

of the phosphate as counterion thereby probably forming the photoactive MV^{2+} -EDTA complex also reported recently.²³ Similar competition between Br^- and EDTA for MV^{2+} was observed²⁸ where Br^- reduced the MV^{+} yield as expected from our recent findings.⁹

The toxicity of $MV^{2+}(Cl^-)_2$ as a herbicide is believed to occur through its reduction by the photosynthetic system.¹ As discussed in a preliminary account,⁸ this is certainly the major toxic pathway. Our results suggest that the photochemistry of methyl viologen charge-transfer complexes is a potential parallel toxic pathway since it results in the additional formation of a strong reactive oxidizing agent such as $(X^-)_2$. However, it must be added that the importance of this pathway will of course depend on the location of the methyl viologen in the plant cell. At a given location the relative concentrations of the various anions will determine which are associated with MV^{2+} , while the type of counteranion will determine the photoactivity and the extent of absorption in the solar spectrum, and therefore the potential phototoxicity.

Conclusion

The photochemistry of methyl viologen, in general, seems to involve only the complexed form of the species most probably

because the excited states are very short lived. The photochemistry of the halide complexes presents many interesting and unusual features such as the following: very fast intracomplex rearrangement of the counteranion with its radical form, formation of a bonded radical pair, and generation of both strong reducing and oxidizing radicals, and this with a relatively high quantum yield for the final separated species. Potential applications of the photochemistry of methyl viologen include, for example, generation of H_2 and Cl_2 from MV^{+} and $(Cl^-)_2$ with an upper quantum efficiency of 0.2 with use of solar energy. Finally, when used as an herbicide, the photochemistry of methyl viologen complexes may play a role in the phototoxicity.

Acknowledgment. K.S.P. is grateful for the financial support from N.S.F. (N.S.F. CHE-8117519). The authors are grateful for the very useful scientific discussions held with G. Ferraudi and C. Previtali. The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2577 from the Notre Dame Radiation Laboratory.

Registry No. MV^{+} , 25239-55-8; $MV^{2+}SCN^-$, 92525-86-5; $MV^{2+}(SCN^-)_2$, 92525-87-6; SCN^- , 302-04-5.

A Silicon Phthalocyanine and a Silicon Naphthalocyanine: Synthesis, Electrochemistry, and Electrogenerated Chemiluminescence

Bob L. Wheeler,[†] G. Nagasubramanian,[†] Allen J. Bard,^{*†} Lee A. Schechtman,[‡] David R. Dininny,[‡] and Malcolm E. Kenney^{*†}

Contribution from the Department of Chemistry, University of Texas, Austin, Texas 78712, and the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. Received February 21, 1984

Abstract: The synthesis, spectral characterization, and electrochemical behavior of bis(tri-*n*-hexylsiloxy)(2,3-phthalocyaninato)silicon [$SiPc(OR)_2$], its dimer [$RO(SiPcO)_2R$], and its naphthalocyanine analogue [$SiNc(OR)_2$] are described. All compounds show near-UV absorption corresponding to Soret and N bands and intense absorption in the visible-near-IR region corresponding to Q bands. In CH_2Cl_2 , within the solvent stability limit, there are two reductions and one oxidation for $SiPc(OR)_2$ and two reductions and two oxidations for $RO(SiPcO)_2R$ and $SiNc(OR)_2$; all appear as reversible one-electron waves, although $n = 2$ for the dimer. The difference in the peak potentials of the first oxidation and first reduction waves agrees well with the excitation energy and fluorescence (corresponding to Q bands) of $SiPc(OR)_2$ and $SiNc(OR)_2$. Both compounds emit upon electrochemical generation of reduced and oxidized forms (electrogenerated chemiluminescence, ecl). The corrected ecl maxima are near 684 nm for $SiPc(OR)_2$ and 792 nm for $SiNc(OR)_2$; the latter corresponds to the longest wavelength ecl emission reported so far. The phthalocyanine dimer, $RO(SiPcO)_2R$, is easier to reduce and easier to oxidize than the monomer. The voltammetric waves in this case involve two-electron transfers with peak splittings characteristic of 1e waves, suggesting that the two phthalocyanine rings in the dimer do not strongly interact. No fluorescence or ecl was observed from the dimer.

Phthalocyanine compounds often show high thermal and chemical stability and interesting optical and electrical properties.¹⁻⁵ We and others have been interested in the conductivities of these materials^{6,7} and in their application to the sensitization and stabilization of semiconductor electrodes in photoelectrochemical cells.^{8,9} The group 4 metal phthalocyanines are of interest because various groups can be attached to the axial (or trans) positions.¹⁰ Further, some group 4 phthalocyanines are linear stacked polymers.^{4,11} We describe here the synthesis and the electrochemical and spectroscopic properties of a (trialkylsiloxy)silicon phthalocyanine, bis(tri-*n*-hexylsiloxy)(phthalocyaninato)silicon [$SiPc(OR)_2$], and its 2,3-naphthalocyanine analogue, [$SiNc(OR)_2$] (Figure 1). We also describe the synthesis and properties of the dimeric analogue of the phthalocyanine

[$RO(SiPcO)_2R$]. The presence of the trialkylsiloxy groups on the central Si atom leads to relatively high solubility in these

- (1) Lever, A. B. P. *Adv. Inorg. Chem. Radiochem.* **1965**, *7*, 27.
- (2) Grammatica, S.; Mort, J. *Appl. Phys. Lett.* **1981**, *38*, 445.
- (3) Mizuguchi, J. *Jpn. J. Appl. Phys.* **1981**, *20*, 293.
- (4) Kuznesof, P. M.; Nohr, R. S.; Wynne, K. J.; Kenney, M. E. *J. Macromol. Sci., Chem.* **1981**, *A16*, 299.
- (5) Lever, A. B. P.; Licocchia, S.; Ramaswamy, B. S.; Kandil, A.; Stynes, D. V. *Inorg. Chim. Acta* **1980**, *51*, 169.
- (6) (a) Van Ewyk, R. L.; Chadwick, A. V.; Wright, J. D. *J. Chem. Soc., Faraday Trans.* **1981**, *77*, 73. (b) Diel, B. N.; Inabe, T.; Lyding, J. W.; Schoch, K. F., Jr.; Kannewurf, C. R.; Marks, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 1539.
- (7) Nohr, R. S.; Kuznesof, P. M.; Wynne, K. J.; Kenney, M. E.; Siebenman, P. G. *J. Am. Chem. Soc.* **1981**, *103*, 4371.
- (8) (a) Leempoel, P.; Castro-Acuna, M.; Fan, F.-R. F.; Bard, A. J. *J. Phys. Chem.* **1982**, *86*, 1396. (b) Jaeger, C. D.; Fan, F.-R. F.; Bard, A. J. *J. Am. Chem. Soc.* **1980**, *102*, 2592.
- (9) Shepard, V. R., Jr.; Armstrong, N. R. *J. Phys. Chem.* **1979**, *83*, 1268.

[†]University of Texas.

[‡]Case Western Reserve University.

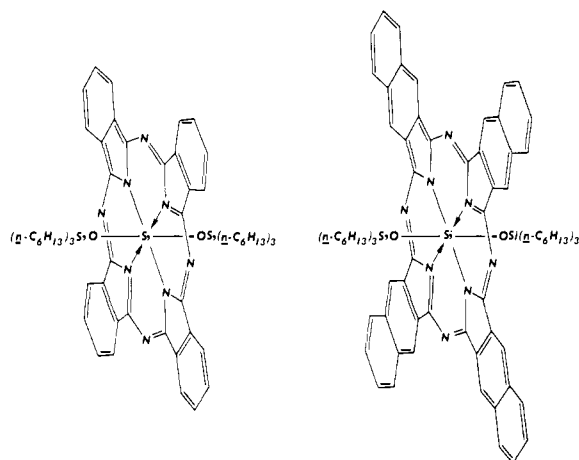


Figure 1. Structures of $\text{SiPc}[\text{OSi}(n\text{-C}_6\text{H}_{13})_3]_2$ and $\text{SiNc}[\text{OSi}(n\text{-C}_6\text{H}_{13})_3]_2$.

compounds and permits studies of solutions of them at the millimolar level.

