Synthesis and Photochemical Properties of Aluminum, Gallium, Silicon, and Tin Naphthalocyanines

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The synthesis and characterization of 30 Al, Ga, Si, and Sn naphthalocyanines relevant to the search for improved photodynamic therapy agents are reported. The compounds that have been studied are AlNcCl, AlNcOH, AlNcOSi(n-C_6H_{13})$_3$, (AlNcF)$_n$, GaNcCl, GaNcOH, GaNcOH·2H_2O, GaNcOSi(n-C_6H_{13})$_3$, (GaNcF)$_n$, SiNc(O-n-C_8H_{17})$_2$, SiNc[$(OCH_2CH_2)_{\sim 17}OCH_3$]$_2$, SiNc[$(OCH_2CH_2)_{\sim 43}OCH_3$]$_2$, SiNc[4-$OCH_2CH_2)_{\sim 26}OC_6H_4C(CH_3)_2CH_2C(CH_3)_3$]$_2$, SiNc[4-$OC_6H_4CO(OCH_2CH_2)_3OCH_3$]$_2$, SiNc[OSi($n$-$C_4H_9$)$_2$($n$-$C_{18}H_{37}$)]$_2$, SiNc[OSi($i$-$C_4H_9$)$_2$($n$-$C_{18}H_{37}$)]$_2$, SiNc[$OSi(CH_3)_2(CH_2)_{10}COOCH_3$]$_2$, SiNc(2/3-Cl)$_4Cl_2$, SiNc(2/3-Cl)$_4$(O-$n$-$C_8H_{17}$)$_2$, SiNc(2/3-Cl)$_4$[OSi($n$-$C_6H_{13}$)$_3$]$_2$, SiNc[2/3-Cl)$_4(OH)_2$, SiNc(2/3-Br)$_4Cl_2$, SiNc(2/3-Br)$_4$(O-$n$-$C_8H_{17}$)$_2$, SiNc(2/3-Br)$_4$[OSi($n$-$C_6H_{13}$)$_3$]$_2$, SiNc(2/3-Br)$_4(OH)_2$, SnNcCl$_2$, SnNc, SnNcI$_2$, SnNc(OH)$_2$, and SnNc[OSi($n$-$C_6H_{13}$)$_3$]$_2$. For nine of these compounds and for an additional compound, SiNc[OSi(n-C_6H_{13})$_3$]$_2$, one or more of the following photoproperties have been determined: λ_Q, the Q(0,0)-band absorption maximum; Φ_T, the triplet-state quantum yield or Φ_T', an approximation of Φ_T; $\Delta\epsilon_T$ the triplet-minus-ground-state extinction coefficient difference at 590 nm; τ_T, the triplet-state lifetime in the absence of O_2; and k_{ox}, the bimolecular rate constant for the quenching of the triplet state by O_2. The values obtained show that λ_Q is essentially independent of the kinds of atoms in the 2 and 3 positions of the macrocycle and that Φ_T is moderately and directly dependent on the atomic numbers of the atoms in the center and the 2 and 3 positions of the ring. In the case of the silicon naphthalocyanines, they show in addition that λ_Q, Φ_T', and τ_T are moderately dependent on the type of axial ligand present.

Introduction

Photodynamic therapy is a promising therapy for neoplastic disease. One of the essential components of this therapy is a photosensitizing agent. This agent should have an optical absorbance spectrum that meets several criteria. It should be in the deep-red spectral region, where absorption by hemoglobin and other tissue absorbers and scattering by melanin and other tissue scatterers are minimal. In addition, it should be well matched by the output spectrum of a readily available laser beam, and it should be intense. Besides meeting these special criteria, the agent must have the appropriate photophysical characteristics, be chemically stable, and be nontoxic in the absence of light. It also should localize preferentially in target tissues and clear promptly from all tissues after it has served its function.

