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Axial Reactivity of Soluble Silicon(IV) Phthalocyanines

Zhiyong Li and Marya Lieberman*

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556

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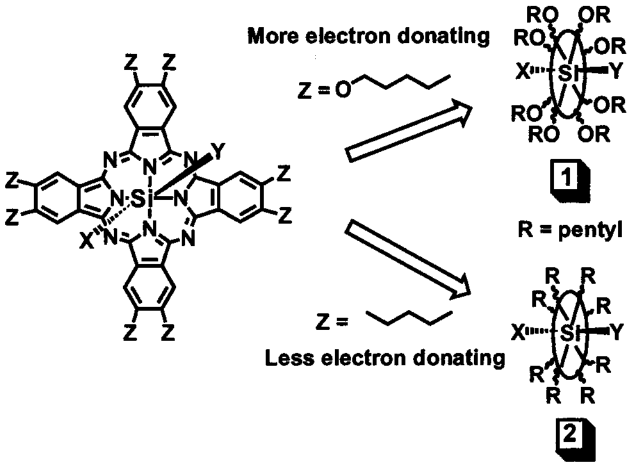
The axial reactivity of peripherally octasubstituted soluble silicon(IV) phthalocyanines ($SiPcZ_8$, Z = OC_5H_{11} or Z = C_5H_{11}) was studied in order to explore new synthetic routes for preparing axially functionalized SiPc monomers and dimers. Self-exchange of the axial methoxide in methylmethoxy $SiPcZ_8$ was about 10 times faster for Z = OC_5H_{11} than for Z = C_5H_{11}. The Pc rings of these two complexes do not differ in electron-richness; their first oxidation potentials (−0.880 and −0.875 V, respectively) are the same within experimental error. The axial alkoxide ligand in methylisopropoxy $SiPcZ_8$ monomer (**1c**″, **2c**″) could be quantitatively replaced by mercaptoethanol to yield O-bound methylmercaptoethoxy $SiPcZ_8$ (**1h**, **2h**). Condensation of methylhydroxy $SiPcZ_8$ monomers yielded μ-oxo-bridged bismethyl $SiPcZ_8$ dimers (**1k**, **2k**) without formation of oligomeric byproducts. Photolysis of such methyl-capped dimers in the presence of mercaptoethanol yielded μ-oxo-bridged bismercaptoethoxy $SiPcZ_8$ dimers (**1n**, **2n**) which are of interest as precursors for oriented self-assembled monolayers (SAMs) of oligomeric phthalocyanines.

1. Introduction

Unsubstituted Pcs (Pc = phthalocyanine) are notoriously insoluble, which for many years hindered efforts to characterize axial reactivity. Kenney's group found that the axial Si−OH bond in the parent $(OH)_2SiPc$ compound can be derivatized with bulky trialkylsilanes to form siloxy-SiPcs with good solubility.[1] They reported that axial Ge−Me and Si−Me bonds could be photolyzed with ease, in contrast with their resistance to chemical attack. An alternative way to enhance solubility of Pcs was later developed by Hanack and others, who introduced peripheral alkoxy and alkyl substituents into the macrocycle phthalocyanine ring.[2] This provides a convenient way to increase the solubility of these compounds while freeing up the axial positions for other roles (Scheme 1).

The effect of different peripheral substituents toward Pc structure and physical properties has been studied in both theoretical and experimental areas.[3] But how the substituents might affect the axial reactivity has been barely discussed in the literature. Only recently, Lemke and co-workers investigated the axial reactivity of Si(IV) with octahedral geometry in another macrocycle system, porphyrins.[4] They concluded that the electron-donating ability of substituents in the porphyrin periphery could alter the axial Si−Cl bond reactivity. The more electron-rich the substituents, the more reactive the axial Si−Cl bond.

Scheme 1. Structures of Two Series of Silicon Phthalocyanines



One of the more interesting axial reactions that octahedral silicon phthalocyanines undergo is oligomerization. The electronic properties of the resulting μ-oxo bridged silicon(IV) phthalocyanine polymers include one-dimensional hole conduction, photoconductivity, and changes in conductivity in response to oxidizing or reducing gases. Since potential device applications, such as sensors,[5] often take advantage of thin films of Pc oligomers, several efforts have been made to fabricate well-ordered Pc monolayers using the self-assembled monolayer

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(SAM) technique.[6-8] This technique depends largely on the design and synthesis of soluble thiol-functionalized phthalocyanines, which led us to study the axial reactivity of octahedral silicon(IV) phthalocyanines as a synthetic route toward novel thiol-functionalized phthalocyanines and phthalocyanine oligomers.

In this study, we compare axial reactivity in two different peripherally substituted SiPcs, one with octapentyloxy substituents, another with octapentyl substituents, and describe how axial reactivity can be used to prepare novel thiol functionalized SiPc monomers and dimers.

2. Results and Discussion

2.1. Synthesis of Soluble Octasubstituted SiPc Monomers. The general synthesis procedures for these octasubstituted silicon phthalocyanines were adapted from Hanack[2] and Kenney[1] et al.

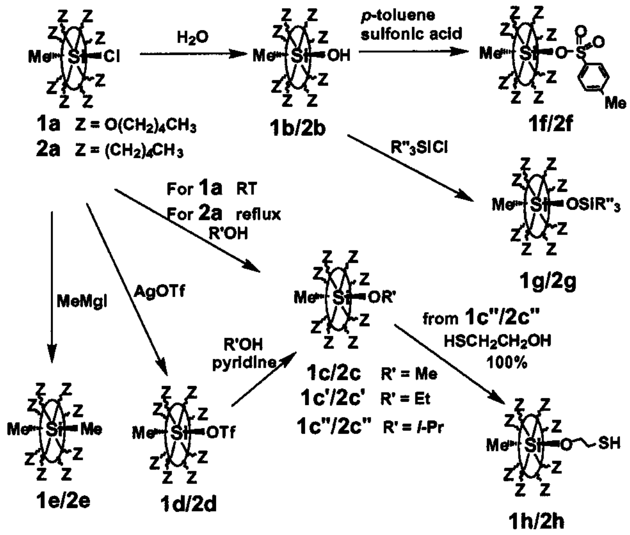
Soluble silicon phthalocyanines with eight peripheral pentyloxy or pentyl groups were synthesized from the corresponding disubstituted diiminoisoindolines. For dipentyloxydiiminoisoindoline, catechol was first brominated, then the phenolic oxygen was coupled to pentyl bromide under basic conditions to give dibromodipentyloxybenzene. The yield was 76% from catechol. For dipentyl diiminoisoindoline, Grignard coupling of *o*-dichlorobenzene with pentylbromomagnesium was carried out with Ni(DPPP)Cl_2 as the catalyst. Bromination at 0 °C with an iron/iodide catalyst gave dibromodipentylbenzene. The isolated yield was 36% from dichlorobenzene. Benzylic bromination can be controlled effectively by using only a stoichiometric amount of bromine and by keeping the temperature low.

The aromatic bromides were then substituted by cyanide in a Sandmeyer reaction with a typical yield of 40−60%, and the resulting phthalonitriles were converted into diiminoisoindolines by addition of gaseous ammonia in methanol. Copper phthalocyanines were obtained as a side product in the Sandmeyer reaction.[9]

Methylchloro $SiPcZ_8$ (Z = pentyl, pentyloxy) was made by refluxing disubstituted diiminoisoindoline and excess $MeSiCl_3$ in dry quinoline for 1 h. The green precipitates were washed with dry acetonitrile in a Soxhlet extractor under Ar for 24 h to remove impurities. The isolated yield for this condensation varies from 30% to 50%. (The synthetic schemes are shown in the Supporting Information) The axial Si−Cl bond in these SiPcs is extremely sensitive to water, which yields methylhydroxy-SiPc. When alcohol is used instead of acetonitrile in the washing step for the workup, the corresponding methylalkoxy-SiPcs were formed. The detailed reactivity of these axial Si−Cl, Si−OH and Si−OR bonds is further discussed in the next section.