Experimental Section

Synthesis of $\text{SiNc}[\text{OSi}(n\text{-C}_6\text{H}_{13})_3]_2$ and $\text{SiPc}[\text{OSi}(n\text{-C}_6\text{H}_{13})_3]_2$. **2,3-Naphthalenedicarbonitrile.** The procedure is a modification of one used by Luk'yanets.¹² A mixture of $\alpha,\alpha,\alpha',\alpha'$ -tetrabromo-*o*-xylene (200 g), fumaronitrile (64 g), NaI (200 g), and dry dimethylformamide (2 L) was heated at 75 °C for 5.5 h. The resultant was allowed to cool to 65 °C and then poured into a mixture of ice and water (3 L). Sodium bisulfite was added to the suspension obtained (which was dark red), until it turned yellow-tan (65 g). The product was filtered off, washed, vacuum dried (70 °C), and weighed (65 g, 78%).

A small portion of this product was sublimed (160 °C) in air at atmospheric pressure: mp 256 °C (lit.¹² 251 °C); IR (Nujol) 2220 ($\text{C}\equiv\text{N}$) cm^{-1} ; NMR (200 MHz, CDCl_3) δ 8.37 (s, 1,4-H); 8.00 (m, 5,8-H), 7.81 (m, 6,7-H); mass spectrum, m/z (rel intensity) 178 (M^+ , 100), 151 (20). Anal. Calcd for $\text{C}_{12}\text{H}_6\text{N}_2$: C, 80.88; H, 3.40; N, 15.72. Found: C, 80.83; H, 3.56; N, 15.68.

The sublimed compound is composed of small, colorless needles. The synthesis product is a beige color and is satisfactory for use as an intermediate.

1,3-Diiminobenz(*f*)isoindoline. The synthesis used by Esposito for 1,3-diiminoisoindoline¹³ served as a model. Anhydrous NH_3 was slowly bubbled through a stirred mixture of 2,3-naphthalenedicarbonitrile (10.2 g), sodium methoxide (1.5 g), and dry methanol (90 mL) for 45 min. With continued NH_3 introduction, the mixture was refluxed for 3 h. After the resultant had cooled, the product was collected by filtration, washed, air dried, and weighed (9.2 g, 82%): IR (Nujol) 3285, 3200, 3080, 1700, 1640, 1545, 1520 cm^{-1} ; NMR (100 MHz, $(\text{CD}_3)_2\text{SO}$) δ 8.31 (s, 1,4-H), 8.08 (m, 5,8-H), 7.68 (m, 6,7-H); mass spectrum, m/z (rel intensity) 196 (70), 195 (M^+ , 100), 179 (68), 126 (51), 63 (59), 51 (55).

From batch to batch the product ranges from yellow to green. Attempts made to purify it by recrystallization and sublimation failed. As obtained, the product is sufficiently pure for use as a naphthalocyanine precursor.

SiNcCl_2 . A mixture of 1,3-diiminobenz(*f*)isoindoline (6.0 g), SiCl_4 (5.4 mL), dry tetrahydronaphthalene (40 mL), and dry tri-*n*-butylamine (20 mL) was refluxed for 2.5 h. The resultant was allowed to cool and then diluted with methanol (30 mL). The product was filtered off, washed, air dried, and weighed (5.8 g): IR (Nujol) 475 (m, Si-Cl) cm^{-1} .

The product is quite impure, containing perhaps as much as 20–40% impurities. It is dark green and has very low solubility in a variety of organic solvents. It also has little volatility. Attempts made to purify it failed.

$\text{SiNc}(\text{OH})_2$. A mixture of SiNcCl_2 (5.8 g) and concentrated H_2SO_4 (200 mL) was stirred for 2 h and then poured over ice (600 g). The solid was filtered off and washed with water and an acetone–water solution. A mixture of this solid and concentrated NH_4OH (150 mL) was refluxed

for 1 h and allowed to cool. The resulting solid was filtered off, vacuum dried, and weighed (5.6 g). Part of it (4.3 g) was extracted with pyridine in a Soxhlet extractor, washed, vacuum dried, and weighed (2.8 g).

A pure sample of the hydroxide was obtained by hydrolysis of $\text{SiNc}[\text{OSi}(n\text{-C}_6\text{H}_{13})_3]_2$ (see below). A mixture of chromatographed $\text{SiNc}[\text{OSi}(n\text{-C}_6\text{H}_{13})_3]_2$ (100 mg), water (3 mL), 1,2-dimethoxyethane (60 mL), and concentrated HCl (0.06 mL) was refluxed for 5 h. The resulting suspension was allowed to cool, and the solid was collected by filtration, washed, vacuum dried, and weighed (29 mg, 50%): IR (Nujol) 3435 (O-H), 840 (Si-O) cm^{-1} . Anal. Calcd for $\text{C}_{48}\text{H}_{26}\text{N}_8\text{O}_2\text{Si}$: C, 74.40; H, 3.38; Si, 3.62. Found: C, 74.04; H, 3.71; Si, 3.52.

The compound is green. It is, at best, only slightly soluble in a variety of organic solvents. The product of the SiNcCl_2 synthesis is generally satisfactory for use as an intermediate.

$\text{SiNc}[\text{OSi}(n\text{-C}_6\text{H}_{13})_3]_2$. For the synthesis of this compound, a mixture of $\text{SiNc}(\text{OH})_2$ made from SiNcCl_2 (600 mg), tri-*n*-hexylchlorosilane (3.0 mL), dry tri-*n*-butylamine (2.0 mL), and dry 3-picoline (70 mL) was refluxed for 1.5 h. The solution obtained was allowed to cool and then filtered (no residue). The filtrate was poured into an ethanol–water solution (1:1, 100 mL), and the product was separated by filtration from the resulting suspension. After being washed, it was vacuum dried and weighed (808 mg, 78%).

The product was chromatographed on alumina (activity I) with a toluene–hexane solution (3:1) as the eluant: mp 278 °C; IR (Nujol) 1250 (Si-CH₂), 1040 (Si-O-Si) cm^{-1} ; NMR (200 MHz, CDCl_3) δ 10.11 (s, 1,4-Nc), 8.69 (m, 5,8-Nc), 7.94 (m, 6,7-Nc), 0.61 (m, ϵ -CH₂), 0.41 (t, CH₃), 0.22 (m, δ -CH₂) 0.06 (m, γ -CH₂), -0.98 (m, β -CH₂), -2.05 (m, α -CH₂). Anal. Calcd for $\text{C}_{84}\text{H}_{102}\text{N}_8\text{O}_2\text{Si}_3$: C, 75.29; H, 7.67; Si, 6.29. Found: C, 75.05; H, 7.69; Si, 6.03.

The compound is green. It is stable and soluble in a variety of non-polar and chlorinated organic solvents. However, it is insoluble in acetonitrile. As shown by its NMR spectrum, the synthesis product contains a small amount of the dimer $(n\text{-C}_6\text{H}_{13})_2\text{SiO}(\text{SiNcO})_2\text{Si}(n\text{-C}_6\text{H}_{13})_2$.

$\text{SiPc}[\text{OSi}(n\text{-C}_6\text{H}_{13})_3]_2$. A synthetic procedure similar to that described by Douglass¹⁴ was followed. A mixture of $\text{SiPc}(\text{OH})_2$ (0.75 g), tri-*n*-hexylchlorosilane (5.0 mL), and dry pyridine (75 mL) was refluxed for 5 h. After the solution obtained had been allowed to cool, it was filtered (no residue) and concentrated under vacuum. The resulting oil was mixed with pentanes (10 mL), and the slurry formed was filtered. The solid was washed with pentanes (10 mL) and an acetone–water solution, vacuum dried, and weighed (0.78 g). To recover additional product, the pentane filtrates were combined, concentrated, and filtered. The solid was washed, vacuum dried, and weighed (0.28 g, combined yield 78%).

