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Synthesis of amphiphilic phthalocyanines and Langmuir-Blodgett film balance studies of these compounds

Batzel, Daniel Austin, Ph.D.

Case Western Reserve University, 1990
SYNTHESIS OF AMPHIPHILIC PHTHALOCYANINES AND
LANGMUIR-BLODGETT FILM BALANCE STUDIES OF THESE COMPOUNDS

by

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Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy

Thesis Advisor: Malcolm E. Kenney

Department of Chemistry
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January 1990
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GRADUATE STUDIES

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SYNTHESIS OF AMPHIPHILIC PHTHALOCYANINES AND LANGMUIR-BLODGETT FILM BALANCE STUDIES OF THESE COMPOUNDS

Abstract

by

DANIEL AUSTIN BATZEL

This thesis describes the synthesis and spectroscopic characterization of the Langmuir-Blodgett film-forming phthalocyanines (n-C₆H₁₃)₃SiO(SiPcO)₁₋₂H, C₁₈H₃₇(C₄H₉)₂SiO(SiPcO)₁₋₂H, (n-C₆H₁₃)₃SiO-(SiPcO)₃C(0)CCl₃, C₁₈H₃₇(C₄H₉)₂SiO(SiPcO)₃C(0)CCl₃, (n-C₆H₁₃)₃SiO-SiPcOGePcOH, C₁₈H₃₇(C₄H₉)₂SiOSiPcOGePcOH, and C₁₈H₃₇(C₄H₉)₂SiO-SiPcOAlPc (where Pc is the phthalocyaninato dianion). It also describes the synthesis and characterization of some of the precursors of these compounds including (n-C₆H₁₃)₃SiO(SiPcO)₁₋₄Si(n-C₆H₁₃)₃, C₁₈H₃₇(C₄H₉)₂SiO(SiPcO)₁₋₄Si(C₄H₉)₂C₁₈H₃₇, CH₃GePcCl, CH₃GePcOH, and C₁₈H₃₇(C₄H₉)₂SiOAlPc.

In addition, the thesis describes the formation and properties of monolayers of (n-C₆H₁₃)₃SiOSiPcOGePcOH, C₁₈H₃₇(C₄H₉)₂SiOSiPcOGePcOH, C₁₈H₃₇(C₄H₉)₂SiOSiPcOAlPc, (n-C₆H₁₃)₃SiO(SiPcO)₁₋₂H, and C₁₈H₃₇(C₄H₉)₂SiO(SiPcO)₁₋₂H from solutions of these compounds and monolayers of (n-C₆H₁₃)₃SiO(SiPcO)₃H and C₁₈H₃₇(C₄H₉)₂SiO(SiPcO)₃H from solutions of (n-C₆H₁₃)₃SiO(SiPcO)₃C(0)CCl₃ and C₁₈H₃₇(C₄H₉)₂SiO(SiPcO)₃C(0)CCl₃. It is shown from co-area data that the phthalocyanine rings of the (n-C₆H₁₃)₃SiO(SiPcO)₁₋₃H, C₁₈H₃₇(C₄H₉)₂SiO(SiPcO)₁₋₃H, (n-C₆H₁₃)₃SiOSiPcOGePcOH, and C₁₈H₃₇(C₄H₉)₂SiOSiPcOGePcOH monolayers are oriented parallel to the
plane of the monolayer, while the phthalocyanine rings of the
C_{18}H_{37}(C_{4}H_{9})_{2}SiOSiPcOAlPc monolayers are not. This is attributed to
the presence of OH head groups and R_{3}SiO tail groups on the central
metal. From phase-transition pressure data and compressive creep
curves it is concluded that the stability of the (n-C_{6}H_{13})_{3}SiO-
(SiPcO)_{2-3}H and (n-C_{6}H_{13})_{3}SiOSiPcOGePcOH monolayers is greater than
the stability of the (n-C_{6}H_{13})_{3}SiOSiPcOH monolayers. This is at-
tributed to the thicker ring profile of the two- and three-ring
compounds.

Finally, a summary of the results of collaborative work on the
preparation, characterization, and properties of Langmuir-Blodgett
multilayers of (n-C_{6}H_{13})_{3}SiOSiPcOGePcOH is given. It is shown by X-
ray and electron diffraction experiments that the multilayer films
are highly anisotropic and the phthalocyanine rings are parallel to
the plane of the substrate. Furthermore, metal-insulator-metal and
gas-sensing device studies incorporating these multilayer films indi-
cate that they have high thermal, electrical, chemical, and photo-
chemical stability.
To my mother

Lillian E. Batzel

and

In memory of my father

Edward Morris Batzel
1921-1989
ACKNOWLEDGMENTS

My sincerest gratitude is extended to Professor Malcolm E. Kenney for the confidence-instilling guidance he provided throughout the course of this work.

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C_{18}H_{37}(C_{4}H_{9})_{2}SiOSiPcOH  

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\[(\text{C}_6\text{H}_{13})_3\text{SiOGePcOH}\]

Double Ring Well-Characterized Axially Unsymmetrically Substituted Phthalocyanines Containing Two Metals

\[\text{C}_{18}\text{H}_{37}(\text{C}_4\text{H}_9)_2\text{SiOSiPcOAlPc}\]

\[(\text{C}_6\text{H}_{13})_3\text{SiOSiPcOGePcOH}\]

\[\text{C}_{18}\text{H}_{37}(\text{C}_4\text{H}_9)_2\text{SiOSiPcOGePcOH}\]

Double Ring NMR-Characterized Axially Unsymmetrically Substituted Phthalocyanines Containing Two Metals

\[(\text{C}_6\text{H}_{13})_3\text{SiOSiPcOAlPc}\]

Triple Ring NMR-Characterized Axially Unsymmetrically Substituted Phthalocyanines Containing Two Metals

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\[(\text{C}_6\text{H}_{13})_3\text{SiOSiPcOGePcOSiPcCH}_3\]

\[(\text{C}_6\text{H}_{13})_3\text{SiOSiPcOGePcOSiPcOH}\]

Other Phthalocyanines

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\[\text{GaPc(Cl)}_\text{16(Cl)}\]

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INTRODUCTION

The phthalocyanines are a class of aromatic compounds that are known for their diverse organic, coordination, and polymer chemistry. A monograph\(^1\) and several reviews\(^2-4\) dealing with this class of compounds are available.

The phthalocyanine ring, Figure 1, is a bivalent, tetradeutate ligand that is noted for its high thermal, chemical, and photochemical stability. It has sixteen sites for substitution and a central cavity capable of bonding to a variety of metals. If the metals are trivalent or tetravalent, one or two additional positions for substitution are available. With silicon as the central metal, for example, two substitution sites are available. These sites can carry identical or different ligands. Figure 2.\(^5,6\)

**Phthalocyanine Conductivity**

Many phthalocyanines have low conductivity. However, some of these poorly conducting phthalocyanines become moderately good conductors when fractionally oxidized, or doped, with oxidants such as I\(_2\).\(^7\) These doped phthalocyanines range in conductivity from semiconducting to superconducting (at low temperatures).

Among the phthalocyanines that are poor conductors, but become moderately good conductors when doped, is a class made up of
Figure 1. The phthalocyaninato ligand.

Figure 2. Structure of the axially unsymmetrically substituted phthalocyanine CH₃SiPcOH.

Figure 3. Structure of the cofacial phthalocyanine polymer [SiPcO]ₙ.
cofacially stacked metal phthalocyanines bridged by atoms such as O or F. Examples include [MPCO]_n, where M is Si or Ge, Figure 3 and [MPCF]_n, where M is Al, Ga, or Cr. Another class is made up of metal phthalocyanines that are not bridged but rather are stacked. Examples include NiPc and CoPc.

Conductivity in these doped phthalocyanines is generally very dependent on the direction of the current. For the doped O- and F-bridged phthalocyanines and for doped NiPc, this anisotropy arises because the transport pathway is formed primarily by a conduction band generated by ring π-π orbital overlap. For doped CoPc the anisotropy arises because the transport pathway is formed primarily by a conduction band generated by overlapping orbitals of the metal centers.

It has been demonstrated that, as would be expected, the conductivity of bulk phthalocyanines is greatly affected by the presence or absence of long range order. For example, a single crystal of nickel phthalocyanine iodide, NiPcI, has a conductivity of 550 Ω⁻¹·cm⁻¹ along the ring stack direction while, in contrast, a pressed pellet of NiPcI crystallites has a conductivity of 0.7 Ω⁻¹·cm⁻¹ in all directions.

A major difference between phthalocyanine conductors and metals is the potential for the conductivity of the former to be substantially varied and highly controlled. One way this can be done is by changing the electronic properties of the phthalocyanine ring through chemical derivatization. Another way is by orienting the rings by various methods.
Phthalocyanines for Microelectronic Device Applications

The variable and anisotropic conduction properties, stability, and diverse chemistry of phthalocyanines has led to a significant interest in their use as active components in microelectronic devices. However, the use of phthalocyanines in such devices presents challenging problems since thin films of them with special properties are often needed.

Among possible ways of forming phthalocyanine films are spin coating, vapor deposition, and Langmuir-Blodgett deposition. Phthalocyanine films formed by the spin coating and vapor deposition methods are often not fully suited to microdevice applications. This is because they usually do not have the reproducible thickness, internal ring orientation, and degree of perfection needed. Phthalocyanine films formed by the Langmuir-Blodgett technique, however, can have the needed properties. This has led to the use of such films in the fabrication of microelectronic devices including gas sensors,\textsuperscript{19-22} electroluminescent diodes,\textsuperscript{19,23,24} bistable switches,\textsuperscript{19} and photovoltaic devices.\textsuperscript{25,26} Several reviews dealing in part with the microdevice applications of phthalocyanine Langmuir-Blodgett films appear in the literature.\textsuperscript{27-31}

Phthalocyanine Langmuir-Blodgett Films

To obtain phthalocyanine Langmuir-Blodgett films, amphiphilic or semiamphiphilic phthalocyanines are spread onto water in a film balance and compressed into a tightly packed monolayer, Figure 4. A portion of the monolayer is then transferred to a substrate surface with dipping, lifting, or rolling methods, Figure 5. Multilayers are
Figure 4. Monolayer formation: (a) amphiphilic phthalocyanine (\(\phi\)) dissolved in a volatile solvent is spread on water surface and solvent allowed to evaporate; (b) resulting film is compressed to a tightly packed monolayer while the surface pressure is being monitored.
Figure 5. Monolayer transfer process: (a) immersion and (b) withdrawal of hydrophobic substrate yielding a Y-type [ref 47] bilayer.
formed by repeated substrate dippings, lifttings, or rollings.

The phthalocyanine Langmuir-Blodgett films that have been made include those composed of phthalocyanines having hydrogen, silicon, or one of a variety of metals in the center of the ring; zero or two axial groups; and zero, three, four, or eight peripheral groups.\textsuperscript{19-26,32-45} Several reviews of the Langmuir-Blodgett technique and its use with a variety of materials have recently appeared.\textsuperscript{46,47}

Needs in Phthalocyanine Films

To allow for full flexibility in the design of devices that utilize phthalocyanine films, phthalocyanine multilayers having rings that are perpendicular to the substrate, parallel to it, or both perpendicular and parallel to it in some specified sequence are needed. Although the work done on phthalocyanine films prior to the work described in this thesis had resulted in a phthalocyanine monolayer on water in which the rings are parallel to the surface\textsuperscript{42}, the formation of a multilayer in which the rings are parallel to the substrate surface had not yet been achieved.

Objectives of This Work

The purpose of this work was to design, synthesize, and characterize phthalocyanines that have the ability to form stable, highly ordered Langmuir-Blodgett multilayers in which the rings are parallel to the substrate surface.
SYNTHETIC DETAILS

Reagents

Generally the commercial reagents and solvents used were of reagent grade or better quality. Both the deuterated benzene and the deuterated pyridine (Aldrich Chemical Co., Milwaukee, WI) had isotopic purities of at least 99.96%, while the deuterated chloroform (Norell, Inc., Landisville, NJ) had an isotopic purity of 99.8%. The tetrachlorophthalonitrile was a generous gift (SDS Biotech Corp., Painesville, OH).

Chromatographic Materials

The substrate used in column chromatography was neutral alumina (Woelm Pharma GmbH & Co., Eschwege, W. Germany, distributed by ICN Biochemicals Division, Cleveland, OH; and Fisher Scientific Co., Fairlawn, NJ). Its activity was adjusted by standard methods. In those cases where mixed-solvent eluants were used, the eluents were formulated on a volume/volume basis.

The thin layer chromatography plates used were aluminum-backed silica plates (neutral, 200 μm) with a fluorescent indicator (E. Merck, Darmstadt, W. Germany; distributed by Alltech Associates, Inc., Deerfield, IN). Again, where mixed-solvent eluants were used, they were formulated on a volume/volume basis.
Techniques

Glassware used in reactions not employing aqueous media generally was oven-dried (-120 °C, 1 atm) for more than 12 h, assembled hot, and cooled. In most cases reaction mixtures were protected from atmospheric moisture with either CaSO₄ drying tubes or dry Ar blankets. The solvents were often dried by distillation (<30% distillate). Other techniques were sometimes used. The solid reagents and the solid products were often dried in a vacuum oven connected to a laboratory vacuum line (~80 torr) or in an Abderhalden drying tube (P₂O₅) connected to a vacuum pump (~0.5 torr).

Generally when solution evaporations were required, the evaporations were carried out with a rotary evaporator (Büchi Laboratoriums-Technik AG, Flawil, Switzerland; distributed by Brinkmann Instruments, Inc., Westbury, NY) equipped with a cold trap (dry ice-acetone) condenser. The evaporator was connected to a vacuum pump (~0.05 torr).

The low light conditions used in some of the syntheses were created by wrapping the glassware in Al foil, turning off the room lights, and pulling down the shades.

In most cases the columns for chromatography separations were constructed with a layer of sand above and below the alumina layer. The alumina layer was formed from a slurry of the alumina and a solvent such as hexanes. The columns were loaded either by the solution technique with the aid of solvents such as toluene, or by the dry loading technique with the aid of adsorbants such as Celite 545 (Johns-Manville Corp., Denver, CO).
Instrumentation

Infrared Spectrometer. A Perkin-Elmer IR 598 (Perkin-Elmer Corp., Norwalk, CT) spectrophotometer was used to record the infrared spectra. CsI plates were used to hold the mulls. Polystyrene was used to calibrate the spectra. Typical instrument settings used are:

- Range: 4000-200 cm\(^{-1}\)
- Atmosphere: air
- Scan Time: 12 min
- Slit Width: medium

NMR Spectrometer. A Varian XL-200 spectrometer (Varian Associates, Inc., Palo Alto, CA) was used to record the NMR spectra. Tetramethyldisilane was used as reference. Typical instrument settings used are:

- Sweep Width: 3,400 or 4,000 Hz
- Number of Points: 13,600 or 16,000
- Transmitter Offset: -400, -500, or -600 Hz
- Acquisition Time: 2.0 sec
- Delay Time: 2.0 or 3.0 sec
- Pulse Width: 6.3 \(\mu\)sec
- Number of Transients: 128, 256, or 512

Externally Acquired Data

Elemental Analyses. The elemental analyses were obtained from Galbraith Laboratories, Inc., Knoxville, TN. Some carbon and hydrogen analyses were done with the aid of a combustion catalyst. The silicon and germanium analyses were done by a procedure involving acid digestion and inductively coupled plasma analysis. The purity of the samples was checked by NMR or IR spectroscopy before they were
submitted for analysis.

Mass Spectra. The high and low resolution fast atom bombardment, FAB, mass spectra were obtained from the Midwest Center for Mass Spectrometry (University of Nebraska-Lincoln, Lincoln, NE). The laser desorption, LD, mass spectra were obtained from the Middle Atlantic Mass Spectrometry Laboratory (Johns Hopkins University, Baltimore, MD).
Chapter 3

SYNTHESES

Some of the procedures used in the following syntheses were carried out with protection from light. These are indicated with the letter p.

Precursor Phthalocyanines

$\beta$-ClGePcCH$_3$. Under Ar, a mixture of CH$_3$GeCl$_3$ (5.69 g, 29.3 mmol), diiminoisoindoline (7.64 g, 52.6 mmol), and distilled, deoxygenated quinoline (60 mL) was heated to reflux over a 30 min period (p). The mixture was refluxed for 1 h (p), cooled (p), and filtered (p). The solid was washed with MeOH (240 mL), air dried, and weighed (5.64 g).

With a procedure originally developed by Esposito for the purification of ClSiPcCH$_3$ as a model, a portion of the solid (2.09 g) was extracted under Ar with dry, deoxygenated chlorobenzene (Soxhlet, fine, 0.3 L, 36 h, p). The extract was cooled (p) and filtered, and the solid was washed with hexanes (100 mL) and diethyl ether (150 mL), dried (~0.5 torr, 80 °C), and weighed (1.14 g, 1.79 mmol, 13.6%, adjusted yield 38%$^{49}$). IR (mineral oil) 1507 (m), 1295 (m), 1245 (w), 1170 (m), 1130 (s), 905 (m), 780 (m), 735 (s), 580 (m) cm$^{-1}$. Anal. Calcd for C$_{33}$N$_8$H$_{19}$GeCl: C, 62.36; H, 3.01; Cl, 5.58. Found: C, 62.18; H, 3.09; Cl, 5.40. The product was a green-transmitting,
red-reflecting crystalline solid.

The compound gives a positive Beilstein test. It is insoluble in a variety of common organic solvents at room temperature, but is presumed to be photosensitive when in solution.

α-ClGePcCH₃. A portion of the pure β-ClGePcCH₃ polymorph (270 mg) was ground to a fine powder and sublimed (2 x 10⁻³ torr, 400 °C, 1 h, air-cooled cold finger, p). The sublimate was isolated and weighed (43.0 mg, 16%): IR (mineral oil) 1300 (w), 1252 (w), 1009 (w), 907 (w), 732 (m), 712 (m), 580 (w), 283 (m) cm⁻¹. The sublimate was a green-transmitting, dull-green-reflecting powder.

This polymorph can be converted to the β-polymorph by digestion in chlorobenzene.

HOGePcCH₃. A mixture of ClGePcCH₃ (17.0 g, 26.7 mmol) and concentrated H₂SO₄ (700 mL) was cooled (0 °C), stirred for 2 h (p), and poured over ice (3 kg, p). The resulting suspension was filtered and the solid was washed with water (2 L), and air dried. It was then extracted with pyridine (p) (Soxhlet, medium, 12 h), air dried, washed with H₂O (500 mL), dried (~80 torr, 85 °C), and weighed (13.6 g, 22.0 mmol, 82%).

An alternative method also gave the compound. In this method, NH₃ was added continuously (~5 mL/min) to a warm (~70 °C), stirred mixture of (n-C₆H₁₃)₃SiOGePcCH₃ (see below, 3.60 g, 4.00 mmol) and pyridine over a period of 8.5 h (p). The resulting suspension was filtered, and the solid was washed with acetone (100 mL) and MeOH (100 mL), dried (~80 torr, 85 °C), and weighed (2.16 g, 3.50 mmol, 88%): IR (mineral oil) 3550 (m br, O-H), 1490 (s), 1293 (m), 1242
(w), 1171 (m), 1128 (s), 990 (w, Ge-OH def), 905 (m), 732 (s), 628 (m, Ge-O) cm$^{-1}$. As obtained the product was a green-transmitting, blue-green-reflecting powder.

It is insoluble at room temperature in a variety of common organic solvents.

On the basis of the yields obtained in reactions in which the two products described above were used as intermediates, it is judged that the second method gives a purer product.

$n$-C$_6$H$_{13}$)$_3$SiOGePcCH$_3$. A mixture of HOGePcCH$_3$ (1.02 g, 1.65 mmol) and toluene (100 mL) was dried by distillation (20 mL of distillate, p) and cooled (p). (n-C$_6$H$_{13}$)$_3$SiOH$_{50}$ (2.5 mL, 7.0 mmol) was added to this mixture (p) and the resulting suspension was refluxed 1 h (p), cooled (p), and filtered (p). The filtrate was evaporated to a viscous suspension (~80 torr, 70 °C, p) and the resultant was washed with cold pentane (0 °C, 75 mL, p), air dried, and weighed (795 mg, 0.884 mmol, 54%): IR (mineral oil) 1611 (w), 1492 (sh), 1289 (m), 1232 (w, Si-CH$_2$), 1121 (m), 990 (m, Ge-O-Si), 900 (m), 734 (s), 575 (m) cm$^{-1}$; NMR (200 MHz, CDCl$_3$, 20 °C) $\delta$ 9.63 (m, 1.4-GePcH), 8.32 (m, 2,3-GePcH), 0.85 (m, $\epsilon$-CH$_2$), 0.71 (q, t-CH$_3$), 0.32 (m, $\delta$-CH$_2$), -0.05 (m, $\gamma$-CH$_2$), -1.35 (m, $\beta$-CH$_2$), -2.58 (m, $\alpha$-CH$_2$), -5.67 (s, Ge-CH$_3$). The product gave impurity resonances at $\delta$ 1.30 and 0.58. It was a green-transmitting, blue-green-reflecting crystalline solid.

The compound is soluble in toluene, CHCl$_3$, and pyridine, slightly soluble in hexanes, and insoluble in EtOH. It is photosensitive when in solution. When heated in wet solvents and when
chromatographed on silica or alumina it decomposes (apparently to HOGPcCH₃).

C₁₈H₃₇(Ç₄H₉)₂SiOSiPcCH₃. A suspension of CH₃SiPcOH₅ (3.32 g, 6.15 mmol) and pyridine (170 mL) was dried by distillation (25 mL of distillate, p) and cooled (p). C₁₈H₃₇(Ç₄H₉)₂SiCl₅ (7.95 g, 18.4 mmol) was added to the remainder (p) and the resulting suspension was refluxed for 1 h (p), cooled (p), and filtered (p). The filtrate was evaporated to a viscous suspension (~80 torr, 70 °C, p).

