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Synthesis, Photochemistry, and Electrochemistry of a Series of Phthalocyanines with Graded Steric Hindrance[†]

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A group of twelve new and three known silicon phthalocyanines having axial ligands and peripheral groups which provide varying amounts of steric protection to the ring face and ring periphery has been assembled. These are SiPc[OSi(n-C_6H_{13})$_3$]$_2$, **1**, (known), SiPc[OSi(i-C_4H_9)$_2$(n-$C_{18}H_{37}$)]$_2$, **2**, SiPc(OEt)$_8$[OH]$_2$, **5**, SiPc(OEt)$_8$[OSi(CH_3)$_3$]$_2$, **6**, SiPc(OnBu)$_8$[OH]$_2$, **8**, (known), SiPc(OnBu)$_8$[OSi(n-C_6H_{13})$_3$]$_2$, **9**, (known), SiPc(OnBu)$_8$[OSi(i-C_4H_9)$_2$(n-$C_{18}H_{37}$)]$_2$, **10**, SiPc(dib)$_4$(OnBu)$_8$[OH]$_2$, **15**, SiPc(dib)$_4$(OnBu)$_8$[F]$_2$, **16**, SiPc(dib)$_4$(OnBu)$_8$[OSi(n-C_6H_{13})$_2$]$_2$, **17**, SiPc(dib)$_4$(OnBu)$_8$[OSi(i-C_4H_9)$_2$(n-$C_{18}H_{37}$)]$_2$, **18**, SiPc(dib)$_4$(OnBu)$_8$[OSi_8O_{12}(C_5H_9)$_7$]$_2$, **19**, SiPc(dib)$_4$(OnBu)$_8$[OH]$_2$, **22**, SiPc(dib)$_4$(OiBu)$_8$[OSi(n-C_6H_{13})$_3$]$_2$, **23**, and SiPc(dib)$_4$(OiBu)$_8$[OSi_8O_{12}-(C_5H_9)$_7$]$_2$, **24**. Syntheses are given for the twelve members of the group that are new. Photophysical and voltammetric investigations of six representative members of the group, **1**, **2**, **10**, **18**, **19**, and **24**, have been carried out. The results show that compounds **1** and **2** (no butoxy substituents at the 1 and 4 positions) have significantly larger values of the first oxidation potential (E_{+1}) than those compounds (**10**, **18**, **19**, and **24**) that do carry these substituents. The values of E_{-1} (first reduction potential) show very little in the way of structural dependence. Alkoxy substitution at the 1,4 positions affects the HOMO energies, and therefore, the addition of an electron from an electrode to the LUMO of a 1,4 substituted silicon phthalocyanine will not be a sensitive function of the substitution pattern. The removal of an electron from the HOMO in an oxidation step on the other hand would be expected to be energetically less demanding for those compounds wherein the HOMO is higher lying. This orbital energy effect of substitution makes it clear why the E_{+1} values for compounds **1** and **2** are significantly lower. Substitution of dibenzobarreleno (*dib*) at the 2,3 positions has only minor effects on the HOMO energy, as shown by the similarities in the position of the Q-band maximum. However, it is very likely that the steric effects of the dibenzobarreleno substituents and the [OSi_8O_{12}(C_5H_9)$_7$] axial cages contribute to the observed trends in E_{+1}. Bimolecular rate constants for quenching of the triplet states of the six target compounds by O_2, by β-carotene, and by chloranil were measured. The first two compounds quench by triplet−triplet (TT) energy transfer, whereas the last is an electron transfer (ET) reactant. All rate parameters were sensitive to the steric crowding of the phthalocyanine π system, but with different degrees. The least sensitive was the ET reaction with chloranil. Thus, it appears that although steric crowding of the triplet state of the silicon phthalocyanines is very effective at reducing the rate constants of exoergic electron exchange energy transfer (TT) reactions, even for a small molecule such as oxygen, it is much less effective at discriminating against electron transfer (ET) processes. These differences may be accounted for on the concept that the overlap requirement for the double electron exchange of TT energy transfer is more stringent compared to the single electron transfer (ET).

Introduction

The transfer of electronic energy between a pair of molecules, in which spin multiplicity changes in the participating molecules are observed, has been widely studied over several decades. When the donor species (D) is in an electronically excited triplet state and the acceptor species (A) is in its electronic ground state, the process is termed “triplet−triplet energy transfer” and can be represented schematically as

$$^3D^* + A \rightleftharpoons D + {}^3A^*$$

Processes such as this are ubiquitous in the photochemistry of organic molecules containing low Z constituents wherein multiplicity is unambiguous. It is the process that underlies the phenomenon of photosensitization, which is responsible for an abundance of photochemical and photobiological effects. Triplet−triplet energy transfer between aromatic hydrocarbons was actually first characterized in rigid solutions at 77 K.[1,2] It was subsequently observed in fluid (benzene) solution at room temperature by Bäckström and Sandros,[3,4] who investigated the effect of acceptor triplet energy on the bimolecular rate constant

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of the transfer. Energy transfer of this type in which spin multiplicity changes occur in the participating entities requires an electron exchange interaction that requires the close approach of the reacting molecules such that significant orbital overlap can occur. Dexter[5] analyzed the electron exchange requirement and developed a relationship between the rate constant and an exponential term involving the distance between the donor and acceptor states. Porter and Wilkinson were the first to use time-resolved techniques (flash photolysis) to investigate the dynamics of T−T energy transfer.[6] Since these early observations, there have been an abundance of studies on the dynamics of T−T energy transfer in solution phase. As a result, it is fair to say that for exoergic reactions the overall process is controlled by the rate at which the participants can encounter each other, viz., diffusion-controlled rate constants are observed.

Unfortunately, measurements of diffusion-limited rate constants offer little insight into the detailed nature of the energy transfer event at the molecular level; such details being obscured inside the diffusion requirement. Students of single electron transfer (ET) reactions overcame similar problems in the early 1980s by affixing their donor and acceptor moieties at the opposite ends of a spacer molecule,[7] effectively creating a "triad" system of donor-spacer-acceptor. In such a system, the electron transfer reaction becomes intramolecular and the requirement for preliminary diffusion steps is obviated. Using this expediency, it became possible for investigators to individually study the effects of overall driving force (by using D and A entities having a range of reduction potentials), of distance (by manipulating the spacer size and structure), and of orientation (by joining the D and A entities to the spacer via axial or equatorial links).[8−10] Two decades of intense activity in such matters has led to major advances in our understanding of electron-transfer reactions, not least of which has been the experimental demonstration of the so-called "inverted region" in which the rate constant of ET diminished as the overall driving force increased.[10−13] This startling effect had been predicted by Marcus[14] some decades earlier.

Another result of note from the ET investigations is that under conditions of constant driving force the rate constant is governed by an intermolecular distance parameter.[9,10] The functional form is

$$k = k_0 \exp(-\beta[R - R_0])$$

where R is the separation distance, R_0 is the van der Waals separation, and β is a scaling parameter that can be thought of as a molecular resistivity. This distance dependence of the rate can be understood through a Fermi Golden Rule treatment of ET as radiationless transition between reactant and product states. Within that formalism, the reaction rate is proportional to the second power of the matrix element (V) that couples the initial and final states, and the distance dependence seen in k is a reflection of the distance dependence of V.

Returning now to TT energy transfer and the Dexter theory of electron exchange,[5] it becomes reasonable to think of triplet−triplet energy transfer in terms of an exchange of two electrons between the HOMO and LUMO of the participating entities. In a formal sense, this amounts to the simultaneous transfer of an electron from the LUMO of the donor to the LUMO of the acceptor, and the transfer of a hole from the HOMO of the donor to the HOMO of the acceptor. Within this framework it can be shown[15] that

$$\beta^{TT} = \beta^{ET} + \beta^{HT}$$

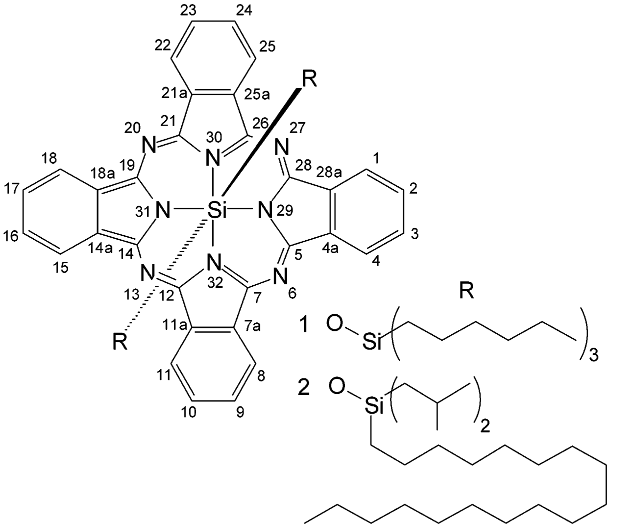


Figure 1. Structure and numbering scheme for SiPc[R]$_2$ compounds (alkyl chain conformations arbitrary).

where the HT superscript denotes hole transfer. This result was confirmed by a series of experiments carried out in the Closs laboratory, employing the donor−spacer−acceptor paradigm that had worked so effectively for the electron-transfer investigations.[16, 17]

More recently, investigations of TT energy transfer have centered on the role of the intervening, disorganized medium (e.g., solvent) that separates donor and acceptor in bimolecular reactions in fluid media. Model systems that are aimed to address such questions are those in which one of the reactant pair is incorporated as a guest entity within the body of a hemicarcerand host and the other reactant is free to diffuse within the solvent phase in which the host is dispersed.[18,19] In these instances, TT (and ET) reactions are required to occur through the molecular wall of the host. The results of these studies showed that the rate constants for TT excitation transfer displayed a pronounced dependence on the total internal reorganization energy of the reactant pair. A variant of this approach is to use synthetic routes to construct a covalently linked molecular sheath around a putative reaction site, thereby restricting access to the site. When the sheathed reaction site is a light-absorbing moiety, it is possible to describe it as a hindered or encapsulated chromophore. Dendrimeric structures with photoactive cores have recently been constructed that attenuate ET reaction rates[20] or can sensitize the generation of singlet oxygen.[21]

Our interest in encapsulated chromophores stems from our long time involvement in the design, synthesis, and excited state properties of metallophthalocyanines that are potentially useful as photoinitiators for energy transfer and electron-transfer reactions.[22−28] Surrounding the chromophore both at the periphery of the π plane and axially via covalent links to the metal center can potentially hinder the approach of molecular species that are putative energy/electron transfer reactants with an excited state of the chromophore. To provide a basis for examination of this, we have assembled a group of 15 new and known silicon phthalocyanines having axial ligands and ring substituents which are of such sizes and are so placed, as to provide widely varying amounts of steric protection to the face and periphery of the ring. Five peripheral groups and six axial ligands are present in these phthalocyanines, Figures 1−5. Figure 6 shows views of a computer-generated low energy conformation of compound **24**. We have conducted photophysical and voltammetric investigations on six representative

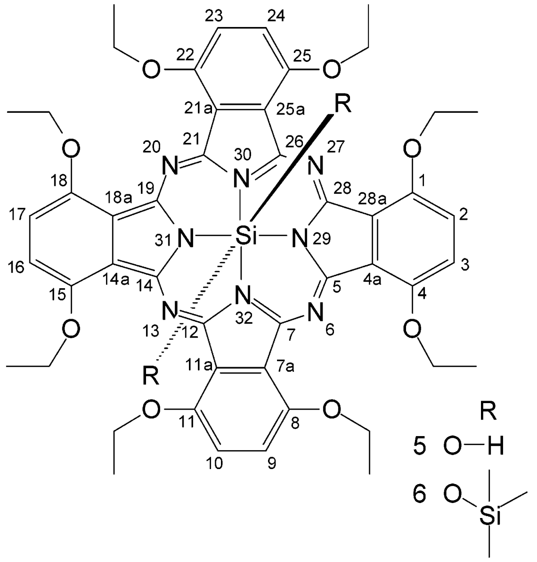


Figure 2. Structure and numbering scheme for $SiPc(OEt)_8[R]_2$ compounds.

