohol groups of the first, second, and third generation of Fréchet's dendrons, respectively.[16] The structures of **1**–**3** were confirmed by ^{1}H NMR spectroscopy and FAB-MS. The ^{1}H NMR spectra are particularly informative, as the strong ring current of the Pc macrocycle helps to differentiate protons of similar type. For example, the aromatic protons at the sites labeled b, e, and h in the structural formula of **3** give rise to well-resolved doublets (^3J(H,H) $\approx$ 1 Hz) at $\delta = 3.50$, 6.30, and 6.65, respectively. The purity of each material was confirmed by elemental analysis and thin layer chromatography.



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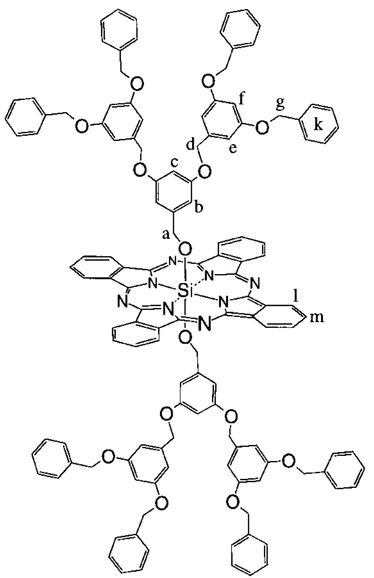

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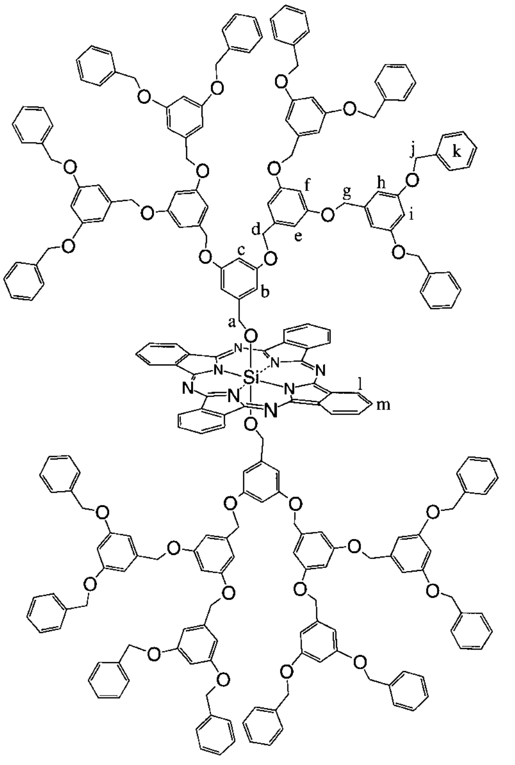

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Compounds **1**–**3** are all soluble (although **1** only sparingly so) in common aprotic solvents such as THF, toluene, and chloroform but not in diethyl ether and hexane. Slow diffusion of diethyl ether into a concentrated solution of **2** in toluene gave single crystals suitable for X-ray structure analysis. This method failed to yield suitable crystals of **1** or **3** and gave a microcrystalline powder and a clear glass, respectively. Figure 1 shows ORTEP plots of the molecular structure of **2**. The asymmetric unit consists of half a molecule. The Si atom lies on a center of symmetry, and the other half of the molecule is generated by inversion. The O-Si-O bond angle is

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[**] This work was supported by a grant from the EPSRC.