The suspension was chromatographed in portions (Al₂O₃ III, Woelm, hexanes slurry; dry loading, Celite, CH₂Cl₂; hexanes-toluene solutions; filtration; p), and weighed (4.95 g, 5.12 mmol, 83%): NMR (200 MHz, CDCl₃, 20 °C) δ 9.64 (m, 1,4-SiPcH), 8.32 (m, 2,3-SiPcH), 1.31 (m, η-ρ-CH₂), 1.07 (m, ζ-CH₂), 0.88 (m, η-C₁₈-CH₃), 0.80 (m, ε-CH₂), 0.36 (m, δ-CH₂), 0.00 (m, overlapping γ-C₁₈-CH₂, γ-C₄-CH₂, and τ-C₄-CH₃), -1.33 (m, β-C₁₈-CH₂, β-C₄-CH₂), -2.51 (m, α-C₁₈-CH₂, α-C₄-CH₂), -6.36 (s, Si-CH₃). As obtained the compound was a green-transmitting, velvet-green-reflecting solid.

The compound is soluble in CHCl₃, toluene, and benzene, slightly soluble in hexane, and insoluble in EtOH and diethyl ether. It is photosensitive when in solution.

C₁₈H₃₇(Ç₄H₉)₂SiOSiPcOGePcCH₃. A suspension of an intimate mixture of dry HOGPcCH₃ (2.09 g, 3.39 mmol) and C₁₈H₃₇(Ç₄H₉)₂SiCSiPcOH (see p 25) (3.21 g, 3.31 mmol) in dry 1,2,4-trimethylbenzene (400 mL) was refluxed 4.5 h (p), and filtered (p). The solid was extracted with CH₂Cl₂ (200 mL, p) and the extract and the filtrate were combined (p) and evaporated to a viscous blue suspension (~5 torr, 80
0°C, p). The suspension was washed with pentane (50 mL, p), and the remaining solid was air dried and weighed (2.56 g).

Most of the solid (2.44 g) was chromatographed (Al2O3 III, Fisher, hexanes slurry; dry loading, Celite, CH2Cl2; hexanes-toluene solutions, CHCl3; filtration; p) and weighed (605 mg).

The extract from the pentane treatment (above) was evaporated to a viscous suspension (-80 torr, p), and the suspension was chromatographed (Al2O3 I, Fisher, hexanes slurry; dry loading, Celite, CH2Cl2; hexanes-toluene solutions, toluene-CH2Cl2 solution, filtration; p) and weighed (168 mg). The products from the two separations were combined and weighed (773 mg, 0.493 mmol, 15%, adjusted yield 16%49): NMR (200 MHz, CDCl3, 20 °C) δ 9.08 (m, 1,4-Si or GePcH), 9.01 (m, 1,4-Si or GePcH), 8.40 (m, 2,3-Si or GePcH), 8.32 (m, 2,3-Si or GePcH), 1.33 (m, ζ-CH2), 1.01 (m, η-CH2), 0.93 (t, β-C18-CH3), 0.80 (m, ζ-CH2), 0.42 (m, ε-CH2), -0.18 (m, δ-CH2), -0.41 (t, α-C4-CH3), -0.64 (m, γ-C18-CH2, γ-C4-CH2), -2.29 (m, β-C18-CH2, β-C4-CH2), -3.54 (m, α-C18-CH2, α-C4-CH2), -7.43 (s, Ge-CH3). As obtained the compound was a blue-transmitting, blue-reflecting solid.

The compound is soluble in CHCl3 and toluene, slightly soluble in hexanes, and insoluble in EtOH and diethyl ether. It is photosensitive when in solution.

\((n-\text{C}_6\text{H}_{13})_3\text{SiO(SiPcO)}_n\text{Si(n-\text{C}_6\text{H}_{13})}_3\) (where n is small). With a modification of the method developed by Dininny52 for the synthesis of \((n-\text{C}_6\text{H}_{13})_3\text{SiO(SiPcO)}_n\text{Si(n-\text{C}_6\text{H}_{13})}_3\) as a model, a mixture of dry SiPc(OH)2 (15.5 g, 27.0 mmol), dry SiPcCl2 (8.49 g, 13.9 mmol), Ar purged quinoline (0.4 L), and tributylamine (30 mL) was refluxed for
40 minutes and cooled (0 °C). While being vigorously stirred, the resulting suspension was diluted over 3 h with concentrated HCl (400 mL), and the diluted suspension was warmed (room temperature) and filtered. The solid was washed with CH₃OH (1.5 L) and air dried.

A mixture of this solid (23.3 g) and concentrated H₂SO₄ (400 mL) was stirred for 3 h while being kept cool (0 °C), and then poured over crushed ice (5 kg). The resultant was allowed to settle and the supernatant liquid was decanted. With vigorous stirring, the remainder was mixed with a pyridine-concentrated NH₄OH solution (1:1, 1.5 L) and the suspension formed was stirred for 3 h, diluted with H₂O (1 L), allowed to settle, and filtered. The solid was washed with H₂O (1 L), a CH₃OH-H₂O solution (1:1, 1 L), and air dried.

The dried solid was mixed with 2-picoline (500 mL), and the suspension formed was dried by distillation (80 mL of distillate) and cooled. Tri-n-hexylchlorosilane (34.6 g, 108 mmol) was added to the remainder, and the resulting mixture was refluxed for 3.5 h, cooled, and filtered. The solid was extracted while still on the filter with toluene (1 L), and both the extract and the solid were retained. The extract and the filtrate were combined and evaporated to a viscous blue suspension (~5 torr, 60 °C). After this suspension had been diluted with EtOH (1 L), it was filtered and the solid recovered was air dried and weighed (10.1 g). A mixture of a portion of the solid retained from the extraction (5.90 g) and 2-picoline (1 L) was dried by distillation (150 mL of distillate) and cooled. Tri-n-hexylchlorosilane (4.79 g, 15.0 mmol) was added to the remainder, and the resulting suspension was refluxed for 1.75 h, cooled, and filtered.
The solid was washed with toluene (200 mL), and the washings and the filtrate were combined and evaporated to a viscous suspension (~5 torr, 60 °C). After the suspension had been diluted with EtOH (500 mL), it was filtered and the solid was air dried and weighed (1.06 g). The remaining solid retained from the extraction was subjected in four portions to the same treatment and the products were combined and weighed separately (2.10 g total).

The resulting six products were then separated in portions by chromatography (Al₂O₃ III, Fisher, hexanes slurry; dry loading, Celite, CH₂Cl₂; hexanes-toluene solutions; filtration) into three fractions. These were shown by thin layer chromatography and by NMR spectroscopy to be the dimer (i.e., \( (n-C₆H₁₃)_₃SiO(SiPcO)₂Si(n-C₆H₁₃)_₃ \)), the trimer, and the tetramer.

\( (n-C₆H₁₃)_₃SiO(SiPcO)₂Si(n-C₆H₁₃)_₃ \). The impure dimer was chromatographed (Al₂O₃ III, Woelm, hexanes slurry; dry loading, CH₂Cl₂; hexanes-toluene solutions; filtration), and weighed (665 mg, 0.392 mmol, 1.9% total yield based on SiPc(OH)₂ and SiPcCl₂): TLC (silica gel, n-hexane-EtOAc, 5:1) \( R_f \) 0.51; IR (Nujol) 1252 (w, Si-CH₂), 1030 (s, Si_cap-O-Si_Pc), 979 (s, Si_Pc-O-Si_Pc) cm⁻¹; NMR (200 mHz, C₆D₆, 70 °C) δ 9.20 (m, 1.4-SiPch), 8.08 (m, 2,3-SiPch), 0.58 (m, overlapping ε-CH₂ and γ-CH₃), 0.07 (m, δ-CH₂), -0.38 (m, γ-CH₂), -1.86 (m, β-CH₂), -3.16 (m, α-CH₂). As obtained the compound was a blue-transparent, blue-reflecting solid.

The compound is soluble in toluene, CHCl₃, and pyridine, slightly soluble in hot hexanes, and insoluble in diethyl ether and EtOH.
(n-C₆H₁₃)₃SiO(SiPC0)₃Si(n-C₆H₁₃)₃. The impure trimer was chromatographed in portions (Al₂O₃ III, Woelm, hexanes slurry; dry loading, Celite, CH₂Cl₂; hexanes-toluene solutions; filtration). The resultant was combined with additional like material isolated during the separation of the tetramer (see below) and the combined amount was weighed (3.84 g, 1.70 mmol, 13% based on SiPC(OH)₂ and SiPCCl₂): TLC (silica gel, n-hexane-EtOAc, 5:1) Rf 0.43; IR (Nujol) 1013 (s, Si₃C₆P-O-SiPC), 981 (s, SiPC-O-SiPC) cm⁻¹; NMR (200 MHz, C₆D₆, 70 oC) δ 8.75 (m, terminal 1,4-SiPC$_{H}$), 8.69 (m, center 1,4-SiPC$_{H}$), 8.21 (m, center 2,3-SiPC$_{H}$), 7.84 (m, terminal 2,3-SiPC$_{H}$), 0.36 (m, overlapping ε-CH₂ and τ-CH₃), -0.23 (m, δ-CH₂), -0.71 (m, γ-CH₂), -2.30 (m, β-CH₂), -3.65 (m, α-CH₂). As obtained the compound was a blue-transmitting, blue-reflecting solid.

A similarly prepared product was further characterized by elemental analysis. Anal. Calcd for C₃₂H₆₀N₂₄Si₂O₄: C, 70.37; H, 5.64; Si, 6.23. Found: C, 70.30; H, 5.88; Si, 5.95.

The compound is soluble in toluene, CHCl₃ and pyridine, slightly soluble in hot hexanes, and insoluble in diethyl ether and EtOH.

(n-C₆H₁₃)₃SiO(SiPC0)₄Si(n-C₆H₁₃)₃. The impure tetramer was chromatographed in portions (Al₂O₃ III, Woelm, hexanes slurry; dry loading, Celite, CH₂Cl₂; hexanes-toluene solutions; filtration), and weighed (1.77 g, 0.630 mmol, 6.2% based on SiPC(OH)$_₂$ and SiPCCl₂): TLC (silica gel, n-hexane-EtOAc, 5:1) Rf 0.37; IR (Nujol) 1029 (s, Si₃C₆P-O-SiPC), 1000 (s, SiPC-O-SiPC) cm⁻¹; NMR (200 MHz, C₆D₆, 70 oC) δ 8.47 (m, terminal 1,4-SiPC$_{H}$), 8.25 (m, inner 1,4-SiPC$_{H}$), 8.01 (m, inner 2,3-SiPC$_{H}$), 7.65 (m, terminal 2,3-SiPC$_{H}$), 0.24 (m, overlap-
ping ε-CH₂ and τ-CH₃), -0.39 (m, δ-CH₂), -0.89 (m, γ-CH₂), -2.53 (m, β-CH₂), -3.89 (m, α-CH₂). As obtained the compound was a blue-
transmitting, red-reflecting solid.

A similarly prepared product was further characterized by elemental analysis. Anal. Calcd for C₁₆₄H₅₄₂N₃₂Si₆O₅: C, 70.11; H, 5.09; Si, 6.00. Found: C, 70.04; H, 5.22; Si, 5.65.

The compound is soluble in toluene, CHCl₃, and pyridine, and insoluble in hexanes, diethyl ether, and EtOH.

C₁₈H₃₇(C₄H₉)₂SiO₂SiPcO)nSi(C₄H₉)₂C₁₈H₃₇ (where n is small). A mixture of dry SiPc(OH)₂ (7.28 g, 12.7 mmol), dry SiPcCl₂ (3.86 g, 6.31 mmol), Ar purged quinoline (0.65 L), and tributylamine (15 mL) was refluxed for 40 minutes and then cooled (0 °C). While being vigorously stirred, the resulting suspension was diluted over 3 h with concentrated HCl (0.45 L), and the diluted suspension was warmed (room temperature) and filtered. The solid was washed with H₂O (2 L) and air dried.

A mixture of this solid (11.52 g) and concentrated H₂SO₄ (500 mL) was stirred for 1 h while being kept cool (0 °C), and then poured over crushed ice (4 kg). The resultant was allowed to settle and the supernatant liquid was decanted. With vigorous stirring, the remainder was mixed with a pyridine-concentrated NH₄OH solution (1:1, 400 mL), and the resulting suspension was stirred for 0.5 h, diluted with H₂O (2 L), allowed to settle, and filtered. The solid was washed with H₂O (1 L), air dried, and weighed (9.76 g).

The dried solid was mixed with 2-picoline (1 L) and the suspension formed was dried by distillation (300 mL of distillate) and
cooled. C_{18}H_{37}(C_4H_9)_2SiCl_{51} (15.28 g, 35.48 mmol) was added to the remainder and the resulting suspension was refluxed for 1 h, and filtered hot. The solid was extracted with hot toluene (0.2 L) and the extract and filtrate were combined and evaporated to a viscous suspension (~5 torr, 60 °C). The suspension was combined with Celite (43.0 g) and toluene (150 mL), evaporated to a free-flowing powder (~5 torr, 40 °C), and weighed (75.9 g).

The powder was separated in portions by chromatography (Al_{2}O_{3} III, Fisher, hexanes slurry; dry loading; hexanes-toluene solutions; filtration) into four fractions. These were shown by thin-layer chromatography and by NMR spectroscopy to be the dimer (i.e., C_{18}H_{37}(C_4H_9)_2SiO(SiPcO)_2Si(C_4H_9)_2C_{18}H_{37}), trimer, tetramer, and pentamer.

C_{18}H_{37}(C_4H_9)_2SiO(SiPcO)_2Si(C_4H_9)_2C_{18}H_{37}. The impure dimer fractions were chromatographed in portions (Al_{2}O_{3} III, Woelm, hexanes slurry; dry loading, Celite, CH_{2}Cl_{2}; hexanes-toluene solutions; filtration), and weighed (4.37 g, 2.28 mmol, 24% based on SiPc(OH)$_2$ and SiPcCl$_2$): TLC (silica gel, n-hexane-EtOAc, 5:1) $R_f$ 0.59; IR (mineral oil) 1035 (s, Si$_{cap}$-O-SiPc), 980 (m, SiPc-O-SiPc) cm$^{-1}$; NMR (200 MHz, C$_6$D$_6$, 70 °C) $\delta$ 9.20 (m, 1,4-SiPcH), 8.09 (m, 2,3-SiPcH), 1.36 (m, $\gamma$-C$_{18}$-CH$_2$), 1.11 (m, $\eta$-CH$_2$), 0.92 (m, $\tau$-C$_{18}$-CH$_3$), 0.62 (m, $\epsilon$-CH$_2$), 0.11 (m, $\delta$-CH$_2$), -0.19 (t, $\tau$-C$_4$-CH$_3$), -0.36 (m, $\gamma$-C$_{18}$-CH$_2$, $\gamma$-C$_4$-CH$_2$), -1.90 (m, $\beta$-C$_{18}$-CH$_2$, $\beta$-C$_4$-CH$_2$), -3.17 (m, $\alpha$-C$_{18}$-CH$_2$, $\alpha$-C$_4$-CH$_2$) ($\xi$-CH$_2$ obscured by $\tau$-C$_{18}$-CH$_3$). Anal. Calcd for C$_{116}$N$_{16}$H$_{142}$Si$_{4}$O$_3$: C, 72.54; H, 7.45; Si, 5.85. Found: C, 72.86; H, 7.62; Si, 6.20. As obtained the compound was a blue-transmitting, blue-reflecting solid.
The compound is soluble in toluene, CHCl₃, and pyridine, slightly soluble in hexanes, and insoluble in diethyl ether and EtOH.

C₁₈H₃₇(C₄H₉)₂Si(O(SiPcO)₃Si(C₄H₉)₂C₁₈H₃₇. The impure trimer was chromatographed in portions (Al₂O₃ III, Woelm, hexanes slurry; dry loading, Celite, CH₂Cl₂; hexanes-toluene solutions; filtration), and weighed (3.53 g, 1.42 mmol, 22% based on SiPc(OH)₂ and SiPcCl₂): TLC (silica gel, n-hexane-EtOAc, 5:1) Rₛ 0.52; IR (mineral oil) 1029 (s, Sicap-O-SipC), 988 (s, SipC-O-SipC) cm⁻¹; NMR (200 MHz, C₆D₆, 70 °C) δ 8.76 (m, terminal 1,4-SipCH), 8.70 (m, center 1,4-SipCH), 8.22 (m, center 2,3-SipCH), 7.85 (m, terminal 2,3-SipCH), 1.33 (m, t-CH₂), 0.93 (m, t-C₁₈-CH₃), 0.76 (m, 3-CH₂), 0.41 (m, 3-CH₂), -0.17 (m, 3-CH₂), -0.47 (t, 3-C₄-CH₃), -0.69 (m, γ-C₁₈-CH₂, γ-C₄-CH₂), -2.31 (m, β-C₁₈-CH₂, β-C₄-CH₂), -3.64 (m, α-C₁₈-CH₂, α-C₄-CH₂) (η-CH₂, θ-CH₂ obscured by t-C₁₈-CH₃ and t-CH₂). As obtained the compound was a blue-transmitting, blue-reflecting solid.

The compound is soluble in toluene, CHCl₃, and pyridine, slightly soluble in hexanes, and insoluble in diethyl ether and EtOH.

C₁₈H₃₇(C₄H₉)₂Si(O(SiPcO)₄Si(C₄H₉)₂C₁₈H₃₇: The impure tetramer was chromatographed (Al₂O₃ III, Woelm, hexanes slurry; dry loading, Celite, CH₂Cl₂; hexanes-toluene solutions; filtration), and weighed (1.15 g, 0.379 mmol, 8.0% based on SiPc(OH)₂ and SiPcCl₂): TLC (silica gel, n-hexane-EtOAc, 5:1) Rₛ 0.47; IR (mineral oil) 1030 (s, Sicap-O-SipC), 1002 (s, SipC-O-SipC); NMR (200 MHz, C₆D₆, 70 °C) δ 8.47 (m, terminal 1,4-SipCH), 8.25 (m, center 1,4-SipCH), 8.01 (m, inner 2,3-SipCH), 7.65 (m, terminal 2,3-SipCH), 1.30 (m, t-CH₂), 0.92 (m, t-C₁₈-CH₃), 0.63 (m, 3-CH₂), 0.26 (m, 3-CH₂), -0.37 (m, θ-CH₂),
CH₂), -0.63 (t, t-C₄-CH₃), -0.88 (m, γ-C₁₈-CH₂, γ-C₄-CH₂), -2.55 (m, β-C₁₈-CH₂, β-C₄-CH₂), -3.90 (m, α-C₁₈-CH₂, α-C₄-CH₂) (η-CH₂, ζ-CH₂ obscured by t-C₁₈-CH₃ and i-ρ-CH₂). As obtained the compound was a blue-transmitting, red-reflecting solid.

The compound is soluble in toluene, CHCl₃, and pyridine, slightly soluble in hot hexanes, and insoluble in EtOH and diethyl ether.

C₁₈H₃₇(C₄H₉)₂SiO(SiPcO)₅Si(C₄H₉)₂C₁₈H₃₇. The impure pentamer was chromatographed (Al₂O₃ V, Woelm, hexanes slurry; dry loading, Celite, CH₂Cl₂; hexanes-toluene solutions; filtration), and weighed (75.1 mg): TLC (silica gel, n-hexane-EtOAc, 5:1) Rf 0.37; NMR (200 MHz, toluene-d₈, 100 °C) δ 8.21 (m, terminal 1,4-SiPcH), 7.88 (m, inner 1,4-SiPcH), 7.81 (m, inner 2,3-SiPcH), 7.78 (m, center 1,4-SiPcH), 7.71 (m, center 2,3-SiPcH), 7.51 (m, terminal 2,3-SiPcH), 1.26 (m, ι-ρ-CH₂), 0.89 (t, t-C₁₈-CH₃), 0.76 (m, η-CH₂), 0.55 (m, ζ-CH₂), 0.13 (m, ε-CH₂), -0.51 (m, δ-CH₂), -0.78 (t, t-C₄-CH₃), -1.02 (m, γ-C₁₈-CH₂, γ-C₄-CH₂), -2.70 (m, β-C₁₈-CH₂, C₄-CH₂), -4.10 (m, α-C₁₈-CH₂, α-C₄-CH₂) (θ-CH₂ obscured by ι-ρ-CH₂). As judged on the basis of its NMR spectrum the product contained ~60% pentamer. Accordingly, the contained yield based on SiPc(OH)₂ and SiPcCl₂ was 0.33%. The product was a blue-transmitting red-reflecting solid.

The compound is soluble in CHCl₃ and hot toluene, and insoluble in hexanes. Chromatography on alumina does not separate it efficiently from the trimer and tetramer.
Single Ring Well-Characterized Axially Unsymmetrically Substituted
Silicon Phthalocyanines

$(n$-$C_6H_{13})_3SiOSiPcOH$. A preparation of this compound involving
the photolysis of $(n$-$C_6H_{13})_3SiOSiPcCH_3$ has been reported previous-
ly. In the preparation developed in this work, a solution of $(n$-$C_6H_{13})_3SiOSiPcOsi(n$-$C_6H_{13})_3$ \(^{52}\) (chromatographed, 2.16 g, 1.90 mmol) and
toluene (250 mL) was dried by distillation (50 mL of distillate) and
cooled. Under Ar, $Cl_3CC(0)OH$ (recrystallized\(^ {48}\), 618 mg, 3.78
mmol) was added to the solution and the mixture formed was stirred 2
h and filtered. The filtrate was evaporated to dryness (~0.05 torr,
0 °C), and the residue was mixed with a pyridine-$H_2O$ solution (4:1,
125 mL) and stirred for 10 h while being warmed (50 °C). The result-
ing suspension was filtered, and the solid was washed with a $MeOH$-
$H_2O$ solution (1:1, 200 mL). It was then air dried and quickly washed
with warm (~50 °C) hexanes (200 mL).