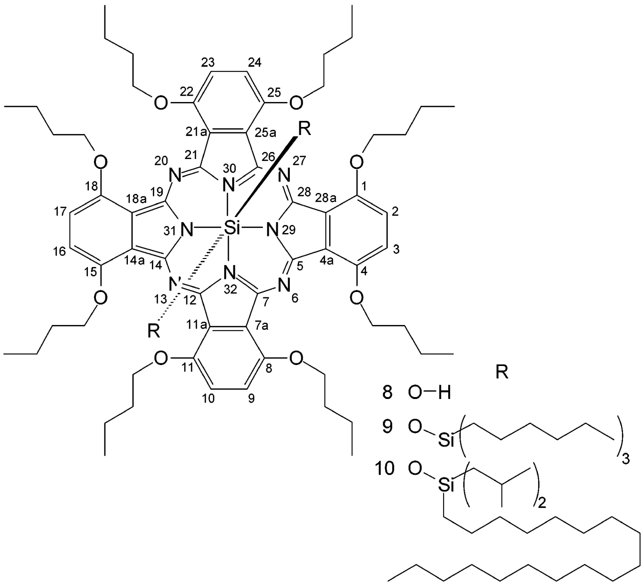


Figure 3. Structure and numbering scheme for $SiPc(OnBu)_8[R]_2$ compounds (alkyl chain conformations arbitrary).

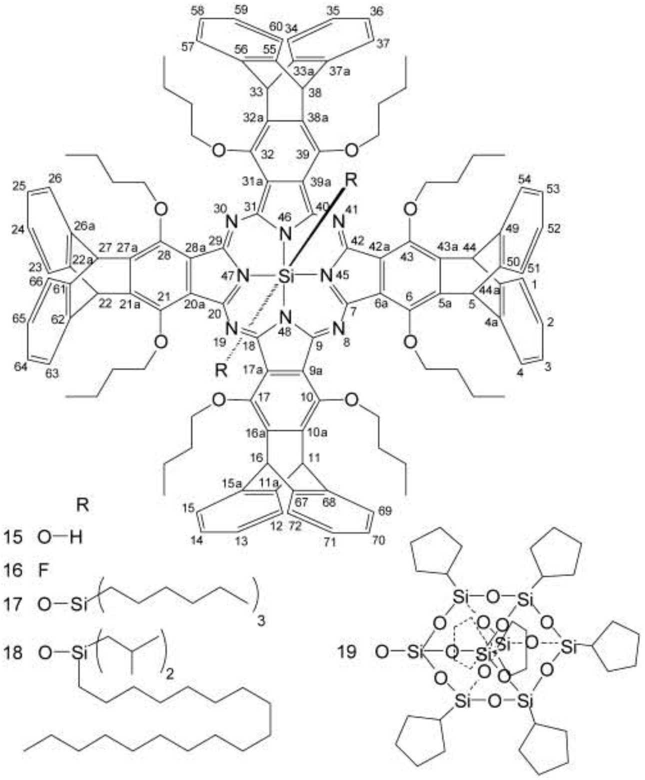


Figure 4. Structure and numbering scheme for $SiPc(dib)_4(OnBu)_8$-$[R]_2$ compounds (alkyl chain conformations arbitrary).

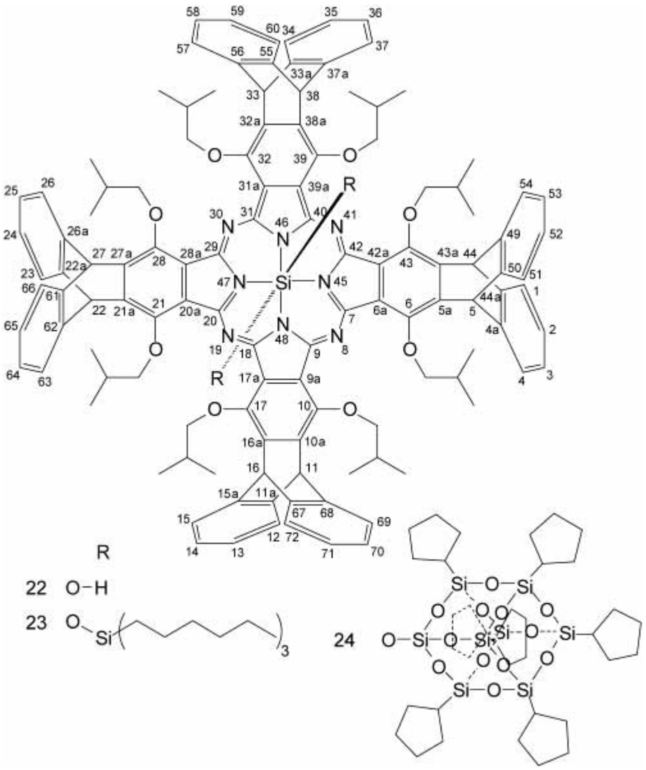


Figure 5. Structure and numbering scheme for $SiPc(dib)_4(OiBu)_8[R]_2$ compounds (alkyl chain conformations arbitrary).

compounds from the series and have found that these properties are profoundly affected by the amount of steric hindrance that has been built into them. It becomes apparent that the reactivity of the central chromophore can indeed be modulated by the nature of the molecular sheath.

Experimental Procedures

Syntheses. *Materials.* The reagents and solvents used in the syntheses whose source is not specified were from commercial vendors.

*SiPc[OSi(n-C_6H_{13})$_3$]$_2$, Pc 162, **1**.* See Wheeler et al.[29] UV−vis (toluene) λ_{max}, nm: 669. It is soluble in CH_2C1_2, toluene and hexanes.

*SiPc[OSi(i-C_4H_9)$_2$(n-$C_{18}H_{37}$)]$_2$, Pc 163, **2**.* A mixture of SiPc-$[OH]_2$ (163 mg), (*i*-C_4H_9)$_2$(*n*-$C_{18}H_{37}$)SiCl[30] (200 μL) and pyridine (20 mL) was refluxed for 4 h, concentrated by rotary evaporation (∼50 °C), diluted with hexanes (30 mL), and filtered. The filtrate was concentrated by rotary evaporation (∼50 °), and the concentrate was chromatographed (Al_2O_3 III, hexanes−toluene solution), vacuum-dried (room temperature), and weighed (132 mg, 34%). UV−vis (toluene) λ_{max}, nm: 670. NMR (C_6D_6): δ 9.75 (m, 1,4-Ar H), 7.94 (m, 2, 3-Ar H), 1.50−1.20 (m, SiR_{od}-7−17 CH_2), 1.08 (m, SiR_{od}-6 CH_2), 0.93 (t, SiR_{od} CH_3), 0.69 (m, SiR_{od}-5 CH_2), 0.39 (m, SiR_{od}-4 CH_2), −0.28

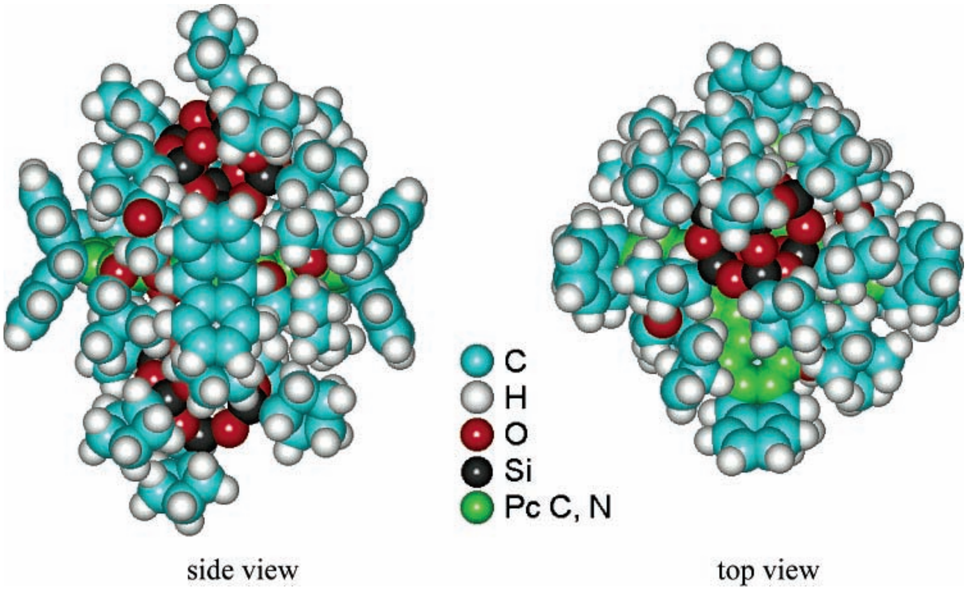


Figure 6. Computer-generated side and top views of a low energy conformation of $SiPc(dib)_4(OiBu)_8[OSi_8O_{12}(C_5H_9)_7]_2$, **24** (note that approach to the phthalocyanine ring is highly restricted).

(m, SiR_{od}-3 CH_2; SiR_b CH_3), −0.59 (m, SiR_b-2 CH), −0.90 (m, SiR_{od}-2 CH_2), −2.04 (m, SiR_{od}-1 CH_2; SiR_b-1 CH_2). MS−HRFAB exact mass, *m*/*z*: calc for $C_{84}H_{127}N_8O_2Si_3$ $(M + H)^+$, 1363.9390; found, 1363.9395, 1363.9334.

The compound is a blue solid. It is soluble in CH_2C1_2, toluene, and hexanes.

3,6-Diethoxy-1,2-benzenedicarbonitrile, ***3***. Work of Cook was used as a guide for this synthesis.[31] Under N_2, a mixture of 3,6-dihydroxy-1,2-benzenedicarbonitrile (3.2 g), iodoethane (8 mL), K_2CO_3 (12.4 g) and acetone (100 mL) was refluxed for 72 h, and concentrated by rotary evaporation (∼30 °C). The concentrate was treated with H_2O (50 mL) and filtered, and the solid was washed (acetone), vacuum-dried (room temperature), and weighed (3.5 g, 81%). NMR ($CDCl_3$): δ 7.26 (s, Ar H), 4.13 (q, OR CH_2), 1.48 (t, OR CH_3).