2.2. Axial Reactivity of SiPc Monomers. The chloro species **1a** and **2a** undergo hydrolysis and alcoholysis, similar to the known reactivity of the parent compounds and the axial reactivity in hexacoordinate silicon porphyrins reported by Lemke.[4] They react with silver triflate to give methyltriflato-SiPc, which can further react with alcohol in the presence of pyridine to give the corresponding alkoxy-SiPc (Scheme 2).

Scheme 2. Axial Reactions of Chloride and Hydroxide Silicon Phthalocyanines



1a and **2a** also react with methylmagnesium iodide to give bismethyl SiPc, characterized by NMR (the integral ratio of the axial methyl peak vs the Pc ring protons is 6:8). We were unable to isolate the bismethyl SiPc, and efforts to synthesize bismethyl-SiPc directly from the precursor diiminoisoindolines and dimethyldichlorosilane were also unsuccessful. This could be explained either by the high light sensitivity of the Si−Me axial ligand or by the cationic nature of hexacoordinated Si, which prefers to ligate with atoms of higher electronegativity (such as oxygen or chloride).

The methylhydroxy species **1b** and **2b** react with *p*-toluenesulfonic acid in dichloromethane solution to give methyl-*p*-toluenesulfonato-SiPc. This readily reversible reaction is useful in characterization because the hydroxy silicon phthalocyanines have very broad ^{1}H NMR spectra, but the tosyl adducts show sharp NMR peaks. As reported for the unsubstituted SiPc species,[11] the methylhydroxy species can also react with trialkylchlorosilanes such as TMSCl to form methylsiloxy SiPc species.

Axial alkoxide ligands can be exchanged by other nucleophiles. The relative lability of the alkoxide ligand decreases with the decreasing bulkiness in the sequence of ^{i}PrO > EtO > MeO. Thus, axial isopropoxide can be displaced by ethanol or methanol, but axial methoxide is not displaced by either 2-propanol or ethanol. By mixing methylisopropoxyl-SiPcs **1c″** and **2c″** with mercaptoethanol in dry dichloromethane solution, methylmercaptoethoxy SiPc species were formed with 100% yield. The mercaptoethanol binds via its oxygen rather than its sulfur, as evidenced by the formation of a single compound in the NMR and the observation of the S−H IR stretch at 2594 cm^{-1}. This competition experiment demonstrates the preference of hexacoordinated Si for oxygen instead of sulfur and provides a simple synthetic route for making thiol-functionalized SiPc species. We have found that these axial thiol-functionalized phthalocyanines form well-oriented self-assembled monolayers on gold surfaces.[10]

In contrast with the reactivity of the axial Si−Cl, Si−OH, and Si−OR bonds toward various nucleophiles, the axial Si−

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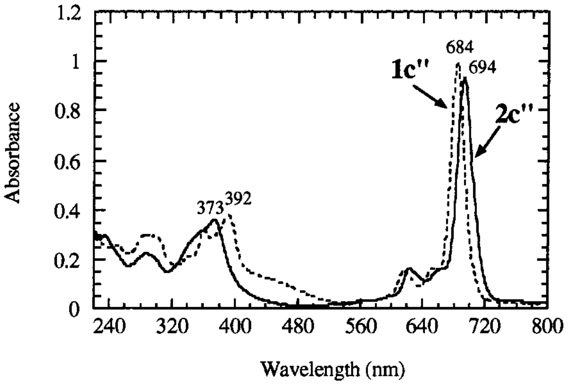

Figure 1. The absorption spectra of SiPc monomers with different peripheral substituents.

Me group remains stable under all these chemical attacks as long as light is excluded. But exposure to ambient light in the lab for several hours can photolyze the Si−Me bond in these methyl $SiPcZ_8$ monomers, as Kenney and others noted in methyl-germanium and methyl-silicon phthalocyanines.[11] The detailed mechanism of this photolytic procedure is not clear at this moment, but one likely explanation would be homolysis of the Si−Me bond followed by reaction with oxygen in the solution and decomposition of the resulting peroxy radical.

2.3. Comparison of Spectroscopic and Electrochemical Properties. We noticed that axial methoxide species **1c** could be made at room temperature by washing the chloride species **1a** with methanol, whereas synthesis of **2c** required refluxing **2a** with methanol. To investigate the effect of peripheral substituents toward the axial reactivity, we compared the spectroscopic and electrochemical properties of SiPcs bearing eight alkoxy substituents (**1a**−**c**) with those bearing eight alkyl substituents (**2a**−**c**).

The absorption spectra of **1c**″ and **2c**″ are shown in Figure 1. The maximum absorption peak (Q-band) was blue-shifted by about 10 nm in the octapentyloxy-SiPc species. The broad band centered around 450 nm in the octapentoxy-substituted SiPc, which is assigned as an oxygen-to-ring $n-\pi^*$ charge transfer,[12] was absent in the octapentyl-substituted SiPc. All the absorption spectra were recorded right after the solutions were made. We did notice that the absorption spectra changed slightly after exposing the solutions to the ambient light for a short time period (spectra not shown); longer exposure (overnight) to ambient light could completely decolor the SiPc solutions.

Cyclovoltammetric measurements of these SiPc monomers were performed in a drybox in a standard three-electrode cell. Shown in Figure 2 are the CV spectra of **1c** and **2c** in 0.1 M $(TBA)BF_4$ methylene chloride solution. In addition to the reversible first oxidation ($SiPc^{-2}/SiPc^{-1}$) and two reduction processes ($SiPc^{-2}/SiPc^{-3}$ and $SiPc^{-3}/SiPc^{-4}$), which were similar to those reported by Kenney's group[15] for bis(trihexylsiloxy)-SiPc, an irreversible second oxidation was observed at around 1.5 V. This second oxidation can be assigned to be the further oxidation of the Pc ring, forming $SiPc^0$, which then decomposes, presumably by loss of an axial group.

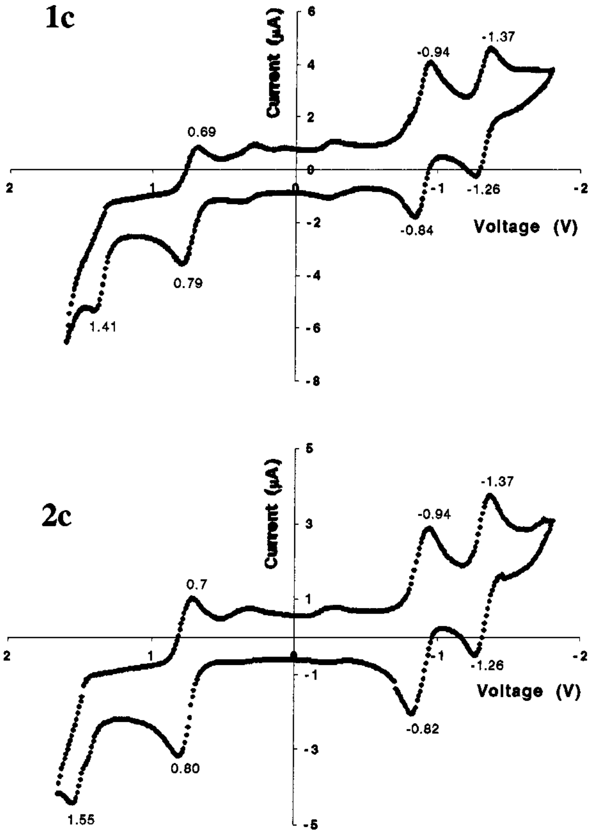

Figure 2. CV of **1c** and **2c** in 0.1 M $(TBA)BF_4$ in CH_2Cl_2 at the Pt electrode. Scan rate = 100 mV/s, SiPc monomer concentration = 0.5 mM.