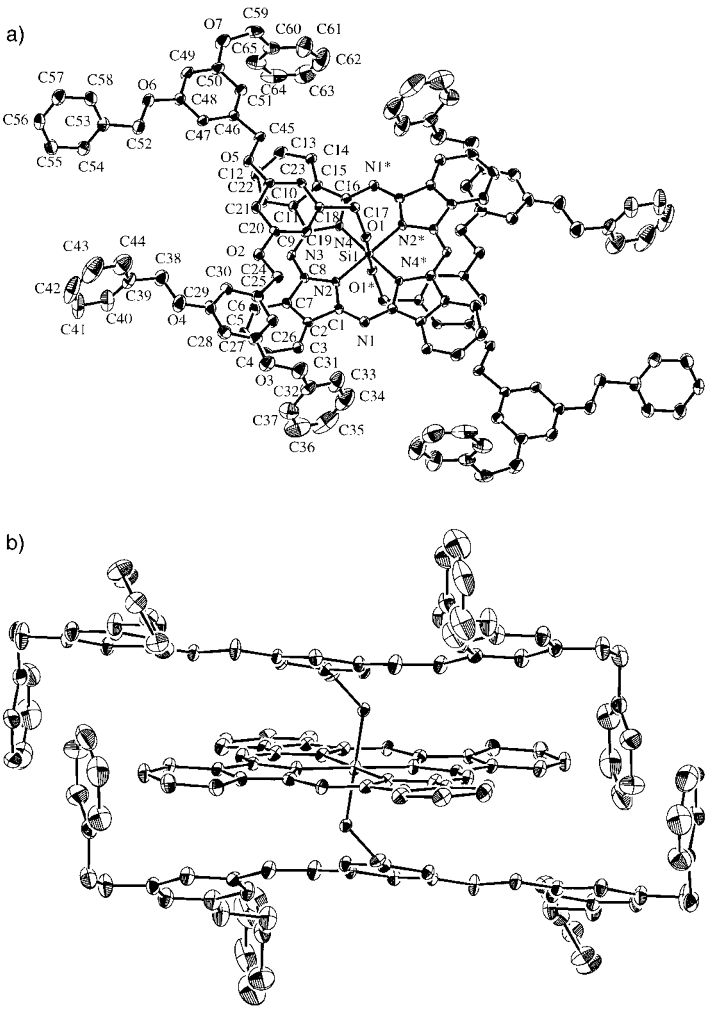

Figure 1. An ORTEP diagram of the molecular structure of **2** with a) crystallographic numbering scheme. b) The symmetrical arrangement of the two dendritic substituents. The Si atom lies on a center of symmetry.

almost linear (179°), and the Pc core is essentially planar. The benzyl group directly attached to the silicon atom forms an angle of 15.64° to the Pc core, with which it appears to interact strongly, as indicated by the short intramolecular distances (e.g., N4 ⋯ C18 3.177(7) Å). The axial substituents result in a distance between the cofacial Pc subunits of 14 Å along the *a* axis of the crystal (Figure 2). This distance is too large for significant exciton coupling. However, there are short edge-to-edge contacts between adjacent Pc cores (e.g., C5 ⋯ C21 3.348(9) Å).

The UV/Vis spectra of spin-coated thin films of **1**–**3** also illustrate the extent to which the axial dendritic substituents suppress cofacial intermolecular excitonic interactions. Only relatively weak edge-to-edge exciton interactions are present, as is evident from the bathochromic shift of the Q band of the films relative to the spectra in solution.[17] The magnitude of these interactions can be gauged by the extent of the red shift ($\Delta\lambda_{max}$) and the broadening (ΔW) of the Q band (Table 1). These values show that edge-to-edge interactions are small for **2** and **3** and that these spin-coated films resemble true solid solutions. Polarized optical microscopy suggests that the films derived from **2** and **3** are uniform and isotropic (nonbirefringent), whereas the spin-coated film of **1** has a microcrystalline structure. Each of the Pcs **1**–**3** displays a distinct glass transition on cooling from the melt ($T_g = 139$, 124, and 110 °C, respectively). Therefore, films can also be readily fabricated by melt processing.