The compound is a white solid. It is slightly soluble in acetone.

$H_2Pc(OEt)_8$ Pc 126, ***4***.[31] Under N_2, a suspension of 3,6-diethoxy-1,2-benzenedicarbonitrile (900 mg) and xylenes (50 mL) which had been dried by distillation (10 mL of distillate), ethanol (absolute, 10 mL), and Li (shot, 150 mg) was refluxed for 4 h and treated with H_2O (15 mL). The resulting slurry was extracted with CH_2Cl_2 (3 times, 20 mL each time), and the extracts were combined, washed (saturated NaCl solution, H_2O), dried (Na_2SO_4), and evaporated to dryness by rotary evaporation (∼30 °C). The solid was chromatographed (Al_2O_3 V, CH_2Cl_2-ethyl acetate solution), vacuum-dried (∼65 °C), and weighed (440 mg, 48%). UV−vis (toluene) λ_{max}, nm: 733, 758. NMR (C_6D_6): δ 7.48 (s, Ar H), 4.88 (q, OR CH_2), 1.69 (t, OR CH_3), 0.14 (s, NH). MS−HRFAB exact mass *m*/*z*: calc for $C_{48}H_{51}N_8O_8$ $(M + H)^+$, 867.3831; found, 867.3801, 867.3857.

The compound is a green solid. It is soluble in CH_2Cl_2, and toluene, and insoluble in hexanes.

$SiPc(OEt)_8[OH]_2$, Pc 127, ***5***. Work of Aoudia et al. provided a basis for this synthesis.[25] A mixture of $H_2Pc(OEt)_8$ (106 mg), $HSiCl_3$ (0.2 mL), $(n\text{-}C_3H_7)_3N$ (4 mL), and CH_2Cl_2 (40 mL) was stirred for 48 h and then was treated with H_2O (20 mL) and $(C_2H_5)_3N$ (10 mL). The resultant slurry was extracted with CH_2Cl_2 (3 times, 20 mL each time), and the extracts were combined, washed (H_2O), dried (Na_2SO_4), filtered, and evaporated to dryness by rotary evaporation (∼45 °C). The solid was chromatographed (Al_2O_3 III, CH_2Cl_2-ethyl acetate-CH_3OH solution), vacuum-dried (∼60 °C), and weighed (98 mg, 87%). UV−vis (toluene) λ_{max}, nm: 747. NMR (C_6D_6): δ 7.45 (s, Ar H), 4.81 (q, OR CH_2), 1.65 (t, OR CH_3). MS−HRFAB exact mass, *m*/*z*: calc for $C_{48}H_{50}N_8O_{10}Si$ $(M)^+$, 926.3419; found, 926.3390, 926.3377.

The compound is a green solid. It is soluble in CH_2Cl_2 and toluene, and insoluble in hexanes.

$SiPc(OEt)_8[OSi(CH_3)_3]_2$, Pc 128, ***6***. Under N_2, a mixture of $SiPc(OEt)_8[OH]_2$ (19 mg), Me_3SiCl (0.2 mL), and pyridine (20 mL) was refluxed for 2 h and evaporated to dryness by rotary evaporation (∼45 °C). The solid was dissolved in a hexanes−toluene solution (4:1), and the solution was filtered and evaporated to dryness by rotory evaporation (∼50 °C). The resulting solid chromatographed (Al_2O_3 V, toluene-ethyl acetate solution), vacuum-dried (∼65 °C), and weighed (17 mg, 78%). UV−vis (toluene) λ_{max}, nm: 746. NMR (C_6D_6): δ 7.46 (s, Ar H), 4.87 (q, OR CH_2), 1.64 (t, OR CH_3), −2.37 (s, SiR CH_3). MS−HRFAB exact mass, *m*/*z*: calc for $C_{54}H_{67}N_8O_{10}Si_3$ $(M + H)^+$, 1071.4289; found, 1071.4316, 1071.4308.

The compound is a green solid. It is soluble in CH_2C1_2, toluene and hexanes.

$H_2Pc(OnBu)_8$, Pc 164, ***7***. See Aoudia et al.[25]

$SiPc(OnBu)_8[OH]_2$, Pc 165, ***8***. See Aoudia et al.[25]

$SiPc(OnBu)_8)[OSi(n\text{-}C_6H_{13})_3]_2$, Pc 166, ***9***. See Aoudia et al.[25]

$SiPc(OnBu)_8[OSi(i\text{-}C_4H_9)_2(n\text{-}C_{18}H_{37})]_2$, Pc 167, ***10***. A mixture of $SiPc(OnBu)_8[OH]_2$ (48 mg), $(i\text{-}C_4H_9)_2(n\text{-}C_{18}H_{37})SiCl$[30] (125 μL), pyridine (5 mL), and toluene (20 mL) was refluxed for 4 h, concentrated by rotary evaporation (∼50 °C), diluted with hexanes (30 mL), and filtered. The filtrate was concentrated by rotary evaporation (∼50 °C), and the concentrate was chromatographed (Al_2O_3 III, hexanes−toluene solution), vacuum-dried (room temperature), and weighed (53 mg, 65%). UV−vis (toluene) λ_{max}, nm: 749. NMR (C_6D_6): δ 7.59 (m, Ar H) 5.02 (t, OR-1 CH_2), 2.25 (m, OR-2 CH_2), 1.79 (m, OR-3 CH_2), 1.40−1.20 (m, SiR_{od}-7−17 CH_2), 1.08 (m, SiR_{od}-6 CH_2; OR CH_3), 0.92 (t, SiR_{od} CH_3), 0.72 (m, SiR_{od}-5 CH_2), 0.53 (m, SiR_{od}-4 CH_2), −0.30 (m, SiR_{od}-3 CH_2; SiR_b CH_3), −0.35 (m, SiR_b-2 CH), −0.62 (m, SiR_{od}-2 CH_2), −1.82 (m, SiR_{od}-1 CH_2;

SiR_b-1 CH_2). MS−HRFAB exact mass, *m/z*: calc for $C_{116}H_{191}N_8O_{10}Si_3$ $(M + H)^+$, 1940.3991; found, 1940.4018, 1940.3952.

The compound is a green oil. It is infinitely miscible with CH_2C1_2, toluene, and hexanes.

2,3-Dibromo-9,10-dihydro-9,10[1′,2′]-benzenoanthracene-1,4-dione, ***11***. Work of Rihter et al. was used as a model for this synthesis.[23] A solution of 4a,9,9a,10-tetrahydro-9,10[1′,2′]-benzenoanthracene-1,4-dione (prepared from 1,4-benzoquinone and anthracene;[23] 7.5 g) and glacial acetic acid (150 mL) was treated *dropwise* with a solution of Br_2 (4.1 mL) and glacial acetic acid (20 mL), refluxed for 3 h, and filtered. The solid was washed (glacial acetic acid then hexanes), chromatographed (Al_2O_3 III, $CHCl_3$), vacuum-dried (∼60 °C), and weighed (6.4 g, 56%). NMR ($CDCl_3$): δ 7.43 (m, 5, 8, 3′,6′-Ar H), 7.02 (m, 6,7,4′,5′-Ar H), 5.88 (s, 9,10-CH).

The compound is an orange solid. It is soluble in CH_2Cl_2 and slightly soluble in toluene and insoluble in hexanes.

9,10-Dihydro-1,4-dihydroxy-9,10[1′,2′]-benzenoanthracene-2,3-dicarbonitrile, ***12***.[23] A mixture of 2,3-dibromo-9,10-dihydro-9,10[1′,2′]-benzenoanthracene-1,4-dione (0.17 g) and C_2H_5OH (5 mL) was treated dropwise with a solution of KCN (0.11 g) in H_2O (1 mL) and stirred for 3.5 h. The reaction mixture was diluted with H_2O (40 mL), refluxed overnight, and treated with HCl (concentrated, 10 mL) (CAUTION, USE TRAP). The acidified solution was extracted with $CHCl_3$ (4 times, 15 mL each time), and the extracts were combined, dried (Na_2SO_4), filtered, and evaporated to dryness by rotary evaporation (∼45 °C). The solid was washed (toluene then ethyl acetate), vacuum-dried (∼60 °C), and weighed (52 mg, 41%). NMR (CD_3OD): δ 7.42 (m, 5,8,3′,6′-Ar H), 7.03 (m, 6,7,4′,5′-Ar H), 5.99 (s, 9,10-CH).

The compound is a white solid. It is insoluble in CH_2C1_2, toluene and hexanes.

Because the dibromodione gives a product that is easier to purify it, it is a better reactant than the analogous dichlorodione.

9,10-Dihydro-1,4-di(1-butoxy)-9,10[1′,2′]-benzenoanthracene-2,3-dicarbonitrile, ***13***.[23] Under Ar, a mixture of 9,10-dihydro-1,4-dihydroxy-9,10[1′,2′]-benzenoanthracene-2,3-dicarbonitrile (0.72 g), 1-iodobutane (2.0 mL), K_2CO_3 (5.1 g), and acetone (50 mL) was refluxed for 16 h and filtered. The filtrate was evaporated to dryness by rotary evaporation (∼30 °C), and the solid was chromatographed (Al_2O_3 I, CH_2Cl_2), vacuum-dried (∼60 °C), and weighed (0.29 g, 30%). NMR ($CDCl_3$): δ 7.41 (m, 5,8,3′,6′-Ar H), 7.06 (m, 6,7,4′,5′-Ar H), 5.82 (s, 9,10-CH), 4.17 (t, OR-1 CH_2), 1.92 (m, OR-2 CH_2), 1.62 (m, OR-3 CH_2), 1.06 (t, OR CH_3).

The compound is a white solid. It is soluble in CH_2Cl_2 and toluene, and insoluble in hexanes.

$H_2Pc(dib)_4(OnBu)_8$, Pc 148, ***14***.[23] Under Ar, a refluxing solution of 9,10-dihydro-1,4-di(1-butoxy)-9,10[1′,2′]-benzenoanthracene-2,3-dicarbonitrile (372 mg) and 1-butanol (10 mL) was treated with Li (shot, 0.11 g), refluxed for 45 min, diluted with H_2O (10 mL), and extracted with CH_2Cl_2 (4 times, 10 mL each time). The extracts were combined, filtered, and evaporated to dryness by rotary evaporation (∼45 °C), and the solid was washed (pentane then methanol), chromatographed (Al_2O_3 III, toluene-ethyl acetate solution), washed with pentane, vacuum-dried (∼60 °C), and weighed (210 mg, 56%). UV−vis (toluene) λ_{max}, nm: 731, 758. NMR (C_6D_6): δ 7.62 (m, 1,4,12,15,23,26,34,37,51,54,57,60,63,66,69,72-Ar H[32a]), 6.97 (m, 2,3,13,14,24,25,35,36,52,53,58,59,64,65,70,71-Ar H[32b]), 6.79 (s, 5,11,16,22,27,33,38,44-CH[32c]), 5.20 (t, OR-1 CH_2), 2.33 (m, OR-2 CH_2), 1.65 (m, OR-3 CH_2), 1.13 (t, OR CH_3), −0.17 (s, NH).