The first oxidation potentials for both **1c** (0.745 V vs Ag RE) and **2c** (0.750 V vs Ag RE) are lower than that of a SiPc derivative which does not bear peripheral substituents (∼1.0 V vs Ag RE for bis(trihexylsiloxy) SiPc[15]). This suggests that the alkoxide and alkyl groups both donate electrons to the phthalocyanine ring to make the ring easier to oxidize. The difference between the first oxidation potential of these two species is very slight, 0.005 V, indicating that the alkoxide group has only slightly better electron-donating ability to the Pc ring than the alkyl group.

2.4. Kinetic Study of Axial Reactivity. To further explore how factors such as peripheral substituents might affect axial ligand exchange, we studied the self-exchange of an axial methoxy ligand in compounds **1c** and **2c** with deuterated methanol by monitoring the ^1H NMR spectrum.

In a typical experiment, 3.0 mg each of **1c** and **2c** were mixed under argon in a valved NMR tube with 0.5 mL of dry benzene-d_6. After 5 μL of dry deuterated methanol (an excess) was injected into the NMR tube, the sample was immediately taken for an initial NMR spectrum. Then the NMR tube was heated in an oil bath, and each spectrum was taken after a time interval. During the whole experiment, the NMR tube was wrapped with aluminum foil to exclude light. By conducting the kinetic runs simultaneously for both compounds in the same NMR tube, we could be sure that the effective pH, temperature, and deuteriomethanol concentrations were identical for **1c** and **2c**.

Figure 3 shows the time course of the exchange of the methoxide in **1c** and **2c**. The peaks at −1.2 and −1.4 ppm are the axial methoxide of **1c** and **2c**, respectively, and the peaks at −5.4 and −5.6 ppm are the axial methyl ligand of **1c** and **2c** respectively. For each compound, the ratio of the methoxide peak area to that of the methyl peak area drops over time as

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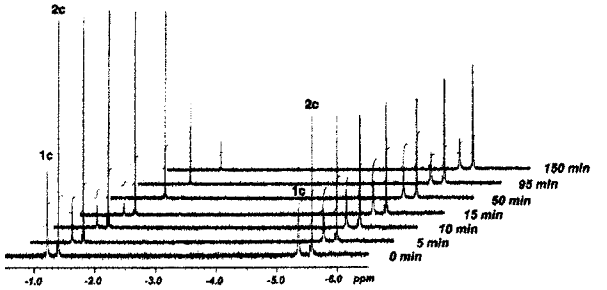


Figure 3. NMR of the axial methoxide self-exchange in a mixture of **1c** and **2c** at 60 °C.

Table 1. The Relationship of Self-exchange Rate and the Concentration of Methanol-d_4 at 40 °C

	1c		**2c**	
$[CD_3OD]$ (mol L^{-1})	k_{obs} (s^{-1})	R_{ex} (mol L^{-1} s^{-1})	k_{obs} (s^{-1})	R_{ex} (mol L^{-1} s^{-1})
0.044	8.7×10^{-5}	4.1×10^{-7}		
0.089	1.6×10^{-4}	7.5×10^{-7}	7.8×10^{-6}	4.1×10^{-8}
0.22	4.7×10^{-4}	2.2×10^{-6}	1.8×10^{-5}	9.4×10^{-8}

the $-OCH_3$ is replaced by $-OCD_3$. The axial methyl groups do not exchange under the conditions of this experiment, and neither methylhydroxy SiPc nor SiPcOSiPc dimers were observed.

The peak integral data was analyzed using the McKay equation[13] for self-exchange reactions (eq 1),

$$\ln(1 - F) = -R_{ex}\frac{C_{SiPc} + C_{CD_3OD}}{C_{SiPc}C_{CD_3OD}}t \tag{1}$$

where F represents the fraction of exchange, R_{ex} is the exchange reaction rate, and C_{SiPc} and C_{CD_3OD} are the total concentration of SiPc and deuterated methanol, respectively.

Since the concentration of deuterated methanol is in large excess, $1 - F$ in this particular self-exchange reaction can be represented by the ratio of axial methoxy peak area to axial methyl peak area and eq 1 can be written as

$$\ln\left(\frac{A_{OCH_3}}{A_{CH_3}}\right) = -\frac{R_{ex}}{C_{SiPc}}t \tag{2}$$

The experimental data give a linear plot of $\ln(A_{OCH3}/A_{CH3})$ vs time; the slope of the plot is k_{obs}. k_{obs} changes proportionally with the concentration of deuterated methanol as shown in Table 1, indicating that self-exchange is first-order in methanol.

The self-exchange reaction was done at different temperatures to extract kinetic parameters. The values for $\ln(k/T)$ vs $1/T$ are plotted in Figure 4. From the plot, the entropy and enthalpy of the transition state was derived. For **1c,** $\Delta H^{\ddagger} = 86.9 \pm 13.8$ kJ/mol, $\Delta S^{\ddagger} = -24 \pm 43$ J/molK; for **2c**, $\Delta H^{\ddagger} = 87.6 \pm 10.6$ kJ/mol, $\Delta S^{\ddagger} = -42 \pm 32$ J/molK. These thermodynamic data, despite large error ranges, indicate that both the octapentyl- and octapentyloxy-SiPcs have the same self-exchange mechanisms. The relatively large enthalpy of activation is consistent with a large degree of bond breaking in the transition state, and the fact that the reaction is first-order in deuteriomethanol suggests a bimolecular transition state.

It is known that Lewis acids can catalyze the polymerization of silicon phthalocyanine monomers,[14] so the effects of acid and base catalysis on the self-exchange rate were studied. Addition of pyridine does not affect the self-exchange rate at all, whereas acid accelerates self-exchange. In the presence of a tiny amount of dry *p*-toluenesulfonic acid, self-exchange of the axial methoxide in both **1c** and **2c** is finished within 1 min at room temperature (the half-life for both these compounds without acid at room temperature is about 1 day). This suggests that self-exchange in the presence of acid follows a different mechanism than in neutral or basic solution.

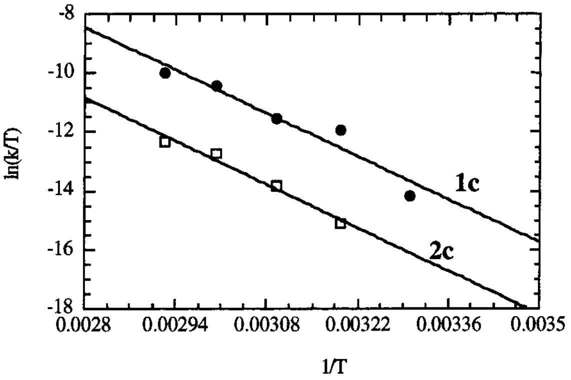
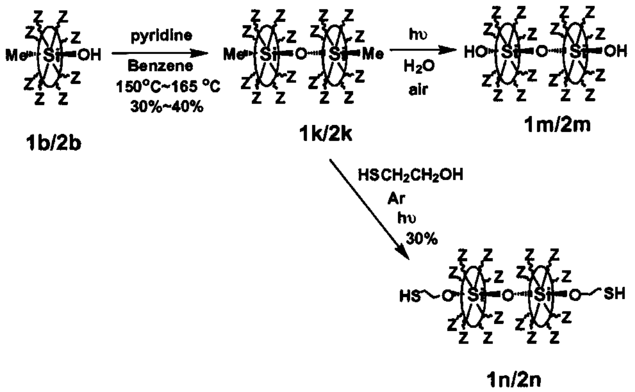


Figure 4. Plot of ln(*k*/*T*) vs 1/*T* for **1c** and **2c**.