The washed solid was extracted with chloroform (200 mL), the
extract was evaporated to a solid (~80 torr, 70 °C), and the solid
was weighed (892 mg, 1.04 mmol, 55%): TLC (silica gel, $EtOAc$-
hexanes, 5:1) $R_f$ 0.70; IR (mineral oil) 3500 (w, O-H), 1521 (m),
1340 (s), 1255 (w, Si-CH$_2$), 1125 (s), 1038 (m, Si-O-Si), 1005 (sh),
916 (s), 841 (w, Si-OH), 739 (s), 538 (m), 425 (m) cm$^{-1}$ (these data
agree with and expand upon previous data)\(^ {53}\); NMR (200 MHz, $C_6D_6$, 2.3
× 10$^{-2}$H, 60 °C) $\delta$ 9.23 (1,4-$SiPcH$), 7.86 (2,3-$SiPcH$), 0.78 (m, $\epsilon$-
CH$_2$), 0.62 (m, $\epsilon$-CH$_3$), 0.37 (m, $\delta$-CH$_2$), 0.03 (m, $\gamma$-CH$_2$), -1.15 (m, $\beta$-
CH$_2$), -2.33 (m, $\alpha$-CH$_2$), -3.02 (br s, O-H). As obtained the compound
was a blue-transmitting, blue-reflecting powder.
In a separate experiment the compound was chromatographed (Al₂O₃ V, Woelm, toluene slurry; dry loading, Celite, CH₂Cl₂; toluene, CHCl₃; filtration). The product was washed with EtOH (100 mL) and was shown to be pure (n-C₆H₁₃)₃SiOSiPcOH by NMR spectroscopy (36% of load).

The compound is soluble in pyridine, toluene, and benzene, partly soluble in hot hexanes, and insoluble in EtOH and diethyl ether.

C₁₈H₃₇(C₄H₉)₂SiOSiPcOH. C₁₈H₃₇(C₄H₉)₂SiOSiPcCH₃ (4.94 g, 5.11 mmol) was dissolved in toluene (4 L), and the resulting solution was irradiated with direct sunlight for 1 h and filtered. The filtrate was evaporated to dryness (~80 torr, 70 °C), and the residue was washed with n-hexane (0.5 L, sonication), air dried, and weighed (3.07 g, 3.17 mmol, 62%): IR (mineral oil) 3500 (m, O-H), 1521 (m), 1340 (s), 1198 (w), 1125 (s), 1035 (m, Si-O-Si), 1005 (sh), 916 (m), 840 (w, Si-OH), 739 (s), 535 (m), 425 (m) cm⁻¹; NMR (200 MHz, C₆D₆, 8.7 × 10⁻³M, 20 °C) δ 9.13 (m, 1,4-SiPcH), 7.61 (m, 2,3-SiPcH), 1.34 (m, η-CH₂), 1.03 (m, β-CH₂), 0.92 (m, α-C₁₈-CH₃), 0.81 (m, ε-CH₂), 0.36 (m, δ-CH₂), 0.01 (m, overlapping γ-C₁₈-CH₂, γ-C₄-CH₂, and τ-C₄-CH₃). -1.26 (m, β-C₁₈-CH₂, β-C₄-CH₂), -2.38 (m, α-C₁₈-CH₂, α-C₄-CH₂).

Anal. Calcd for C₅₈N₈H₇₂Si₂O₂: C, 71.86; N, 11.56; H, 7.49. Found: C, 71.75; N, 11.60; H, 7.32. As obtained the compound was a blue-transmitting, blue-reflecting powder.

The compound is soluble in CHCl₃, toluene, and benzene, partly soluble in hot hexanes, and insoluble in EtOH and diethyl ether.
Single Ring NMR-Characterized Axially Unsymmetrically Substituted
Silicon Phthalocyanines

C₈H₁₇SiPcOH. A mixture of dry diiminoisoindoline (10.0 g, 69.1
mmol), C₈H₁₇SiCl₃ (8.81 g, 35.6 mmol), and dry deoxygenated quinoline
(70 mL) was heated to 200 °C over a period of 2.5 h (with vigorous
stirring, p), kept at this temperature for an additional 3 h (p), and
slowly cooled (p). The resulting suspension was diluted with MeOH
(100 mL, p) and filtered (p). The solid was extracted with CHCl₃
(500 mL), and the extract was evaporated to dryness (~80 torr, 70 °C)
and air dried (1.28 g).

A mixture of a portion of this solid (502 mg) and concentrated
H₂SO₄ (0.250 L) was stirred 6 h (p), and then poured over ice (1 kg,
p). The resulting suspension was filtered, and the remaining solid
was mixed with a pyridine-concentrated NH₄OH solution (1:1, 200 mL).
The mixture formed was stirred 1 h, diluted with H₂O (1 L), and
filtered. The solid was washed with MeOH (500 mL) and extracted with
CHCl₃ (300 mL, p). The extract was filtered (p), and the filtrate was
evaporated to dryness (~80 torr, 70 °C, p), and weighed (288 mg).

A portion of this solid (100 mg) was chromatographed (Al₂O₃ V,
Woelm, toluene slurry; solvent loading, toluene-CHCl₃, 1:1, 6 mL;
toluene-CHCl₃ solutions; filtration; p), and weighed (33.2 mg, 0.0495
mmol, 0.29%, adjusted yield 2.1±4⁹): IR (mineral oil) 3490 (m, O-
H), 1614 (w), 1512 (m), 1339 (s), 840 (w, Si-OH), 799 (m), 733 (s),
530 (w) cm⁻¹; NMR (200 MHz, CDCl₃, 20 °C) δ ~9.35 (m, 1,4-SiPC₆H₅),
~8.25 (m, 2,3-SiPC₆H₅), ~6.30 (m, α-CH₂). As obtained the compound
was a bright-green-transmitting, green-reflecting powder.
The compound is soluble in CHCl₃, slightly soluble in toluene, and insoluble in MeOH and hexanes. It is photosensitive in solution.

The yield of this synthesis may be improved using a low temperature procedure discussed on p 70.

C₁₈H₃₇(C₄H₉)₂SiOSiPcCl. Pyridine (80 mL, distilled from CaH₂) was transferred by cannula (Ar) to a flask containing dry C₁₈H₃₇(C₄H₉)₂SiOSiPcOH (1.00 g, 1.03 mmol), and the resulting solution was cooled (0 °C). Thionyl chloride (distilled, 8.0 mL, 110 mmol) was slowly added to the solution by syringe, and the resulting mixture was stirred for 45 min while being kept cool (0 °C) and then stirred for an additional 2 h after being allowed to warm (room temperature). The resulting suspension was evaporated to a solid (0.5 torr, 0 °C).

The residue was extracted with dry toluene (100 mL), and the extract was evaporated to dryness (0.5 torr, 0 °C). The residue washed with dry n-hexane (150 mL), air dried, and weighed (0.650 g, 0.625 contained mmol, 61% contained yield): NMR (200 MHz, C₆D₆, 6.5 x 10⁻³M, 20 °C) δ 9.61 (m, 1,4-SiPcH), 7.87 (m, 2,3-SiPcH), 1.34 (m, α-CH₂), 0.92 (m, overlapping ε-CH₂ and γ-C₁₈-CH₃), 0.56 (m, δ-CH₂), 0.20 (m, overlapping γ-C₁₈-CH₂, γ-C₄-CH₂, and ε-C₄-CH₃), -0.97 (m, β-C₁₈-CH₂, β-C₄-CH₂), -2.05 (m, α-C₁₈-CH₂, α-C₄-CH₂). On the basis of its NMR spectrum, it was judged that the product was ~95% pure. As obtained the compound was a blue-green transmitting, blue-reflecting powder.

The compound gives a positive Beilstein test. It is soluble in pyridine, toluene, benzene, and CHCl₃, and insoluble in hexanes. It
hydrolyzes rapidly when in solution in wet solvents, but is stable when in solution in dry solvents.

\[ \text{C}_{18}\text{H}_{37}\text{(C}_4\text{H}_9)\text{O}_2\text{SiOSiPC}_{18}\text{H}_37 \] A solution of \[ \text{C}_{18}\text{H}_{37}\text{(C}_4\text{H}_9)\text{O}_2\text{SiOSiPC}_{18}\text{H}_37 \] (1.08 g, 1.11 mmol) and toluene (250 mL) was dried by distillation (50 mL of distillate), and cooled. Dry MeOH\(^4\) (12 mL) was added to the solution, and the mixture was concentrated by distillation (50 mL of distillate). Three successive additions of MeOH (10 mL each) were made to the concentrate. After each of these, the concentrate was reduced in volume by distillation (35 mL, 20 mL, 5 mL of distillate). The resultant was evaporated to dryness (~80 torr, 70 °C), and the solid was washed with MeOH (100 mL, sonicating), dried (~80 torr, 80 °C), and weighed (798 mg, 0.811 mmol, 73%). NMR (200 MHz, CDCl\(_3\), 20 °C) \( \delta \): 9.64 (\text{m, 1,4-SiPcH}), 8.33 (\text{m, 2,3-SiPcH}), 1.31 (\text{m, } \eta\text{-p-CH}_2), 1.08 (\text{m, } \zeta\text{-CH}_2), 0.89 (\text{m, overlapping } \epsilon\text{-CH}_2, \tau\text{-C}_{18}\text{-CH}_3), 0.37 (\text{m, } \delta\text{-CH}_2), 0.04 (\text{m, overlapping } \gamma\text{-C}_{18}\text{-CH}_2, \gamma\text{-C}_4\text{-CH}_2, \text{ and } \tau\text{-C}_4\text{-CH}_3), -1.28 (\text{m, } \beta\text{-C}_{18}\text{-CH}_2, \beta\text{-C}_4\text{-CH}_2), -1.82 (\text{s, } 0\text{-CH}_3), -2.43 (\text{m, } \alpha\text{-C}_{18}\text{-CH}_2, \alpha\text{-C}_4\text{-CH}_2). As obtained the compound was a blue-transmitting, blue-reflecting powder.

The compound is soluble in CHCl\(_3\), toluene, pyridine and benzene, and insoluble in EtOH, and pentane.

\( (n\text{-C}_6\text{H}_{13})_3\text{SiOSiPcOCH}_2\text{OC(CH}_2\text{OH)}_3 \) A mixture of \( (n\text{-C}_6\text{H}_{13})_3\text{SiOSiPcOCH}_2\text{OC(CH}_2\text{OH)}_3 \) (prepared by photolysis\(^5\), 152 mg, 0.177 mmol), pentaerythritol (2.35 g, 17.3 mmol), and distilled, deoxygenated DMF (50 mL) was heated to 120 °C, and the resulting mixture was stirred for 2 h while being warmed. The resulting solution was cooled, diluted with H\(_2\)O (50 mL), and filtered. The solid was washed with H\(_2\)O (50 mL),
dried (-80 torr, 90 °C), and weighed (157 mg, 0.161 mmol, 91%): NMR (200 MHz, CDCl₃, 20 °C) δ 9.65 (m, 1,4-SiPcH), 8.36 (m, 2,3-SiPcH), 1.21 (d, CCH₂O), 0.80 (m, ε-CH₂), 0.70 (t, τ-CH₃), 0.33 (m, δ-CH₂), 0.14 (t, OH), 0.03 (m, γ-CH₂), -1.30 (m, β-CH₂), -2.12 (s, SiOCH₂), -2.44 (m, α-CH₂). As obtained the compound was a blue-transmitting, blue-reflecting solid.

The compound is soluble in DMF, DMSO, CHCl₃, toluene, benzene, and pyridine, and insoluble in hexanes, EtOH, MeOH, and H₂O.

(n-C₆H₁₃)₃SiOSiPcO(SiOCH₃)₃. A mixture of SiCl₄ (0.4 mL, 3.49 mmol), (n-C₆H₁₃)₃SiOSiPcOH (prepared by photolysis⁵³, 101 mg, 0.118 mmol) and distilled dimethylaniline (70 mL) was stirred for 4 h while being warmed (50 °C). Dry MeOH⁴⁸ (0.60 mL, 15 mmol) was added to the warm solution (CAUTION⁵⁴), and the resultant was stirred for 30 min, cooled, and evaporated to dryness (-15 torr, 90 °C). The residue was extracted with diethyl ether (~100 mL), and the extract was evaporated to a solid (~80 torr, 0 °C).

The solid was recrystallized from dry methylocyclohexane (5 mL), air dried, and weighed (15.1 mg, 0.0154 mmol, 13%): NMR (200 MHz, CDCl₃, 20 °C) δ 9.65 (m, 1,4-SiPcH), 8.33 (m, 2,3-SiPcH), 1.22 (s, OCH₃), 0.82 (m, ε-CH₂), 0.69 (m, τ-CH₃), 0.36 (m, δ-CH₂), 0.05 (m, γ-CH₂), -1.26 (m, β-CH₂), -2.41 (m, α-CH₂). As obtained the compound was a blue-transmitting, purple-reflecting crystalline solid.

The compound is soluble in diethyl ether, CHCl₃, toluene, and pyridine, and is insoluble in MeOH and pentane.
Double Ring Well-Characterized Axially Unsymmetrically Substituted Silicon Phthalocyanines

\((n\text{-}C_6H_{13})_3SiO(SiPcO)_2Si(n\text{-}C_6H_{13})_3\). A mixture of \((n\text{-}C_6H_{13})_3SiO(SiPcO)_2Si(n\text{-}C_6H_{13})_3\) (chromatographed, 598 mg, 0.353 mmol) and toluene (80 mL) was dried by distillation (20 mL of distillate) and cooled. Under dry Ar, Cl₃CC(O)OH (recrystallized, 118 mg, 0.722 mmol) was added to the solution, and the mixture was stirred 1.5 h and filtered. The solid was washed with toluene (50 mL) and the washings and filtrate were combined and evaporated to a solid (-0.5 torr, 0 °C). This was washed with n-hexane (200 mL, sonication).

The washed solid was mixed with a pyridine-H₂O solution (4:1, 100 mL), and the resulting suspension was stirred while being warmed (50 °C) for 6 h and filtered. The solid was washed with an EtOH-H₂O solution (1:1, 100 mL), air dried, and weighed (298 mg).

A portion of this solid (232 mg) was extracted with pyridine (70 mL, sonication), and the extract was diluted with H₂O (50 mL) and filtered. The solid was washed with MeOH (100 mL) and n-hexane (100 mL), dried (-0.5 torr, 80 °C), and weighed (188 mg, 0.133 mmol, 38%, adjusted yield 48%49): TLC (silica gel, n-hexane-EtOAc, 5:1) Rₚ 0.70; IR (mineral oil) 3500 (w br, O-H), 1433 (m), 1257 (w, Si-CH₂), 1030 (m, Siₚc-0-Siₚc), 980 (m, Siₚc-0-Siₚc), 739 (s), 428 (m) cm⁻¹; NMR (200 MHz, pyridine-d₅, 5.0 x 10⁻³M, 20 °C) δ 9.32 (m, 1,4-S1OSiPcH), 9.21 (m, 1,4-HOSiPcH), 8.45 (m, 2,3-HOSiPcH), 8.38 (m, 2,3-S1OSiPcH), 0.51, (m, overlapping ε-CH₂, δ-CH₃), -0.04 (m, δ-CH₂), -0.44 (m, γ-CH₂), -1.96 (m, β-CH₂), -3.18 (m, α-CH₂). MS-HRFAB exact mass m/z calcd. for \(^{13}\text{C}C_{81}H_{72}N_{16}Si_{13}O_{3}\) (M)⁺: 1413.5315. Found:
1413.5240. Anal. Calcd for C₈₂H₇₂N₁₆Si₃O₃:  C, 69.66; H, 5.13; N, 15.85; Si, 5.96. Found:  C, 69.31; H, 4.92; N, 16.46; Si, 5.35. As obtained the compound was a blue-transmitting, purple-reflecting solid.

In a separate experiment a similarly prepared sample of the compound (197 mg) was chromatographed (Al₂O₃ V, Woelm, toluene slurry; dry loading, Celite, CH₂Cl₂; toluene-CHCl₃ solutions; filtration; p). The product was washed with EtOH (50 mL), dried (2 x 10⁻³ torr, 90 °C), weighed (134 mg), and shown to be pure (n-C₆H₁₃)₃SiO(SiPcO)₂H by NMR spectroscopy.

The compound is soluble in CHCl₃, warm pyridine, and warm toluene, and insoluble in hexane and EtOH.

C₁₈H₃₇(C₄H₉)₂SiO(SiPcO)₂H. A mixture of C₁₈H₃₇(C₄H₉)₂Si-O-Si(C₄H₉)₂C₁₈H₃₇ (chromatographed, 1.01 g, 0.526 mmol) and toluene (130 mL) was dried by distillation (30 mL of distillate) and cooled. Under Ar, Cl₃CC(O)OH (recrystallized⁴⁸, 186 mg, 1.14 mmol) was added to the solution, and the mixture was stirred 3 h and filtered. The solid was washed with toluene (100 mL) and the washings and filtrate were combined and evaporated to a solid (~0.5 torr, 0 °C). This was washed with n-hexane (300 mL, sonication).

The washed solid was mixed with a pyridine-H₂O solution (4:1, 125 mL) and the resulting suspension was stirred for 6 h while being warmed (50 °C) and then filtered. The solid was washed with a H₂O-EtOH solution (1:1, 100 mL), air dried, and weighed (528 mg).

A portion of the washed solid (450 mg) was extracted with CH₂Cl₂ (100 mL) and the extract was evaporated to dryness (~80 torr, room
temperature). The residue was washed with n-hexane (100 mL), dried (-0.5 torr, 78 °C), and weighed (370 mg, 0.242 mmol, 46%, adjusted yield 54%): TLC (silica gel, n-hexane-EtOAc, 5:1) Rf 0.74; IR (mineral oil) 3500 (w br, O-H), 1524 (m), 1341 (m), 1020 (m, Si_{cap}-O-Si_{PC}), 980 (m, Si_{PC}-O-Si_{PC}), 837 (w), 740 (s), 540 (m) cm\(^{-1}\); NMR (200 MHz, C\(_6\)D\(_6\), 2.6 x 10\(^{-3}\)M, 70 °C) \(\delta\) 8.99 (m, 1,4-SiOSiPc\(\text{H}\)), 8.72 (m, 1,4-HOSiPc\(\text{H}\)), 7.91 (m, overlapping 2,3-HOSiPc\(\text{H}\) and 2,3-SiOSiPc\(\text{H}\)), 1.32 (m, \(\theta-\rho-\text{CH}_2\)), 1.06 (m, \(\eta-\text{CH}_2\)), 0.90 (m, \(\tau-\text{C}_18-\text{CH}_3\)), 0.52 (m, \(\epsilon-\text{CH}_2\)), -0.01 (m, \(\delta-\text{CH}_2\)), -0.31 (t, \(\tau-\text{C}_4-\text{CH}_3\)), -0.50 (m, \(\gamma-\text{C}_18\text{CH}_2, \gamma-\text{C}_4-\text{CH}_2\)), -2.02 (m, \(\beta-\text{C}_18-\text{CH}_2, \beta-\text{C}_4-\text{CH}_2\)), -3.32 (m, \(\alpha-\text{C}_18-\text{CH}_2, \alpha-\text{C}_4-\text{CH}_2\)) (\(\tau-\text{CH}_2\) obscured by \(\tau-\text{C}_18-\text{CH}_3\)). Anal. Calcd for C\(_{90}\)N\(_{16}\)H\(_{88}\)Si\(_{30}\): C, 70.84; N, 14.69; H, 5.81; Si, 5.52. Found: C, 70.35; N, 15.32; H, 5.42; Si, 5.49. As obtained the compound was a blue-transmitting and purple-reflecting solid.

The compound is soluble in pyridine, CHCl\(_3\), hot toluene, and hot benzene, and insoluble in hexane, EtOH, and diethyl ether.

**Triple Ring Well-Characterized Axially Unsymmetrically Substituted Silicon Phthalocyanines**

\((n-\text{C}_6\text{H}_{13})_3\text{SiO(SiPcO)}_3\text{C(O)CCl}_3\). A mixture of \((n-\text{C}_6\text{H}_{13})_3\text{SiO(SiPcO)}_3\text{Si}(n-\text{C}_6\text{H}_{13})_3\) (chromatographed, 1.48 g, 0.657 mmol) and toluene (600 mL) was dried by distillation (100 mL of distillate) and cooled. Under dry Ar, Cl\(_3\)CC(O)OH (recrystallized\(^{68}\), 139 mg, 0.851 mmol) was added to the remainder, and the resulting mixture was stirred for 3 h and filtered. The filtrate was evaporated to dryness (-0.5 torr, 0 °C), and the residue was quickly washed with dry
n-hexane twice (1.5 L, 1L, hot), dried (10^{-3} torr, 30 °C), and weighed (801 mg).