The compound is a green solid. It is soluble in CH_2C1_2 and toluene, and slightly soluble in hexanes.

$SiPc(dib)_4(OnBu)_8[OH]_2$, Pc 168, ***15***. Method 1. Under Ar, a mixture of $HSiCl_3$ (0.35 mL) and a solution of $H_2Pc(dib)_4(OnBu)_8$ (149 mg), tetrahydrofuran (40 mL), CH_3CN (35 mL), and $(n\text{-}C_3H_7)_3N$ (10 mL) that had been dried by distillation (∼10 mL of distillate) was refluxed for 3 h, treated with $HSiCl_3$ (0.10 mL), stirred for 64 h, again treated with $HSiCl_3$ (0.10 mL), and refluxed for 2 h. The resulting slurry was treated with H_2O (∼40 mL) and $(C_2H_5)_3N$ (30 mL), and the mixture was extracted with CH_2Cl_2 (4 times, 50 mL each time). The extracts were combined, filtered and evaporated to dryness by rotary evaporation (∼40 °C), and the solid was chromatographed (Al_2O_3 III, toluene-ethyl acetate solution), vacuum-dried (∼60 °C), and weighed (70 mg, 45%).

Method 2. A solution of $SiPc(dib)_4(OnBu)_8[OSi(n\text{-}C_6H_{13})_3]_2$, **17** (see below, 40 mg), Cl_3CCOOH (0.10 g), and benzene (10 mL) was refluxed for 3 h, treated with hydrochloric acid (concentrated, 3.5 mL), and refluxed for 12 h. The resulting solution was treated with $(C_2H_5)_3N$ (10 mL) and extracted with toluene. The extract was washed (H_2O, 2 times, 10 mL each time) and evaporated to dryness by rotary evaporation (∼45 °C), and the solid was chromatographed (Al_2O_3 III, CH_2Cl_2), rechromatographed (BioBeads S−X4, Bio-Rad Laboratories, Hercules, CA; toluene), vacuum-dried (∼60 °C), and weighed (28 mg, 91%). UV−vis (toluene, 1.8 μM) λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 745 (2.7×10^5). NMR (C_6D_6): δ 7.64 (m, 1,4-Ar H), 7.01 (m, 2,3-Ar H), 6.75 (s, 5,44-CH), 5.06 (t, OR-1 CH_2), 2.34 (m, OR-2 CH_2), 1.63 (m, OR-3 CH_2), 1.18 (t, OR CH_3), −5.40 (s, br, OH). MS−HRFAB exact mass, *m/z*: calc for $C_{120}H_{114}N_8O_{10}Si$ $(M)^+$, 1854.8427; found, 1854.8504, 1854.8451.

The compound is a green solid. It is soluble in CH_2C1_2 and toluene, and slightly soluble in hexanes.

While circuitous, method 2 gives a purer product. It probably can be shortened by omission of the Cl_3CCOOH step.

$SiPc(dib)_4(OnBu)_8[F]_2$, Pc 169, ***16***. Under Ar, a mixture of $SiPc(dib)_4(OnBu)_8[OSi(n\text{-}C_6H_{13})_3]_2$ (see below, 15 mg), $BF_3 \cdot O(C_2H_5)_2$ (2.0 mL), and toluene (3 mL) was refluxed for 30 min and diluted with toluene (5 mL). The resultant was treated with pyridine (8 mL) and H_2O (20 mL) and extracted with toluene (5 times, 5 mL each time). The extracts were combined, filtered, and evaporated to dryness by rotary evaporation (∼45 °C), and the solid was chromatographed (Al_2O_3 III, toluene-CH_2Cl_2 solution), washed (pentane), vacuum-dried (∼60 °C), and weighed (10 mg, 87%). UV−vis (toluene) λ_{max}, nm: 755. NMR (C_6D_6): δ 7.64 (m, 1,4-Ar H), 7.02 (m, 2,3-Ar H), 6.73 (s, 5,44-CH), 4.50 (t, OR-1 CH_2), 2.31 (m, OR-2 CH_2), 1.62 (m, OR-3 CH_2), 1.18 (t, OR CH_3). MS−HRFAB exact mass, *m/z*: calc for $C_{120}H_{111}N_8O_8F_2Si$ $(M - H)^+$, 1857.8262; found, 1857.8333, 1857.8337.

The compound is a green solid. It is soluble in CH_2C1_2 and toluene and slightly soluble in hexanes. Its solubility in toluene and $CHCl_3$ is significantly less than that of the other members of this family.

The evaporation of mixtures of hydrofluoric acid (48%), pyridine and $SiPc(dib)_4(OnBu)_8[OSi(n\text{-}C_6H_{13})_3]_2$ or $SiPc(dib)_4(OnBu)_8[OH]_2$ yielded the unreacted phthalocyanine.

$SiPc(dib)_4(OnBu)_8[OSi(n\text{-}C_6H_{13})_3]_2$, Pc 170, ***17***. Under Ar, a mixture of $SiPc(dib)_4(OnBu)_8[OH]_2$ (55 mg), $(n\text{-}C_6H_{13})_3SiCl$ (0.15 mL), pyridine (2 mL), and toluene (30 mL) was refluxed for 3 h and evaporated to dryness by rotary evaporation (∼45 °C). The solid was dissolved in hexanes (25 mL), and the solution was filtered and evaporated to dryness by rotary evaporation (∼45 °C). The resulting solid was chromatographed

(Al$_2$O$_3$ III, CH$_2$Cl$_2$), rechromatographed (BioBeads S−X4, toluene), vacuum-dried (∼60 °C), and weighed (56 mg, 78%). UV−vis (toluene, 2.0 μM) λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 741 (2.9×10^5). NMR (C$_6$D$_6$): δ 7.58 (m, 1,4-Ar H), 6.95 (m, 2,3-Ar H), 6.77 (s, 5,44-CH), 5.40 (t, OR-1 CH$_2$), 2.44 (m, OR-2 CH$_2$), 1.80 (m, OR-3 CH$_2$), 1.23 (t, OR CH$_3$), 0.43 (m, SiR-5 CH$_2$; SiR CH$_3$), 0.18 (m, SiR-4 CH$_2$), 0.00 (m, SiR-3 CH$_2$), −0.91 (m, SiR-2 CH$_2$), −2.06 (m, SiR-1 CH$_2$). MS−HRFAB exact mass m/z: calc for $C_{156}H_{190}N_8O_{10}Si_3$ (M)$^+$, 2419.3912; found, 2419.3959, 2419.3855.

The compound is a green solid. It is soluble in CH$_2$C1$_2$, toluene, and hexanes.

SiPc(dib)$_4$(OnBu)$_8$[OSi(i-C$_4$H$_9$)$_2$(n-C$_{18}$H$_{37}$)]$_2$, Pc 171, **18**. Under Ar, a mixture of SiPc(dib)$_4$(OnBu)$_8$[OH]$_2$ (50 mg), (*i*-C$_4$H$_9$)$_2$(*n*-C$_{18}$H$_{37}$)SiCl[30] (500 μL), pyridine (8 mL), and toluene (50 mL) was refluxed for 6 h and evaporated to dryness by rotary evaporation (∼45 °C). The solid was dissolved in pentane (25 mL), and the solution was filtered and evaporated to dryness by rotary evaporation (∼45 °C). The resulting solid was chromatographed (Al$_2$O$_3$ III, hexanes−toluene solution), rechromatographed (BioBeads S−X4, toluene), vacuum-dried (∼60 °C), and weighed (53 mg, 74%). UV−vis (toluene, 2.2 μM) λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 745 (2.7×10^5). NMR (C$_6$D$_6$): δ 7.57 (m, 1,4-Ar H), 6.93 (m, 2,3-Ar H), 6.78 (s, 5,44-CH), 5.40 (t, OR-1 CH$_2$), 2.47 (m, OR-2 CH$_2$), 1.78 (m, OR-3 CH$_2$), 1.22 (t, OR CH$_3$), 1.2−1.4 (m, SiR$_{od}$−7−17 CH$_2$), 0.90 (t, SiR$_{od}$ CH$_3$), 0.54 (m, SiR$_{od}$-6 CH$_2$), 0.52 (m, SiR$_{od}$-5 CH$_2$), 0.29 (m, SiR$_{od}$-4 CH$_2$), 0.10 (m, SiR$_{od}$-3 CH$_2$), −0.58 (m, SiR$_b$ CH; SiR$_b$ CH$_3$), −0.92 (m, SiR$_{od}$-2 CH$_2$), −2.00 (m, SiR$_{od}$-1 CH$_2$), −2.14 (d, SiR$_b$ CH$_2$). MS−HRFAB exact mass, m/z: calc for $C_{172}H_{222}N_8O_{10}Si_3$ (M)$^+$, 2643.6416; found, 2643.6449, 2643.6330.

The compound is a green solid. It is soluble in CH$_2$C1$_2$, toluene, and hexanes.

SiPc(dib)$_4$(OnBu)$_8$[OSi$_8$O$_{12}$(C$_5$H$_9$)$_7$]$_2$, Pc 144, **19.** Under Ar, a mixture of SiPc(dib)$_4$(OnBu)$_8$[OH]$_2$ (12 mg), 3,5,7,9,11,13,15-heptacyclopentylpentacyclo[9.5.1.1.^{3,9}1.^{5,15}1^{7,13}]octasiloxan-1-ol ((C$_5$H$_9$)$_7$Si$_8$O$_{12}$OH; 300 mg), and pyridine (15 mL) was slowly distilled for 7 h (8 mL distillate) and evaporated to dryness by rotary evaporation (∼30 °C). The solid was chromatographed twice (silica gel, cyclohexane-CH$_2$Cl$_2$ solution), rechromatographed (Al$_2$O$_3$ III, cyclohexane-CH$_2$Cl$_2$ solution), vacuum-dried (room temperature), and weighed (15 mg, 63%). UV−vis (toluene, 4.9 μM) λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 748 (2.8×10^5). NMR (pyridine- d_5): δ 7.89 (m, 1,4-Ar H), 7.28 (m, 2,3-Ar H), 6.88 (s, 5,44-CH), 4.99 (m, OR-1 CH$_2$), 2.60 (m, OR-2 CH$_2$), 2.21 (m, OR-3 CH$_2$), 1.54 (t, OR CH$_3$), −1.45 to −0.22 (m, C$_5$H$_9$CH$_2$). MS-MALDI, m/z: calc for $C_{190}H_{239}N_8O_{34}Si_{17}$ (M + H)$^+$, 3656; found, 3652.

The compound is a green solid. It is soluble in CH$_2$Cl$_2$ and toluene, and slightly soluble in hexanes.