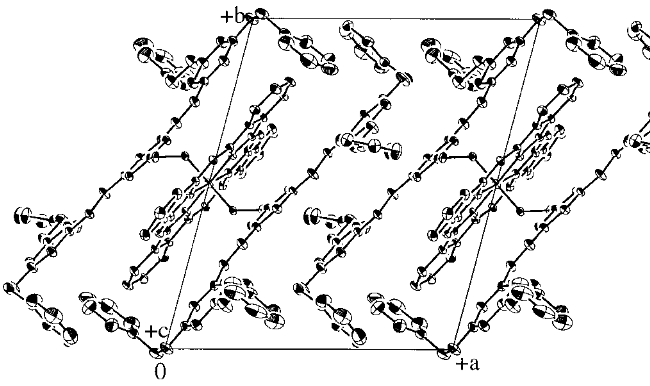

Figure 2. The crystallographic packing of **2** viewed along the *c* axis. The cofacial distance between Pc cores is 14 Å.

Table 1. Comparison of the UV/Vis spectroscopic data of **1**–**3**.

	1	2	3
$\lambda_{max}{}^{[a]}$ [nm]	678	680	680
$\lambda_{max}{}^{[b]}$ [nm]	704	692	688
$\Delta\lambda_{max}{}^{[c]}$ [nm]	26	12	8
$\Delta W^{[d]}$ [nm]	18	5	2

[a] In toluene. [b] In spin-coated film. [c] λ_{max}(film) – λ_{max}(solution). [d] Width of peak at half height.

This study has yielded robust, nonscattering glasses which appear indefinitely stable with respect to crystallization. These easily processable solid solutions are suitable materials for optical studies, which are now in progress.

Experimental Section

Typical synthesis: **2**: Sodium hydride (0.055 g, 2.3 mmol) was added to a mixture of dichloro(phthalocyaninato)silicon (0.2 g, 0.33 mmol) and 3,5-di-[3′,5′-(dibenzyloxy)benzyloxy]benzyl alcohol (1.15 g, 1.32 mmol) in dry toluene (2 mL). After heating under nitrogen at 80 °C for 96 h, the reaction mixture was poured into water, and the aqueous layer was extracted with toluene (3 × 50 mL), dried over magnesium sulfate, and evaporated to dryness under reduced pressure. The product was purified by column chromatography (silica, toluene) followed by recrystallization from toluene/diethyl ether to give **2** as green prismatic crystals (0.310 mg, 46 %).

1: Yield 14 %; m.p. 253 °C (THF); $T_g = 139$ °C; 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; ^{1}H NMR (500 MHz, $CDCl_3$, 60 °C): $\delta = -0.69$ (s, 4H, ^{a}CH$_2$), 3.58 (d, ^3J(H,H) = 1 Hz, 4H, ^{b}CH), 4.11 (s, 8H, ^{d}CH$_2$), 5.64 (t, ^3J(H,H) = 1 Hz, 2H, ^{c}CH), 7.05–7.30 (m, 20H, ^{k}C$_6$H$_5$), 8.20–8.31 (m, 8H, ^{l}CH), 9.52–9.62 (m, 8H, ^{m}CH); UV/Vis (toluene): $\lambda_{max}(\varepsilon) = 678$ nm (250 000); FAB-MS: *m/z*: 1178 [M^+].

2: Yield 46 %; m.p. 168 °C (toluene/diethyl ether); $T_g = 124$ °C; 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; ^{1}H NMR (500 MHz, $CDCl_3$, 60 °C): $\delta = -0.69$ (s, 4H, ^{a}CH$_2$), 3.54 (d, ^3J(H,H) = 1 Hz, 4H, ^{b}CH), 4.02 (s, 8H, ^{d}CH$_2$), 4.96 (s, 16H, ^{g}CH$_2$), 5.64 (t, ^3J(H,H) = 1 Hz, 2H, ^{c}CH), 6.32 (d, ^3J(H,H) = 1 Hz, 8H, ^{e}CH), 6.46 (t, ^3J(H,H) = 1 Hz, 4H, ^{f}CH), 7.20–7.32 (m, 40H, ^{k}C$_6$H$_5$), 8.12–8.14 (m, 8H, ^{l}CH), 9.49–9.52 (m, 8H, ^{m}CH); UV/Vis (toluene): λ_{max} (ε) = 680 nm (250 000); FAB-MS: *m/z*: 2028 [M^+].