The combined solids were chromatographed as described by Janson¹⁵ on alumina (activity I) with a toluene–hexanes solution (1:2) as the eluant: mp 175 °C (lit.¹⁵ 175 °C); IR (Nujol) 1250 (Si-CH₂), 1040 (Si-O-Si) cm^{-1} ; NMR (200 MHz, CDCl_3) δ 9.63 (m, 3,6-Pc), 8.31 (m, 4,5-Pc), 0.82 (m, ϵ -CH₂), 0.71 (t, CH₃), 0.36 (m, δ -CH₂), 0.02 (m, γ -CH₂), -1.28 (m, β -CH₂), -2.45 (m, α -CH₂). Anal. Calcd for $\text{C}_{68}\text{H}_{94}\text{N}_8\text{O}_2\text{Si}_3$: C, 71.66; H, 8.31; Si, 7.39. Found: C, 71.60; H, 8.37; Si, 7.41.

In accordance with expectations, the compound is stable and is blue when finely divided. It can be sublimed under vacuum at elevated temperatures and is soluble in many organic solvents including mixed pentanes. The synthesis product contains, as is evident from its NMR spectrum, a small amount of $(n\text{-C}_6\text{H}_{13})_2\text{SiO}(\text{SiPcO})_2\text{Si}(n\text{-C}_6\text{H}_{13})_2$.¹⁴

$(n\text{-C}_6\text{H}_{13})_2\text{SiO}(\text{SiPcO})_2\text{Si}(n\text{-C}_6\text{H}_{13})_2$. The procedure used earlier¹⁶ for a similar dimer was employed as a model. A mixture of $\text{SiPc}(\text{OH})_2$ (540 mg), SiPcCl_2 (294 mg), dry tri-*n*-butylamine (1.0 mL), and dry, nitrogen-purged quinoline (65 mL) was refluxed for 15 min. The resulting suspension was allowed to cool, mixed with concentrated HCl (46 mL), and filtered. The solid obtained was washed. A mixture of this solid and concentrated H_2SO_4 (50 mL) was stirred for 2 h and then poured over ice (200 g). The solid was filtered off and washed. A mixture of the solid, concentrated NH_4OH (150 mL), and pyridine (10 mL) was refluxed for 1 h, cooled, and filtered. The resulting hydroxy-capped oligomers were washed, vacuum-dried, and weighed (763 mg, 96%).

A mixture of the oligomers (707 mg), tri-*n*-hexylchlorosilane (0.5 mL), and dry pyridine (125 mL) was refluxed for 2.5 h. The solution obtained was filtered while hot (46 mg of residue) and evaporated to dryness under vacuum. After being washed, the solid was air dried and weighed (1.13 g).

(10) Krueger, P. C.; Kenney, M. E. *J. Org. Chem.* **1963**, *28*, 3379.

(11) (a) Joyner, R. D.; Kenney, M. E. *Inorg. Chem.* **1962**, *1*, 717. (b) Hanack, M.; Mitulla, K.; Pawlowski, G.; Subramanian, L. R. *J. Organomet. Chem.* **1981**, *204*, 315.

(12) Kovshov, E. I.; Puchnova, V. A.; Luk'yanets, E. A. *J. Org. Chem. USSR (Engl. Transl.)* **1971**, *7*, 364; *Zh. Org. Khim.* **1971**, *7*, 369.

(13) Lowery, M. K.; Starshak, A. J.; Esposito, J. N.; Krueger, P. C.; Kenney, M. E. *Inorg. Chem.* **1965**, *4*, 128.

(14) Douglass, S. L. Ph.D. Dissertation, Case Western Reserve University, Cleveland, OH, 1975.

(15) Janson, T. R. Ph.D. Dissertation, Case Western Reserve University, Cleveland, OH, 1971.

(16) Mezza, T. M.; Armstrong, N. R.; Ritter, G. W., II; Iafalice, J. P.; Kenney, M. E. *J. Electroanal. Chem.* **1982**, *137*, 227.

This solid was chromatographed on alumina (activity III). The desired product was eluted with a toluene-hexanes solution (1:3) (376 mg, 32% overall): mp 201 °C; IR (Nujol) 1250 (Si-CH₂), 1025 (SiR-O-SiPc), 970 (SiPc-O-SiPc) cm⁻¹; NMR (200 MHz, CDCl₃) δ 9.00 (m, 3,6-Pc), 8.31 (m, 4,5-Pc), 0.43 (overlapping m, CH₃ and ε-CH₂), -0.30 (m, δ-CH₂), -0.65 (m, γ-CH₂), -2.29 (m, β-CH₂), -3.54 (m, α-CH₂).

The compound is a blue solid that is soluble in common organic solvents. Further elution of the column yielded the trimer, the tetramer, and a mixture with a substantial pentamer content.

Elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, TN.

Electrochemical Measurements. The solvent, methylene chloride (CH₂Cl₂, MCB Omnisolv grade; EM Science, Gibbstown, NJ), was dried by vacuum distillation over molecular sieves and stored in a helium-filled Vacuum Atmosphere Corp. (Hawthorne, CA) glovebox. Polarographic grade tetra-*n*-butylammonium perchlorate (TBAP), which was recrystallized twice from acetone-ether and dried under a vacuum of better than 10⁻⁵ torr for 2 days, was used as the supporting electrolyte at 0.1 M concentration. For electrochemical measurements a three-compartment electrochemical cell of 25-mL capacity was used. A Pt disk of ~0.03 cm² area was used as the working electrode. A large area (>40 cm²) Pt gauze, separated from the working electrode by a fine porosity glass frit, was the counter electrode. The reference electrode, a quasi-reference Ag electrode, denoted as AgRE, was also separated from the main compartment by a fine-porosity glass frit and the reference and counter electrodes were immersed in a solution containing the solvent, CH₂Cl₂, and 0.1 M TBAP. In a typical experiment, before the addition of the phthalocyanine or naphthalocyanine compounds, the CH₂Cl₂-0.1 M TBAP solution was stirred with activated alumina (Woelm Neutral Alumina, activity Super I, Woelm Pharma GmbH and Co., Eschwege, BRD) to remove any residual water and was then placed in all three cell compartments. The concentrations of the SiPc(OR)₂, RO(SiPcO)₂R, and SiNc(OR)₂ in the working electrode compartment were around 2.2, 1.0, and 1.4 mM, respectively. All the experiments were carried out inside the glovebox. At the conclusion of the experiments the cell was taken out of the glovebox, and the potential of the AgRE was measured against the aqueous saturated calomel electrode (SCE). Because of the slow shift in the AgRE, mainly due to a seepage of redox couple into the reference compartment, potentials reported vs. SCE were within ±100 mV for SiNc(OR)₂ and ±10 mV for SiPc(OR)₂ and RO(SiPcO)₂R. Positive-feedback *i*R compensation was used to minimize the uncompensated resistance during cyclic voltammetric experiments.

A Princeton Applied Research (PAR) Model 173 potentiostat and a PAR Model 175 universal programmer equipped with a Houston Instruments (Austin, TX) model 2000 X-Y recorder was used to obtain cyclic voltammograms and, with a time-base module, for chronoamperometry. For ac voltammetry, a Soltec (Sun Valley, CA) Model 6432, X-Y₂ recorder was employed. For the ac voltammetry, the lock-in amplifier technique which yields the in-phase (0° component) and the out-of-phase (90° component) components of a sine wave superimposed on a linear potential ramp was employed. For the above measurement a PAR Model 5204 lock-in amplifier was used, which output simultaneously the phase angle and the in-phase component. The low harmonic distortion ac signal (12 mV_{pk-pk}) at different frequencies was obtained for input into the potentiostat from a Model 200 CD wide-range oscillator (Hewlett-Packard, Palo Alto, CA).