9,10-Dihydro-1,4-di(2-methyl-1-propoxy)-9,10[1′,2′]-benzenoanthracene-2,3-dicarbonitrile, **20**. Under Ar, a mixture of 9,10-dihydro-1,4-dihydroxy-9,10[1′,2′]-benzenoanthracene-2,3-dicarbonitrile (200 mg), **9**, 1-iodo-2-methylpropane (2 mL), K$_2$CO$_3$ (1.2 g), and acetone (12 mL) was refluxed for 14 h and evaporated to dryness by rotary evaporation (∼30 °C). The solid was extracted into CH$_2$Cl$_2$ (50 mL), recovered by rotary evaporation (∼30 °C) after the extract had been filtered, chromatographed (Al$_2$O$_3$ III, toluene), vacuum-dried (room temperature), and weighed (230 mg, 86%). NMR (CDC1$_3$): δ 7.43 (m, 5,8,3′,6′-Ar H), 7.08 (m, 6,7,4′,5′-Ar H), 5.85 (s, 9,10-CH), 3.96 (d, OR-1 CH$_2$), 2.29 (m, OR-2 CH), 1.22 (d, OR CH$_3$).

The compound is a light-yellow solid. It is soluble in CH$_2$Cl$_2$ and toluene, and insoluble in hexanes.

H$_2$Pc(dib)$_4$(OiBu)$_8$, Pc 150, **21**. Under Ar, a refluxing solution of 9,10-dihydro-1,4-di(2-methyl-1-propoxy)-9,10[1′,2′]-benzenoanthracene-2,3-dicarbonitrile (200 mg) and 2-methyl-1-propanol (18 mL) was treated with Li (shot, 20 mg), refluxed for 3 h, and treated with H$_2$O (20 mL). The mixture was extracted with toluene (3 times, 100 mL each time), and the extracts were combined, dried (Na$_2$SO$_4$), filtered, and evaporated to dryness by rotary evaporation (∼30 °C). The solid was washed (CH$_3$OH), chromatographed (silica gel, toluene), vacuum-dried (room temperature), and weighed (50 mg, 25%). UV−vis (toluene) λ_{max}, nm: 737, 764. NMR (C$_6$D$_6$): δ 7.63 (m, 1,4-Ar H), 6.98 (m, 2,3-Ar H), 6.84 (s, 5,44-CH), 4.92 (d OR-1 CH$_2$), 2.85 (m, OR-2 CH), 1.35 (d, OR CH$_3$), 0.01 (s, NH). MS−HRFAB exact mass, m/z: calc for $C_{120}H_{115}N_8O_8$ (M + H)$^+$, 1795.8838; found, 1795.8774, 1795.8745.

The compound is a green solid. It is slightly soluble in CH$_2$C1$_2$ and toluene, and insoluble in hexanes.

SiPc(dib)$_4$(OiBu)$_8$[OH]$_2$, Pc 151, **22**. A mixture of H$_2$Pc(dib)$_4$(OiBu)$_8$ (82 mg), HSiCl$_3$ (1.2 mL), toluene (40 mL), CH$_3$CN (40 mL), CH$_2$Cl$_2$ (60 mL), and (*n*-C$_3$H$_7$)$_3$N (8 mL) was stirred for 5 days, treated with a stream of Ar, and then evaporated to dryness by rotary evaporation (∼30 °C). The solid was stirred with toluene (50 mL), CH$_2$Cl$_2$ (50 mL), (*n*-C$_3$H$_7$)$_3$N (10 mL), and aqueous NaHCO$_3$ (saturated, 120 mL), and the mixture was extracted with toluene (4 times, 200 mL each time). The extracts were combined, dried (Na$_2$SO$_4$), and evaporated to dryness by rotary evaporation (∼30 °C), and the solid was chromatographed (silica gel, toluene-ethyl acetate solution), vacuum-dried (room temperature), and weighed (34 mg, 41%). UV−vis (toluene) λ_{max}, nm: 750. NMR (C$_6$D$_6$): δ 7.65 (m, 1,4-Ar H), 7.01 (m, 2,3-Ar H), 6.82 (s, 5,44-CH), 4.77 (d, OR-1 CH$_2$), 2.83 (m, OR-2 CH), 1.35 (d, OR CH$_3$).

The solid is a green solid. It is soluble in CH$_2$C1$_2$ and toluene and insoluble in hexanes.

SiPc(dib)$_4$(OiBu)$_8$[OSi(n-C$_6$H$_{13}$)$_3$]$_2$, Pc 142, **23**. Under Ar, a mixture of SiPc(dib)$_4$(OiBu)$_8$[OH]$_2$ (7 mg), (*n*-C$_6$H$_{13}$)$_3$SiCl (60 mg), pyridine (1 mL) and toluene (4 mL) was refluxed for 2 h and evaporated to dryness by rotary evaporation (∼30 °C). The solid was chromatographed (Al$_2$O$_3$ III, hexanes−CH$_2$Cl$_2$ solution), rechromatographed (Bio Beads S−X3, toluene), again rechromatographed (silica gel, hexanes−CH$_2$Cl$_2$ solution), vacuum-dried (room temperature), and weighed (4 mg, 44%). UV−vis (toluene) λ_{max}, nm: 748. NMR (C$_6$D$_6$): δ 7.59 (m, 1,4-Ar H), 6.95 (m, 2,3-Ar H), 6.82 (s, 5,44-CH), 5.12 (m, OR-1 CH$_2$), 2.94 (m, OR-2 CH), 1.46 (d, OR CH$_3$), 0.39 (m, SiR-5 CH$_2$; SiR CH$_3$), 0.15 (m, SiR-4 CH$_2$), 0.01 (m, SiR-3 CH$_2$), −0.88 (m, SiR-2 CH$_2$), −2.02 (m, SiR-1 CH$_2$). MS−HRFAB exact mass, m/z: calc for $C_{156}H_{191}N_8O_{10}$ Si_3 (M + H)$^+$, 2420.3913; found, 2420.3875, 2420.3937.

The compound is a green solid. It is soluble CH$_2$C1$_2$, toluene, and hexanes.

SiPc(dib)$_4$(OiBu)$_8$[OSi$_8$O$_{12}$(C$_5$H$_9$)$_7$]$_2$, Pc 143, **24**. Under Ar, a mixture of SiPc(dib)$_4$(OiBu)$_8$[OH]$_2$ (12 mg), (C$_5$H$_9$)$_7$Si$_8$O$_{12}$OH (300 mg), and pyridine (15 mL) was slowly distilled for 6 h (8 mL distillate) and evaporated to dryness by rotary evaporation (∼30 °C). The solid was chromatographed twice (silica gel, cyclohexane-toluene solution), rechromatographed twice (Bio Beads S−X1, toluene), vacuum-dried (room temperature), and weighed (15 mg, 63%). UV−vis (toluene, 2.9 μM) λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 749 (2.6×10^5). NMR (pyridine-d_5): δ 7.88 (m, 1,4-Ar H), 7.26 (m, 2,3-Ar H), 6.92 (s, 5,44-CH), 3.07 (m, OR-2 CH), 1.65 (d, OR CH$_3$), 1.45 to −0.05 (m, C$_5$H$_9$CH$_2$). MS-MALDI, m/z: calc for $C_{190}H_{239}N_8O_{34}Si_{17}$ (M + H)$^+$, 3656; found 3656.

The compound is a green solid. It is soluble in CH$_2$C1$_2$ and toluene, and slightly soluble in hexanes.

9,10-Dihydro-1,4-di(2,2-dimethyl-1-propoxy-9,10[1′,2′]-benzenoanthracene-2, 3-dicarbonitrile, ***25***. Under Ar, a cooled (ice bath) mixture of 9,10-dihydro-1,4-dihydroxy-9,10[1′,2′]-benzenoanthracene-2,3-dicarbonitrile (400 mg), NaH (mineral oil dispersion, 60%, 200 mg), and dimethylformamide (16 mL) was stirred for 3 h, treated with $(CH_3)_3CCH_2I$ (3.0 mL), refluxed for 24 h, cooled, and mixed with aqueous $NaHCO_3$ (saturated, 100 mL). The reaction mixture was extracted with CH_2Cl_2 (four times, 100 mL each time), and the extracts were combined, dried (Na_2SO_4), and evaporated to dryness by rotary evaporation (∼30 °C). The solid was chromatographed (A1$_2$O$_3$ III, toluene), vacuum-dried (room temperature), and weighed (335 mg, 60%). NMR ($CDCl_3$): δ 7.43 (m, 5,8,3′,6′-Ar H), 7.09 (m, 6,7,4′,5′-Ar H), 5.87 (s, 9,10-CH), 3.82 (s, OR-1 CH$_2$), 1.26 (s, OR CH$_3$).

The compound is a light-yellow solid. It is soluble in CH_2Cl_2 and toluene, and insoluble in hexanes.

$H_2Pc(dib)_4(OneoPen)_8$, ***26***. Attempts to cyclotetramerize dicarbonitrile **25** by the same route used to cyclotetramerize dicarbonitrile **20** to its corresponding phthalocyanine, **21,** failed.

Cyclic Voltammetry. Cyclic dc and differential voltammetry (OSWV) were carried out with a BAS 100A electrochemical analyzer (Bioanalytical Systems, Inc.), which was interfaced to an IBM PC. A three-electrode cell assembly was used in electrochemical measurements with working platinum, pseudo-reference Ag/Ag+ (0.01 M $AgNO_3$ and 0.1 M TBAP in benzonitrile), and coiled platinum auxiliary electrodes. Experimental parameters for a typical OSWV run, such as frequency, step, quiet time, and sensitivity are given in the figure captions. All measurements were made in 0.1 M TBAP in dichloromethane. Ferrocene was used as an internal reference with known ferrocenium/ferrocene reduction potential, E_0 (Fe3+/2+) = 0.45 V against NHE.[33]

Time-Resolved Kinetic Spectrometry. The instrumentation and methods for measuring the absorption spectra and dynamics of the triplet states of silicon phthalocyanines in dilute solutions in toluene have been adequately described in earlier publications from this laboratory.[25,27] Throughout this investigation, the silicon phthalocyanine concentrations were less that 5 μM, ensuring no aggregation.

Results

Photophysical and Voltammetric Work. *Phthalocyanines Selected for Physical Examination.* Six of the fifteen silicon phthalocyanines considered in this study were chosen for photophysical and voltammetric work. These are compounds **1**, **2**, **10**, **18**, **19**, and **24**. These six compounds have phthalocyanine rings that range from relatively unhindered, that in **1**, to highly hindered, that in **24**.

Ground-State Absorption Spectra. Figure 7 shows representative UV−vis absorption spectra of the two of the six compounds. The spectrum of compound **1**, Figure 7A, is typical of silicon phthalocyanines that lack peripheral alkoxy ring substituents, and that of compound **18**, Figure 7B, is typical of those that have eight 1,4-alkoxy substituents. As has been observed in earlier work from this laboratory,[22,25] substitution at the eight 1,4 positions causes the major Q-band to shift from ca. 670 nm to ca. 750 nm.

Voltammetric Measurements. Cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSWV) measurements were performed on compounds **1**, **2**, **10**, **18**, **19**, and **24**. One oxidation and two reduction waves were observed for compound **1** (Figure 8, upper panel). Two reduction and two oxidation waves were observed in the solvent working window for the other compounds (compound **18** is depicted in Figure 8, lower panel). The reversibility of the reduction and oxidation processes was probed by measuring the ratio of the cathodic and anodic peaks, which was found to be close to unity in all cases. The potentials (vs Ag/Ag$^+$) for the first oxidation and reduction waves are collected in Table 1.