While the agent currently undergoing clinical trials, Photofrin II, meets some of these criteria, agents with better property sets are clearly needed. This has led to the study of a variety of compounds and mixtures of compounds.[1] Included among these are complexes of metal-free naphthalocyanine, H_2Nc (or more formally 37H,39H-tetranaphtho[2,3-b:2′,3′-g:2″,3″-l:2‴,3‴-q]-tetraporphyrazine, Figure 1), and mixtures of substituted metal-free naphthalocyanines.[2-13]

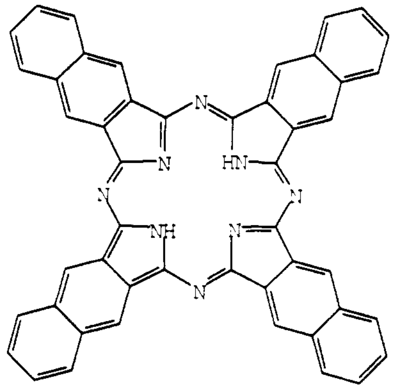

Figure 1. Structure of H_2Nc.

In this paper, we report on the synthesis and characterization of some naphthalocyanines that are relevant to the search for better photodynamic therapy agents and whose synthesis and characterization either have not been described or have not been described in detail.[14] We also report on the photophysics of some

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(1) For a review of phototherapy agents see: Kreimer-Birnbaum, M. *Semin. Hematol.* **1989**, *26*, 157–173.

(2) Firey, P. A.; Rodgers, M. A. J. *Photochem. Photobiol.* **1987**, *45*, 535–538.

(3) Firey, P. A.; Jones, T. W.; Chang, H.-Y.; Kenney, M. E.; Rodgers, M. A. J. *NATO ASI Ser., Ser. H* **1988**, *15*, 77–79.

(4) Firey, P. A.; Ford, W. E.; Sounik, J. R.; Kenney, M. E.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1988**, *110*, 7626–7630.

(5) Yates, N. C. *NATO ASI Ser., Ser. H* **1988**, *15*, 365–368.

(6) Ford, W. E.; Rihter, B. D.; Kenney, M. E.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1989**, *111*, 2362–2363.

(7) Völcker, A.; Adick, H.-J.; Schmidt, R.; Brauer, H.-D. *Chem. Phys. Lett.* **1989**, *159*, 103–108.

(8) Cuomo, V.; Jori, G.; Rihter, B.; Kenney, M. E.; Rodgers, M. A. J. *Br. J. Cancer* **1990**, *62*, 966–970.

(9) Henderson, B. W.; Mayhew, E. *Proc. SPIE-Int. Soc. Opt. Eng.* **1990**, *1203*, 126–135.

(10) Ho, Y.-k.; Pandey, R. K.; Sumlin, A. B.; Missert, J. R.; Bellnier, D. A.; Dougherty, T. J. *Proc. SPIE-Int. Soc. Opt. Eng.* **1990**, *1203*, 293–400.

(11) Paquette, B.; Ouellet, R.; Ali, H.; Langlois, R.; van Lier, J. E. *Proc. SPIE-Int. Opt. Eng.* **1990**, *1203*, 246–252.

(12) Krasnovsky, A. A., Jr.; Rodgers, M. A. J.; Galpern, M. G.; Kenney, M. E.; Luk'yanets, E. A. *Sov. J. Bioorg. Chem.* (*Engl. Transl.*) **1991**, *16*, 806–810; *Bioorg. Khim.* **1990**, *16*, 1413–1418.

(13) Zuk, M. M.; Rihter, B. D.; Kenney, M. E.; Rodgers, M. A. J.; Kreimer-Birnbaum, M. *J. Chromatogr.* **1991**, *568*, 437–444.

(14) Preliminary accounts of some of the syntheses described in this paper have been given earlier.[15-19]

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of these new materials and on the photophysics of a naphthalocyanine whose synthesis and characterization have been given earlier.[20]

Experimental Section

AlNcCl. With a procedure of Mikhalenko and Luk'yanets[21] as a guide, a mixture of 2,3-naphthalenedicarbonitrile (2.40 g), $AlCl_3$ (0.78 g), and dry quinoline (20 mL) was refluxed for 2 h and cooled. The reaction product was filtered, and the solid was washed (toluene, EtOH), air-dried, and weighed (1.26 g, 48%).

Some of the product was vacuum-sublimed (535 °C, $<10^{-3}$ Torr): IR (Nujol) 1261 (w), 1082 (s), 882 (m), 759 (s), 468 (m), 445 (m, AlCl) cm^{-1}. Anal. Calcd for $C_{48}H_{24}AlClN_8$: C, 74.37; H, 3.12; Cl, 4.57. Found: C, 74.39; H, 3.33; Cl, 4.40.