Spectral Studies. The electronic spectra of the two compounds were recorded with a Cary 17D (Varian Associates, Sunnyvale, CA) spectrophotometer. Infrared spectra were obtained with a Perkin-Elmer 598 infrared spectrophotometer (Perkin-Elmer Corp., Norwalk, CT). A Varian HA-100 NMR spectrometer equipped for Fourier-transform operation was used to record the 100-MHz spectrum while a Varian XL-200 instrument was used to record the 200-MHz spectra. Mass spectra were obtained with an AEI MS-30 spectrometer (Associated Electrical Industries, Manchester, England). The samples were introduced by means of a heated solid probe (350 °C) and ionized by electron impact (70 eV). For fluorescence studies an Aminco-Bowman spectrophotometer with appropriate slits to achieve a band-pass of 5 nm for both excitation and emission was used. A photomultiplier tube R928 (Hamamatsu TV Co., Ltd., Middlesex, NJ) in conjunction with a grating monochromator Model 7240 (Oriol Corporation, Stamford, CT) with 1-μm blaze and slits for 30-nm bandwidth were used for recording the eel spectra. The procedure used was similar to that reported previously.¹⁷

Results and Discussion

Synthetic Considerations. The syntheses for SiNcCl₂ and SiNc(OR)₂ and the synthesis for SiNc(OH)₂ from SiNcCl₂ are

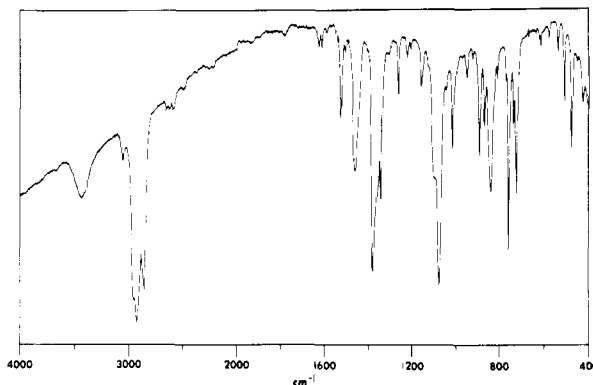


Figure 2. Infrared spectrum of SiNc(OH)₂ in a Nujol mull (KBr plates).

modeled on analogous syntheses for the corresponding phthalocyanines.^{13,14,18} In view of the nature of the routes previously found to be useful for the preparation of silicon phthalocyanines¹⁹ and the satisfactory character of the synthesis for SiNcCl₂, it seems probable that SiNcCl₂ will generally be found to be a good entry point for the synthesis of silicon naphthalocyanines. Further, since the synthesis for SiNc(OH)₂ is also satisfactory, it appears the SiNcCl₂ and SiNc(OH)₂ will be generally found to be good intermediates for the preparation of silicon naphthalocyanines.

Chemical and Physical Properties. The chemical stability of the SiNc system is illustrated by its ability to survive intact during the concentrated H₂SO₄ hydrolysis of SiNcCl₂. In large part the resistance of the ring in this system to degradation can be attributed to its aromaticity while the resistance of the silicon to expulsion from the system can be associated with the macrocyclic (chelate) effect. The nonlability of the silicon of this system is of interest because the silicon is bound by Si-N bonds. The parallel nonlability of the silicon in the SiPc system has previously been noted as being of interest for the same reason.¹⁸

On the basis of the available data, it is clear that the solubility, volatility, and melting point characteristics of SiNcCl₂, SiNc(OH)₂, and SiNc[OSi(*n*-C₆H₁₃)₃]₂ are directly associated with the size and nature of their axial ligands. These properties can be understood in terms of the relative strengths of the π-π and other intermolecular interactions involved.

In accordance with expectations, the shapes and positions of the naphthalocyanine bands in the infrared spectra of the three naphthalocyanines are quite similar. Also in accordance with expectations, the pattern of the naphthalocyanine bands is, as is illustrated by the spectrum of SiNc(OH)₂ (Figure 2) comparatively simple.

The NMR spectrum of SiNc[OSi(*n*-C₆H₁₃)₃]₂ (Figure 3) shows that the naphthalocyanine ring produces, not surprisingly, a large ring-current effect. Because of this, the assignments of the individual resonances of the hexyl compound are straightforward. However, it is of interest that, although the hexyl resonances of this compound and those of SiPc[OSi(*n*-C₆H₁₃)₃]₂ are similarly positioned, the resonances of the inner hexyl protons of the naphthalocyanine are shifted upfield less than the resonances of the corresponding protons of the phthalocyanine. Conversely, the resonances of the outer hexyl protons of the naphthalocyanine are shifted more. Since the chains are probably similarly extended and positioned in the two compounds (in solution), it appears that for comparable regions above the rings and near their centers the ring-current effect is somewhat less for the naphthalocyanine ring, but that for comparable regions above and further out the effect is somewhat greater. The greater ring-current effect of the naphthalocyanine ring further out can be ascribed to its greater spread.

Comparison of the positions of like protons in the hexyl chains of SiPc[OSi(*n*-C₆H₁₃)₃]₂ and (*n*-C₆H₁₃)₃SiO(SiPcO)₂Si(*n*-C₆H₁₃)₃ shows that the hexyl protons of the dimer are upfield of those of

(18) Joyner, R. D.; Kenney, M. E. *Inorg. Chem.* **1962**, *1*, 236.

(19) Pommier, J. C. *Rev. Silicon, Germanium, Tin, Lead Compd.* **1979**, *4*, 91.

(17) Keszthelyi, C. P.; Tachikawa, H.; Bard, A. J. *J. Am. Chem. Soc.* **1972**, *94*, 1522.

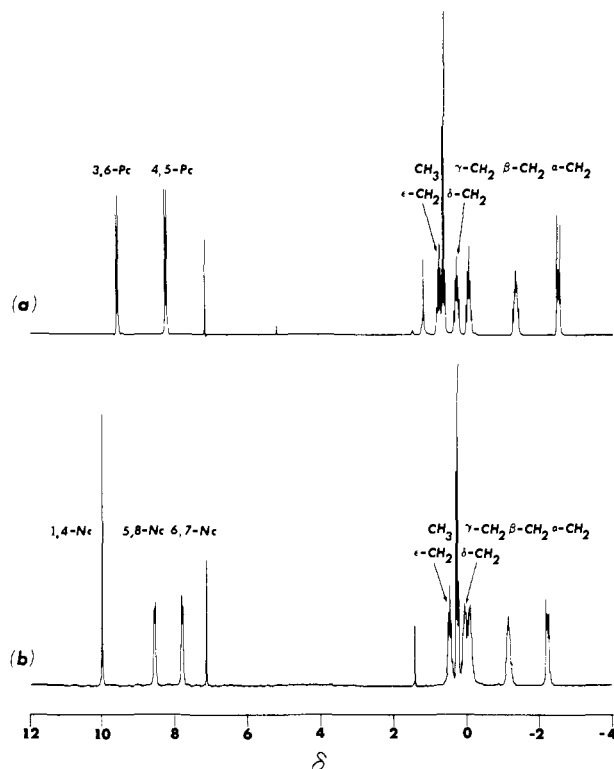


Figure 3. NMR spectra, 200 MHz, of (a) $\text{SiPc}[\text{OSi}(n\text{-C}_6\text{H}_{13})_3]_2$ and (b) $\text{SiNc}[\text{OSi}(n\text{-C}_6\text{H}_{13})_3]_2$ in CDCl_3 .