Scheme 3. Synthesis of μ-Oxo SiPc Dimers and Their Photoreactivity



2.5. Synthesis of μ-Oxo Silicon Phthalocyanine Dimers. μ-Oxo silicon phthalocyanine dimers were synthesized in a sealed tube by dehydration of **1b** or **2b** in benzene in the presence of pyridine (Scheme 3). The temperature of 150−165 °C needed for this dimerization in the octasubstituted SiPcs is lower than the 190 °C solid-phase reaction required for unsubstituted SiPcs reported by Kenney and others.[15] Furthermore, only dimers are formed in this solution phase condensation. The stable Si−Me axial cap prevents formation of higher oligomers, such as trimers or tetramers. As expected from our study of axial reactivity discussed in the previous section, the octapentyloxy substituted SiPc, **1b**, dimerizes at lower temperature (150 °C) and finishes in less time (12 h) with higher isolated yield (40%) than the octapentyl-substituted one, **2b**. *p*-Toluenesulfonic acid was tried as a catalyst in an attempt to increase the yield; the reaction time was shortened, but the yield of dimers was the same.

2.6. Photoreactivity of μ-Oxo Silicon Phthalocyanine Dimers. The SiPc dimers with axial methyl capping groups can be photolyzed to form bis(hydroxy) dimer species just as the monomers can. Quantitative removal of the axial methyl groups was obtained by exposing a solution of dimers **1k** or **2k** in wet deuterated benzene to irradiation from a 350 nm mercury lamp for 30 min. The formation of bis(hydroxy)-SiPc dimers was confirmed by mass spectroscopy.

By photolysis of dimers **1k** or **2k** in the presence of mercaptoethanol under argon, novel bis(mercaptoethoxy)-SiPc

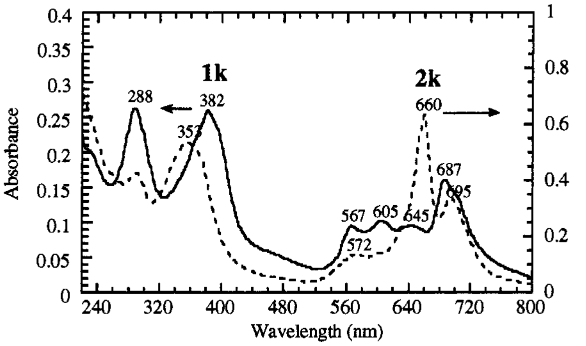


Figure 5. The absorption spectra of SiPc dimers **1k** and **2k** in CH_2Cl_2.

dimer species **1n** and **2n** were produced. However, cleavage of the Si−O−Si bond in the dimers **1k** and **2k** was observed by NMR. This cleavage yields the major byproduct, bis(mercaptoethoxy)-SiPc monomers, which were not isolated because they stuck to and decomposed on the chromatography column. Although the dimer **1n** could not be isolated from the reaction mixture by alumina or silica column chromatography, **2n** was successfully separated from the reaction mixture by alumina column chromatography, with an isolated yield of 30%. **2n**, as expected, forms self-assembled monolayers on Au(111) surfaces.[10]

2.7. Spectroscopic and Electrochemical Properties of *μ*-Oxo-Bridged SiPc Dimers. The absorption spectra of the methyl-capped dimers **1k** and **2k** in dichloromethane are quite different from the monomers. The spectra are compared in Figure 5. The octapentyloxy-SiPc dimer has four low-intensity peaks at 687, 645, 605, and 566 nm in the Q-band region. The octapentyl SiPc dimer shows a much more intense absorption at 660 nm, as well as weaker absorption at 695 and 572 nm.

According to Hanack,[16] octaalkyloxy-substituted SiPc dimers have two reasonable isomers with adjacent ring rotation angles of 20° and 45°. In nonaromatic solvents only the isomer with a rotation angle of 20° is stable, giving a multipeaked spectrum, while in aromatic solvents, the second isomer with rotation angle of 45° is stabilized, giving a single Q-band. This solvatochromic behavior can be observed in **1k** by changing the solvent from dichloromethane to benzene (spectra not shown).

For **2k**, which has octaalkyl peripheral substituents, no similar solvatochromic behavior was found. From the similarity of its optical spectrum (intense band at 660 nm) with the known 45° alkyloxy dimers, we conclude that the 45° gauche conformation is preferable in **2k**, regardless of solvents. The different spectroscopic properties of **1k** and **2k** suggest that minor changes in steric bulk at the ring periphery (O vs CH_2 attachment) play a significant role in determining the geometry of the adjacent rings.

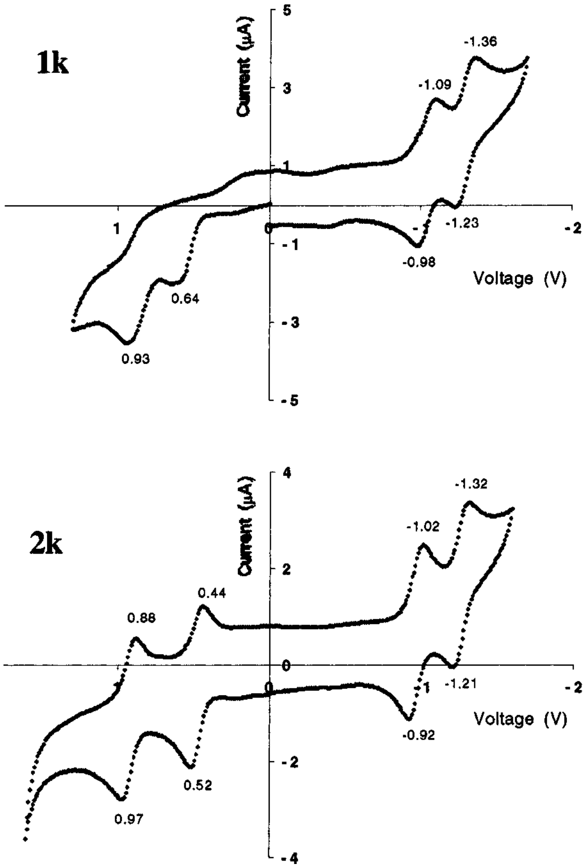


Figure 6. The CV of *μ*-oxo-bridged SiPc dimers **1k** and **2k** in 0.1 M $(TBA)BF_4$ in CH_2Cl_2 at the Pt electrode; potential in V vs Ag reference electrode, scan rate = 100mV/s, dimer concentration = 0.4 mM.

CV spectra of the SiPc dimers **1k** and **2k** are shown in Figure 6. The redox peaks of **2k** are similar to those of the SiPc dimers reported by Kenney's group.[15] Two reversible one-electron oxidation peaks at 0.48 and 0.93 V vs Ag RE correspond to $\mathrm{SiPc^{-2}{-}O{-}SiPc^{-2}/SiPc^{-2}{-}O{-}SiPc^{-1}}$ and $\mathrm{SiPc^{-2}{-}O{-}SiPc^{-1}/SiPc^{-1}{-}O{-}SiPc^{-1}}$, respectively. Comparing these potentials to the two oxidation potentials of Kenney's peripherally unsubstituted bis(trihexylsiloxy) SiPc dimer,[15] (0.55 and 1.06 V vs Ag RE), it is clear that the peripheral alkyl substituents make the Pc ring more electron rich. The large separation of two reversible redox processes suggests an electrochemically generated stable mixed-valence species ($\mathrm{SiPc^{-2}{-}O{-}SiPc^{-1}}$) with a comproportion constant of 3.6×10^7. In contrast, the alkyloxy-substituted dimer **1k** gave two irreversible oxidation processes. This result is not surprising in view of the greater axial reactivity of the alkyloxy-SiPc species.