A portion of the solid (244 mg) was mixed with a dry toluene-triethylamine solution (250:0.3, 250 mL) and the resulting suspension was stirred for 2 h and filtered. The filtrate was evaporated to dryness (-0.5 torr, 0 °C), and the residue was washed with dry n-hexane (200 mL, sonication), dried (10^{-3} torr, 30 °C), and weighed (107 mg, 0.0506 mmol, 7.7%, adjusted yield 25%): IR (mineral oil) 1730 (m, C=O), 1339 (s), 1018 (m, Si-O-Si), 848 (w), 735 (s), 538 (m) cm^{-1}; NMR (200 MHz, pyridine-d5, 2.4 x 10^{-3}M, 20 °C) δ 8.86 (m, overlapping terminal 1,4-COSiPcH and 1,4-SiOSiPcH), 8.77 (m, inner 1,4-SiPcH), 8.50 (m, inner 2,3-SiPcH), 8.17 (m, overlapping terminal 2,3-COSiPcH and 2,3-SiOSiPcH), 0.34 (m, overlapping ε-CH₂ and ε-CH₃), -0.28 (m, δ-CH₂), -0.75 (m, γ-CH₂), -2.38 (m, β-CH₂), -3.61 (m, α-CH₂). Anal. Calcd for C_{116}H_{24}N_{24}H_{87}Si_{4}Cl_{3}O_{5}: C, 65.85; H, 4.14; Cl 5.03. Found: C, 66.22; H, 4.08; Cl, 5.10. As obtained the compound was a blue-transmitting and purple-reflecting solid.

The compound is soluble in pyridine and chloroform, slightly soluble in toluene and benzene, and insoluble in hexane and EtOH. It decomposes to (n-C₆H₁₃)₃SiO(SiPcO)₃H when in contact with wet solvents, silica gel, and alumina.

Triple Ring NMR- or IR-Characterized Axially Unsymmetrically Substituted Silicon Phthalocyanines

(n-C₆H₁₃)₃SiO(SiPcO)₃H. A mixture of (n-C₆H₁₃)₃SiO(SiPcO)₃C(O)CCl₃ (207 mg, 0.0978 mmol), pyridine (200 mL), and H₂O (20 mL)
was stirred 12 h and filtered. The solid was washed with EtOH (100 mL), air dried, and weighed (145 mg, 0.0736 mmol, 75%): IR (mineral oil) 3515 (w br, O-H), 1340 (m), 1294 (m), 1126 (m), 985 (m, Si-O-Si), 913 (m), 735 (s), 537 (w) cm⁻¹. As obtained the compound was a blue-transmitting, purple-reflecting solid.

The compound is very slightly soluble in pyridine and CHCl₃, and insoluble in toluene, benzene, and hexane.

C₁₈H₃₇(C₄H₉)₂S₁₀(SiPcO)₃C(O)CCl₃. A mixture of C₁₈H₃₇(C₄H₉)₂S₁₀(SiPcO)₃Si(C₄H₉)₂C₁₈H₃₇ (chromatographed, 1.42 g, 0.573 mmol) and toluene (550 mL) was dried by distillation (90 mL of distillate) and cooled. Under dry Ar, C₁₃CC(O)OH (recrystallized⁴⁸, 116 mg, 0.710 mmol) was added to the solution and the resulting mixture was stirred for 2 h and filtered. The filtrate was evaporated to dryness (~0.5 torr, 0 °C), and the residue was quickly washed with dry n-hexane twice (200 mL, 200 mL, hot). The solid was dried (~0.5 torr, 55 °C), and weighed (836 mg).

A portion of this (504 mg) was mixed with a dry toluene-triethylamine solution (500:0.6, 500 mL), and the mixture was stirred for 3 h and filtered. The filtrate was evaporated to dryness (~0.5 torr, 0 °C), and the residue was washed with dry n-hexane (300 mL, sonication), dried (~0.5 torr, 55 °C), and weighed (279 mg, 0.125 mmol, 22%, adjusted yield 36%⁴⁹): IR (mineral oil) 1730 (m, C=O), 1290 (m), 1012 (m, Si-O-Si), 848 (w), 734 (s), 533 (m) cm⁻¹; NMR (200 MHz, pyridine-d₅, 2.6 x 10⁻³M, 20 °C) δ 8.87 (m, overlapping terminal 1,4-COSiPC₃H and 1,4-SiOSiPC₃H), 8.77 (m, inner 1,4-SiPC₃H), 8.50 (m, inner 2,3-SiPC₃H), 8.17 (m, overlapping terminal 2,3-COSiPC₃H)
and 2,3-SiOSiPcH), 1.31 (m, \( \theta - \rho \)-CH\(_2\)), 0.92 (m, \( \tau - C_{18} \)-CH\(_3\)), 0.76 (m, 
\( \xi \)-CH\(_2\)), 0.38 (m, \( \epsilon \)-CH\(_2\)), -0.23 (m, \( \delta \)-CH\(_2\)), -0.50 (t, \( \tau - C_{4} \)-CH\(_3\)), -0.74
(m, \( \gamma - C_{18} \)-CH\(_2\), \( \gamma - C_{4} \)-CH\(_2\)), -2.39 (m, \( \beta - C_{18} \)-CH\(_2\), \( \beta - C_{4} \)-CH\(_2\)), -3.62 (m, 
\( \alpha - C_{18} \)-CH\(_2\), \( \alpha - C_{4} \)-CH\(_2\)) (\( \eta - \)CH\(_2\) obscured by \( \tau - C_{18} \)-CH\(_3\)). As obtained the compound was a blue-transmitting, purple-reflecting solid.

The compound is soluble in pyridine and CHCl\(_3\), slightly soluble in toluene and benzene, and insoluble in hexane and EtOH. It decomposes to \( C_{18}H_{37}(C_{4}H_{9})_{2}SiO(SiPcO)_{3}H \) when in contact with wet solvents, silica gel, and alumina.

**Single Ring NMR-Characterized Axially Unsymmetrically Substituted Phthalocyanines Containing Other Metals**

\( C_{18}H_{37}(C_{4}H_{9})_{2}SiOAlPc \). A mixture of AlPcOH\(^{55} \) (0.708 g, 1.27 mmol), tributylamine (2.0 mL, 8.4 mmol), and pyridine (130 mL) was dried by distillation (20 mL of distillate), and cooled.

\( C_{18}H_{37}(C_{4}H_{9})_{2}SiCl_{51} \) (3.3 g, 7.7 mmol) was added to the remainder, and the resulting suspension was refluxed 0.5 h, cooled, and filtered. The filtrate was evaporated to a viscous suspension (\(-80\) torr, 70 \(^{\circ}\)C), and the suspension was washed with pentane (100 mL, 0 \(^{\circ}\)C) and EtOH (150 mL), air dried, oven dried (\(-80\) torr, 85 \(^{\circ}\)C), and weighed (615 mg, 0.646 mmol, 51\%): IR (mineral oil) 1520 (m), 1340 (s), 1295 (m), 1169 (m), 1125 (s), 1084 (s br), 1048 (sh, Si-O-Al), 909 (m), 737 (s), 522 (m) cm\(^{-1}\); NMR (200 MHz, C\(_6\)D\(_6\), 60 \(^{\circ}\)C) \( \delta \) -9.21 (m, 1,4-AlPcH), -7.87 (m, 2,3-AlPcH), --2.08 (m, \( \alpha - C_{18} \)-CH\(_2\), \( \alpha - C_{4} \)-CH\(_2\)). As obtained the compound was a blue-transmitting, blue-reflecting powder.
The compound is soluble in CHCl₃, pyridine, and hot toluene, and insoluble in hexane and EtOH. It decomposes when in contact with silica gel and alumina, and when heated with wet solvents.

(n-C₆H₁₃)₃SiOGePcOH. A cold (0 °C) solution of (n-C₆H₁₃)₃SiOGePcCH₃ (0.654 g, 0.727 mmol) and toluene (3 L) was irradiated with direct sunlight for 1 h and filtered. The filtrate was evaporated to dryness (~0.05 torr, 0 °C), and the residue was chromatographed (Al₂O₃ V, Woeim, hexanes slurry; solvent loading, toluene; CHCl₃), and weighed (0.210 g, 0.214 contained mmol, 29% contained yield): NMR (200 MHz, CDCl₃, 20 °C) δ ~9.15 (m, 1,4-GePcH), ~8.21 (m, 2,3-GePcH), ~2.59 (m, α-CH₂). As judged on the basis of its NMR spectrum the product contained ~8% impurities. It was a blue-transmitting, blue-reflecting powder.

The compound is soluble in CHCl₃, pyridine, and toluene, slightly soluble in hexanes, and insoluble in EtOH.

Double Ring Well-Characterized Axially Unsymmetrically Substituted Phthalocyanines Containing Two Metals

C₁₈H₃₇(C₄H₉)₂SiOSiPcOAlPc. A mixture of dry C₁₈H₃₇(C₄H₉)₂SiOAlPc (387 mg, 0.407 mmol), dry C₁₈H₃₇(C₄H₉)₂SiOSiPcOH (994 mg, 1.03 mmol), and dry p-xylene (200 mL) was refluxed for 2.5 h and filtered hot. The filtrate was evaporated to a solid (~1 torr, 30 °C).

The solid was extracted with hexanes three times (~100 mL each time, Soxhlet, cellulose, medium, 6 h each time, grinding each time). It was then extracted with dry benzene (HPLC grade, 15 mL, Soxhlet,
cellulose, medium, 4 h), and the extract was cooled (5 °C). The resulting suspension was separated by centrifugation while cool, and the solid was washed with benzene (HPLC grade, 5 mL, sonication, centrifugation, 0 °C), and with n-hexane (HPLC grade, 15 mL, sonication, centrifugation, 0 °C). It was then air dried, ground to a fine powder, vacuum dried (-0.5 torr, 78 °C), and weighed (128 mg, 0.0849 mmol, 21%): IR (mineral oil) 1618 (m), 1340 (s), 1171 (m), 1053 (m), 739 (s), 580 (m), 420 (m) cm⁻¹; NMR (200 MHz, C₆D₆, 2.5 x 10⁻³ M, 60 °C) δ 8.80 (m, 1,4-SiPcH), 8.59 (m, 1,4-AlPcH), 7.77 (m, overlapping 2,3-AlPcH and 2,3-SiPcH), 1.32 (m, -ρ-CH₂), 0.93 (m, t-C₁₈-CH₃), 0.85 (m, ˚-CH₂), 0.50 (m, ε-CH₂), -0.01 (m, δ-CH₂), -0.31 (t, t-C₄-CH₃), -0.48 (m, γ-C₁₈-CH₂, γ-C₄-CH₂), -1.93 (m, β-C₁₈-CH₂, β-C₄-CH₂), -3.15 (m, α-C₁₈-CH₂, α-C₄-CH₂) (η-CH₂ obscured). MS-HRFAB exact mass m/z calcd. for 1₃C₈₉H₈₇N₁₆Si₂AlO₂ (M)+: 1507.6585. Found: 1507.6585. Anal. Calcd for C₉₀H₈₇N₁₆Si₂AlO₂: C, 71.69; H, 5.82; N, 14.86. Found (average of four determinations): C, 72.20 ± 0.25; H, 5.74 ± 0.12; N, 15.27 ± 0.09. As obtained the compound was a blue-transmitting, red-reflecting solid.

The compound is soluble in CHCl₃, pyridine, hot toluene, and hot benzene, and insoluble in hexane, EtOH, and diethyl ether. It decomposes when in contact with silica gel and alumina, and when heated in wet solvents. Solutions and suspensions of the compound are difficult to filter.

(n-C₆H₃)₃SiOSiPcGePcOH. An intimate mixture of CH₃GePcOH (2.17 g, 3.52 mmol) and (n-C₆H₃)₃SiOSiPcOH (prepared by photolysis)₃S₅₃, 3.15 g, 3.67 mmol) was suspended in 1,2,4-trimethylbenzene
(150 mL), refluxed for 4 h (p) and filtered (p). The solid was washed with toluene (p), and the washings and the filtrate were combined (p) and evaporated to a viscous suspension (~5 torr, 70 °C, p). The suspension was washed with pentane (100 mL, p), and the resulting solid was dried (~80 torr, 85 °C) and weighed (3.91 g).

A cold (0 °C) solution of this solid (3.14 g) and toluene (3 L) was irradiated with direct sunlight for 75 min, and the resulting solution was evaporated to dryness (~5 torr, 30 °C). The solid was dried (~80 torr, 85 °C) and weighed (2.77 g).

A portion of the solid (1.46 g) was chromatographed (Al2O3 V, Woelm, hexanes slurry; dry loading, Celite, CH2Cl2; toluene-CHCl3 (EtOH stabilized) solutions; filtration; p), and weighed (839 mg).

Some of the resultant (394 mg) was rechromatographed (Al2O3 V, Woelm, toluene slurry; solvent loading, toluene-CHCl3 (5:1); toluene-CHCl3 (EtOH stabilized) solutions; filtration; p) and weighed (141 mg). Part of this (0.072 g) was mixed with a pyridine-H2O solution (4:1, 25 mL), and the resulting suspension was stirred for 1 h while being warmed (60 °C) and then filtered. The solid was washed with H2O, dried (~80 torr, 85 °C), and weighed (0.059 g, 0.040 mmol, 1.1%, adjusted yield 9.1%49): IR (mineral oil) 3500 (w br, O=H), 1250 (w, Si-CH2), 1025 (m, Si-O-Si), 940 (m, Si-O-Ge) cm⁻¹; NMR (200 MHz, CDCl3, 4.1 x 10⁻³M, 20 °C) δ 8.92 (m, 1,4-SiPcH), 8.87 (m, 1,4-GePcH), 8.31 (m, 2,3-GePcH), 8.25 (m, 2,3-SiPcH), 0.42 (m, ε-CH2, τ-CH3), -0.20 (m, δ-CH2), -0.65 (m, γ-CH2), -2.29 (m, β-CH2), -3.53 (m, α-CH2); MS-FAB m/z 1442 (M - OH)⁺, 1143 (M - OSI(C6H13)3)⁺, 840 (M - OGePcOH)⁺, 603 (M - OSiPcOSi(C6H13)3)⁺, 558 (M - OGePcOSi(C6H13)3)⁺.
Anal. Calcd for C_{82}H_{72}N_{16}Si_{2}GeO_{3}: C, 67.54; H, 4.98; Ge, 4.98.

Found: C, 67.12; H, 5.03; Ge, 4.52. As obtained the compound was a blue-transmitting, blue-reflecting solid.

The compound is soluble in pyridine, CHCl₃, and warm toluene, and insoluble in hexanes, EtOH, and diethyl ether. It undergoes self-condensation to (n-C₆H₄₃)₃SiOSiPcO(GePcO)₂SiPcOSi(n-C₆H₄₃)₃ at ~150 °C when in solution.

C_{18}H_{37}(C₄H₉)₂SiOSiPcOGePcOH. A cold (0 °C) solution of C_{18}H_{37}(C₄H₉)₂SiOSiPcOGePcCH₃ (604 mg, 0.385 mmol) and toluene (600 mL) was irradiated with direct sunlight for 1 h, and the resulting solution was evaporated to dryness (~1 torr, 0 °C), air dried, and weighed (597 mg).

A portion of this product (588 mg) was chromatographed (Al₂O₃ V, Fisher, toluene slurry; solvent loading, toluene (100 mL); toluene-chloroform (EtOH stabilized) solutions; filtration; p) and weighed (316 mg). Part of this (210 mg) was mixed with a pyridine-H₂O solution (2.5:1, 70 mL), and the resulting suspension was stirred for 1.5 h while being warmed (60 °C) and then filtered. The solid was washed with a pyridine-H₂O solution (1:2, 100 mL) and extracted with CH₂Cl₂ (100 mL). The extract was evaporated to dryness (~80 torr, 20 °C), and the residue was dried (0.05 torr, 78 °C) and weighed (146 mg, 0.0930 mmol, 24%, adjusted yield 37449): IR (mineral oil) 3490 (br w, 0-H), 1525 (m), 1339 (s), 1019 (m, Si-O-Si), 940 (m, Ge-O-Si), 735 (s) cm⁻¹; NMR (200 MHz, CDC1₃, 3.2 x 10⁻³M, 20 °C) δ 8.96 (m, overlapping 1,4-SiPcH and 1,4-GePcH), 8.34 (m, 2,3-GePcH), 8.28 (m, 2,3-SiPcH), 1.32 (m, θ-ρ-CH₂), 0.92 (m, t-C₈H₃), 0.79 (m, γ-CH₂),
0.43 (m, \(\epsilon\)-CH₂), -0.19 (m, \(\delta\)-CH₂), -0.44 (t, \(\epsilon\)-C₄-CH₃), -0.66 (m, \(\gamma\)-C₁₈-CH₂, \(\gamma\)-C₄-CH₂), -2.27 (m, \(\beta\)-C₁₈-CH₂, \(\beta\)-C₄-CH₂), -3.49 (m, \(\alpha\)-C₁₈-CH₂, \(\alpha\)-C₄-CH₂) \((\eta\)-CH₂ obscured); MS-FAB m/z 1554 (M-OH)+, 1143 (M - OSi(C₄H₉)₂C₁₈H₃₇)+, 952 (M - OGePcOH)+, 603 (M - OSiPcOSi(C₄H₉)₂C₁₈H₃₇)+, 558 (M - OGePcOSi(C₄H₉)₂C₁₈H₃₇)+. Anal. Calcd for C₉₀H₈₈N₁₆S₁₂GeO₃: C, 68.83; H, 5.65; Ge, 4.62. Found: C, 68.91; H, 5.72; Ge, 4.61. As obtained the compound was a blue-transmitting, blue-reflecting powder.

The compound is soluble in pyridine, CHCl₃, and warm toluene, and insoluble in hexanes, EtOH, and diethyl ether. It undergoes self-condensation to C₁₈H₃₇(C₄H₉)₂SiOSiPcO(GePcO)₂SiPcO-Si(C₄H₉)₂C₁₈H₃₇ at -150 °C when in solution.

Double Ring NMR-Characterized Axially Unsymmetrically Substituted Phthalocyanines Containing Two Metals

\((n-C₆H₁₃)₃SiOSiPcOAlPc\). An intimate mixture of dry \((n-C₆H₁₃)₃SiOSiPcOH\) (prepared by photolysis\(^{53}\), 314 mg, 0.366 mmol), dry AlPcOH\(^{55}\) (216 mg, 0.388 mmol), and distilled 1,2,4-trimethylbenzene (15 mL) was refluxed for 4 h and slowly cooled. The resulting suspension was filtered, and the solid was washed with toluene (100 mL) and air dried (303 mg).

A portion of the solid (298 mg) was recrystallized from dry p-xylene (20 mL), and the solid was air dried, and weighed (161 mg, 0.115 mmol, 31%, adjusted yield 32%\(^{69}\)). IR (mineral oil) 1613 (w), 1516 (m), 1335 (s), 1165 (m), 1121 (s), 1049 (m), 735 (s), 578 (w) cm⁻¹; NMR (200 MHz, C₆D₆, 70 °C) \(\delta\) -8.93 (m, 1,4-SiPcH), -8.82 (m,
1,4-AlPcH), -7.89 (m, overlapping 2,3-SiPcH, 2,3-AlPcH), -3.02 (m, α-CH₂). The product gave an impurity resonance at δ 1.3. It was a blue-transmitting, red-reflecting solid.

The compound is slightly soluble in pyridine, CHCl₃, hot toluene, and hot benzene, and insoluble in DMSO and hexanes. It decomposes when in contact with silica gel and alumina and when heated in wet solvents. Solutions and suspensions of the compound are difficult to filter.

An alternative isolation method for compounds of this type also was developed (see C₁₈H₃₇(C₆H₉)₂SiOSiPcOAlPc, p 36).

Triple Ring NMR-Characterized Axially Unsymmetrically Substituted Phthalocyanines Containing Two Metals

(n-C₆H₁₃)₃SiOSiPcOGePcOGePcCH₃. An intimate mixture of (n-C₆H₁₃)₃SiOSiPcOGePcOH (52 mg, 0.036 mmol) and HOGePcCH₃ (23 mg, 0.037 mmol) was refluxed in 1,2,4-trimethylbenzene (5 mL) for 2 h (p), and the resulting suspension was cooled (p) and filtered (p). The solid was washed with toluene (50 mL, p), and the washings and the filtrate were combined (p), evaporated to dryness (~80 torr, 70 °C, p), and weighed (40 mg).

A similarly prepared product (140 mg) was chromatographed (Al₂O₃ III, Woelm, CCl₄ slurry; dry loading, Celite, CH₂Cl₂; hexanes-toluene solutions, toluene-CHCl₃ solution; filtration; p) and weighed (23 mg): NMR (200 MHz, CDCl₃, 20 °C) δ 8.55 (m, terminal 1,4-Si or GePcH), 8.49 (m, terminal 1,4-Si or GePcH), 8.36 (m, overlapping inner 1,4-GePcH and inner 2,3-GePcH), 8.10 (m, terminal 2,3-Si or
GePcH), 8.02 (m, terminal 2,3-Si or GePcH), 0.27 (m, overlapping ε-CH₂, τ-CH₃), -0.45 (m, δ-CH₂), -0.93 (m, γ-CH₂), -2.67 (m, β-CH₂), -3.92 (m, α-CH₂), -8.01 (s, Ge-CH₃). As judged on the basis of its NMR spectrum the product contained ~10% impurities. It was a blue-transmitting, blue-reflecting powder.

The compound is soluble in CHCl₃, pyridine, and toluene, and insoluble in hexane and EtOH. It is photosensitive when in solution.

(n-C₆H₁₃)₃SiOSiPcOGePcOSiPcCH₃. An intimate mixture of (n-C₆H₁₃)₃SiOSiPcOGePcOH (547 mg, 0.375 mmol) and HOSiPcCH₃ (218 mg, 0.381 mmol) was refluxed in 1,2,4-trimethylbenzene for 70 min (p), and the resulting suspension was cooled (p), and filtered (p). The solid was extracted with CHCl₃ (100 mL, p), and the extract and filtrate were combined (p), evaporated to dryness (~80 torr, 70 °C, p) and weighed (514 mg).