3: Yield 54 %; $T_g = 110$ °C; elemental analysis calcd for $C_{242}H_{198}O_{30}N_8Si$: C 78.00, H 5.36, 3.00; found: C 78.06, H 5.55, N 2.93; ^{1}H NMR (500 MHz,

$CDCl_3$, 60 °C): $\delta = -0.71$ (s, 4H, ${}^{a}CH_2$), 3.50 (d, ${}^{3}J(H,H) = 1$ Hz, 4H, ${}^{b}CH$), 3.97 (s, 8H, ${}^{d}CH_2$), 4.87 – 5.00 (m, 48H, ${}^{g}CH_2 + {}^{j}CH_2$), 5.65 (t, ${}^{3}J(H,H) = 1$ Hz, 2H, ${}^{c}CH$), 6.30 (d, 8H, ${}^{e}CH$), 6.44 (t, ${}^{3}J(H,H) = 1$ Hz, 4H, ${}^{f}CH$), 6.54 (t, ${}^{3}J(H,H) = 1$ Hz, 8H, ${}^{i}CH$), 6.65 (d, ${}^{3}J(H,H) = 1$ Hz, 16H, ${}^{h}CH$), 7.24 – 7.38 (m, 80H, ${}^{k}C_6H_5$), 8.12 – 8.14 (m, 8H, ${}^{l}CH$), 9.49 – 9.52 (m, 8H, ${}^{m}CH$); UV/Vis (toluene): λ_{max} (ε) = 680 nm (250000), FAB-MS: m/z: 3726 [M^+].

Crystal structure analysis of **2**: $C_{130}H_{102}N_8O_{14}Si$, $M_r = 2028.37$, green prismatic crystal, crystal dimensions 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, $\alpha = 103.62(2)$, $\beta = 109.30(2)$, $\gamma = 71.83(2)^\circ$, $V = 2585(1)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.303$ g cm^{-3}, $\mu = 0.9$ cm^{-1}; Rigaku AFC5R diffractometer, monochromatized $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å), 20 °C, $\omega - 2\theta$ scan mode; $2\theta_{max} = 50.1^\circ$; 9709 measured reflections, 9175 unique reflections ($R_{int} = 0.102$), 691 parameters refined, 4023 reflections included in the refinement. Lorentzian, polarization, and absorption corrections were carried out (transmission factors = 0.9331 – 1.0000; $\mu = 0.9$ cm^{-1}). A decay correction based on a 4.5 % decrease in the intensity of three standard reflections was also applied. The structure was determined by direct methods (SHELXS86) and expanded by 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 full-matrix least-squares methods 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}. Crystallographic data (excluding structure 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).

Received: October 13, 1997 [Z11027IE]
German version: *Angew. Chem.* **1998**, *110*, 1185 – 1187

Keywords: dendrimers · phthalocyanines · silicon · steric hindrance

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Determination of the Disordered Structure of $Gd_2Ba_2CaCu_2Ti_3O_{14}$ with Multiple-Edge EXAFS and Powder Diffractograms[**]

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The structures of solids are defined by local and long-range order, both of which must be determined to characterize a material. Systems in which perfect crystalline order does not exist and local structural features are important include superconducting oxides, alloys, zeolites containing entrapped molecular species, ferroelectric materials, materials that exhibit high magnetoresistance, and intercalation compounds. The structures of such materials are often determined by separate analyses of data collected by a variety of techniques, sometimes with conflicting results, or an averaged structure is determined by analysis of diffraction data alone.

The structure of the complex oxide $Gd_2Ba_2CaCu_2Ti_3O_{14}$ was determined by using a combination of extended X-ray absorption fine structure (EXAFS) data for all five of the metals with powder X-ray diffraction data and refined with a single set of coordinates consistent with all the experimental data. This combined analysis approach, illustrated here, is a

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[**] This research was supported by the EPSRC through grants X46R352 and GR/J27053 and a studentship for M.J.P.