Both **1k** and **2k** show two sucessive reductions in the region -1 to -1.4 V, which correspond to $\mathrm{SiPc^{-2}{-}O{-}SiPc^{-2}/SiPc^{-2}{-}O{-}SiPc^{-3}}$ and $\mathrm{SiPc^{-2}{-}O{-}SiPc^{-3}/SiPc^{-3}{-}O{-}SiPc^{-3}}$. These reductions are reversible for **2k**. The alkyloxy species **1k** is slightly (<60 mV) more difficult to reduce in each case, and the second reduction is only quasireversible judging from the 170 mV peak separation and disparity between i_c and i_a.

3. Conclusions

The axial reactivity of SiPc with octaalkyloxy and octaalkyl peripheral substituents was explored with an ultimate goal of seeking new synthetic routes for thiol-functionalized SiPc species. The self-exchange of axial methoxide in octaalkyl-substituted SiPc (**2c**) is slower than that of octaalkyloxy-substituted species (**1c**). Regardless of peripheral substituents, exchange reactions of methylisopropoxy-SiPc (**1c″** and **2c″**) with mercaptoethanol produce novel species (**1h** and **2h**) with one thiol functional group in the axial position of SiPc monomers. We have found that this attachment makes phthalocyanine rings adopt a flat orientation in self-assembled monolayers on Au(111).[10]

The successful use of the axial methyl ligand as a blocking group in the synthesis of *μ*-oxo SiPc dimers provides a way to make dimers selectively without formation of higher oligomers as byproducts. The dimers so formed can be photolyzed in wet

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solvents to form hydroxy-SiPc dimers. Furthermore, by carrying out photolysis in dry solvents in the presence of mercaptoethanol, new μ-oxo SiPc dimers functionalized with thiol groups were generated. These dimers form a "double-decker" self-assembled monolayer on gold surfaces with an extra thiol linkage projecting away form the surface. The preparation and properties of such monolayers will be discussed in a future report.[10]

4. Experimental Section

General. The following materials were commercially available and were used without purification: bromine, iodine, 1-bromopentane, catechol, copper(I) cyanide, potassium carbonate, magnesium, dichloro[1,3-bis(diphenylphosphino)propane]nickel(II), tetrabutylamonium tetrafluroborate, *p*-toluenesulfonic acid, and 3 M methylmagnesium iodide in ether (Aldrich); and anhydrous ammonia (Air Products). Quinoline (Aldrich) contained a yellow impurity and was vacuum distilled from barium oxide; dichloromethane, pyridine, and acetonitrile were dried over calcium hydride and then vacuum transferred and stored in a drybox under Ar; toluene, benzene and d_6-benzene were dried over sodium, vacuum transferred, and stored in a drybox under Ar; methyltrichlorosilane and tetrachlorosilane were dried over calcium hydride, vacuum transferred, and stored under Ar; mercaptoethanol and deuterated methanol were dried over activated 3 Å molecular sieves, vacuum transferred, and stored under Ar; methanol, ethanol, and 2-propanol were dried by storage over activated 3 Å molecular sieves; and other organic solvents were used directly without further treatment. All the precursors were prepared according to literature methods.[17−19]

^{1}H NMR spectra were taken on Varian Unity+ 300 or GN300 instruments. ^{29}Si NMR was also tried for SiPcs, but insufficient signal was achieved. IR spectra were taken as thin films (from evaporation of benzene or dichloromethane solutions) on KBr plates or as Nujol mulls prepared in a drybox for air-sensitive samples and were analyzed on a Perkin-Elmer Paragon 1000 FT-IR spectrometer. UV−vis spectra were obtained with a Perkin-Elmer Lambda 11 UV/vis spectrometer. Elemental analysis was performed by M−H−W Laboratories, Phoenix, AZ. Mass spectra of the phthalocyanines and their precursors were obtained on a JEOL JUS-AX505 HA mass spectrometer using a JEOL 102517 electrospray source (for phthalocyanine monomers) or MALDI (for phthalocyanine dimers).

The cyclovoltammetric measurement of these SiPc species in solution was performed in a drybox using an EG&G Instruments PAR 283 potentiostat/galvanostat. A standard three-electrode setup was used. A platinum disk electrode with geometric surface area of ~0.02 cm^2 was used as the working electrode, a coiled platinum wire was used as a counter electrode, and the reference electrode was a silver wire inserted in a 0.1 M solution of (TBA)BF$_4$ in methylene chloride separated from the working solution by a fine porous glass frit.

Photolysis of SiPc species was carried out in a Rayonet photochemical reactor. The light source was a mercury lamp with a center wavelength of 350 nm.

$[CH_3(CH_2)_4O]_8PcSi(CH_3)Cl$ (1a) and $[CH_3(CH_2)_4]_8PcSi(CH_3)Cl$ (2a). The procedure was modified from the method used by Hanack and Kenney.[2,11] All procedures were carried out in the dark as much as possible. In a typical synthesis, 1,3-diimino-5,6-bis(pentenyloxy)isoindoline (0.20 g) was stirred with 2 mL of dry quinoline under Ar, then 0.1 mL of methyltrichlorosilane was added by syringe. The mixture was brought quickly to 180 °C and kept at this temperature for 1 h. After the reaction cooled, 10 mL of dry CH_3CN was added, and the mixture was filtered to separate the dark green product. The crude product was washed in a Soxhlet apparatus with dry CH_3CN for 24 h under Ar. The final product was extracted from the Soxhlet apparatus using dry CH_2Cl_2 under Ar, followed by removal of solvent and vacuum-drying (yield for **1a**, 90 mg (45%); for **2a**, 88 mg (42%)). Due to the small scale of the reaction, partial hydrolysis occurred even though moisture was avoided in each step as much as possible, which caused poor elemental analysis results. Also due to the high water sensitivity of the samples, mass spectra do not reflect any molecular ions of the coresponding SiPcs. Further purification by recrystallization or column was unsuccessful, due to hydrolysis and sticking to the silica.

1a: ^{1}H NMR (C_6D_6) δ 9.23 (b, 8H), 3.75 (b, 16H), 1.89 (b, 16H), 1.36 (b, 32H), 0.99 (b, 24H), −5.49 (s, 3H, axial methyl) ppm; IR (in Nujol) 1604 (m), 1526 (m), 1469 (vs), 1428 (s), 1393 (s), 1365 (m), 1280 (s), 1209 (s), 1098 (vs), 1057 (m), 1012 (w), 851 (w), 754 (m) cm^{-1}. Elemental analysis observed (calcd): C, 72.21 (68.49); H, 9.06 (7.79); N, 6.43 (8.75); Cl, 3.12 (2.77).

2a: ^{1}H NMR (C_6D_6) δ 9.68 (b, 8H), 3.06 (t, 16H, J = 8.0 Hz), 1.87 (m, 16H), 1.38 (m, 32H), 0.98 (t, 24H, J = 6.9 Hz) −5.35 (s, 3H, axial methyl) ppm; IR (in Nujol) 1621 (w), 1522 (w), 1462 (vs), 1417 (m), 1376 (s), 1347 (s), 1267 (m), 1099 (s), 1082 (s), 886 (m), 758 (m) cm^{-1}. Elemental analysis observed (calcd): C, 78.38 (76.10); H, 9.60 (8.66); N, 7.69 (9.72); Cl, 4.47 (3.08).