A portion of the product (220 mg) was chromatographed (Al₂O₃ III, Woelm, hexanes slurry; dry loading, Celite, CH₂Cl₂; hexanes-toluene solutions; filtration; p) and weighed (22 mg, 0.010 contained mmol, 2.7% contained yield, adjusted contained yield 6.5%): NMR (200 MHz, CDCl₃, 20 °C) δ 8.50 (m, terminal 1,4-SiPcH), 8.40 (m, 1,4-GePcH), 8.32 (m, 2,3-GePcH), 8.04 (m, terminal 2,3-SiPcH), 0.26 (m, overlapping ε-CH₂, τ-CH₃), -0.46 (m, δ-CH₂), -0.93 (m, γ-CH₂), -2.65 (m, β-CH₂), -3.92 (m, α-CH₂), -8.84 (s, SiPc-CH₃). As judged on the basis of its NMR spectrum, the product contained ~5% of a dimeric phthalocyanine impurity. It was a blue-transmitting, blue-reflecting powder.

The compound is soluble in CHCl₃, pyridine, and toluene, and
insoluble in hexanes and EtOH. It is photosensitive when in solution.

\((\text{C}_6\text{H}_{13})_3\text{SiOSiPcOGePcOSiPcOH}\). A solution of \((\text{C}_6\text{H}_{13})_3\text{SiOSiPcOGePcOSiPcCH}_3\) (19 mg, 0.0090 contained mmol) in toluene (400 mL) was irradiated with direct sunlight for 1 h and the resulting suspension was filtered. The filtrate was evaporated to dryness (-80 torr, 70 °C), and the residue was weighed (18 mg, 0.0085 contained mmol, 94%):

NMR (200 MHz, CDCl\(_3\), 20 °C) \(\delta\ ~8.48\) (m, overlapping terminal 1,4-SiOSiPcH and 1,4-HOSiPcH), \(\sim 8.39\) (m, 1,4-GePcH), \(\sim 8.29\) (m, 2,3-GePcH), \(\sim 8.02\) (m, overlapping terminal 2,3-SiOSiPcH and 2,3-HOSiPcH), \(\sim 3.91\) (m, \(\alpha\)-CH\(_2\)). As judged on the basis of its NMR spectrum, the product retained the dimeric impurity in the starting material.

The compound is a blue-transmitting, blue-reflecting powder. It is slightly soluble in CHCl\(_3\), pyridine, and toluene, and insoluble in hexanes and EtOH.

Other Phthalocyanines

AlPc(Cl)\(_{16}\)(Cl). Under N\(_2\), a mixture of tetrachlorophthalonitrile (1.02 g, 3.84 mmol), sublimed AlCl\(_3\) (463 mg, 3.47 mmol), and dry, deoxygenated quinoline (17 mL) was heated to reflux over a 30 minute period and then refluxed for an additional hour. The resulting suspension was cooled slowly and filtered. The solid was washed with MeOH (200 mL), dried \((10^{-3}\ \text{torr}, 120 \, ^\circ\text{C})\), and weighed (245 mg, 0.218 mmol, 23%): IR (mineral oil) 1507 (m), 1390 (m), 1213 (m), 1080 (m), 949 (s), 612 (m), 519 (m), 470 (m, Al-Cl) cm\(^{-1}\); MS-LD \(m/z\) 1124.4 ± 1.8 (M\(^+\)), 1087.8 ± 1.8 (M-Cl\(^+\)). As obtained the compound
was a green-transmitting, blue-green reflecting crystalline solid.

The compound is not soluble in a variety of common organic solvents.

GaPc(Cl)_{16}(Cl). Under N\textsubscript{2}, a mixture of tetrachlorophthalonitrile (7.60 g, 28.6 mmol), GaCl\textsubscript{3} (5.0 g, 28 mmol), and dry deoxygenated 1-chloronaphthalene (60 mL) was heated to reflux over a 30 minute period and then refluxed for an additional 30 min. The resulting suspension was slowly cooled and filtered. The solid was washed with toluene (200 mL), acetone (100 mL), air dried, and weighed (429 mg, 0.367 mmol, 5%): IR (mineral oil) 1493 (m), 1390 (m), 1210 (m), 1085 (m), 943 (s), 600 (m), 509 (s), 352 (w, Ga-Cl) cm\textsuperscript{-1}. As obtained the compound was a green-transmitting, blue-green reflecting crystalline solid.

The compound is not soluble in a variety of common organic solvents.
LANGMUIR-BLODGETT DATA COLLECTION

Apparatus

Film Balance. A modified Model P MGW Lauda continuous compression film balance (MGW Lauda, Lauda, W. Germany; distributed by Brinkmann Instruments, Inc.) was used to obtain the pressure-area isotherms, Figure 6. It was equipped with a custom Teflon-coated trough (0.6 x 15 x 70 cm) and a custom Teflon-coated moving barrier. The potentiometer of the moving barrier system yielded the surface area data, and the inductive linear transducer of the floating barrier system yielded the surface pressure.

A vibration isolation table was used to reduce vibrations transmitted to the balance. To control the temperature of the balance, a Model 90 Fisher circulating water bath was used. A class 10 laminar flow area located in a class 100 clean room having a relative humidity of 35-40% (designed by Environmental Air Control, Inc., Hagerstown, MD) was used to provide the environment for the balance.

Computer. An IBM-PC computer (International Business Machines Corp., Armonk, NY) was utilized to control the balance and to record the output data. It was connected to the balance with a previously described interface and was run with previously described software.
Water Purification System. A custom water purification system was used to supply water for the balance. This system had water softening, filtration-adsorption, and reverse osmosis-deionization sections. In addition it had distillation, storage, and UV sterilization sections. Details of the system have been given elsewhere.57-59

Water Quality Equipment. A Model PM-512 Sybron/Barnsted resistivity meter (Barnsted-Thermolyne Corp., Dubuque, IA) was used to measure the resistivity of the purified water, and a Model 21 Fisher Tensiomat was used to measure the surface tension of the purified water.

Glassware, Syringe, and Micropipeter. Class A Pyrex volumetric flasks with glass stoppers (Corning Glass Works, Corning, NY) were used in the preparation of the amphiphile solutions. A 100 μL Hamilton Gastight syringe (Hamilton Co., Reno, NV) equipped with a Hamilton 90° beveled tip was used to dispense the amphiphile solutions in the pressure-area isotherm experiments. A 100 μL Drummond Digital Microdispenser (Drummond Scientific Co., Broomall, PA) equipped with glass micropipets was used to dispense the amphiphile solutions in the compressive creep studies.

Water. The water used in the trough had been distilled <3 h before use and had a resistivity of ≥18.0 MΩ. One sample of the water had a surface tension of 72.4 mN/m.

Chemicals. The stearic acid (Fluka Chemical Corp., Ronkonkoma, NY) was >99.5%, the H₂SO₄ (Fisher) was reagent grade, the CHCl₃ (Aldrich) was amylene stabilized HPLC grade, and the CH₂Cl₂ was HPLC
grade (Aldrich). Before use the phthalocyanines were redried (−0.5 torr, 55 °C).

**Apparatus Preparation**

**Glassware, Syringe, and Micropipets.** The glassware was cleaned by soaking it in a freshly prepared H₂SO₄-Nochromix (Godax Laboratories, NY, NY) bath⁶⁰ (−6 h), thoroughly rinsing it in purified water, soaking it in a freshly prepared EtOH-KOH bath⁶⁰ (~30 min), thoroughly rinsing it in purified water, and drying it in a Model 1620D VWR class 100 drying oven (VWR Scientific, Inc., San Francisco, CA). The syringe and the micropipets were cleaned by flushing them with CHCl₃.

**Trough Filling.** All wettable surfaces of the trough, the moving barrier, and the floating barrier were first carefully wiped with class 100 cloths (Berkshire Corp., Great Barrington, MA) wetted with CH₂Cl₂. Then trough was carefully filled to overflowing with water and aspirated dry. Finally, it was filled with the subphase medium to a height ~2 mm above its rim.

**Subphase Temperature Adjustment.** The circulating bath was adjusted to give a subphase temperature of 20.0 ± 0.2 °C.

**Floating Barrier Adjustment.** After the trough had been filled, the floating barrier was positioned with Teflon forceps so that it appeared to float without binding. Its ability to actually do so was verified by zeroing the linear transducer, momentarily deflecting the barrier with the forceps, and observing the pressure reading after the barrier had returned to rest. If the pressure was less than
±0.2 mN/m, the barrier was considered to be operational.

Pressure System Linearity and Calibration. The linearity of the output of the pressure measurement system was tested by gathering voltage measurements for five known pressures (generated by known weights) and constructing a pressure-voltage curve. The curve was found to be linear by a least squares fit of the data points (0.99 correlation) over the pressure range of interest (0-60 mN/m).

Before each experiment a pressure-voltage calibration curve based on the use of one weight was constructed. The pressure measurement system is estimated by Lauda to have a sensitivity of 0.1 mN/m and an uncertainty in the absolute values of measured film pressures of ±5%.

Area System Linearity and Calibration. The linearity of the output of the area measurement system was tested by gathering voltage measurements for a series of known positions of the moving barrier and constructing an area-voltage calibration curve. The curve was found to be linear by a least squares fit of the data points (0.99 correlation) over an area sufficiently large to permit full compression isotherms of all compounds studied (0-300 cm²).

Before each experiment the position-voltage readings for several positionings of the moving barrier were checked against the calibration curve. The uncertainty in the area measurement was estimated to be ±2% when the barriers were 5 cm apart and ±0.5% when the barriers were 20 cm apart.

Solvent Residue Interference Test. The presence of an interference from residues left by evaporation of the spreading solvent
was tested for by spreading a typical volume of the CHCl₃ on the
trough, and moving the moving barrier to zero while reading the
pressure. Within experimental error, no change in pressure was
detected.

Trough Sealing Test. The integrity of the trough sealing system
was tested by spreading a small amount of talc on a stearic acid film
under compression and searching for talc outside the enclosed area.
No talc was found.

Experimental Procedures

Solution Preparation. A small sample of the amphiphile (10.0-
15.0 mg) was transferred from an aluminum foil wrapped sample vial to
an aluminum foil wrapped glass weighing boat, the weight of the
sample was determined to ±0.1 mg, and the sample was transferred to
an aluminum foil wrapped volumetric flask (25 or 50 mL). Then the
flask was filled with the CHCl₃ and the weight and the temperature of
the CHCl₃ were determined. Next, the contents of the flask were
mixed (sonication), and the solution was checked for suspended par-
ticles with a low power microscope. If none were found, the solution
was accepted and its concentration was calculated.

The solutions of \((n-C₆H₁₃)₃SiO(SiPcO)₃C(0)CCl₃\) and
\(C₁₈H₃₇(C₄H₉)₂SiO(SiPcO)₃C(0)CCl₃\) were used immediately. Those solu-
tions of the other amphiphiles were used within a day.

Acquisition of Pressure-Area Isotherms. The balance was cleaned
and filled with H₂O in the case of the phthalocyanine experiments, or
0.01 N H₂SO₄ in the case of the stearic acid experiments. Then the
moving barrier was positioned to give a suitable surface area (>450 cm²), and ten or more portions of the amphiphile solution (total volume 49.6 ± 0.6μL) were placed on different parts of the water surface. Next, the bottom of the trough was searched for amphiphile solution droplets, and if none were found the experiment was continued by allowing the system to stand for at least 20 min. Finally, the film was compressed (16.2 cm²/min) and the pressure-area data were collected.

Acquisition of Compressive Creep Data. The balance was cleaned and filled with H₂O. Then the moving barrier was positioned to give a suitable surface area (>675 cm²) and five or more portions of the phthalocyanine solution (total volume 100-200 μL) were placed on different parts of the water surface. Next the bottom of the trough was searched for phthalocyanine droplets, and if none were found the experiment was continued by allowing the system to stand for at least 20 min. Finally, the film was brought to a given pressure and the area-time data were collected.
DISCUSSION OF COMPOUNDS SYNTHESIZED

Synthesis of Compounds of the Type $R_3SiO(SiPcO)_nSiR_3$

Mixtures of compounds of the type $R_2R'SiO(SiPcO)_nSiR'R_2$ where $R$ is alkyl, siloxy or $H$, $R'$ is alkyl, and $n$ is small have been prepared previously by four routes:

Route 1

$$SiPc(OH)_2 + HOSiPcOSiR_2R' \xrightarrow{\text{vacuum}} 300 \, ^\circ\text{C} \quad R_2R'SiO(SiPcO)_nSiR'R_2$$

(1)

Route 2

$$SiPc(OH)_2 + (R_2R'Si)_2NH \xrightarrow{\text{py}} -110 \, ^\circ\text{C} \xrightarrow{\text{NaOH, py-H}_2\text{O}} \text{reflux} \quad HO(SiPcO)_nH$$

$$\xrightarrow{(R_2R'Si)_2NH} \xrightarrow{\text{py}} R_2R'SiO(SiPcO)_nSiR'R_2$$

(2)

Route 3

$$SiPcCl_2 + KOCMe_3 \xrightarrow{\text{toluene-reflux}} \xrightarrow{\text{NaOMe-H}_2\text{O-reflux}} HO(SiPcO)_nH$$

$$\xrightarrow{\text{MeC(OSiMe_3)NSiMe_3}} \xrightarrow{\text{py}} Me_3SiO(SiPcO)_nSiMe_3$$

(3)
Route 4

\[
\begin{align*}
\text{SiPc(OH)}_2 + \text{SiPcCl}_2 & \xrightarrow{\text{(Bu)}_3\text{N, quinoline, reflux 15 min}} \text{H}_2\text{SO}_4 \xrightarrow{\text{1}} \text{HO(SiPcO)}_n\text{H} \\
& \xrightarrow{\text{2. NH}_4\text{OH}} \text{R}_3\text{SiCl} \\
& \xrightarrow{\text{pyridine}} R_3\text{SiO(SiPcO)}_n\text{SiR}_3^{52} 
\end{align*}
\]

(4)

In the present study stacked-ring oligomer mixtures of this type have been made by variations of Route 4:

Route 5

\[
\begin{align*}
\text{SiPc(OH)}_2 + \text{SiPcCl}_2 & \xrightarrow{\text{(Bu)}_3\text{N, quinoline, reflux 40 min}} \text{H}_2\text{SO}_4 \xrightarrow{\text{1}} \text{HO(SiPcO)}_n\text{H} \\
& \xrightarrow{\text{2. NH}_4\text{OH}} \text{R}_2\text{R'}\text{SiCl} \\
& \xrightarrow{\text{2-picoline}} R_2\text{R'}\text{SiO(SiPcO)}_n\text{SiR'R}_2 
\end{align*}
\]

(5)

Route 6

\[
\begin{align*}
\text{SiPc(OH)}_2 + \text{SiPcCl}_2 & \xrightarrow{\text{(Bu)}_3\text{N, quinoline, reflux 40 min}} \text{H}_2\text{SO}_4 \xrightarrow{\text{1}} \text{HO(SiPcO)}_n\text{H} \\
& \xrightarrow{\text{2. NH}_4\text{OH}} \text{R}_2\text{R'}\text{SiOH} \\
& \xrightarrow{\text{2-picoline}} R_2\text{R'}\text{SiO(SiPcO)}_n\text{SiR'R}_2 
\end{align*}
\]

(6)

where \( R = \text{C}_4\text{H}_9 \) and \( R' = \text{C}_{18}\text{H}_{37} \), or \( R = R' = \text{C}_6\text{H}_{13} \).

Route 1 is not attractive because it does not allow for adequate control of the oligomer formation process. Route 2 is not attractive because it requires silazanes that are not readily available. However, the results of exploratory work on the oligomerization of \( \text{SiNc(OH)}_2 \) (\( \text{Nc} \) = naphthalocyanine ligand) suggest that \((\text{Me}_3\text{Si})_2\text{NLi}\) can be used in a route like Route 2. Route 3 is unattractive because it
gives low yields of the higher oligomers. Routes 4-6 are reasonable but cumbersome.

Route 4 was examined by Dininny. He showed that short reaction times (−15 min) lead to products rich in dimer, and somewhat longer reaction times (−40 min) lead to products rich in trimer and tetramer. Additionally, he showed that still longer reaction times (−1 h) lead to a decrease in the total yield of soluble oligomers. Observations made in the present work with Routes 5 and 6 suggest that reaction time has a similar effect on them. The effects of reaction time on Route 4 and its apparent effects on Routes 5 and 6 are those that would normally be expected in oligomerizations.

On the basis of the information at hand, the yields of tetramer and pentamer appear to be smaller in Route 6 than in Route 5. This is attributed to a low reactivity of R₃SiOH with the tetramer and pentamer.

The solubility and column chromatographability of the oligomers with (C₆H₁₃)₃SiO and C₁₈H₃₇(C₄H₉)₂SiO end groups is good. While the trimers and tetramers with C₁₈H₃₇(C₄H₉)₂SiO end groups appear to be more soluble than their (C₆H₁₃)₃SiO analogues, they do not seem to be more chromatographable. This is understandable since both have enough solubility to be suitable for column chromatography and since neither interacts with the column in a strongly preferential manner.

Particular problems were met in trying to isolate the pentamers because the ends of the tetramer bands on the column overlapped with the pentamer bands. Since, as expected, the yield of the pentamers in the reaction mixtures was low, this problem proved to be signifi-
cant. No column chromatographic solution to it was found.

Clearly simpler and more efficient routes to individual oligomers are needed. Some work has been done indicating that these can be found. For example, Dininny showed that the reaction:

\[
2 \text{(C}_6\text{H}_{13})_3\text{SiOSiPCOH} \xrightarrow{\text{1,2,4-trimethylbenzene}} \text{reflux} \rightarrow \text{(C}_6\text{H}_{13})_3\text{SiO(SiPCO)}_2\text{Si(C}_6\text{H}_{13})_3
\]  

(7) takes place. In the present studies exploratory work showed that the reaction:

\[
\text{(C}_6\text{H}_{13})_3\text{SiOSiPCl} + \text{HOSiPCOSi(C}_6\text{H}_{13})_3 \xrightarrow{\text{pyridine}} \text{50 °C} \rightarrow \text{(C}_6\text{H}_{13})_3\text{SiO(SiPCO)}_2\text{Si(C}_6\text{H}_{13})_3
\]  

(8) also takes place. On the basis of these results it seems likely that good routes to the individual higher oligomers that involve similar condensations can be developed.

In some cases compounds of the type \( R_3\text{SiO(SiPCO)}_n^- \) \((\text{GePCO})_2(\text{SiPCO})_n\text{SiR}_3\) could be of interest as alternatives to compounds of the type \( R_3\text{SiO(SiPCO)}_n\text{SiR}_3 \). These mixed-metal compounds might prove to be reasonably accessible since hydroxy germanium phthalocyanines condense readily to \( \mu \)-oxo species. A possible route to such a mixed-metal compound is:

\[
\text{R}_3\text{SiOSiPCOGePCOH} \xrightarrow{\text{p-xylene}} \text{reflux} \rightarrow \text{R}_3\text{SiOSiPCO(GePCO)}_2\text{SiPCOSiR}_3
\]  

(9)
Synthesis of Axially Unsymmetrically Substituted Phthalocyanines by Condensation

As described in Chapter 3, compounds of the types \( R_3SiOSiPcOAlPc \), \( R_2R'SiOSiPcOGePcCH_3 \), \( R_3SiOSiPcOGePcOGePcCH_3 \), and \( R_3SiO-SiPcOGePcOSiPcCH_3 \) have been prepared in this study. The routes used can be summarized as:

Route 7
\[
R_3SiOSiPcOH + HOAlPc \xrightarrow{1,2,4-trimethylbenzene; reflux} R_3SiOSiPcOAlPc \tag{10}
\]

Route 8
\[
R_2R'SiOSiPcOH + HOGePcCH_3 \xrightarrow{1,2,4-trimethylbenzene; dark} R_2R'SiOSiPcOGePcCH_3 \tag{11}
\]

Route 9
\[
R_3SiOSiPcOGePcOH + HOGePcCH_3 \xrightarrow{1,2,4-trimethylbenzene; dark} R_3SiOSiPcOGePcOGePcCH_3 \tag{12}
\]

Route 10
\[
R_3SiOSiPcOGePcOH + HOSiPcCH_3 \xrightarrow{1,2,4-trimethylbenzene; dark} R_3SiOSiPcOGePcOSiPcCH_3 \tag{13}
\]

In addition, attempts were made in this study to synthesize compounds of the types \( R_3SiOSiPcOSiPcCH_3 \), \( R_3SiOSiPcOSiPcC_8H_{17} \), and \( R_3SiO-SiPcO)_{2}C_8H_{17} \) by related condensation routes. A summary of data for representative examples of Routes 7-10 and for the attempts to make compounds of the types \( R_3SiOSiPcOSiPcCH_3 \), \( R_3SiOSiPcOSiPcC_8H_{17} \), and \( R_3SiO-SiPcO)_{2}C_8H_{17} \) is given in Tables I and II.
<table>
<thead>
<tr>
<th>Rte.</th>
<th>Target</th>
<th>Reactants</th>
<th>Time (h)</th>
<th>Yld. (%)</th>
<th>Byproducts</th>
</tr>
</thead>
</table>
| 7    | Hx₃SIO₃PcOAlPc               | Hx₃SIO₃PcOH        | 4        | 32       | Hx₃SIO₃PcO₂S₃Hₓ₃ c  
|      |                               |                    |          |          | Hx₃SIO₃AlPc c  
|      |                               |                    |          |          | AlPcOAlPc d |
| 8    | Hx₃SIO₃PcOGePcCH₃            | Hx₃SIO₃PcOH        | 4        | 19       | Hx₃SIO₃PcO₂S₃Hₓ₃ c  
|      |                               |                    |          |          | Hx₃SIO₃GePcCH₃ c  
|      |                               |                    |          |          | CH₃GePcOGePcCH₃ c |
| 8    | Od(Bu)₂SIO₃PcOGePcCH₃        | Od(Bu)₂SIO₃PcOH    | 4.5      | 16       | Od(Bu)₂SIO₃-  
|      |                               |                    |          |          | (SIPcO)₂S₁(Bu)₂Od c  
|      |                               |                    |          |          | Od(Bu)₂SIO₃GePcCH₃ c  
|      |                               |                    |          |          | CH₃GePcOGePcCH₃ c |
| 9    | Hx₃SIO₃PcOGePcOGePcCH₃      | Hx₃SIO₃PcOGePcOH   | 2        | 8        | Hx₃SIO₃PcO-  
|      |                               |                    |          |          | (GePcO)₂S₁PcOS₁Hₓ₃ c  
|      |                               |                    |          |          | Hx₃SIO₃GePcCH₃ c  
|      |                               |                    |          |          | CH₃GePcOGePcCH₃ c |
| 10   | Hx₃SIO₃PcOGePcOSiPcCH₃      | Hx₃SIO₃PcOGePcOH   | 1.2      | 7        | Hx₃SIO₃PcO-  
|      |                               |                    |          |          | (GePcO)₂S₁PcOS₁Hₓ₃ c  
|      |                               |                    |          |          | Hx₃SIO₃SiPcCH₃ c |

a. Hx = C₆H₁₃, Od = C₁₈H₃₇, Bu = C₆H₉; b. Adjusted percent yield [ref 49];

c. Determined by NMR; d. Determined by IR.
<table>
<thead>
<tr>
<th>Att.</th>
<th>Target</th>
<th>Reactants</th>
<th>Time (h)</th>
<th>Yld. (%)</th>
<th>Byproducts</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hx₃SiOSiPcO⁻SiPcCH₃</td>
<td>Hx₃SiOSiPcOH, CH₃SiPcOH</td>
<td>4</td>
<td>0</td>
<td>Hx₃SiO(SiPcO)₂SiHₓ₃, Hx₃SiOSiPcCH₃</td>
</tr>
<tr>
<td>2</td>
<td>Hx₃SiOSiPcO⁻SiPcC₈H₁₇</td>
<td>Hx₃SiOSiPcOH, C₈H₁₇SiPcOH</td>
<td>2</td>
<td>0</td>
<td>Hx₃SiO(SiPcO)₂SiHₓ₃</td>
</tr>
<tr>
<td>3</td>
<td>Hx₃SiOSiPcO⁻SiPcOC₈H₁₇</td>
<td>Hx₃SiOSiPcOH, C₈H₁₇OSiPcOH</td>
<td>2 &lt;5</td>
<td></td>
<td>Hx₃SiO(SiPcO)₂SiHₓ₃</td>
</tr>
</tbody>
</table>

a. Hx = C₆H₁₃; b. Determined by NMR.
A precedent for Route 7 can be found in the reaction:

\[
\text{SiPc(OH)}_2 + \text{AlPcOH} \xrightarrow{\text{reflux 4 h}} \text{AlPcOSiPCoAlPc}^{55,66}
\]

The relatively low yield of Route 7 probably can be attributed mainly to the insolubility of AlPcOH.