Table I. Values of E° (V vs. SCE) for $\text{SiPc}(\text{OR})_2$, $\text{RO}(\text{SiPcO})_2\text{R}$, and $\text{SiNc}(\text{OR})_2$ in CH_2Cl_2

	$\text{SiPc}(\text{OR})_2$, V vs. SCE	$\text{SiNc}(\text{OR})_2$, V vs. SCE	$\text{RO}(\text{SiPcO})_2\text{R}$, V vs. SCE
2nd ox.		+1.24	+1.20
1st ox.	+1.00	+0.58	+0.71
1st red.	-0.90	-1.01	-0.81
2nd red.	-1.48	-1.55	-1.21
$-\Delta H^\circ$, eV	1.8 ± 0.1	1.5 ± 0.1	
singlet emission energy, eV	1.86	1.61	

the monomer. This is attributed to the additivity of the shielding effects of the rings in the dimer.²⁰

Electrochemical Measurements. The stability limits of CH_2Cl_2 with 0.1 M TBAP were +1.6 to -2.3 V vs. AgRE. In the working potential window two reductions and one oxidation of $\text{SiPc}(\text{OR})_2$ and two reductions and two oxidations of $\text{RO}(\text{SiPcO})_2\text{R}$ and $\text{SiNc}(\text{OR})_2$ were observed. Typical cyclic voltammograms at 20 mV/s are shown in Figure 4. From their general shape, all waves appear to be reversible one-electron transfers. Such multiple oxidation and reduction waves have been reported for other phthalocyanines in nonaqueous media.^{11,16,21} The average values of the peak potentials obtained at several scan rates are given in Table I. Note that while it is easier to oxidize $\text{SiNc}(\text{OR})_2$ than $\text{SiPc}(\text{OR})_2$, the reduction potentials of both are nearly the same. The lack of observation of a second oxidation wave in the $\text{SiPc}(\text{OR})_2$ species probably can be attributed to the onset of background oxidation before its appearance. Ac voltammetry experiments performed with benzonitrile as the solvent indicate a second oxidation wave near the solvent limit at +2.1 V vs. SCE, 1.1 V positive of the first oxidation wave in this solvent. The difference in potential in CH_2Cl_2 between the first and second

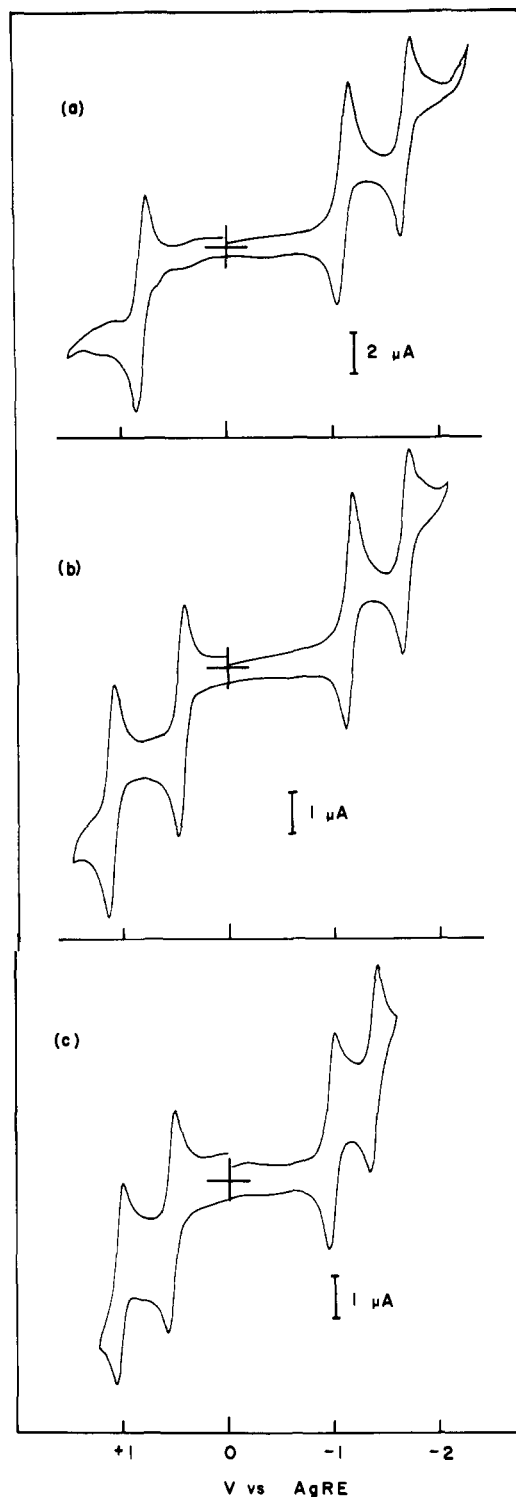


Figure 4. Cyclic voltammogram of (a) 2.2 mM $\text{SiPc}[\text{OSi}(n\text{-C}_6\text{H}_{13})_3]_2$, (b) 1.4 mM $\text{SiNc}[\text{OSi}(n\text{-C}_6\text{H}_{13})_3]_2$, and (c) 1.0 mM $(n\text{-C}_6\text{H}_{13})_3\text{SiO}(\text{SiPcO})_2\text{Si}(n\text{-C}_6\text{H}_{13})_3$ in CH_2Cl_2 , 0.1 M TBAP. Scan rate = 20 mV/s.

reduction waves, 0.5 V, agrees with that found by Lever et al.^{21c} for $\text{PcSi}(\text{O-tert-amy})_2$ in DMF. Further information about the electrochemical processes were obtained by investigating the dependence of peak currents (i_p) and potentials (E_p) on scan rate (v) and by ac voltammetric methods. For the first reduction peaks of all these compounds $i_{pc}/v^{1/2}$ was constant and $i_{pc} = i_{pa}$ for v between 0.005 and 2.0 V/s. Similar results were obtained for the first oxidation waves. These results demonstrate that the products of the first oxidation and reduction are stable on the cyclic voltammetric time scale and the waves are diffusion limited. Although it is more difficult to obtain quantitative data for the later peaks, the general shape and behavior of these also suggest

(20) Jansen, T. R.; Kane, A. R.; Sullivan, J. F.; Knox, K.; Kenney, M. E.; *J. Am. Chem. Soc.* **1969**, *91*, 5210.

(21) (a) Clack, D. W.; Hush, N. S.; Woolsey, I. S. *Inorg. Chim. Acta* **1976**, *19*, 129. (b) Lever, A. B. P.; Wiltshire, J. P. *Inorg. Chem.* **1978**, *17*, 1145. (c) Lever, A. B. P.; Licocchia, S.; Magnell, K.; Minor, P. C.; Ramaswamy, B. S. *Adv. Chem. Ser.* **1982**, *201*, 237.