$[CH_3(CH_2)_4O]_8PcSi(CH_3)(OH)$ (1b) and $[CH_3(CH_2)_4]_8PcSi(CH_3)(OH)$ (2b). 1b and **2b** can be made by adding a few drops of water to a dichloromethane solution of the methylchloro-SiPc **1a** and **2a**. The product is isolated by removing solvent and drying under vacuum overnight. **1b** and **2b** were formed when wet solvents were used in the workup for **1a** and **2a**.

1b: ^{1}H NMR (C_6D_6) δ 9.26 (b, 8H), 4.03 (b, 16H), 1.89 (b, 16H), 1.36 (b, 32H), 0.99 (b, 24H), −5.89 (s, 3H, axial methyl) ppm; IR (in Nujol) 3475 (w), 1605 (m), 1512 (s), 1463 (vs), 1424 (m), 1378 (s), 1282 (s), 1207 (m), 1105 (m), 1084 (s), 1058 (m), 921 (w), 886 (w), 854 (w), 784 (m) cm^{-1}.

2b: ^{1}H NMR (C_6D_6) δ 9.02 (b, 8H), 3.17 (b, 16H), 1.84 (b, 16H), 1.36 (b, 32H), 1.03 (b, 24H), −5.98 (s, 3H, axial methyl) ppm; IR (in Nujol) 3443 (w), 1619 (w), 1514 (m), 1462 (vs), 1415 (m), 1377 (s), 1348 (m), 1263 (w), 1098 (m), 1078 (m), 894 (w), 803 (m) cm^{-1}.

Alcoholysis of $R_8PcSi(CH_3)Cl$. Use of dry alcohols such as methanol, ethanol, or 2-propanol to work up the methylchloro-SiPc intermediates **1a** or **2a** yielded the corresponding methylalkoxy-SiPcs (**1c, 1c′, 1c″** and **2c, 2c′, 2c″**), which can be isolated in pure form by Soxhlet extraction with dry dichloromethane. The following are the various yields: for the methanolysis products, $[CH_3(CH_2)_4O]_8PcSi(CH_3)(OCH_3)$ **(1c)**, 46%; $[CH_3(CH_2)_4]_8PcSi(CH_3)(OCH_3)$ **(2c)**, 45%; for ethanolysis products, $[CH_3(CH_2)_4O]_8PcSi(CH_3)(OCH_2CH_3)$ **(1c′)**, 37%; $[CH_3(CH_2)_4]_8PcSi(CH_3)(OCH_2CH_3)$ **(2c′)**, 40%; and for 2-propanolysis products, $[CH_3(CH_2)_4O]_8PcSi(CH_3)(OCH(CH_3)_2)$ **(1c″)**, 19%; $[CH_3(CH_2)_4]_8PcSi(CH_3)(OCH(CH_3)_2)$ **(2c″)**, 21%.

1c: ^{1}H NMR (C_6D_6) δ 9.15 (s, 8H), 3.99 (t, b, 16H), 1.84 (m, 16H), 1.35 (m, 32H), 0.95 (t, 24H, J = 7.0 Hz), −1.18 (s, 3H, SiOCH_3), −5.42 (s, 3H, SiCH_3) ppm; IR (in Nujol) 1604 (m), 1515 (m), 1466 (vs), 1424 (s), 1391 (s), 1362 (m), 1281 (s), 1207 (s), 1097 (vs), 1058 (m), 1015 (w), 923 (w), 885 (w), 856 (w), 758 (m) cm^{-1}; MS (electrospray) calcd for $C_{74}H_{102}O_9N_8Si$ *m*/*e* 1275.7, found *m*/*e* 1277.2. Elemental analysis observed (calcd): C, 69.60 (69.67); H, 7.85 (8.06); N, 8.54 (8.78).

1c′: ^{1}H NMR (C_6D_6) δ 9.18 (s, 8H), 3.99 (t, b, 16H), 1.83 (m, 16H), 1.35 (m, 32H), 0.93 (t, 24H, J = 7.0 Hz), −1.46 (q, 2H, SiOCH_2CH$_3$), −1.64 (t, 3H, SiOCH$_2$$CH_3$), −5.36 (s, 3H, Si$CH_3$) ppm; IR (in Nujol) 1604 (m), 1515 (m), 1463 (vs), 1424 (s), 1390 (vs), 1361 (m), 1282 (s), 1207 (s), 1096 (vs), 1057 (s), 1016 (w), 923 (w), 885 (w), 856 (w), 760 (m) cm^{-1}; MS (MALDI) calcd for $C_{75}H_{104}O_9N_8Si$ *m*/*e* 1289.8, found *m*/*e* 1291.0. Elemental analysis observed (calcd): C, 70.00 (69.84); H, 8.10 (8.13); N, 8.51 (8.69).

1c″: ^{1}H NMR (dry C_6D_6) δ 9.05 (s, 8H), 3.90 (t, b, 16H), 1.84 (m, 16H), 1.33 (m, 32H), 0.95 (t, 24H, J = 6.9 Hz), −1.98 (d, 6H, SiOCH(CH_3)$_2$, J = 6.0 Hz), −2.17 (m, 1H, SiOCH (CH$_3$)$_2$, J = 6.0 Hz), −4.87 (s, 3H, SiCH_3) ppm; IR (in Nujol) 1603 (s), 1513 (s), 1463 (vs), 1424 (s), 1389 (vs), 1360 (s), 1282 (vs), 1207 (s), 1095 (vs), 1057 (s), 1010 (m), 923 (m), 884 (w), 855 (m) cm^{-1}; MS (electrospray) calcd for $C_{76}H_{106}O_9N_8Si$ *m*/*e* 1303.8, found *m*/*e* 1307.3. Elemental analysis observed (calcd): C, 69.96 (70.01); H, 8.06 (8.19); N, 8.50 (8.59).

2c: ^{1}H NMR (C_6D_6) δ 9.73 (s, 8H), 3.07 (t, 16H, J = 8.0 Hz), 1.88 (m, 16H), 1.42 (m, 32H), 0.96 (t, 24H, J = 7.0 Hz), −1.38 (s, 3H, SiOCH_3), −5.56 (s, 3H, SiCH_3) ppm; IR (in Nujol) 1621 (w), 1514

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(m), 1459 (vs), 1416 (m), 1377 (s), 1349 (s), 1268 (m), 1185 (m), 1098 (s), 888 (w), 764 (m) cm^{-1}; MS (electrospray) calcd for $\mathrm{C_{74}H_{102}ON_8Si}$ *m*/*e* 1147.8, found *m*/*e* 1148.4. Elemental analysis observed (calcd): C, 77.60 (77.44); H, 8.76 (8.96); N, 9.90 (9.76).

2c′: ^{1}H NMR ($\mathrm{C_6D_6}$) δ 9.73 (s, 8H), 3.06 (t, b, 16H), 1.86 (m, 16H), 1.42 (m, 32H), 0.96 (t, 24H, $J = 7.2$ Hz), −1.63 (q, 2H, $\mathrm{SiO}\mathit{CH}_2\mathrm{CH_3}$), −1.84 (t, 3H, $\mathrm{SiOCH_2}\mathit{CH}_3$), −5.61 (s, 3H, $\mathrm{Si}\mathit{CH}_3$) ppm; IR (in Nujol) 1620 (m), 1513 (s), 1456 (vs), 1416 (s), 1377 (s), 1347 (s), 1261 (m), 1185 (m), 1093 (vs), 892 (s), 761 (s) cm^{-1}; MS (MALDI) calcd for $\mathrm{C_{75}H_{104}ON_8Si}$ *m*/*e* 1161.8, found *m*/*e* 1165.6. Elemental analysis observed (calcd): C, 76.36 (77.54); H, 8.85 (9.02); N, 8.87 (9.65). The poor elemental analysis results may be due to hydrolysis of the axial ethoxide.