An example in the literature that is like Routes 8-10 is the reaction:

\[
\text{Ge(OEP)(OH)}_2 + \text{HOSiPCO(C}_6\text{H}_{13})_3 \xrightarrow{\text{o-xylene reflux}} \text{HOGe(OEP)OSiPCOSi(C}_6\text{H}_{13})_3^{67}
\]

where OEP is the octaethylporphyrin dianion. However, Routes 8-10 give low yields while the literature reaction gives good yields. Probably this is due mostly to the insolubility of CH₃SiPcOH and CH₃GePcOH.

In an exploratory NMR study of the reaction of Route 10 with \((\text{C}_6\text{H}_{13})_3\text{SiOSiPCOGePcOH}\) and \(\text{CH}_3\text{SiPcOH}\) as reactants, it was found that the ratio of \((\text{C}_6\text{H}_{13})_3\text{SiOSiPCO(GePcO)}_2\text{SiPcOSi(C}_6\text{H}_{13})_3\) to \((\text{C}_6\text{H}_{13})_3\text{SiO-SiPcOGePcOSiPcCH}_3\) shifted in favor of \((\text{C}_6\text{H}_{13})_3\text{SiOSiPCOGePcOSiPcCH}_3\) over a period of 5 h. This suggests that the kinetically favored product of this reaction is \((\text{C}_6\text{H}_{13})_3\text{SiOSiPCO(GePcO)}_2\text{SiPcOSi(C}_6\text{H}_{13})_3\) whereas the thermodynamically favored product is \((\text{C}_6\text{H}_{13})_3\text{SiOSiPCOGePcOSiPcCH}_3\). If so, this would not be surprising because the Si-O-Ge bond should be stronger than the Ge-O-Ge bond (but of course all other bonds must be considered too).
A precedent for Attempts 1-3 is provided by the reaction:

\[
\begin{align*}
2 \text{(C}_6\text{H}_{13})_3\text{SiOSiPcOH} & \quad \xrightarrow{189 \, ^\circ\text{C}} \quad (\text{C}_6\text{H}_{13})_3\text{SiO(SiPcO)}_2\text{Si(C}_6\text{H}_{13})_3 \quad (16) \\
& \quad \text{30 min}
\end{align*}
\]

The failure of Attempt 1 is attributed largely to the insolubility of \text{CH}_3\text{SiPcOH}. The failure of Attempts 2 and 3 cannot be ascribed to reactant insolubility since both \text{C}_8\text{H}_{17}\text{SiPcOH} and \text{C}_8\text{H}_{17}\text{OSiPcOH} are soluble. However, it appears that they are not stable under the reaction conditions used and that this underlies the failure of these attempts.

Although the data presented here and elsewhere on the condensation of hydroxy phthalocyanines with themselves and with other hydroxy phthalocyanines is too fragmentary to permit firm conclusions about the relative ease of the various condensations, it appears that the order of ease of condensation of aluminum, silicon, and germanium hydroxy phthalocyanines with the SiPcOH unit is AlPcOH > GePcOH > SiPcOH. Similarly it appears that the order of ease of condensation of silicon and germanium hydroxy phthalocyanines with the GePcOH unit is GePcOH > SiPcOH.

On the basis of what has been done, it is clear that other unsymmetrically substituted phthalocyanines can be made. A group that appears to be possible is given in Table III along with suggested precursors.

**Synthesis of Axially Unsymmetrically Substituted Phthalocyanines by Ligand Exchange**

Compounds of the type \text{R}_3\text{SiO(SiPcO)}_n\text{H} where \text{n} is small and
compounds of the type $R_3SiO(SiPcO)_3C(O)CCl_3$ have been prepared in this study by Routes 11-14:

Route 11

$R_3SiOSiPcO SiR_3 + Cl_3CC(O)OH \xrightarrow{1. \text{toluene}} R_3SiOSiPcOH \xrightarrow{2. \text{py-H}_2O, 50 \, ^{\circ}C} \rightarrow R_3SiOSiPcO SiOH$ (17)

TABLE III. POTENTIAL CONDENSATION-DERIVED AXIALLY UNSYMMETRICALLY SUBSTITUTED PHTHALOCYANINES

<table>
<thead>
<tr>
<th>Compound</th>
<th>Precursors</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Hx_3SiO(SiPcO)<em>2C_6H_4C(CH_3)</em>{3-p}$</td>
<td>$Hx_3SiOSiPcOH, HOSiPcOC_6H_4C(CH_3)_{3-p}$</td>
</tr>
<tr>
<td>$Hx_3SiOGePcOSiPcCH_3$</td>
<td>$Hx_3SiOGePcOH, HOSiPcCH_3$</td>
</tr>
<tr>
<td>$Hx_3SiOSiPcOGaPc$</td>
<td>$Hx_3SiOSiPcOH, HOGaPc$</td>
</tr>
<tr>
<td>$Hx_3SiOGePcOAlPc$</td>
<td>$Hx_3SiOGePcOH, HOAlPc$</td>
</tr>
<tr>
<td>$Hx_3SiO(SiPcO)_2GePcCH_3$</td>
<td>$Hx_3SiO(SiPcO)_2H, HOGePcCH_3$</td>
</tr>
<tr>
<td>$Hx_3SiO(SiPcO)_2AlPc$</td>
<td>$Hx_3SiO(SiPcO)_2H, HOAlPc$</td>
</tr>
<tr>
<td>$Hx_3SiO(SiPcO)GePcOAlPc$</td>
<td>$Hx_3SiO(SiPcO)GePcOH, HOAlPc$</td>
</tr>
</tbody>
</table>

a. $Hx = C_6H_{13}$

Route 12

$R_2R'SiO(SiPcO)_2SiR_2R' + Cl_3CC(O)OH \xrightarrow{1. \text{toluene}} \rightarrow R_2R'SiO(SiPcO)_2H \xrightarrow{2. \text{py-H}_2O, 50 \, ^{\circ}C}$ (18)

Route 13

$R_2R'SiO(SiPcO)_3SiR_2R' + Cl_3CC(O)OH \xrightarrow{1. \text{toluene}} \rightarrow \rightarrow R_2R'SiO(SiPcO)_3C(O)CCl_3$ (19)
Route 14
\[ \text{R}_2\text{R'}\text{SiO(SiPcO)_3C(O)CCl}_3 \xrightarrow{\text{py-H}_2\text{O}} \text{R}_2\text{R'}\text{SiO(SiPcO)_3H} \] (20)

In addition, attempts were made to synthesize compounds of the type \( \text{R}_3\text{SiO(SiPcO)_3H} \) by treating a compound of the type \( \text{R}_3\text{SiO(SiPcO)_3SiR}_3 \) with acetic acid. A summary of the data for representative examples of Routes 11-14 and of the data on attempts to make compounds of the type \( \text{R}_3\text{SiO(SiPcO)_3H} \) are given in Tables IV and V.

Routes 11-13 are related to a reaction sequence often used for the preparation of \( \text{HOSiNcOH} \):

\[ \text{C}_8\text{H}_{17}\text{OSiNcOC}_{8}\text{H}_{17} \xrightarrow{\text{1. xs HCl, toluene}} \text{HOSiNcOH}_{51} \xrightarrow{\text{2. N\textsubscript{3}H}_4\text{OH, pyridine}} \]

where \( \text{Nc} \) is the naphthalocyanine dianion. In Routes 11-13, however, a much smaller amount of acid is used. This leads, as desired, to cleavage of only one axial ligand from a substantial fraction of the reactant oligomers.

It appears on the basis of spectroscopic data and the known basicity of the aza nitrogens of the phthalocyanine ring\(^{68, 69} \) that the major intermediates in Routes 11 and 12 are \( \text{R}_3\text{SiO(SiPcO)_3CCl}_3\cdot\text{xCl}_3\text{CC(O)OH} \) and \( \text{R}_2\text{R'}\text{SiO(SiPcO)_2CCl}_3\cdot\text{xCl}_3\text{CC(O)OH} \). Thus, one function of the pyridine in the second step of Routes 11 and 12 is to liberate the phthalocyanine rings. Another function of the pyridine in these routes is to assist in the displacement of the \( \text{Cl}_3\text{CC(O)} \) (or \( \text{Cl}_3\text{CC(O)O} \) group). Similarly, in Route 14 the function of the pyridine is to assist in the displacement of this group.

In an exploratory study with \( \text{(C}_6\text{H}_{13})_3\text{SiO(SiPcO)_2Si(C}_6\text{H}_{13})_3 \) and
<table>
<thead>
<tr>
<th>Rte.</th>
<th>Target</th>
<th>Precursor</th>
<th>Ratio Acid:Pe</th>
<th>Yld. (%)</th>
<th>Byproducts</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>Hx₃SiOSiPcOH</td>
<td>Hx₃SiOSiPcO₃Hx₃</td>
<td>2:1</td>
<td>55</td>
<td>Hx₃SiOSiPcO₃Hx₃&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>SiPc(OH)&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>12</td>
<td>Hx₃SiO(SiPcO)₂H</td>
<td>Hx₃SiO(SiPcO)₂Hx₃</td>
<td>2:1</td>
<td>48</td>
<td>Hx₃SiO(SiPcO)₂Hx₃&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HO(SiPcO)&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>12</td>
<td>Od(Bu)&lt;sub&gt;2&lt;/sub&gt;SiO(SiPcO)₂H</td>
<td>Od(Bu)&lt;sub&gt;2&lt;/sub&gt;SiO(SiPcO)₂</td>
<td>2:1</td>
<td>54</td>
<td>Od(Bu)&lt;sub&gt;2&lt;/sub&gt;SiO(SiPcO)₂SIOd(Bu)&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SIOd(Bu)&lt;sub&gt;2&lt;/sub&gt;</td>
<td></td>
<td></td>
<td>HO(SiPcO)&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>13</td>
<td>Hx₃SiO(SiPcO)₃-C(O)CCl₃</td>
<td>Hx₃SiO(SiPcO)₃Hx₃</td>
<td>4:3</td>
<td>25</td>
<td>Hx₃SiO(SiPcO)₃Hx₃&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CCl₃C(O)O(SiPcO)₃C(O)CCl₃&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>13</td>
<td>Od(Bu)&lt;sub&gt;2&lt;/sub&gt;SiO(SiPcO)₃-C(O)CCl₃</td>
<td>Od(Bu)&lt;sub&gt;2&lt;/sub&gt;SiO(SiPcO)₃-SIOd(Bu)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>6:5</td>
<td>36</td>
<td>Od(Bu)&lt;sub&gt;2&lt;/sub&gt;SiO(SiPcO)₃SIOd(Bu)&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SIOd(Bu)&lt;sub&gt;2&lt;/sub&gt;</td>
<td></td>
<td></td>
<td>CCl₃C(O)O(SiPcO)₃C(O)CCl₃&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>14</td>
<td>Hx₃SiO(SiPcO)₃H</td>
<td>Hx₃SiO(SiPcO)₃-C(O)CCl₃</td>
<td>75</td>
<td></td>
<td>HO(SiPcO)₃H&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Hx = C₆H₁₃, Od = C₈H₁₇, Bu = C₄H₉; <sup>b</sup> Adjusted percent yield [ref 49]; <sup>c</sup> Determined by NMR and TLC; <sup>d</sup> Determined by IR.
<table>
<thead>
<tr>
<th>Att.</th>
<th>Target</th>
<th>Precursor</th>
<th>Ratio Acid:Pc</th>
<th>Yield&lt;sup&gt;b&lt;/sup&gt; (%)</th>
<th>Byproducts&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Hx&lt;sub&gt;3&lt;/sub&gt;SiO(SiPcO)&lt;sub&gt;3&lt;/sub&gt;C(O)CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Hx&lt;sub&gt;3&lt;/sub&gt;SiO(SiPcO)&lt;sub&gt;3&lt;/sub&gt;SiHx&lt;sub&gt;3&lt;/sub&gt;</td>
<td>6:5</td>
<td>0</td>
<td>Hx&lt;sub&gt;3&lt;/sub&gt;SiO(SiPcO)&lt;sub&gt;3&lt;/sub&gt;SiHx&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>5</td>
<td>Hx&lt;sub&gt;3&lt;/sub&gt;SiO(SiPcO)&lt;sub&gt;3&lt;/sub&gt;C(O)CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Hx&lt;sub&gt;3&lt;/sub&gt;SiO(SiPcO)&lt;sub&gt;3&lt;/sub&gt;SiHx&lt;sub&gt;3&lt;/sub&gt;</td>
<td>6:5</td>
<td>0</td>
<td>Hx&lt;sub&gt;3&lt;/sub&gt;SiO(SiPcO)&lt;sub&gt;3&lt;/sub&gt;SiHx&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Hx = C<sub>6</sub>H<sub>13</sub>; <sup>b</sup> Determined by NMR and TLC.
Cl₃CC(O)OH, it was found that (C₆H₁₃)₃Sio(SiPcO)₂Si(C₆H₁₃)₃ is favored when the acid-to-phthalocyanine ratio is less than two, that (C₆H₁₃)₃Sio(SiPcO)₂CCl₃ is favored when the ratio is two, and that Cl₃CC(O)O(SiPcO)₂CCl₃ is favored when the ratio is greater than two. Probably the need for a ratio greater than one arises because of the basic nature of theaza nitrogens of the phthalo-cyanine ring.

The yields in the examples of Routes 11-14 tried are acceptable to good. Better yields with these routes might be obtained by adding a dilute solution of the Cl₃CC(O)OH in toluene slowly to a solution of the oligomer in toluene that is being vigorously stirred.

Attempts 4 and 5 probably failed because CH₃C(O)OH is too weak an acid.

In some cases compounds of the type R₃SiO(GePcO)ₙH could be of interest. These compounds might be accessible by axial ligand exchange reactions such as:

\[
\text{GePc(OSiR₃)₂ + Cl₃CC(O)OH} \xrightarrow{\text{toluene, py-H₂O}} \text{R₃SiOGePcOH} \quad (22)
\]

\[
\text{R₃SiOGePcOH} \xrightarrow{\text{p-xylene, reflux}} \text{R₃SiO(GePcO)₂SiR₃} \quad (23)
\]

1. Cl₃CC(O)OH, toluene \xrightarrow{} R₃SiO(GePcO)₂H
2. py-H₂O

**Synthesis of Axially Unsymmetrically Substituted Phthalocyanines by Photolysis**

Compounds of the types R₂R'SiOSiPcOH, R₃SiOGePcOH,
R₂R'SiOSiPcOGePcOH, and R₃SiOSiPcOGePcOSiPcOH have been prepared in this study by Routes 15-18:

Route 15
\[ R₂R'SiOSiPcCH₃ \xrightarrow{\text{toluene, H₂O \text{, } h\nu}} R₂R'SiOSiPcOH \] (24)

Route 16
\[ R₃SiOGePcCH₃ \xrightarrow{\text{toluene, H₂O \text{, } 0 \degree C \text{, } h\nu}} R₃SiOGePcOH \] (25)

Route 17
\[ R₂R'SiOSiPcOGePcCH₃ \xrightarrow{\text{toluene, H₂O \text{, } 0 \degree C \text{, } h\nu}} R₂R'SiOSiPcOGePcOH \] (26)

Route 18
\[ R₃SiOSiPcOGePcO SiPcCH₃ \xrightarrow{\text{toluene, H₂O \text{, } h\nu}} R₃SiOSiPcOGePcO SiPcOH \] (27)

In an extension of this work, attempts were made to synthesize (C₆H₁₃)₃SiOSiPcOGePcOGePcOH. A summary of data for representative examples of Routes 15-18 and of data for the attempt to make (C₆H₁₃)₃SiOSiPcOGePcOGePcOH are given in Table VI. A precedent for Routes 15 and 18 is provided by the photolysis:

\[ (CH₃)₃C(CH₃)₂SiOSiPcCH₃ \xrightarrow{\text{toluene, H₂O \text{, } h\nu}} (CH₃)₃C(CH₃)₂SiOSiPcOH \] (28)

The yields obtained from the examples of Routes 15 and 18 studied are comparable to the yield obtained in the literature photolysis. However, the yields obtained from the examples of Routes 16 and 17 studied are lower than the yields of the examples of
TABLE VI. SYNTHESIS OF AXIALLY UNSYMMETRICALLY SUBSTITUTED PHTHALOCYANINES BY PHOTOLYSISa

<table>
<thead>
<tr>
<th>Route</th>
<th>Target</th>
<th>Precursor</th>
<th>Yield (%)</th>
<th>Byproducts</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>Od(Bu)₂S10SiPcOH</td>
<td>Od(Bu)₂S10SiPcCH₃</td>
<td>62b</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>Hx₃S10GePcOH</td>
<td>Hx₃S10GePcCH₃</td>
<td>29b</td>
<td>Hx₃S₁₀(GePcO)₂SiHₓ₃C GePc(OH)₂d</td>
</tr>
<tr>
<td>17</td>
<td>Hx₃S10SiPcOGePcOH</td>
<td>Hx₃S10SiPcOGePcCH₃</td>
<td>15b, e</td>
<td>Hx₃S₁₀SiPcO(GePcO)₂-S1PcOHS₁₀Hₓ₃C Hx₃S₁₀SiPcOHC</td>
</tr>
<tr>
<td>17</td>
<td>Od(Bu)₂S10SiPcOGePcOH</td>
<td>Od(Bu)₂S10SiPcOGePcCH₃</td>
<td>37b</td>
<td>Od(Bu)₂S₁₀SiPcO(GePcO)₂-S₁₀PcOHS₁₀(Bu)₂dC</td>
</tr>
<tr>
<td>18</td>
<td>Hx₃S10SiPcOGePcO₃PcOH</td>
<td>Hx₃S10SiPcOGePcO₃PcCH₃</td>
<td>94b</td>
<td></td>
</tr>
</tbody>
</table>

Attempt

<table>
<thead>
<tr>
<th>Route</th>
<th>Target</th>
<th>Precursor</th>
<th>Yield (%)</th>
<th>Byproducts</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>Hx₃S₁₀SiPcOGePcOGePcOH</td>
<td>Hx₃S₁₀SiPcOGePcOGePcCH₃</td>
<td>5c</td>
<td>Hx₃S₁₀SiPcOGePcOHC</td>
</tr>
</tbody>
</table>

a. Od = C₁₈H₃₇, Bu = C₄H₉, Hx = C₆H₁₃; b. Percent adjusted yield [ref 49];
c. Determined by NMR; d. Determined by IR; e. Precursor was impure.
Routes 15 and 18. The lower yields in these routes are probably due to more byproduct formation rather than to resistance of the GeCH₃ group to photolysis. Evidence provided by other workers involving the photodissociation of the Ge-C bond in compounds of the type Ge(TPP)R₂ (where TPP is the tetraphenylporphyrin dianion and R is phenyl or benzyl) suggest that R⁻ and a zwitterionic intermediate of the type RGe⁺(TPP)⁻ are formed.⁷⁰ If similar intermediates are formed in examples of Routes 15-18, the greater byproduct formation obtained from examples of Routes 16 and 17 may be due to a greater reactivity of the germyl cation towards species other than H₂O.