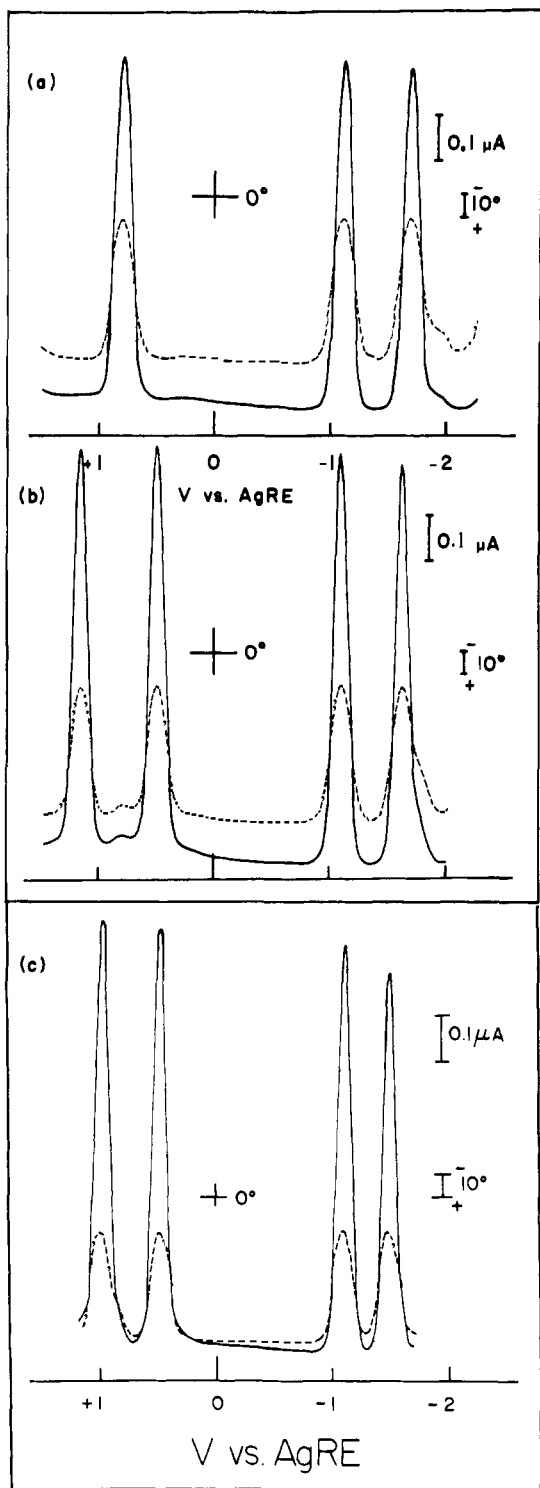


Figure 5. (a) Ac voltammogram of $\text{SiPc}[\text{OSi}(n\text{-C}_6\text{H}_{13})_3]_2$, 2.2 mM, in CH_2Cl_2 , 0.1 M TBAP; (b) ac voltammogram of $\text{SiNc}[\text{OSi}(n\text{-C}_6\text{H}_{13})_3]_2$, 1.4 mM, in CH_2Cl_2 , 0.1 M TBAP; (c) ac voltammogram of $(n\text{-C}_6\text{H}_{13})_3\text{SiO}(\text{SiPcO})_2\text{Si}(n\text{-C}_6\text{H}_{13})_3$, 1.0 mM, in CH_2Cl_2 , 0.1 M TBAP. For all, ac frequency = 50 Hz, scan rate = 2 mV/s, in phase (—), phase angle (---).

stability of the product of the second reduction for all compounds and the product of the second oxidation of $\text{RO}(\text{SiPcO})_2\text{R}$ and of $\text{SiNc}(\text{OR})_2$. The waves also appear to be Nernstian ones with peak splittings ($\Delta E_p = E_{pa} - E_{pc}$) of the order of 80 mV. Deviation of ΔE_p from the rigorous Nernstian value of about 60 mV can probably be attributed to effects of uncompensated resistance in this relatively resistive solvent. Further evidence for the rapidity of the heterogeneous electron-transfer reactions of all of the waves was obtained by ac voltammetric measurements (Figure 5). The in-phase (0°) component of the ac current and the phase angle

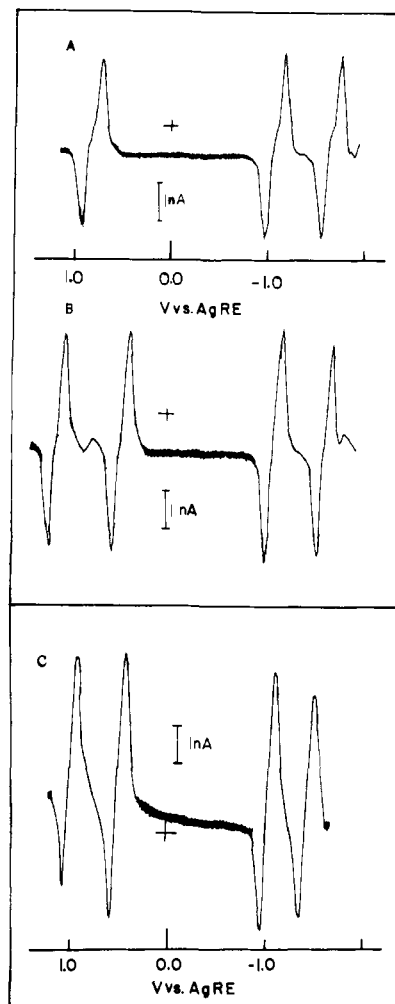


Figure 6. (A) Second harmonic ac voltammogram for the solution in Figure 5a; (B) same for solution in Figure 5b; (C) same for solution in Figure 5c. For all, ac fundamental frequency = 200 Hz, scan rate = 2 mV/s.

of this current with respect to the superimposed 50-Hz potential variation are essentially equal for all waves. The deviation of the phase angle from the expected Nernstian value of 45° again can probably be attributed to uncompensated resistance. If the phase angle is adjusted to 90° in the region where no faradaic current flows ($+0.1$ – 0.8 V vs. AgRE), by manipulating the lock-in phase shifter, the phase angle at the peak potentials equals $45 \pm 2^\circ$. Similarly, the second harmonic ac voltammetric peaks,²² with an applied signal at 200 Hz are all essentially equal (Figure 6), again suggesting rapid electron-transfer rates. Controlled potential coulometry at the first reduction waves of $\text{SiPc}(\text{OR})_2$ and $\text{SiNc}(\text{OR})_2$ yield n_{app} values (Faradays/mole) of 1.0 and 1.1, respectively. Cyclic voltammetry of the reduced solutions, with an initial anodic scan, showed essentially the same pattern of waves as the original solution of parent compound. Reoxidation of these solutions consumed essentially the same number of faradays as the initial reduction and regenerated the starting solution. Parallel behavior was found for coulometric oxidation at the first waves, with n_{app} values of 1.1 (Pc) and 1.0 (Nc). These results confirm the one-electron nature of the cyclic voltammetric waves and the high stability of the one-electron reduced and oxidized products.

For the dimer $\text{RO}(\text{SiPcO})_2\text{R}$, however, bulk electrolysis gave $n_{\text{app}} = 2.0$ for oxidation at the first anodic wave and $n_{\text{app}} = 2.2$ for reduction at the first cathodic wave. That the reduction and oxidation products were stable was clear from voltammetric scans following bulk electrolysis as well as the ability to regenerate the

(22) Bard, A. J.; Faulkner, L. R. "Electrochemical Methods. Fundamentals and Applications"; Wiley: New York, 1980.

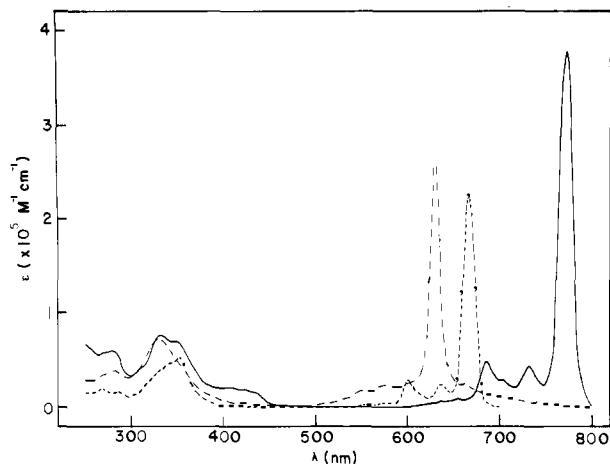


Figure 7. Electronic absorption spectra of 1.1×10^{-5} M SiPc[OSi(n -C₆H₁₃)₃]₂ (---), 1.2×10^{-5} M RO(SiPcO)₂R (···), and 2.5×10^{-6} M SiNc[OSi(n -C₆H₁₃)₃]₂ (—) in CH₂Cl₂.

original parent solution electrolytically. Thus, although the voltammetric wave shapes are characteristic of one-electron reactions (e.g., $\Delta E_p \approx 70$ mV), these clearly represent two-electron transfers. Waves of this type have been observed before and are ascribed to molecules which have two identical non-interacting systems.²³ This would suggest that there is no or little interaction between the two SiPc groups in the dimeric molecule, with each accepting or losing an electron independently. However, in previous cases of noninteracting systems the potentials for electron transfer in the multi-centered species were very near those of the monomer, while in this case the potential for oxidation of the dimer is shifted by about 0.3 V toward less positive potentials (Table I), with a smaller (~ 90 mV) shift of the first reduction wave. This shift might be attributable to an inductive (electron donating) effect of the SiPc(OR) group compared to the (OR) group. Alternatively the groups may be interacting, but that a rearrangement occurs following the first electron transfer which promotes the second. Because both oxidation and reduction of the dimer show the same 2e nature with peak splittings similar to the monomer, this latter proposal seems unlikely. In a previous study of the electrochemistry of closely related SiPc compounds,¹⁶ in which the (n -C₆H₁₃)₃ groups attached to the Si were replaced by (CH₃)₂(*t*-Bu), the oxidation and reduction waves of the dimeric species were attributed to one-electron reactions on the basis of thin layer coulometric studies of 10^{-6} M solutions. The reason for this difference in behavior is not clear and bears further investigation.