2c″: ^{1}H NMR (dry $\mathrm{C_6D_6}$) δ 9.76 (s, 8H), 3.08 (t, b, 16H, $J = 8.1$ Hz), 1.88 (m, 16H), 1.45 (m, 32H), 0.97 (t, 24H, $J = 7.2$ Hz), −2.04 (m, 7H, $\mathrm{SiO}\mathit{CH}(\mathit{CH}_3)_2$), −5.60 (s, 3H, $\mathrm{Si}\mathit{CH}_3$) ppm; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 9.48 (s, 8H), 3.45 (t, b, 16H), 2.05 (m, 16H), 1.50 (m, 32H), 1.00 (t, 24H), −2.29 (d, 6H, $\mathrm{Si{-}OCH}(\mathit{CH}_3)_2$, $J = 6.0$ Hz), −2.66 (m, 1H, $\mathrm{SiO}\mathit{CH}(\mathrm{CH_3})_2$, $J = 6.0$ Hz), −6.35 (s, 3H, $\mathrm{Si}\mathit{CH}_3$) ppm; IR (in Nujol) 1620 (m), 1513 (s), 1456 (vs), 1415 (s), 1358 (s), 1345 (s), 1264 (m), 1168 (m), 1128 (m), 1092 (vs), 1014 (s), 894 (s),762 (s) cm^{-1}; MS (MALDI) calcd for $\mathrm{C_{76}H_{106}ON_8Si}$ *m*/*e* 1175.8, found *m*/*e* 1146.9 (M − $\mathrm{2CH_3}$). Elemental analysis observed (calcd): C, 77.44 (77.64); H, 8.92 (9.09); N, 8.77 (9.53).

$\mathbf{[CH_3(CH_2)_4O]_8PcSi(CH_3)(OTf)}$ (1d) and $\mathbf{[CH_3(CH_2)_4]_8PcSi(CH_3)(OTf)}$ (2d). Compound **1a** or **2a** (30 mg) was dissolved in 10 mL of dry toluene, and 300 mg of AgOTf was added. The mixture was stirred under Ar for 1 h. The precipitate formed in the reaction was filtered off under Ar, and the filtrate containing the dark brown (**1d**) or green (**2d**) product was dried under vacuum. The crude product was extracted into dry dichloromethane, in which AgOTf is insoluble. The triflates react with alcohols, such as ethanol, in the presence of pyridine to give corresponding alkoxide SiPcs, e.g. **1c′** or **2c′**.

1d: IR (in Nujol) 1601 (m), 1486 (s), 1465 (vs), 1431 (s), 1392 (s), 1377 (s), 1286 (vs), 1231 (m), 1213 (s), 1169 (m), 1095 (m), 1054 (m), 1026 (m), 927 (w), 885 (w), 856 (w), 752 (m) cm^{-1}; MS (FAB) calcd for $\mathrm{C_{74}H_{99}O_{11}N_8SiSF_3}$ *m*/*e* 1393.8, found *m*/*e* 1394.7.

2d: ^{1}H NMR ($\mathrm{C_6D_6}$) δ 9.75 (s, 8H), 3.04 (t, 16H), 1.88 (m, 16H), 1.43 (m, 32H), 0.98 (t, 24H), −5.33 (s, 3H, $\mathrm{Si}\text{-}\mathit{CH}_3$) ppm; IR (in Nujol) 1773 (w), 1707 (w), 1618 (m), 1522 (m), 1463 (vs), 1421 (m), 1377 (s), 1349 (s), 1300 (s), 1229 (vs), 1172 (s), 1081 (m), 1027 (s), 896 (w), 811 (w), 756 (m) cm^{-1}; MS (FAB) calcd for $\mathrm{C_{74}H_{99}O_3N_8SiSF_3}$ *m*/*e* 1265.8, found *m*/*e* 1266.8.

$\mathbf{[CH_3(CH_2)_4O]_8PcSi(CH_3)(OTs)}$ (1f) and $\mathbf{[CH_3(CH_2)_4]_8PcSi(CH_3)(OTs)}$ (2f). Compound **1b** or **2b** (3 mg) was dissolved in 1 mL of dry $\mathrm{C_6D_6}$ with 1 mg of *p*-toluenesulfonic acid in a valved NMR tube, and the mixture was heated at 50 °C for 6 h. After the solvent was removed from the tube, the dark brown solid for **1f** or the green solid for **2f** was dried under vacuum, and then washed with dry acetone under Ar to remove excess *p*-toluenesulfonic acid.

1f: ^{1}H NMR ($\mathrm{C_6D_6}$) δ 9.20 (s, 8H), 5.74 (d, 2H, $J = 8.1$ Hz), 5.44 (d, 2H, $J = 8.1$ Hz), 4.01 (m, 16H), 1.85 (m, 16H), 1.39 (m, 32H), 0.97 (t, 24H, $J = 6.9$ Hz), −5.15 (s, 3H, $\mathrm{Si}\text{-}\mathit{CH}_3$) ppm; MS (MALDI) calcd for $\mathrm{C_{80}H_{106}O_{11}N_8SiS}$ *m*/*e* 1415.9, found *m*/*e* 1415.6;

2f: ^{1}H NMR ($\mathrm{C_6D_6}$) δ 9.72 (s, 8H), 5.67 (d, 2H, $J = 7.5$ Hz), 5.35 (d, 2H, $J = 6.9$ Hz), 3.07 (t, 16H, $J = 8.1$ Hz), 1.88 (m, 16H), 1.44 (m, 32H), 0.99 (t, 24H, $J = 6.9$ Hz), −5.43 (s, 3H, $\mathrm{Si}\text{-}\mathit{CH}_3$) ppm; MS (MALDI) calcd for $\mathrm{C_{80}H_{106}O_3N_8SiS}$ *m*/*e* 1287.9, found *m*/*e* 1287.1.

$\mathbf{[CH_3(CH_2)_4O]_8SiPc(CH_3)(OCH_2CH_2SH)}$ (1h) and $\mathbf{[CH_3(CH_2)_4]_8SiPc(CH_3)(OCH_2CH_2SH)}$ (2h). Compound **1c″** or **2c″** (30 mg) was dissolved in 10 mL of dry toluene. Then 0.5 mL of dry $\mathrm{HSCH_2CH_2OH}$ was added, and the solution was stirred at room temperature for 0.5 h. The solvent and excess mercaptoethanol were removed under vacuum, leaving behind analytically pure dark green solid (yield ∼100% for **1h** and **2h**).

1h: ^{1}H NMR (dry $\mathrm{C_6D_6}$) δ 9.06 (s, 8H), 3.91 (t, b, 16H), 1.83 (t, b, 16H), 1.29 (m, 32H), 0.95 (t, 24H, terminal methyl in the substitutents), −0.47 (m, 2H, axial $-\mathrm{OCH_2}\mathit{CH}_2\mathrm{SH}$), −1.31 (t, 1H, axial $-\mathrm{OCH_2CH_2}\mathit{SH}$), −1.64 (t, 2H, axial $-\mathrm{O}\mathit{CH}_2\mathrm{CH_2SH}$), −5.03 (s, 3H, axial methyl) ppm; IR (Nujol mull) 2594.5 (w, SH vibration), 1603.1 (s), 1514.8 (s), 1462.1 (vs), 1424.1 (s), 1390.9 (vs), 1361.5 (s), 1281.8 (vs), 1236.4 (m), 1208.2 (vs), 1095.4 (vs), 1056.1 (s), 1012.0 (m), 922.5 (m), 884.4 (m), 855.0 (m), 758.1 (s) cm^{-1}. Elemental analysis observed (calcd): C, 67.98 (68.15); H, 7.89 (7.93); N, 8.42 (8.48); S, 2.26 (2.42).