It was thought that the selectivity of the GeCH₃ photolysis reactions might be improved by lowering the reaction temperature. However, in exploratory photolyses of (C₆H₁₃)₃SiOSiPcOGePcCH₃ in undried toluene at -18 °C and -72 °C the distribution of products was unchanged. Perhaps a more promising way to improve the selectivity of the germanium reactions is to use a larger ratio of water to phthalocyanine in the reaction mixture. This could be done by using, for example, a THF-toluene-water mixture in which the water concentration was appreciable.

The attempted synthesis of (C₆H₁₃)₃SiOSiPcOGePcOGePcOH, Attempt 6, probably failed because the complexity of the molecule allowed for a number of competing byproduct reactions.

In an exploratory reaction it was found that the photolysis of (C₆H₁₃)₃SiOSiPcCH₃ in a dry isopropanol-toluene solution gave mainly (C₆H₁₃)₃SiOSiPcOCH(CH₃)₂. This is not surprising since Choy⁶³ found that the photolysis of ((CH₃)₃SiO)₂(CH₃)SiOSiPcCH₃ in an
NH₂(CH₂)₆OH-CDCl₃ solution gave mostly ((CH₃)₃SiO)₂(CH₃)SiO-
SiPcO(CH₂)₆NH₂. Based on these results it may be possible to synthe-
size complex alkoxy silicon and germanium phthalocyanines in good
yield using similar methodology. An example of a possible reaction
is:

\[(\text{C}_6\text{H}_{13})_3\text{SiOSiPcCH}_3 + \text{HOCH}_2\text{C(CH}_2\text{OH)}_3 \xrightarrow{\text{toluene}}\]

\[\text{hv}\]

\[(\text{C}_6\text{H}_{13})_3\text{SiOSiPcOCH}_2\text{C(CH}_2\text{OH)}_3\]

(29)

Synthesis of Axially Unsymmetrically Substituted Phthalocyanines

Using Other Approaches

Synthesis of ClGePcCH₃. The synthesis of the silicon analogue
of ClGePcCH₃, ClSiPcCH₃, was described earlier by Esposito⁵:

\[
\begin{align*}
\text{C}_6\text{H}_{13} & + \text{CH}_3\text{SiCl}_3 \xrightarrow{\text{quinoline}} \xrightarrow{\text{reflux, dark}} \\
& \xrightarrow{\text{hot filtration}} \xrightarrow{\text{dark}} \text{ClSiPcCH}_3
\end{align*}
\]

(30)

This synthesis provides a precedent for the synthesis of ClGePcCH₃
described in the present study:

\[
\begin{align*}
\text{C}_6\text{H}_{13} & + \text{CH}_3\text{GeCl}_3 \xrightarrow{\text{quinoline}} \xrightarrow{\text{reflux, dark}} \\
& \xrightarrow{\text{slowly}} \xrightarrow{\text{cool, dark}} \text{ClGePcCH}_3
\end{align*}
\]

(31)

Since ClSiPcCH₃ occurs in two forms, α and β, it is not surpri-
sing that ClGePcCH₃ also occurs in two forms, and it appears likely that α-ClSiPcCH₃ and α-ClGePcCH₃ are isomorphous and β-ClSiPcCH₃ and β-ClGePcCH₃ are also isomorphous. Either form of ClGePcCH₃ can be produced by Reaction 31. Probably the rate of reaction product cooling governs the form produced.

**Synthesis of C₈H₁₇SiPcCl and C₈H₁₇SiPcOH.** The low yield of the synthesis used for C₈H₁₇SiPcOH:

\[
\begin{align*}
\text{quinoline} & \quad \text{200 °C, dark} \\
\text{1. H₂SO₄} & \quad \text{2. py-NH₄OH} \\
\end{align*}
\]

\[
\text{C₈H₁₇SiPcCl} \quad \text{C₈H₁₇SiPcOH}
\]

is due to the low yield of the first step of the synthesis. The low yield of this step is attributed to a lack of stability of C₈H₁₇SiPcCl at 200 °C. Support for this conclusion is provided by the fact that C₈H₁₇SiPcCl has been made recently in good yield at 150 °C.⁷¹

**Synthesis of C₁₈H₃₇(C₄H₉)₂SiOSiPcOAlPc.** The reaction used to make C₁₈H₃₇(C₄H₉)₂SiOSiPcOAlPc:

\[
\begin{align*}
2 \text{C₁₈H₃₇(C₄H₉)₂SiOSiPcOH} + \text{AlPcOSi(C₄H₉)₂C₁₈H₃₇} \xrightarrow{\text{p-xylene} \quad \text{reflux, 2.5 h}} \\
\text{C₁₈H₃₇(C₄H₉)₂SiOSiPcOAlPc} + \text{C₁₈H₃₇(C₄H₉)₂SiOSiPcOSi(C₄H₉)₂C₁₈H₃₇}
\end{align*}
\]

\[
(33)
\]

gave only acceptable yields when C₁₈H₃₇(C₄H₉)₂SiOSiPcOH produced by the trichloroacetic acid hydrolysis of C₁₈H₃₇(C₄H₉)₂SiOSiPcO-
Si(C₄H₉)₂C₁₈H₃₇ was used, but good yields when C₁₈H₃⁷(C₄H₉)₂SiOSiPcOH produced by the photolysis of C₁₈H₃⁷(C₄H₉)₂SiOSiPcCH₃ was used. The cause of this difference is unknown. The mild conditions required by this reaction show it proceeds by some easy route. Perhaps this involves a backside attack of the SiPcOH grouping on the AlPc grouping.

Stability of Phthalocyanines

In the phthalocyanines investigated in these studies, the bonds of the ring system generally have greater overall resistance to photolytic, thermal, and hydrolytic breakdown than the bonds between the central metal atoms and the axial ligands. This is not surprising since the phthalocyanine ring system is noted for its exceptional stability.¹

Stability of Compounds to Light. It was found, as expected, that solutions of the compounds studied containing PcSi-C or PcGe-C bonds (e.g., ClSiPcC₈H₁₇, HOSiPcC₈H₁₇, (C₆H₁₃)₃SiOGePcCH₃, (C₆H₁₃)₃SiOSiPcOGePcCH₃, (C₆H₁₃)₃SiOSiPcOGePcOGePcCH₃, and (C₆H₁₃)₃SiOSiPcOGePcOGePcOGePcCH₃) are rapidly and fully photolyzed by visible light. However, crystals of these compounds and fine particles of them in suspension are not rapidly photolyzed to an appreciable extent. Perhaps the resistance of the crystals and particles to photolysis is attributable to the formation of protective surface films by photolysis. It may also be that the photolysis process requires solvent assistance. None of the other types of compounds prepared appear to be significantly photosensitive.
Stability of Compounds to Heat. The apparent order of thermal stability of the Si-O-Si or Ge-O-Si groups in compounds such as \((\text{C}_6\text{H}_{13})_3\text{SiO(SiPcO)}_2\text{Si(}\text{C}_6\text{H}_{13})_3\), \((\text{C}_6\text{H}_{13})_3\text{SiOSiPcOGePcOH})\), \((\text{C}_6\text{H}_{13})_3\text{SiPcO(}\text{GePcO)}_2\text{SiPcOSi(}\text{C}_6\text{H}_{13})_3\), and \((\text{C}_6\text{H}_{13})_3\text{SiOGePcSi(}\text{C}_6\text{H}_{13})_3\) is \(\text{PsSi-O-SiPc, PsSi-O-GePc > R}_3\text{Si-O-SiPc, PsGe-O-GePc > R}_3\text{Si-O-GePc}\). This order corresponds to the order observed for the hydrolytic stability of these groups and is probably partially associated with the relative bond strengths of the bonds involved.

The stability of the Si-C\(_8\)H\(_{17}\) group in ClSiPcC\(_8\)H\(_{17}\) at \(-200\) °C in quinoline is much less than that of the PsSi-CH\(_3\) group in ClSiPcCH\(_3\) at 200 °C in quinoline. This is attributed to the ability of Si-alkyl compounds with higher alkyl groups to undergo \(\beta\)-hydride transfer-alkene elimination reactions with ease.\(^7\)

Stability of Compounds to Solvolysis. While \((\text{C}_6\text{H}_{13})_3\text{SiO-}\) (SiPcO)\(_2\)Si(\text{C}_6\text{H}_{13})_3\) and \((\text{C}_6\text{H}_{13})_3\text{SiOSiPcOGePcCH}_3\) are not solvolyzed by water and MeOH at \(-100\) °C, \((\text{C}_6\text{H}_{13})_3\text{SiOGePcCH}_3\) and \((\text{C}_6\text{H}_{13})_3\text{SiOGePcOH}\) are solvolyzed under these conditions. The difference between \((\text{C}_6\text{H}_{13})_3\text{SiO(SiPcO)}_2\text{Si(}\text{C}_6\text{H}_{13})_3\) and \((\text{C}_6\text{H}_{13})_3\text{SiOGePcCH}_3\) and \((\text{C}_6\text{H}_{13})_3\text{SiOGePcOH}\) is attributed to the well-known greater lability of the Si-0-Ge bond system. The difference in solvolysis resistance between \((\text{C}_6\text{H}_{13})_3\text{SiOSiPcOGePcCH}_3\) and \((\text{C}_6\text{H}_{13})_3\text{SiOGePcCH}_3\) and \((\text{C}_6\text{H}_{13})_3\text{SiOGePcOH}\) is attributed largely to differences in the steric hindrance at the Ge-O-Si bond system.

The ease with which the Si-O-C(0)CCl\(_3\) grouping in the compounds \((\text{C}_6\text{H}_{13})_3\text{SiO(SiPcO)}_1\cdot 4\text{C(0)CCl}_3\) can be hydrolyzed is probably due to the good leaving ability of the OC(0)CCl\(_3\) group. The hydrolytic
stability of the compounds \((\text{C}_6\text{H}_{13})_3\text{SiO(SiPcO)}_{1.4}\text{C}(\text{O})\text{CCl}_3\) appears to decrease with increasing number of rings. This may be due to an outward dishing of the rings in the multiring compounds that increases with the number of rings. If significant, this could create steric hindrance and weaken the Si-O-C bond.

The difference in conditions required for the hydrolysis of the Si-Cl bond in \(\text{C}_{18}\text{H}_{37}(\text{C}_4\text{H}_9)_2\text{SiOSiPcCl}\) (H\(_2\)O-py, room temperature) and SiPcCl\(_2\) (NH\(_4\)OH-py, reflux) is attributed mainly to solubility differences (although electronic trans group effects may also play a role). Support for this conclusion comes from the fact that other cases are known where the difference in conditions required for the hydrolysis of the Si-Cl bond of chlorosilicon phthalocyanines appears to be governed by solubility.\(^{73}\)

**Stability of Compounds to Alumina Chromatography.** The separation of the group of oligomers \((\text{C}_6\text{H}_{13})_3\text{SiO(SiPcO)}_{1.4}\text{Si(}\text{C}_6\text{H}_{13})_3\) on alumina columns is efficient if the chromatography is done in \(<1.5\) h. With longer times lower yields and lower purities result. This is probably due to alumina mediated \((\text{C}_6\text{H}_{13})_3\text{Si-O-SiPc} \) bond cleavage.

Although the compounds \((\text{C}_6\text{H}_{13})_3\text{SiOSiPcOH}, (\text{C}_6\text{H}_{13})_3\text{SiO(SiPcO)}_2\text{H},\) and \((\text{C}_6\text{H}_{13})_3\text{SiOSiPcOGePcOH}\) can be chromatographed on alumina, the yields are not as high as those obtained with compounds such as \((\text{C}_6\text{H}_{13})_3\text{SiOSiPcOSi(}\text{C}_6\text{H}_{13})_3\) and \((\text{C}_6\text{H}_{13})_3\text{SiO(SiPcO)}_2\text{Si(}\text{C}_6\text{H}_{13})_3\). This likely arises because the compounds are so polar they adsorb very strongly on the alumina.

The compounds \((\text{C}_6\text{H}_{13})_3\text{SiO(SiPcO)}_{1.2}\text{C}(\text{O})\text{CCl}_3\) decompose to compounds believed to be HO(SiPcO)\(_{1.2}\text{H}\) when attempts are made to chroma-
to graph them on alumina. It is thought that the process underlying this decomposition entails an alumina mediated cleavage of the Si-O-C group followed by a cleavage of the \((C_6H_{13})_3Si-O-SiPc\) group catalyzed by the \(Cl_3CC(O)OH\) that is liberated in the first step.

When attempts are made to chromatograph \(C_{18}H_{37}(C_4H_9)_2SiO-SiPc0AlPc\), decomposition products of the type \(C_{18}H_{37}(C_4H_9)_2SiOSiPcOH\) and \(AlPcOH\) apparently form. Similarly, \(C_{18}H_{37}(C_4H_9)_2SiOAlPc\) apparently yields \(C_{18}H_{37}(C_4H_9)_2SiOH\) and \(AlPcOH\). Probably this arises because the AlPc rings of the compounds are open to backside attack.

Although \((C_6H_{13})_3SiOGePcOH\), \((C_6H_{13})_3SiOSiPcOGePcCH_3\), and \((C_6H_{13})_3SiOSiPcOGePcOHi\) can be chromatographed successfully on alumina, \((C_6H_{13})_3SiOGePcCH_3\) cannot be. Instead it decomposes to what is believed to be \(HOGePcCH_3\) and \((C_6H_{13})_3SiOH\). The reasons for this are not clear. Perhaps the \((C_6H_{13})_3Si-O-GePc\) group in \((C_6H_{13})_3SiO-GePcCH_3\) is weakened by the trans CH$_3$ group.

**NMR Spectra**

**Ring-Current Effects.** The ring-current effect of the phthalocyanine ring has been dealt with in a number of studies.\(^{53,62,74-77}\) Because of the size and aromaticity of the ring, this effect is large. Good examples of the effect are seen in the NMR spectra of the oligomers \(C_{18}H_{37}(C_4H_9)_2SiO(SiPc0)_2-4Si(C_4H_9)_2C_{18}H_{37}\). In the dimer, the cumulative effects of the two rings are sufficient to lead to an isolated resonance for the \(\epsilon-CH_2\) group of the octadecyl chain, while in the trimer and tetramer cumulative effects of the ring stacks are sufficient to lead to isolated resonances for the \(\zeta-CH_2\)
groups of the octadecyl chains, Figure 7.

Concentration Effects. The NMR spectra of all compounds prepared in this study having one axial OH group and one axial siloxy group (e.g., \((C_6H_{13})_3SiOSiPcOH\) and \(C_{18}H_{37}(C_4H_9)_2SiOSiPcOCePcOH\)) are concentration dependent when \(CDCl_3\), benzene-\(d_6\), toluene-\(d_8\), and pyridine-\(d_5\) are used as solvents. With increasing concentration, the OH resonance (when observed) moves to lower field and the siloxy resonances move to a higher field. Based on the observations and conclusions of Sounik with regard to the spectra of \(HSiPcO-Si(CH_3)_2CH_2CH_2C_6H_4CH_2I^6\), these shifts are attributed to the formation of loose cofacial, hydroxy-bridged complexes (which lead to additive ring-current effects).

A concentration effect is also observed for the compounds prepared having an AlPc group at one end of the ring stack (e.g., \(C_{18}H_{37}(C_4H_9)_2SiOSiPc0AlPc\) and \(C_{18}H_{37}(C_4H_9)_2SiOAlPc\)). This effect is likewise attributed to the formation of loose cofacial complexes.

Solvent Effects. Well-resolved spectra of the ring protons of the oligomers \(C_{18}H_{37}(C_4H_9)_2Si0(SiPc0)_{1-5}Si(C_4H_9)_2C_{18}H_{37}\) were obtained with benzene-\(d_6\), toluene-\(d_8\), and pyridine-\(d_5\) as solvents. In \(CDCl_3\) fairly well-resolved spectra of the ring protons of the monomer and dimer were obtained but only poorly resolved spectra of the ring protons of the trimer, tetramer, and pentamer were obtained. However, in \(CDCl_3\) containing a small amount of \(Et_3N\) moderately well resolved spectra of the ring protons of the tetramer were obtained.

Perhaps the spectra of the ring protons of the trimer, tetramer, and pentamer in \(CDCl_3\) were poorly resolved because the \(CDCl_3\)
Figure 7. NMR spectra (200 MHz, C₆D₆, 70 °C):
(a) C₁₈H₃₇(C₄H₂)₂SiO(SiPcO)₂Si(C₄H₂)₂C₁₈H₃₇;
(b) C₁₈H₃₇(C₄H₂)₂SiO(SiPcO)₃Si(C₄H₂)₂C₁₈H₃₇;
(c) C₁₈H₃₇(C₄H₂)₂SiO(SiPcO)₄Si(C₄H₂)₂C₁₈H₃₇.
contained DCl and this reacted with the aza nitrogens of the rings. If this is so, why the nitrogens of the monomer and dimer did not react with the DCl is not certain. It may be that the nitrogens of these compounds are less basic.

Other three-ring and four-ring compounds prepared in this study also gave well resolved ring proton spectra in benzene-$d_6$, toluene-$d_8$, and pyridine-$d_5$ and poorly resolved spectra in CDCl$_3$. Again the cause of the poor resolution of the spectra in the CDCl$_3$ is thought to be associated with salt formation.

Infrared Spectra

Generally, where comparisons can be made, the spectra of the silicon, germanium, and aluminum phthalocyanines prepared in this work are similar to those of like silicon$^{78-80}$, germanium$^{78,80,81}$, and aluminum$^{55,82}$ phthalocyanines described in the literature. However, it is worth pointing out that the spectra of both (C$_6$H$_{13}$)$_3$SiO-(SiPcO)$_3$C(O)CCl$_3$ and C$_{18}$H$_{37}$C$_4$H$_9$)$_2$SiO(SiPcO)$_3$C(O)CCl$_3$ have bands at 1730 cm$^{-1}$. These are attributable to C=O stretching vibrations.$^{83}$ It is also of interest that the spectra of C$_{18}$H$_{37}$C$_4$H$_9$)$_2$SiOAlPc and the known compound (C$_6$H$_5$)$_3$SiOAlPc$^{82}$ have bands at 1049 cm$^{-1}$ and 1052 cm$^{-1}$. These are attributed to the Al-O-Si grouping. Finally, it is of interest that the spectra of both (C$_6$H$_{13}$)$_3$SiOSiPcOAlPc and C$_{18}$H$_{37}$C$_4$H$_9$)$_2$SiOSiPcOAlPc have bands at 1053 cm$^{-1}$ and 1052 cm$^{-1}$. These are ascribed to either or both the Al-O-Si and Si-O-Si vibrations.$^{66}$
Electronic Properties

Some of the physical properties of stacked-ring phthalocyanines are influenced by \( \pi-\pi \) interactions between the rings. For example, the differences in the electronic absorption spectra among the oligomers \((C_6H_{13})_3SiO(SiPcO)_{1-4}Si(C_6H_{13})_3\) and among the oligomers \(((CH_3)_3SiO)_2(CH_3)SiO(SiPcO)_{1-4}Si(CH_3)(OSi(CH_3)_3)\)_2 are attributable to such interactions. Similarly, the substantial differences in the redox potentials among the members of the series \((C_6H_{13})_3SiO-(SiPcO)_{1-4}Si(C_6H_{13})_3\) and among the members of the series \((CH_3)_3C(CH_3)_2SiO(SiPcO)_{1-3}Si(CH_3)_2C(CH_3)_3\) are attributable to such interactions.
Chapter 6

LANGMUIR-BLODGETT FILMS OF AMPHIPHILIC PHTHALOCYANINES

Monolayer Films

Pressure-Area Isotherms. The continuous-compression method is a rapid way to obtain pressure-area isotherms for amphiphilic films. However, the isotherms obtained by this method are only approximations of the true isotherms because the molecules in continuously compressed films are not necessarily in equilibrium with their neighbors.87

As made clear in Chapter 4, the isotherms collected in this study are continuous-compression isotherms. Because they are such, interpretation of them has been limited to the extraction of co-areas (limiting molecular areas) and transition pressures.

Stearic Acid Co-Area. The co-area obtained for stearic acid, 0.202 nm²/molecule, is in substantial agreement with the literature value for it, 0.201 nm²/molecule.88 This indicates that the film balance used in these studies was in proper working condition.

Phthalocyanine Ring Orientation. As pointed out earlier (pp 33, 35), suspensions of the compounds (C₆H₁₃)₃SiO(SiPcO)₃C(O)CCl₃ and C₁₈H₃₇(C₄H₉)₂SiO(SiPcO)₃C(O)CCl₃ quickly undergo hydrolysis to (C₆H₁₃)₃SiO(SiPcO)₃H and C₁₈H₃₇(C₄H₉)₂SiO(SiPcO)₃H. Accordingly, it is assumed that dispersed monolayers of (C₆H₁₃)₃SiO(SiPcO)₃C(O)CCl₃ and C₁₈H₃₇(C₄H₉)₂SiO(SiPcO)₃C(O)CCl₃ also quickly undergo hydrolysis.
to these same products and that the isotherms obtained when dispersed monolayers of these compounds are compressed are thus those for 
(C₆H₁₃)₃SIO(SiPcO)₃H and C₁₈H₃₇(C₄H₉)₂SIO(SiPcO)₃H.