Diffusion coefficients (D) for these compounds were estimated from Cottrell plots²² (current vs. $t^{1/2}$ for potential steps from near the rest potential (0 V vs. SCE) to the diffusion-limited region of the first oxidation and reduction waves). Linear i vs. $t^{1/2}$ plots with zero intercepts were obtained for data between approximately 1 and 10 s. For SiPc(OR)₂, a step from 0 to +1.2 V vs. SCE or from 0 to -1.1 V vs. SCE was employed; from the slope of the i vs. $t^{1/2}$ curve, $D = (5.7 \pm 1.1) \times 10^{-6}$ cm²/s. For SiNc(OR)₂, steps of 0 to +0.8 V or 0 to -1.2 V were used and yielded $D = (5.2 \pm 0.4) \times 10^{-6}$ cm²/s. This slightly smaller D value is consistent with the larger ring size in the Nc species. For RO(SiPcO)₂R, steps from 0 to -1.0 V or 0 to +0.9 V gave $D = (2.2 \pm 0.3) \times 10^{-6}$ cm²/s taking $n = 2$. This comparatively low value is consistent with the bulkier nature of the dimer.

Absorption and Fluorescence. The UV-visible absorption spectra for 1.1×10^{-5} M SiPc(OR)₂, 1.2×10^{-5} M RO(SiPcO)₂R, and 2.5×10^{-6} M SiNc(OR)₂ in CH₂Cl₂ are given in Figure 7. SiPc(OR)₂ and SiNc(OR)₂ have the features expected on the basis of previous work.²⁴⁻²⁶ The spectrum of SiPc(OR)₂ shows the

Table II. Q-Band Absorption and Emission Maxima (nm) of SiPc(OR)₂ and SiNc(OR)₂

	SiPc(OR) ₂		SiNc(OR) ₂	
	absorption	emission	absorption	emission
S ₀ (0) ↔ S ₁ (0)	668	668	772	772
S ₀ (0) ↔ S ₁ (1)	638	708	732	790
S ₀ (0) ↔ S ₁ (2)	612	741	704	
S ₀ (0) ↔ S' ₁ (0)	601		686	
S ₀ (0) ↔ S' ₁ (1)	575		655	
S ₀ (0) ↔ S' ₁ (2)	557		636	

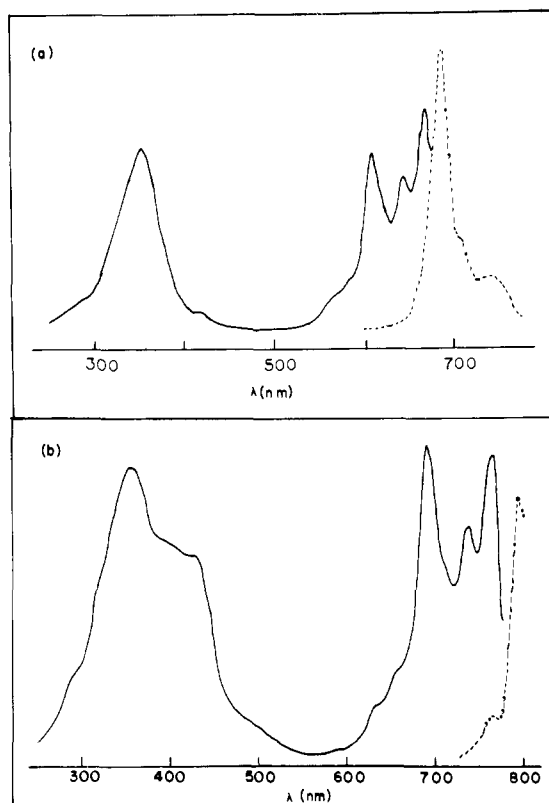


Figure 8. (a) Fluorescence spectrum (uncorrected) of 1.1×10^{-5} M SiPc[OSi(n -C₆H₁₃)₃]₂ in CH₂Cl₂. For excitation spectrum (—), the emission was monitored at 684 nm. For the emission spectrum (---), the excitation was at 350 nm. Bandwidth = 5 nm; (b) fluorescence spectrum (uncorrected) for 1.0×10^{-5} M SiNc[OSi(n -C₆H₁₃)₃]₂ in CH₂Cl₂. For excitation spectrum (—), emission was monitored at 792 nm. For emission spectrum (---), excitation was at 356 nm. Bandwidth = 5 nm.

characteristic absorption for the Soret band at 350 nm, the N band at ~ 270 nm, and the series of peaks due to the Q-band transitions. The absorption in the Q-band region (550–700 nm) appears to be composed of transitions from the ground state to two excited states. The absorption in the Q-band region for SiNc(OR)₂ is similar. The wavelength for these absorptions are listed in Table II.

The shift in the Soret- and Q-band absorptions toward higher energy in the dimer, RO(SiPcO)₂R, relative to SiPc(OR)₂ has been explained previously in terms of exciton coupling of neutral-excitation transitions of the two rings of the dimer.²⁷ The UV-visible absorption spectra of RO(SiPcO)₂R has all the features of the phthalocyanine dimers of these previous works.

Fluorescence is observed from SiPc(OR)₂ and SiNc(OR)₂ in CH₂Cl₂ solution. The uncorrected emission and excitation spectra are given in Figure 8. Both compounds show emissions in the Q-band region for excitation in either Q or the Soret absorption

(23) (a) Flanagan, J. B.; Margel, S.; Bard, A. J.; Anson, F. C. *J. Am. Chem. Soc.* **1978**, *100*, 4248. (b) Ammar, F.; Savéant, J. M. *J. Electroanal. Chem.* **1973**, *47*, 215.

(24) Mikhailenko, S. A.; Luk'yanets, E. A. *J. Gen. Chem. USSR (Engl. Transl.)* **1969**, *39*, 2495; *Zh. Obshch. Khim.* **1969**, *39*, 2554.

(25) Vogler, A.; Kunkely, H. *Inorg. Chim. Acta* **1980**, *44*, L209.

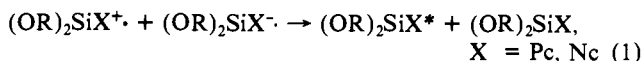
(26) Gouterman, M. "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. III, Chapter 1.

(27) (a) Kane, A. R.; Sullivan, J. F.; Kenny, D. H.; Kenney, M. E. *Inorg. Chem.* **1970**, *9*, 1445. (b) Hush, N. S.; Woolsey, I. S. *Mol. Phys.* **1971**, *21*, 465.

bands. The excitation spectra of these compounds are essentially the same as the absorption spectra and show two sets of three peaks corresponding to absorption from the ground state to two different excited states. The emission spectra are essentially mirror images of the Q-band absorption spectra; the emission peaks are listed in Table II.

A solution of $\text{RO}(\text{SiPcO})_2\text{R}$ exhibited very weak fluorescence. However, the excitation spectrum did not match the absorption spectrum and therefore impurities were suspected as being the emitting species. Thin-layer chromatography confirmed the presence of at least two different impurities. The absence of fluorescence in the pure dimer, like the absorption spectrum, can be explained in terms of the exciton model.²⁸ The lower energy exciton state, which is forbidden and therefore not observed in the absorption spectrum, is a metastable singlet state. This allows for greatly enhanced intersystem crossing into the triplet state. As a result, the singlet emission is quenched.