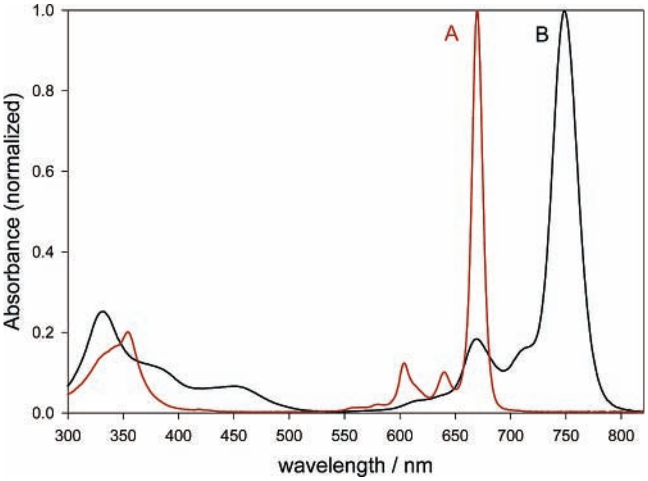


Figure 7. Ground-state absorption spectra for compounds **1** (A) and **18** (B).

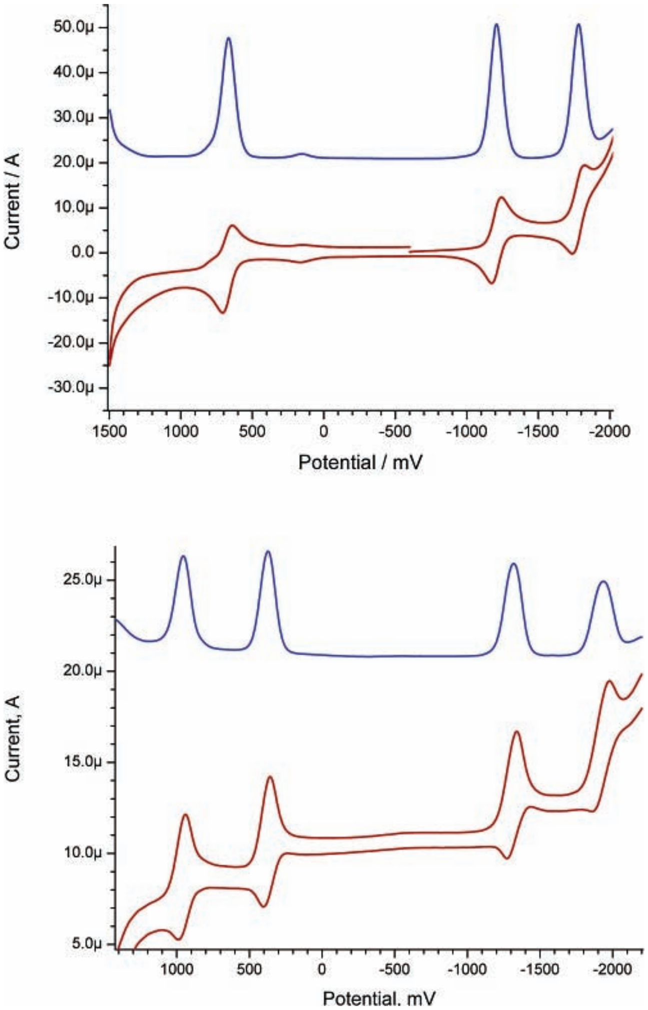


Figure 8. Cyclic DC and AC (OSWV) voltammograms of ∼2 mM compound **1**(top panel) and compound **18** (lower panel) in dichloromethane with 0.1 M TBAP. Scan, 100 mV/s; quiet time, 2 s; sensitivity, 10^{-5} A/V.

TABLE 1[a]

compound	E_{+1}/V[b]	E_{-1}/V[c]
1	0.664	- 1.208
2	0.652	- 1.256
10	0.196	- 1.368
18	0.372	- 1.320
19	0.481	−1.318
24	0.458	−1.3[d]

[a] **1**: SiPc[OSi(n-C_6H_{13})$_3$]$_2$. **2**: SiPc[OSi(i-C_4H_9)(n-$C_{18}H_{37}$)$_2$]$_2$. **10**: SiPc(OnBu)$_8$[OSi(i-C_4H_9)(n-$C_{18}H_{37}$)$_2$]$_2$. **18**: SiPc(dib)$_4$(OnBu)$_8$[OSi(i-C_4H_9)(n-$C_{18}H_{37}$)$_2$]$_2$. **19**: SiPc(dib)$_4$(OnBu)$_8$[OSi$_8$O$_{12}$(C_5H_9)$_7$]. **24**: SiPc(dib)$_4$(OiBu)$_8$[OSi$_8$O$_{12}$(C_5H_9)$_7$]. [b] First oxidation potential vs Ag/Ag$^+$. [c] First reduction potential vs Ag/Ag$^+$. [d] Approximate value only since reduction waves poorly resolved.

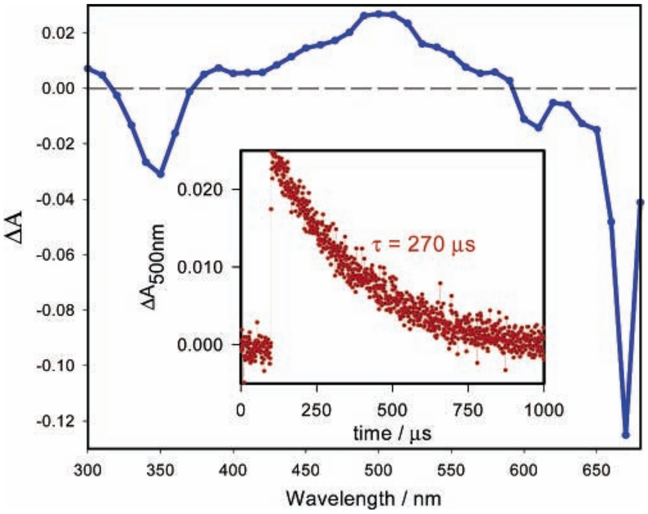


Figure 9. Transient absorption spectrum recorded 11 μs post excitation of compound **1** (5 μM) in toluene by a 6 ns pulse at 660 nm. Inset: time profile at 500 nm, exponential decay with a 270 μs lifetime.

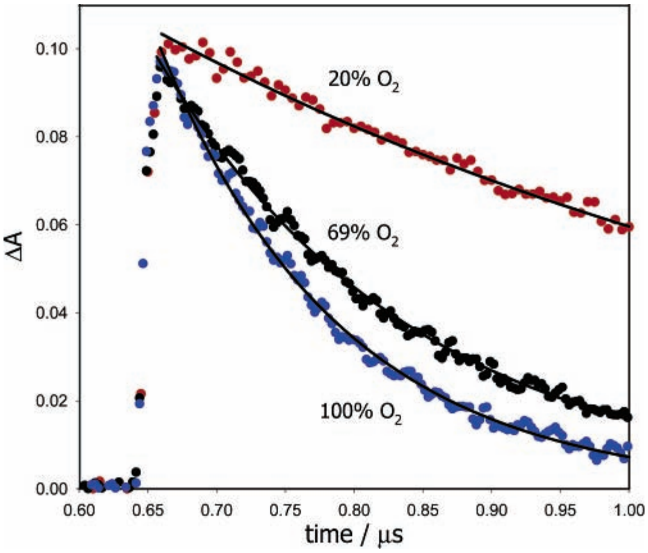


Figure 10. Time profiles of the triplet absorption of compound **1** (5 μM in toluene) at a series of O_2 concentrations.

TABLE 2: Compiled Bimolecular Rate Constants for Triplet-State Quenching of Compounds 1, 2, 10, 18, 19, and 24[a]

compound	$10^{-8}k^{T}_{O2}$/ $M^{-1}s^{-1}$	$10^{-8}k^{T}_{car}$/ $M^{-1}s^{-1}$	$10^{-9}k^{T}_{chl}$/ $M^{-1}s^{-1}$
1	17.1	9.0	3.30
2	18.2	8.3	
10	14.7	1.9	
18	8.4	0.061	3.60
19	0.44	0.0017	1.30
24	1.1	0.0025	0.90

[a] See text for experimental conditions. **1**: SiPc[OSi(n-C_6H_{13})$_3$]$_2$. **2**: SiPc[OSi(i-C_4H_9)(n-$C_{18}H_{37}$)$_2$]$_2$. **10**: SiPc(OnBu)$_8$[OSi(i-C_4H_9)(n-$C_{18}H_{37}$)$_2$]$_2$. **18**: SiPc(dib)$_4$(OnBu)$_8$[OSi(i-C_4H_9)(n-$C_{18}H_{37}$)$_2$]$_2$. **19**: SiPc(dib)$_4$(OnBu)$_8$-[OSi$_8$O$_{12}$(C_5H_9)$_7$]. **24:**SiPc(dib)$_4$(OiBu)$_8$[OSi$_8$O$_{12}$(C_5H_9)$_7$].

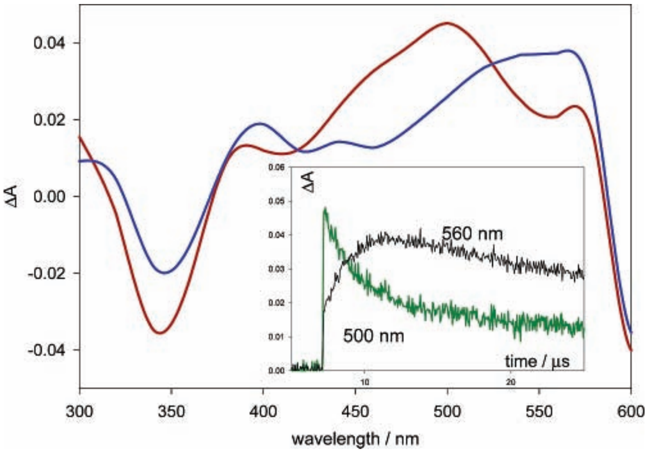


Figure 11. Absorption spectra taken at 200 ns (red) and at 8 μs (blue) after a 355 nm laser pulse incident on a solution of compound **1** (5 μM) and 10^{-4} M chloranil. The inset shows the time profiles at two wavelengths.

Transient Absorption Spectrometry. Air-Free Solutions. Solutions in deaerated toluene containing 5 μM of the silicon phthalocyanines **1**, **2**, **10**, **18**, **19**, and **24** were exposed to 6 ns pulses of light at 355 nm, or at 660 nm, in the sample compartment of a kinetic absorption spectrophotometer. Examples of the transient absorption spectra recorded are shown in Figure 9. It was found that all of the silicon phthalocyanines without butoxy substitution showed immediate postpulse spectra that covered most of the visible spectral region with a maximum near 500 nm; those carrying the butoxy substituents showed maxima near 600 nm. These observations parallel those found earlier with other silicon phthalocyanines[22,23,25,26] and by analogy the observed spectra are assigned to the $T_1 - T_n$ absorption spectra of the six. The time profiles (Figure 9, inset) at the maximum wavelengths were recorded from which kinetic parameters were extracted. In all cases studied in this paper, triplet state decays were cleanly first order, indicating no triplet−triplet annihilation.