An isotherm interpreted as being that of (C₆H₁₃)₃SIO(SiPcO)₃H on the basis of this assumption along with isotherms of (C₆H₁₃)₃SIO-SiPcOH and (C₆H₁₃)₃SIO(SiPcO)₂H are shown in Figure 8. Likewise an isotherm interpreted as being that of C₁₈H₃₇(C₄H₉)₂SIO(SiPcO)₃H along with isotherms of C₁₈H₃₇(C₄H₉)₂SIOSiPcOH and C₁₈H₃₇(C₄H₉)₂SIO-(SiPcO)₂H are shown in Figure 9. Isotherms for (C₆H₁₃)₃SIOSiPCO-GePcOH and (C₆H₁₃)₃SIO(SiPcO)₂H, C₁₈H₃₇(C₄H₉)₂SIOSiPcOGePcOH and 
C₁₈H₃₇(C₄H₉)₂SIO(SiPcO)₂H, and for C₁₈H₃₇(C₄H₉)₂SIOSiPcOAlPc and 
C₁₈H₃₇(C₄H₉)₂SIO(SiPcO)₂H are shown in Figures 10-12.

It is clear from the isotherms that for (C₆H₁₃)₃SIOSiPcOH, 
(C₆H₁₃)₃SIO(SiPcO)₂H, (C₆H₁₃)₃SIOSiPcOGePcOH, C₁₈H₃₇(C₄H₉)₂SIOSiPcOH, 
C₁₈H₃₇(C₄H₉)₂SIO(SiPcO)₂H, and C₁₈H₃₇(C₄H₉)₂SIOSiPcOGePcOH, Figures 8-11, that two structural arrangements occur during compression of films of these compounds. These arrangements may not be phases in the strict thermodynamic sense but they are referred to as such in the present discussion.

On the basis of the data for the co-areas of the first phases of these compounds, Table VII, and data for the packing area of a phthalocyanine ring resting on its face, ~1.44-1.88 nm²/molecule⁸⁹, it is concluded that the rings in these phases are parallel to the water surface. This parallel orientation of the rings is attributed to the presence of hydrophilic OH groups on the center axes of the molecules.
Figure 8. Isotherms of (a) \((C_6H_{13})_3SiOSiPCO\); (b) \((C_6H_{13})_3SiO(SiPCO)H\); (c) \((C_6H_{13})_3SiO(SiPCO)H\) films at 20.0 °C.
Figure 9. Isotherms of (a) $C_{18}H_{37}(C_4H_9)_2SiOSiPcOH$; (b) $C_{18}H_{37}(C_4H_9)_2SiO(SiPcO)_2H$; (c) $C_{18}H_{37}(C_4H_9)_2SiO(SiPcO)_3H$ films at 20.0 °C.
Figure 10. Isotherms of (a) \((\text{C}_6\text{H}_{13})_3\text{SiOSiPcGePcO} \)H and (b) \((\text{C}_6\text{H}_{13})_3\text{SiO(SiPcO)}_2 \)H films at 20.0 °C.
Figure 11. Isotherms of (a) C_{18}H_{37}(C_{4}H_{9})_{2}SO_{2}PeGeOH and (b) C_{18}H_{37}(C_{4}H_{9})_{2}SIO-
(SIPeO)_{2}H films at 20.0 °C.
Figure 12. Isotherms of (a) $C_{18}H_{37}(C_4H_9)_2SiOSiPcOAlPc$ and (b) $C_{18}H_{37}(C_4H_9)_2SiO(SiPcO)_2H$ films at 20.0 °C.
<table>
<thead>
<tr>
<th>Compound</th>
<th>No. of Trials</th>
<th>Co-Area of First or Only Phase b, c (nm²/molecule)</th>
<th>Co-Area of Second Phase b, d (nm²/molecule)</th>
<th>Transition Pressure b, e (mN/m)</th>
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<tr>
<td>Hx₃SiOSiPcOH</td>
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<td>Hx₃SiO(SiPcO)₂H</td>
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<td>1.66</td>
<td>0.947</td>
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<tr>
<td>Od(Bu)₂SiO(SiPcO)₂H</td>
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<td>Stearic Acid</td>
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</table>

a. Hx = C₆H₁₃, Od = C₁₈H₃₇, Bu = C₄H₉; b. Entries associated with multiple trials are averages; c. Reproducibility is within ±3%; d. Reproducibility is within ±6%; e. Reproducibility is within ±5%; f. From hydrolysis of Hx₃SiO(SiPcO)₃C(O)CCl₃; g. From hydrolysis of Od(Bu)₂SiO(SiPcO)₃C(O)CCl₃.
The arrangements of the rings in the second phases are unknown. They could involve tilted or stacked rings.

The situation is less clear with respect to \((C_6H_{13})_3SiO(SiPcO)_3H\) and \(C_{18}H_{37}(C_4H_9)_2SiO(SiPcO)_3H\) since the portions of their isotherms above the initial phase transition pressures, Figures 8 and 9, vary from run to run. On the basis of the data gathered, Table VII, it is concluded that these compounds give initial phases in which the rings are parallel to the water surface and that they may give, in addition, second phases that have unknown structures.

Only one arrangement occurs during the compression of films of \(C_{18}H_{37}(C_4H_9)_2SiOSiPcOAlPc\), Figure 12. Since its co-area, 0.838 nm²/molecule, is considerably less than the packing area of a phthalocyanine ring resting on its face, it is concluded that the rings in this phase are tilted or stacked. Probably the absence of an axial OH group in this compound leads to this behavior.

Molecular Packing and Rearrangement Resistance. As is seen, Table VII, the co-area of the first phase of \((C_6H_{13})_3SiO(SiPcO)_2H\) is larger than that of \((C_6H_{13})_3SiOSiPcO\), and the co-area of the first (or only) phase of \((C_6H_{13})_3Si(SiPcO)_3H\) is larger than that of \((C_6H_{13})_3SiO(SiPcO)_2H\). While the reason for this is not certain, it seems likely that in films of these compounds in which the rings are flat, interdigitation of all the rings becomes progressively more difficult as the ring-stack size increases. If so, this could lead to less efficient packing and give rise to the observed trend.

With \(C_{18}H_{37}(C_4H_9)_2SiOSiPcO\), \(C_{18}H_{37}(C_4H_9)_2SiO(SiPcO)_2H\), and \(C_{18}H_{37}(C_4H_9)_2SiO(SiPcO)_3H\), the co-areas of the first phases of the
first two compounds are similar and the co-area of the first (or only) phase of the third is larger. This suggests that ring-stack size is not the only factor influencing the difficulty of ring interdigitation in films of the compounds in which the rings are flat.

From Table VII it is seen that the phase transition pressures of \((\text{C}_6\text{H}_{13})_3\text{SiOSiPcOH}\) and \((\text{C}_6\text{H}_{13})_3\text{SiO(SiPcO)}_2\text{H}\) are similar and the phase transition pressure (or collapse pressure) of \((\text{C}_6\text{H}_{13})_3\text{SiO(SiPcO)}_3\text{H}\) is considerably higher. Similarly, the phase transition pressures of \(\text{C}_{18}\text{H}_{37}(\text{C}_4\text{H}_9)_2\text{SiOSiPcOH}\) and \(\text{C}_{18}\text{H}_{37}(\text{C}_4\text{H}_9)_2\text{SiO(SiPcO)}_2\text{H}\) are similar and the phase transition pressure of \(\text{C}_{18}\text{H}_{37}(\text{C}_4\text{H}_9)_2\text{SiO(SiPcO)}_3\text{H}\) is considerably higher. The higher pressures of the three-ring compounds are attributed to the shape of the ring-stack in these compounds since it is probably such that it is relatively difficult for the molecules to ride up over each other.

The co-areas and phase transition pressures of \((\text{C}_6\text{H}_{13})_3\text{SiOSiPcOGePcOH}\) and \(\text{C}_{18}\text{H}_{37}(\text{C}_4\text{H}_9)_2\text{SiOSiPcOGePcOH}\) are similar to those of their all-silicon analogues, as expected. Interpretation of the differences that do occur between the co-areas and phase transition pressures of these compounds and those of their all-silicon analogues is deferred until more data are available.

**Compressive Creep Studies.** Compressive creep studies of films of \((\text{C}_6\text{H}_{13})_3\text{SiOSiPcOGePcOH}\) have been reported in a thesis and a paper. The findings from these studies indicate that after 0.5 h the films undergo <1% loss of initial area at 10 mN/m, ~2% loss at 15 mN/m, and ~4% loss at 50 mN/m. These amounts of creep indicate that the films have good stabilities at these pressures.
The compressive creep curves for a film of \((C_6H_{13})_3SiOSiPcOH\) at 6 mN/m, a film of \((C_6H_{13})_3SiO(SiPcO)_2H\) at 8 mN/m, and a film of \((C_6H_{13})_3SiO(SiPcO)_3H\) at 15 mN/m are shown in Figure 13. As is seen, the film of \((C_6H_{13})_3SiO(SiPcO)_2H\) at 8 mN/m is about as stable as the film of \((C_6H_{13})_3SiOSiPcOGePcOH\) at 10 mN/m. This is as expected since the shapes of the molecules of the two compounds are very similar.

As is also seen, the stabilities of the films of the three new compounds at these low pressures increase with ring-stack size. This also is as expected since it has already been concluded on the basis of the isotherms of the compounds that ring-stack size and the resistance of the initial film structures to rearrangement are correlated.

Compressive creep curves for films of \((C_6H_{13})_3SiOSiPcOH\), \((C_6H_{13})_3SiO(SiPcO)_2H\), and \((C_6H_{13})_3SiO(SiPcO)_3H\) at higher pressures are shown in Figure 14. Here the stabilities of the films decrease with ring-stack size and thus are related in the opposite way to ring-stack size.

In this case the structures of the films are not known. However, it seems likely that each is quite different. If so, the structures could be of types that lead to the observed relationship. The large creep associated with the film of the three-ring compound clearly is consistent with the earlier conclusion that this film is in a phase transition at higher pressures.
Figure 13. Compressive creep curves of (a) (C_6H_13)_3SiO(SiPcO)_2H film at 6 mL/min; (b) (C_6H_13)_3SiO(SiPcO)_2H film at 8 mL/min; (c) (C_6H_13)_3SiO(SiPcO)_3H film at 15 mL/min (20.0 °C).
Figure 14. Compressive creep curves of (a) \((C_6H_{13})_3SiOSiPC_{10}H\) film at 41 mN/m; (b) \((C_6H_{13})_3Si(SiPC_{10})_2H\) film at 41 mN/m; (c) \((C_6H_{13})_3SiO(SiPC_{10})_3H\) film at 45 mN/m (20.0 °C).
Multilayer Films of \((\text{C}_6\text{H}_{13})_3\text{SiOSiPC}_{\text{G}}\text{PC}_{\text{OH}}\)

The film work presented in the following sections is the result of collaborative efforts. The collaborators in these efforts include Dr. Chi-Wei Fu, Ms. Hong-Ying Wang, and Professor Wen H. Ko of the Department of Electrical Engineering and Applied Physics, and Dr. Joel D. Shutt, Dr. Casper W.-T. Chiang, Dr. Rashmikant V. Sudiwala, Professor Scott E. Rickert, and Professor Jerome B. Lando of the Department of Macromolecular Science.

Multilayer Formation and Coverage of Substrates. Monolayers of the high co-area arrangement of \((\text{C}_6\text{H}_{13})_3\text{SiOSiPC}_{\text{G}}\text{PC}_{\text{OH}}\) were satisfactorily transferred onto glass, aluminum, and silicon substrates by vertical deposition methods\(^{92,93}\). Contact angle measurements and transfer ratios indicate that after three round trips the dipped areas of the substrates were completely covered with Y-type\(^{47}\) multilayers\(^{93}\) (i.e., multilayers with molecules stacked in a head to head-tail to tail arrangement).

Monolayers were also transferred by a similar method onto more complicated substrates including glass shadowed with aluminum electrodes\(^{58,91}\), silicon patterned with aluminum microelectrodes\(^{93}\), and silicon patterned with gold microelectrodes\(^{93}\). Scanning electron microscopy and electrical measurements indicate that good contact was made between the film and the microelectrodes\(^{93}\).

It was shown by through-film capacitance measurements that the thickness of films on glass carrying multiple aluminum electrodes was not uniform\(^{58,91}\) (this may have been caused by incomplete drainage of the film during the transfer process). However, it was also shown
that at comparable positions the thickness of several of such films was the same.56

The transfer of monolayers of the low co-area arrangement onto substrates was not achieved with the vertical dipping method. This may have been due to the large amount of creep and stress relaxation that this phase undergoes91.

It appears that it would be worthwhile to investigate multilayer formation using a horizontal lifting method since this method can produce X-type47 multilayers (i.e., multilayers with molecules stacked in a head to tail-head to tail arrangement). These multilayers probably would have film properties that differ from those of the Y-type multilayers.

**Multilayer Structure.** The structure of the multilayer formed from (C₆H₁₃)₃SiOSiPCOGePcOH was studied by ellipsometric, x-ray diffraction, and electron diffraction techniques.92 From the results it was concluded that the phthalocyanine rings in each layer are parallel to the substrate surface and pack in a square repeat unit having an area of 2.03 nm². It was also concluded, in agreement with the transfer ratio data, that the layer stacking is of the Y-type. In addition it was concluded that the layer spacing is 11.7 Å.

From the packing data it appears that the area occupied by a ring is larger in a multilayer than in the monolayer (the molecular area is 1.52 nm²/molecule, Table VII). Perhaps this is associated with the simpler structure of the monolayer.

**Physical Properties of Multilayer Microdevices.** If Langmuir-Blodgett films of (C₆H₁₃)₃SiOSiPCOGePcOH and similar compounds are to
be used as elements in multicomponent electronic devices, they must have a variety of properties including thermal, chemical, photochemical, mechanical, and electrical stability. Two device studies give evidence of the extent to which films of $(C_6H_{13})_3SiOSiPcOGePcOH$ have the needed properties.

In one of these studies metal-insulator-metal devices, MIM devices, were fabricated by first transferring from 1 to 29 monolayers of $(C_6H_{13})_3SiOSiPcOGePcOH$ onto glass substrates shadowed with aluminum electrodes. Then properly positioned matching electrodes were vapor deposited onto the films.$^{58,91}$

No short circuits were found in these devices. This indicates that the films are quite perfect and have sufficient mechanical toughness to withstand the vapor deposition process.

The capacitance, resistance, and current-voltage curves of 15-layer devices at room temperature were found to be the same before and after they had been heated to 340 °C.$^{58,94}$ This suggests that the main features of the structure of the films are retained up to temperatures of at least 340 °C. Such behavior is in sharp contrast to that of fatty acid films since such films generally melt at temperatures below 100 °C.

The average dielectric breakdown strength of the films in the devices was determined to be 616 MV/m.$^{58,94}$ This indicates that the films have good durability under high voltage stress. They thus differ considerably from barium stearate films since these have a dielectric breakdown strength of 22 MV/m and accordingly have much less durability.$^{94}$
With the 15-layer devices the capacitance was found to increase from 3.1 nF to 3.8 nF when they were transferred from a dry N₂ environment to a 100% humidity environment and to decrease to 3.2 nF when they were returned to a dry N₂ environment.⁵⁸,⁹⁴ These results indicate that devices containing films of \((C₆H₁₃)₃SiOSiPcOGePcOH\) may not need protection from atmospheric moisture in some cases, thus simplifying packaging of the devices.

In the second of these studies, chemiresistor gas sensors were made.⁹³,⁹⁵,⁹⁶ These were made by a multistep process. In this process first a photoresist was spin-coated onto a silicon wafer imprinted with chips carrying gold interdigitated electrodes and other ancillary microelectronic structures. Then the part of the photoresist over the interdigitated electrode was removed. Next, multilayers of \((C₆H₁₃)₃SiOSiPcOGePcOH\) were deposited. Finally, the remaining photoresist and that portion of the multilayer overlying it were removed.

In the last step of this process, UV decomposition of the photoresist and ultrasonic removal of the degraded photoresist and the overlying multilayer were used. The fact that this process could be used shows that the film has substantial resistance to photodegradation and that when properly supported, it also has substantial resistance to delamination.

In flowing gas stream experiments with these sensors, the conductivity of 29-layer devices at 130 °C was found to increase by 10⁴ when the gas stream was changed from N₂ to N₂ containing 111 ppm Cl₂.⁹⁶ When the stream was changed back to pure N₂ the conductivity
returned to the original value within 1 minute. The conductivity of similar devices was also found to increase significantly when they were exposed to low concentrations of NO₂ and I₂.⁹³,⁹⁵,⁹⁶ These experiments give evidence that the films have a useful variable conductivity.

The devices showed no hysteresis when cycled for short periods between exposures to pure N₂ and N₂ containing NO₂ or Cl₂ at 130 °C.⁹⁶,⁹⁷ These results show the stability of the films to oxidizing gases.

On the basis of the data obtained from all these experiments it is clear that the films have a highly desirable set of properties. Further device-work with the films is in progress.

Concluding Remarks on Phthalocyanine Langmuir-Blodgett Films

Multilayer Langmuir-Blodgett films of (C₆H₁₃)₃SiOSiPcOGePcOH have been shown to have a high degree of perfection and to be anisotropic and stable. In addition they have been shown to be capable of forming the active layer in working gas sensors and metal-insulator-metal devices. It is concluded on the basis of isotherm data, compressive creep data, and structural similarities that most of the other amphiphilic two- and three-ring phthalocyanines prepared in this work should also be capable of forming films useful for devices.

Because these amphiphiles have the potential to be derivatized, they have the potential of leading to films with properties varying over a wide range. It thus appears that this family of films should be useful in microelectronic devices other than those already examined.
INFRARED SPECTRA
Figure 15. Infrared spectrum of β-CH₃CoPcCl (mineral oil mull).
Figure 16. Infrared spectrum of α-CH₃GePcCl (mineral oil melt).
Figure 17. Infrared spectrum of CH₃Ce(OM)(mineral oil mull).
Figure 19. Infrared spectrum of (C₆H₅)₃S(O)₂Si(SiC₆H₅)₃ (Nujol mull).
Figure 20. Infrared spectrum of \((\text{C}_6\text{H}_3)_{3}\text{SiO}3\text{Si(C}_6\text{H}_3)_3\text{(Me}_3\text{SiO)}\text{Me})\).
Figure 24. Infrared spectrum of C18H37(C4H9)2SiO(SiC4H9)4Si(C4H9)2C18H37 (mineral oil mul).
Figure 28. Infrared spectrum of (C₆H₃)₃S(O(CH₂O)₂H (mineral oil mull).
Figure 30. Infrared spectrum of $(C_6H_{13})_3SIO(SiPcO)_3C(O)CCl_3$ (mineral oil mull).
Figure 31. Infrared spectrum of (C₆H₁₃)₃Si(SiPC₁₀)₃H (mineral oil mull).
Figure 32. Infrared spectrum of $C_{18}H_{37}(C_{4}H_{9})_{2}S_{10}(SIPc_{13})_{3}(C\equivO)_{2}Cl_{3}$ (mineral oil mull).
Figure 33. Infrared spectrum of $C_{18}H_{37}(C_{8}H_{9})_{2}SiOAlPe$ (mineral oil mull).
Figure 34. Infrared spectrum of C_{18}H_{37}C_{6}H_{5}C_{6}H_{5}O_{2}SiOSiO_{2}AlPc (mineral oil mull).
Figure 35. Infrared spectrum of (C₆H₅)₃SIO₃PGeO₄GeOH (mineral oil mull).
Figure 36. Infrared spectrum of C_{18}H_{37}(C_{4}H_{9})_{2}SO_{2}PC_{6}H_{4}COOH (mineral oil mull).
Figure 37: Infrared spectrum of AlPc(Cl)_{16}Cl (mineral oil null).
Figure 38. Infrared spectrum of GaPc(C1)16Cl (mineral oil mull).
Appendix

II

NMR SPECTRA
Figure 39. NMR spectrum of (C₆H₄(CH₃)₃SiOSiP(H)OH (C₆D₆, 1 x 10⁻²M, 60 °C).
Figure 40. NMR spectrum of C_{18}H_{37}(C_{4}H_{9})_{2}S_{2}O_{3}S_{2}POH (C_{6}D_{6}, 8.7 \times 10^{-3}M, 20^\circ C).
Figure 41. NMR spectrum of $(\text{C}_6\text{H}_{13})_3\text{SiO(SiPcO)}_2\text{H}$ (pyridine-$d_5$, $5.0 \times 10^3\text{M}$, 20°C).
Figure 4.2. NMR spectrum of $\text{C}_{18}\text{H}_{37}(\text{C}_{4}\text{H}_{9})\text{SiCl}_{2}\text{H} \,(\text{C}_{6}\text{D}_{6}, \, 2.6 \times 10^{-3} \text{M}, \, 70 ^\circ \text{C})$. 

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Figure 43. NMR spectrum of (C₆H₅)₃SIO(SiPcO)₃G(O)CCl₃ (pyridine-d₅, 20 °C).
Figure 44. NMR spectrum of $C_{18}H_{37}(C_4H_9)_2SiO(SiPcO)_{3}C(0)CCl_3$ (pyridine-$d_5$, 20 °C).
Figure 45. NMR spectrum of C$_{18}$H$_{37}$C$_6$H$_9$(C$_6$H$_9$)$_2$S$_4$OSIPEAC$_6$ (C$_6$H$_6$, 2.5 x 10$^{-3}$ M, 60 °C).
Figure 46. NMR spectrum of \((\text{C}_6\text{H}_{13})_3\text{SiOSiGeCOH} (\text{CDCl}_3, 4.1 \times 10^{-3} \text{M}, 20^\circ\text{C})\).
Figure 47. NMR spectrum of C18H37(C6H9)2SiOSiPC6H5OH (CDCl3, 3.2 x 10-3M, 20°C).
Notes and References
NOTES AND REFERENCES


49. Adjusted yield is the yield assuming the complete conversion of all stepwise intermediates.


54. Reaction may form tetramethoxysilane.


56. Shutt, J. D., Georgia Tech Research Institute, personal communication, March 1989.


90. Compressive creep is the change in the area of the film with respect to time at constant pressure.