2h: ^{1}H NMR (dry $\mathrm{C_6D_6}$) δ 9.76 (s, 8H), 3.07 (t, b, 16H), 1.88 (m, 16H), 1.42 (m, 32H), 0.96 (t, 24H, terminal methyl in the substitutents), −0.56 (m, 2H, axial $-\mathrm{OCH_2}\mathit{CH}_2\mathrm{SH}$), −1.34 (t, 1H, $J = 8.1$ Hz, axial $-\mathrm{OCH_2CH_2}\mathit{SH}$), −1.70 (t, 2H, $J = 5.4$ Hz, axial $-\mathrm{O}\mathit{CH}_2\mathrm{CH_2SH}$), −5.56 (s, 3H, axial methyl) ppm.

$\mathbf{\{[CH_3(CH_2)_4O]_8PcSi(CH_3)\}_2O}$ (1k). Compound **1b** (50 mg) was dissolved in 8 mL of dry benzene in a Teflon-valved thick-walled Schlenk tube, and a few drops of pyridine were added to the solution. The tube was sealed under argon and heated at 150 °C for 1 day. After the reaction cooled, the solvent was removed to give a blue powder. The crude product was chromatographed on an alumina (Fisher, 80−200 mesh) column with dichloromethane as eluent. The first fraction was collected and dried to give the final blue product (yield 18 mg, 36%). An NMR reaction was set to monitor the dimerization; no trimer or higher oligomers were found in the NMR tube after heating for 1 day at 150 °C, while unreacted starting material was present. The yield of dimer was 70% by NMR.

^{1}H NMR (dry $\mathrm{C_6D_6}$, 65 °C) δ 9.04 (s, 16H), 4.57 (m, b, 16H), 4.02 (m, b, 16H), 2.06 (m, 32H), 1.66 (m, 32H), 1.53 (m, 32H), 1.09 (t, terminal methyl in the substitutents, $J = 7.2$ Hz), −7.57 (s, 6H, axial methyl) ppm; IR (thin film) 1607 (m), 1514 (m), 1463 (vs), 1425 (s), 1390 (vs), 1357 (m) 1282 (vs), 1202 (s), 1095 (vs), 1058 (s), 970 (m, Si−O−Si), 851 (m), 751 (m) cm^{-1}; MS (MALDI) calcd for $\mathrm{C_{146}H_{198}O_{17}N_{16}Si_2}$ *m*/*e* 2505.5, found *m*/*e* 2507.4. Elemental analysis observed (calcd): C, 69.71 (69.99); H, 7.72 (7.96); N, 8.70 (8.94).

$\mathbf{\{[CH_3(CH_2)_4]_8PcSi(CH_3)\}_2O}$ (2k). Compound **2b** (40 mg) was dissolved in 8 mL of dry benzene with a few drops of pyridine, and the reaction mixture was heated at 165 °C for 2 days. The crude blue product was purified by chromatography on a silica column with $\mathrm{CH_2Cl_2}$/hexanes (2:1) as eluent. The first fraction collected was the dimer (blue powder, yield 13 mg, 30%).

^{1}H NMR (dry $\mathrm{C_6D_6}$, room temperature) δ 9.25 (s, 16H), 3.50 (t, b, 32H, $J = 7.8$ Hz), 2.21 (quintet, b, 32H, $J = 7.5$ Hz), 1.86 (m, 32H), 1.70 (m, 32H, $J = 7.2$ Hz), 1.17 (t, 48H, terminal methyl in the substitutents, $J = 7.2$ Hz), −7.62 (s, 6H, axial methyl) ppm; IR (thin film) 1729 (w), 1620 (w), 1512 (m), 1462 (vs), 1415 (s), 1347 (s), 1259 (w) 1095 (vs), 1077 (s), 980 (s, Si−O−Si), 891 (m), 754 (m), 733 (w) cm^{-1}; MS (MALDI) calcd for $\mathrm{C_{146}H_{198}ON_{16}Si_2}$ *m*/*e* 2249.5, found *m*/*e* 2251.1. Elemental analysis observed (calcd): C, 77.75 (77.96); H, 9.02 (8.87); N, 9.70 (9.96).

$\mathbf{\{[(CH_3(CH_2)_4O]_8PcSi(OCH_2CH_2SH)\}_2O}$ (1n) $\mathbf{\{[CH_3(CH_2)_4]_8PcSi(OCH_2CH_2SH)\}_2O}$ (2n). Compound **1k** or **2k** (10 mg) was dissolved in 1 mL of dry $\mathrm{C_6D_6}$ in a valved NMR tube, and a few drops of dry mercaptoethanol were added. Then the tubes was put in a Rayonet photochemical reactor and photolyzed at 350 nm. After every 10 min, proton NMR spectra were taken to monitor the reaction. After 30 min, all the starting materials were converted to desired products (**1n** or **2n**, >60% yield by NMR) or bis-mercaptoethanoxy-SiPc monomers, as revealed by NMR. The volatile components were removed under vacuum. For **1n**, purification by chromatography was not successful on either alumina or silica gel. For **2n**, the blue solids were purified by alumina column chromatography using $\mathrm{CH_2Cl_2}$/hexanes (3:1) as eluent. The first fraction was collected and removal of the solvent gave the blue solid product, yield 3 mg (∼30%).

1n: ^{1}H NMR ($\mathrm{C_6D_6}$) δ 9.12 (s, 16H), 4.49 (m, b, 16H), 3.86 (m, b, 16H), 1.98 (m, b, 32H), 1.59 (m, 32H), 1.48 (m, 32H), 1.07 (t, 48H, terminal methyl in the substitutents, $J = 7.2$ Hz), −1.42 (m, 4H, axial $-\mathrm{OCH_2}\mathit{CH}_2\mathrm{SH}$), −2.31(t, 2H, axial $-\mathrm{OCH_2CH_2}\mathit{SH}$), −3.10 (t, 4H, axial $-\mathrm{O}\mathit{CH}_2\mathrm{CH_2SH}$) ppm.

2n: ^{1}H NMR (dry $\mathrm{C_6D_6}$) δ 9.26 (s, 16H), 3.47 (t, b, 32H, $J = 7.8$ Hz), 2.20 (m, b, 32H), 1.86 (m, 32H), 1.68 (m, 32H), 1.17 (t, 48H, terminal methyl in the substitutents, $J = 7.2$ Hz), −1.59 (m, 4H, axial $-\mathrm{OCH_2}\mathit{CH}_2\mathrm{SH}$), −2.43 (t, 2H, axial $-\mathrm{OCH_2CH_2}\mathit{SH}$), −3.23 (t, 4H, axial $-\mathrm{O}\mathit{CH}_2\mathrm{CH_2SH}$) ppm; IR (thin film) 2597 (w), 1623 (w), 1620 (w), 1456 (s), 1417 (s), 1352 (s), 1096 (vs), 999 (s, Si−O−Si), 890 (m), 755 (s) cm^{-1}; MS (MALDI) calcd for $\mathrm{C_{148}H_{202}O_3N_{16}Si_2S_2}$ *m*/*e* 2373.6, found *m*/*e* 2376.

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Supporting Information Available: Summary of synthetic routes to soluble SiPcs **1a** and **2a**.This material is available free of charge via the Internet at http://pubs.acs.org.

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