Effect of Oxygen. Time profiles of the triplet−triplet absorptions of the six compounds were recorded in air and oxygen saturated solutions when it was found that the presence of oxygen shortened the lifetimes of the triplet states. Measuring the triplet decay rate constants, Figure 10, as a function of oxygen concentration yielded linear competition plots from which bimolecular rate constants for quenching by oxygen were obtained. The extracted rate constants for the several silicon phthalocyanine triplet states (k^{T}_{O2}) are collected in Table 2.

Effect of Chloranil. Chloranil (tetrachloro-1,4-benzoquinone) has a high electron affinity and has been used as an acceptor of electrons in photoredox reactions. Here it has been employed to investigate the effect of molecular crowding on the rate constant of photoelectron-transfer reactions. Argon-saturated solutions of the silicon phthalocyanines (ca 5 μM) and chloranil (0 to 2 mM) in CH_2C1_2[34] were subjected to 6 ns pulses of 670 nm light and the lifetimes of the triplet states were determined as described above. Figure 11 shows a pair of spectra taken at different times after the laser pulse, and in Figure 12 is a

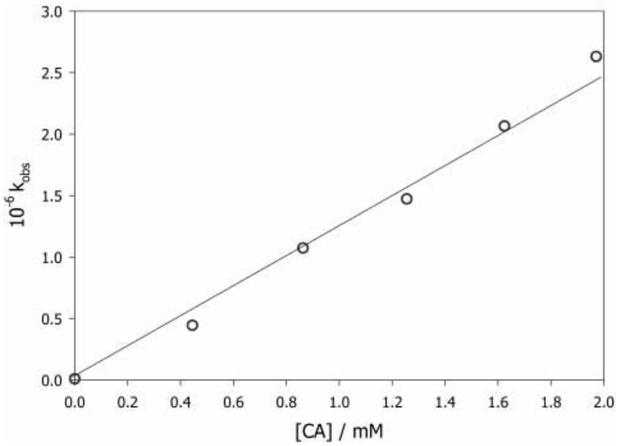


Figure 12. Competition plot for the quenching of the triplet state of compound **1** by chloranil.

SCHEME 1: Synthesis for Silicon Phthalocyanine

$$SiPc[OH]_2 \xrightarrow{(i\text{-}C_4H_9)_2(n\text{-}C_{18}H_{37})SiCl,\ \ C_5H_5N} SiPc[OSi(i\text{-}C_4H_9)_2(n\text{-}C_{18}H_{37})]_2$$

2 Pc 163

representative competition plot for the triplet state decay as a function of chloranil concentration from which bimolecular quenching rate constants (k^{T}_{chl}) were extracted (Table 2).

Effect of trans-β-Carotene. Like oxygen, carotenes have low-lying excited electronic states and carotenes have been employed in many laboratories as acceptors of triplet energy. The effect of adding trans-β-carotene on the lifetime of the triplet states of the six compounds was investigated. Argon-saturated solutions of the silicon phthalocyanines (ca. 5 μM) and β-carotene (0 to 240 μM) in toluene were subjected to 6 ns pulses of 355 nm light, and the lifetimes of the triplet states were determined from exponentially decaying time profiles similar to those shown in Figure 10 for oxygen. The rate constant data were used to construct competition plots (similar to the one shown in Figure 12 for chloranil) from which bimolecular quenching rate constants (k^{T}_{car}) were extracted. These data are collected in Table 2.

Discussion

Preparative Work. *Syntheses.* The syntheses used for the twelve new silicon phthalocyanines are given in Schemes 1−4. Those for eight of these phthalocyanines, **2**, **6**, **10**, **17**, **18**, **19**, **23**, and **24**, utilize, as in seen, familiar condensation chemistry. The synthesis used for $SiPc(OEt)_8(OH)_2$, **5**, Scheme 2, is based on the work of Cook et al.[31] and Aoudia et al.[25] In the cyclization step of this synthesis, the use of ethanol instead of 1-pentanol precludes the formation of troublesome alkoxylation impurities.

The synthesis of $SiPc(dib)_4(OnBu)_8(OH)_2$, **15**, Scheme 3, derives in part from the work of Rihter et al.[23] In the halogenation step of this synthesis, the use of Br_2 instead of Cl_2 circumvents the formation of a vexing impurity which apparently arises from the monohalogenation of one of the benzo rings. The synthesis used for $SiPc(dib)_4(OnBu)_8[F]_2$, **16**, Scheme 3, is unusual. The success of this synthesis and the failure of the known HF synthesis[35] is not understood, but steric hindrance probably plays a significant role. Except for the use of 1-iodo-2-methylpropane in the alkoxylation step, the synthesis for $SiPc(dib)_4(OiBu)_8[OH]_2$, **22**, Scheme 4, is parallel to that used for $SiPc(dib)_4(OnBu)_8[OH]_2$, **15**. The failure of the attempts to make $H_2Pc(dib)_4(OneoPen)_8$, **26**, the neopentoxy analogue of $H_2Pc(dib)_4(OnBu)_8$, **14**, and $H_2Pc(dib)_4(OiBu)_8$, **21**, is attributed to the very great crowding that would be present in the compound if it could be made.

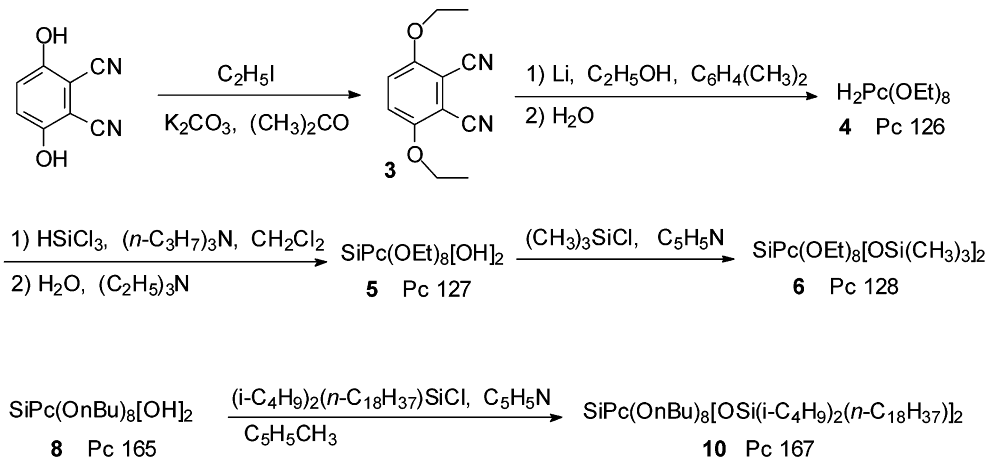
Steric Hindrance. A variety of combinations of steric protection of the ring face and ring periphery exists in the 15 silicon phthalocyanines making up the set. For example, the protection of the face of $SiPc(OEt)_8[OH]_2$, **5**, is low and that of its ring periphery is fairly low. In contrast, the protection of both the face and the periphery of $SiPc(dib)_4(OiBu)_8[OSi_8O_{12}(C_5H_9)_7]_2$, **24**, is so high that they are inaccessible to all but the smallest molecules, Figure 6.

It is important to note that although a variety of combinations of steric protection of the face and periphery of the ring exists in these compounds, all of them are soluble in toluene and CH_2C1_2. This makes them good candidates for physical studies other than those described in this paper.

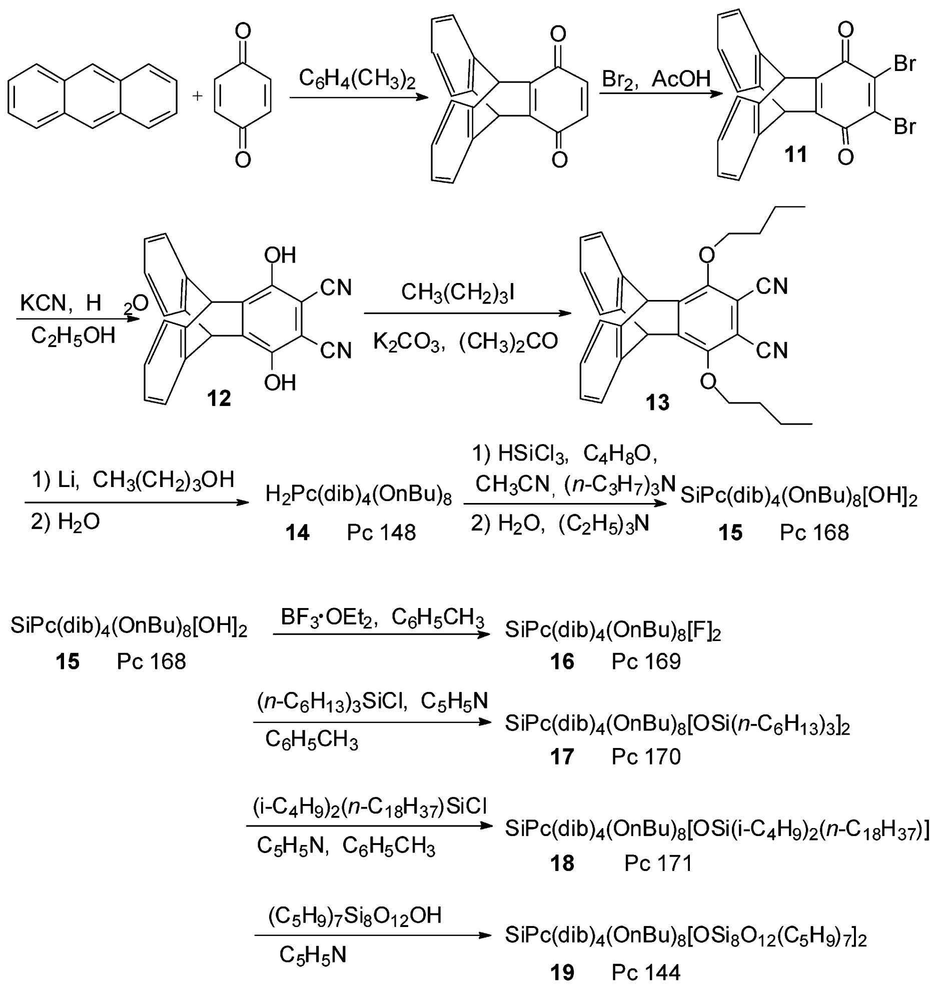
Ground-State Properties. Figure 7 depicts the ground-state absorption spectra of compounds **1** (spectrum A) and **18** (spectrum B). Spectrum A is typical for silicon phthalocyanines that do not have butoxy substituents at the 1 and 4 positions (Figure 1), and spectrum B is typical of those that do have such substituents (Figure 3). The presence of eight such residues causes a spectral red shift of ca. 90 nm (Figure 7). Similar marked red spectral shifts have been observed previously for metallonaphthalocyanines.[25] The substitution of alkoxy residues at the 2 and 3 positions on the benzo-rings has no significant effect on the Q-band maxima.[31,36] This difference can be understood through a consideration of the orbital energies in the different compounds. The HOMO ($a1_u$ in planar D_{4h} symmetry of the Pc ring) has large amplitude at the 1 and 4 positions, much larger than at the 2 and 3 positions.[37] A substituent such as an alkoxy group at the 1 and 4 positions results in an effective upward shift of the energy of this orbital and thus in a diminished HOMO−LUMO (e_g*) gap with respect to the unsubstituted phthalocyanine. The $a1_u$ orbital has much lower amplitude at the 2 and 3 positions, and the presence of substituents at these positions leads to a much less effective upward shift of the orbital energy and no significant spectral shifts.