Electrogenerated Chemiluminescence. The high stability of the oxidized and reduced forms of $\text{SiPc}(\text{OR})_2$ and $\text{SiNc}(\text{OR})_2$ and the fact that both show strong emission upon photoexcitation suggested that these materials were good candidates for ecl studies. There has been only one previous report of ecl from a Pc system, where very weak emission was observed from metal-free Pc.²⁹ Ecl from these compounds is of interest, because there are few systems showing emission in the red and near-infrared region of the spectrum. The energetics of the annihilation process can be estimated from the redox potentials of the relevant species. Thus, the reaction enthalpies can be estimated³⁰ as about 1.8 and 1.5 eV for the $\text{SiPc}(\text{OR})_2$ and $\text{SiNc}(\text{OR})_2$ systems, respectively. The energetics of the lowest 0,0 bands, as estimated from the position of the highest energy emission maximum, are 1.86 and 1.61 eV. Thus, these systems may have sufficient energy to populate the emitting state directly via the electron transfer reaction:



When a Pt electrode immersed in a 1–2 mM solution of the Pc or Nc compound in CH_2Cl_2 was pulsed between potentials for formation of the +1 and –1 species (for $\text{SiPc}(\text{OR})_2$, between –1.2 and +1.1 V and for $\text{SiNc}(\text{OR})_2$ between –1.3 and +0.6 V) at a frequency of 0.5 Hz, weak but easily measurable emission was observed. The ecl spectra are shown in Figure 9. For $\text{SiNc}(\text{OR})_2$ pulsing between potentials for production of the +2 and –2 species produced the same ecl spectra; similar behavior has been seen previously, e.g., in $\text{Ru}(\text{bpy})_3^{2+}$ ^{31a} and rubrene systems,^{31b} and has been attributed to reproporationation reactions that produce the lower oxidized or reduced species. The ecl emissions are shifted to somewhat longer wavelengths as compared to the corresponding fluorescence spectra. This shift probably can be attributed to self-absorption of the emission in ecl, since these compounds have Q bands (absorption peak, Figure 7) located very close to the wavelength of the onset of emission in the ecl spectrum. When corrected for these absorption effects (based on the known absorber concentration, absorptivity, and path length) the corrected ecl spectra are shifted to shorter wavelengths and match the fluorescence spectra. While the energetics of the electron-transfer and emission processes suggest that this may be an “energy sufficient” or “S-route” system, it is marginally so. The difference in emission intensities of the anodic and cathodic pulses, clearly seen in Figure 9, suggests some mechanistic complications. Since both the +1 and –1 forms are quite stable, the difference might be caused by at least some contribution of a “T route” (formation of triplets in the electron-transfer reaction followed by T–T annihilation), with the +1 and –1 forms quenching the triplets at different rates. T–T annihilation has been proposed in the delayed

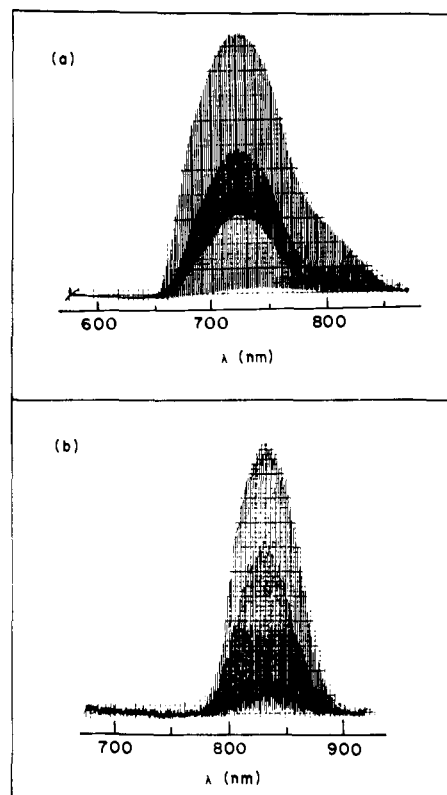


Figure 9. Ecl spectra of (a) $\text{SiPc}[\text{OSi}(n\text{-C}_6\text{H}_{13})_3]_2$, $\lambda_{\text{max}} = 725$ nm, and (b) $\text{SiNc}[\text{OSi}(n\text{-C}_6\text{H}_{13})_3]_2$, $\lambda_{\text{max}} = 828$ nm. Concentrations are 2 and 1.4 mM, respectively, in CH_2Cl_2 , 0.1 M TBAP. Pt electrode pulsed from +1.0 to –1.2 V and +0.6 to –1.3 V vs. AgRE, respectively, at 0.5 Hz. The greater emission for both occurred on the cathodic pulse.

fluorescence of metal-free Pc.³² Finally the ecl of the $\text{SiNc}(\text{OR})_2$ system represents, to our knowledge, the longest wavelength ecl emission yet reported, although other reports of ecl in the red region have appeared.^{29,33} No ecl was observed from $\text{RO}(\text{SiPcO})_2\text{R}$ upon pulsing between either the first oxidation and reduction or the second oxidation and reduction waves.

Conclusions

In view of the structural similarities of SiPc and SiNc systems, and in view of the similarities between the physical and chemical properties of SiNcCl_2 , $\text{SiNc}(\text{OH})_2$, and $\text{SiNc}(\text{OR})_2$ and their phthalocyanine counterparts, it is apparent that pairs of the two types of compounds will be found to be generally similar. Thus the properties of many silicon naphthalocyanines are predictable. In CH_2Cl_2 , within the solvent stability limit, there are two reductions and one oxidation for $\text{SiPc}(\text{OR})_2$ and two reductions and two oxidations for $\text{RO}(\text{SiPcO})_2\text{R}$ and $\text{SiNc}(\text{OR})_2$. These correspond to reversible one-electron waves for $\text{SiNc}(\text{OR})_2$ and $\text{SiPc}(\text{OR})_2$ but are two-electron waves for $\text{RO}(\text{SiPcO})_2\text{R}$. The values of diffusion constants (D , cm^2/s) computed from $i(t)$ vs. $t^{-1/2}$ behavior (potential step experiment) for the neutral $\text{SiPc}(\text{OR})_2$, $\text{RO}(\text{SiPcO})_2\text{R}$, and $\text{SiNc}(\text{OR})_2$ are $(5.7 \pm 1.1) \times 10^{-6}$, $(2.2 \pm 0.3) \times 10^{-6}$, and $(5.2 \pm 0.4) \times 10^{-6}$ cm^2/s , respectively. The compounds show absorptions corresponding to N bands, Soret bands, and intense absorption around 650–700 nm for $\text{SiPc}(\text{OR})_2$, 600–650 nm for $\text{RO}(\text{SiPcO})_2\text{R}$, and 750–800 nm for $\text{SiNc}(\text{OR})_2$ corresponding to Q bands. The corrected ecl maxima are around 684 nm for $\text{SiPc}(\text{OR})_2$ and 792 nm for $\text{SiNc}(\text{OR})_2$. The ecl emission for $\text{SiNc}(\text{OR})_2$ is at the longest wavelength reported so far. No ecl was observed from the dimeric phthalocyanine.

Acknowledgment. We gratefully acknowledge partial support of this work by the Office of Naval Research (ONR), the Army Research Office, and by the Graduate School Annual Alumni Fund of Case Western Reserve University through a fellowship.

(28) Kasha, M. *Radiat. Res.* **1963**, *20*, 55.
 (29) Tokel, N. E.; Keszthelyi, C. P.; Bard, A. J. *J. Am. Chem. Soc.* **1972**, *94*, 4872.
 (30) Faulkner, L. R.; Tachikawa, H.; Bard, A. J. *J. Am. Chem. Soc.* **1972**, *94*, 691.
 (31) (a) Tokel, N. E.; Bard, A. J. *J. Am. Chem. Soc.* **1972**, *94*, 2862. (b) Chang, J.; Hercules, D. M.; Roe, D. K. *Electrochim. Acta* **1968**, *13*, 1197.

(32) Stadelmann, H. R. *J. Lumin.* **1972**, *5*, 171.

(33) Doblhofer, K.; Gerischer, H. *Electrochim. Acta* **1975**, *20*, 215.