Considering the electrochemical properties of the six compounds selected for their gradation in steric hindrance, examination of Table 1 shows that compounds **1** and **2** (no butoxy substituents at the 1 and 4 positions) have significantly larger values of E_{+1} than those compounds (**10**, **18**, **19**, and **24**) that do carry such substituents. At the same time, the values of E_{-1} show very little in the way of structural dependence. As discussed above, 1,4-alkoxy substitution affects the HOMO energies and therefore the addition of an electron from an electrode to the LUMO of a 1,4 substituted silicon phthalocyanine will not be a sensitive function of the substitution pattern. However, removing an electron from the HOMO in an oxidation step would be expected to be energetically less demanding for those compounds wherein the HOMO is higher lying. This orbital energy effect of alkoxy substitution is probably the reason the E_{+1} values for compounds **1** and **2** are significantly larger than those of compounds **10**, **18**, **19**, and **24**. This conclusion may be somewhat overdrawn because it ignores any possible effects of substitution on the oxidation product. In addition to carrying eight butoxy substituents, compounds **18**, **19**, and **24** each carry four dibenzobarreleno (dib) substituents fused at the 2 and 3 positions. According to the above argument, the 2,3 *dib* substitution will have only minor effects on the HOMO energy, as shown by the similarities in the position of the Q-band maximum. Thus, it would be expected that the oxidation

SCHEME 2: Syntheses for Octaalkoxysilicon Phthalocyanines



SCHEME 3: Syntheses for Dibenzobarrelenoocta-*n*-butoxysilicon Phthalocyanines



potentials would also be similar. However, it is noted that there is a clear increase in going from **10**, through **18**, to **19** and then a leveling off to compound **24**. It thus seems very likely that the steric effects of the dibenzobarreleno substituents and the $[OSi_8O_{12}(C_5H_9)_7]$ cages are contributing to these observed trends in E_{+1}. On the other hand, possible effects on the oxidation products cannot be discounted as influencing the observed trend.

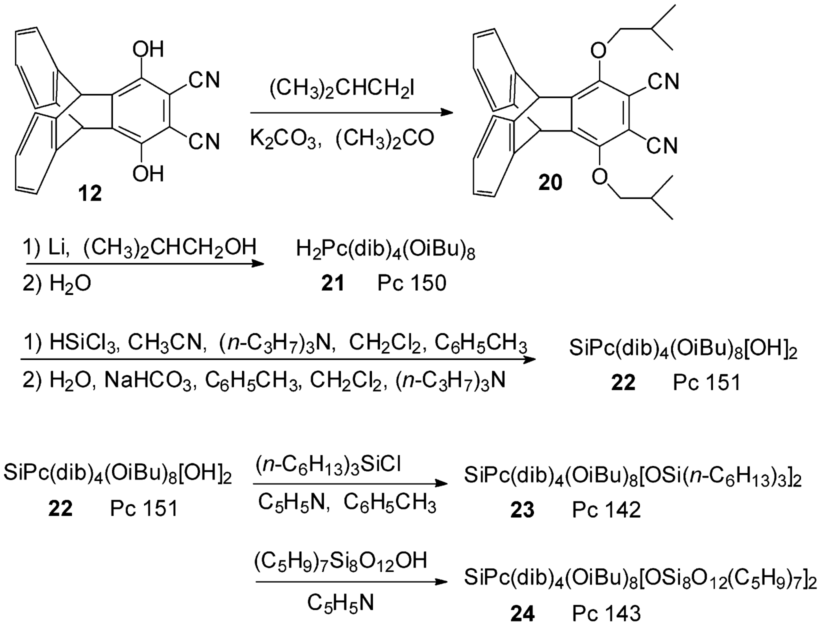
Triplet State Properties. Upon photoexcitation, all compounds showed production of the optical absorption of the T_1 state (Figure 9). The wavelength maximum was either near 600 nm or near 500 nm, depending on whether the phthalocyanine ring carried butoxy substituents or not. In all cases in the absence of oxygen, the triplet state lifetime was close to 300 μs. In the presence of added reactive compounds, the triplet states can be deactivated through energy or electron transfer reactions, typically represented as

$$Pc(T_1) + R \rightarrow Pc(S_0) + R(T_1)$$

or

$$Pc(T_1) + R \rightarrow Pc^+ + R^-$$

SCHEME 4: Syntheses for Dibenzobarrelenooctaisobutoxysilicon Phthalocyanines



Note that the energy transfer reaction regenerates the ground state of the energy donor, but the electron-transfer reaction generates a radical cation of the initial species. The presence of oxygen was shown to enhance the decay rate of the triplet state (Figure 10), and the evaluated bimolecular rate constants for oxygen quenching are listed in Table 2 (second column). For compounds **1**, **2**, and **10**, the bimolecular constants are close to 2×10^9 M^{-1} s^{-1}, and the value that is consistent with exergonic exchange energy transfer.[38,39] Compound **18**, which carries four *dib* residues, is a factor of 2 lower and compounds **19** and **24**, which carry the *dib* residues and the $[OSi_8O_{12}(C_5H_9)_7]$ cages, are lower by more than an order of magnitude. There are several examples of work published from this laboratory[27,38,39] that in situations where the triplet state energy of a compound is lower than that of $O_2(^1\Delta_g)$, the quenching of the triplet state by oxygen has a rate constant that is lower than that for an exergonic energy exchange. The peripheral attachment of *dib* residues causes no change in the energy of the singlet state of silicon phthalocyanines, and it seems therefore reasonable that the triplet energies would also be unaffected. Admittedly, these contain π bonds, but these are insulated from the phthalocyanine π system, and moreover the ground state spectra are unchanged by the substitution of dib residues. Similar considerations apply to the incorporation of the siloxy cages at the axial sites. Thus, we are led to the conclusion that the diminished rate constants for triplet state quenching by oxygen as seen in Table 2 is a consequence of access of oxygen molecules to the donor site being restricted because of steric crowding by the dib residues and even more so by the siloxy cages in compounds **19** and **24**. The views of compound **24** shown in Figure 6 clearly indicate that an approaching O_2 molecule would find itself severely restricted in achieving close proximity to the Pc ring.

The third column of Table 2 shows the bimolecular rate constants that were determined for quenching of the triplet states of the listed compounds by β-carotene. This compound has a low-lying triplet state[40] with an energy in the vicinity of that of $O_2(^1\Delta_g)$, and it will participate in exergonic electron exchange energy transfer reactions with the listed silicon phthalocyanines. Table 2 shows a wide variation in rate constant as the silicon phthalocyanine becomes increasingly more crowded. It is clear that the much greater molecular size of β-carotene, compared to oxygen, causes a much more effective discrimination against the electron exchange process.

In view of the above discussion, it is somewhat surprising that quenching of the silicon phthalocyanine triplet states by chloranil showed so very little steric discrimination (Table 2, column 4). The transient spectra shown in Figure 11 indicate that, at 200 ns post-pulse (the red spectrum), the species present is mainly the triplet state of compound 1 (compare with the spectrum shown in Figure 9). At ca. 8 μs post-pulse, the T_1 spectrum has been replaced (Figure 11, blue); however, the negative absorptions at 350 nm and at >600 nm remain. These latter are due to bleaching of the silicon phthalocyanine ground state, and that these are present when the T_1 state has reacted is a strong indication that the reaction with chloranil does not repopulate the ground state of the silicon phthalocyanine; hence, it is not an energy transfer reaction (see discussion above). Chloranil is known to be a good electron acceptor, and it is concluded that the reaction with silicon phthalocyanine T_1 is an electron-transfer reaction and that the blue spectrum in Figure 11 is that of the radical cation of the phthalocyanine. Thus, it appears that although steric crowding of the triplet state of the silicon phthalocyanines is very effective at reducing the rate constants of exoergic electron exchange energy transfer (TT) reactions, even for a small molecule such as oxygen, it is much less effective at discriminating against electron transfer (ET) processes.

The reason for this can perhaps be understood by a consideration of the work of Closs, Piotrowiak and their coworkers.[15−17] They examined the rates of TT energy transfer, ET, and hole transfer (HT) between a single donor−acceptor pair connected by saturated hydrocarbon bridging units such that donor−acceptor distances were varied. Their data demonstrated that the β values for ET and HT were comparable and that $\beta^{TT} \approx 2\beta^{ET}$. They were able to rationalize this result based on a quantum mechanical exchange integral approach and concluded, in line with Dexter theory, that TT energy transfer can be regarded as a double exchange between electrons associated with the HOMO and LUMO of the reacting pair. The β term is the multiplier of the intermolecule distance parameter in an exponential factor in the electronic coupling element between donor and acceptor orbitals, and the square of this coupling element is proportional to the rate constant for the transfer process. Thus, if $\beta^{TT} \approx 2\beta^{ET}$, then the rate constant for TT transfer (across a spacer) will fall off faster with distance than does the rate constant for the ET reaction. The actual value of k_{TT} corresponding to a given k_{ET} will depend on the values of the preexponential terms in the two rate constant expressions. In an example quoted in a recent review by Piotrowiak[15] (biphenyl as donor; naphthalene as acceptor), although k_{ET} varied by 1 order of magnitude, from 10^9 to 10^8 s^{-1}, k_{TT} varied from ca. 3×10^9 to ca. 10^7 s^{-1}, a lowering of some 300×. In the present situation, it is not possible to make quantitative comparisons because the energy and electron acceptors are not the same compounds, and the nature of the separation is not as strictly controlled as it was in the bridged systems of Closs et al.[16,17] Nevertheless, the more stringent overlap requirement for the double electron exchange compared to the single electron transfer is probably at the root of the lower susceptibility of the ET process to steric hindrance. The same rationale can be used to explain why k_{TT} values for β-carotene are more affected by steric factors than are those for the oxygen quenching reaction. Presumably, the small diatomic can approach the donor excited donor state much more closely than can the much larger caretenoid.

The above discussion has repercussions in mechanistic questions concerning photodynamic therapy, where controversy exists concerning the alternative contributions of energy or electron transfer. From the studies carried out here, it is apparent that steric crowding of the photogenerated excited state is more effective in discriminating against the energy transfer process, even for small energy-accepting entities such as O_2.

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