The compound is blue-green and stable to heat (the residue from the sublimation is AlNcCl). It is insoluble in ethanol and toluene.

AlNcOH. Method 1. A mixture of AlNcCl (1.4 g) and concentrated H_2SO_4 (100 mL) was stirred for 2 h, and the reaction product was poured over ice (400 g). The resulting mixture was filtered, and the solid was washed (H_2O). The washed solid was air-dried and mixed with concentrated NH_4OH (50 mL), and the mixture was refluxed for 3 h. After it had been cooled, the reaction product was filtered, and the solid was washed (H_2O, acetone), vacuum-dried (~100 °C), and weighed (0.99 g, 72%).

Method 2. A mixture of recrystallized AlNcOSi(n-C_6H_{13})$_3$ (see below; 80 mg), H_2O (0.5 mL), and pyridine (10 mL) was refluxed for 1 h and cooled. The reaction product was filtered, and the solid was washed (toluene, acetone–H_2O solution), vacuum-dried, (~100 °C), and weighed (57 mg, 98%): IR (Nujol) 1268 (w), 1088 (s), 900 (m), 895 (m), 762 (s), 470 (m) cm^{-1}. Anal. Calcd for $C_{48}H_{25}AlN_8O$: C, 76.18; H, 3.33; Al, 3.57. Found: C, 75.54, 75.89; H, 3.68; Al, 3.39.

The compound is green. It is insoluble in $CHCl_3$ and toluene, and hydrates readily in humid air.

AlNcOSi(n-C_6H_{13})$_3$. With protection from atmospheric moisture, a mixture of AlNcOH (method 1, 250 mg) and pyridine (40 mL) was dried by distillation (10 mL of distillate). Dry $(C_2H_5)_3N$ (0.20 mL) and then (n-C_6H_{13})$_3$SiCl (0.60 mL) were added to the mixture, and the resultant was refluxed for 1 h and cooled. The reaction product was filtered, and the solid was washed (petroleum ether, acetone–H_2O solution), vacuum-dried (~100 °C), and weighed (249 mg, 73%).

Some of the product was recrystallized (1,2,4-trimethylbenzene): IR (Nujol) 1268 (w), 1250 (w, $SiCH_2$), 1090 (s), 1040 (m, SiOAl), 897 (m), 750 (s), 478 (m) cm^{-1}. Anal. Calcd for $C_{66}H_{63}AlN_8OSi$: C, 76.27; H, 6.11; Al, 2.60; Si, 2.70. Found: C, 76.09; H, 6.22; Al, 2.74; Si, 2.96.

The compound is green and is slightly soluble in 1,2,4-trimethylbenzene.

(AlNcF)$_n$. Recrystallized AlNcOSi(n-C_6H_{13})$_3$ (200 mg) was evaporated to dryness on a steam bath three times with aqueous HF (48%, 10 mL each time). The resulting solid was washed (H_2O, CH_3OH, toluene, petroleum ether), vigorously heated (300 °C) under vacuum ($<10^{-3}$ Torr) for 3 h, and weighed (94 mg, 63%): mp >500 °C (vacuum); IR (Nujol) 1261 (w), 1081 (s), 884 (m), 752 (s), 462 (s) cm^{-1}; powder XRD d (Å) (I/I_0) 16.0 (100), 6.95 (32), 3.62 (33). Anal. Calcd for $C_{48}H_{24}AlFN_8$: C, 75.98; H, 3.19; Al, 3.56; F, 2.50. Found: C, 75.72; H, 3.14; Al, 3.53; F, 2.41.

The compound is green and stable to heat (it does not decompose when heated to 500 °C under vacuum). It is insoluble in methanol and toluene.

GaNcCl. With work of Mikhalenko and Luk'yanets[21] as a basis, a mixture of 2,3-naphthalenedicarbonitrile (3.0 g), $GaCl_3$ (1.0 g), and dry quinoline (30 mL) was refluxed for 2 h and cooled. The reaction product was diluted with toluene (25 mL), and the suspension was filtered. The solid was washed (toluene, ethanol), vacuum-dried (~100 °C), and weighed (1.4 g, 40%).

A portion of the product was vacuum-sublimed (540 °C, $<10^{-3}$ Torr): IR (Nujol) 1260 (w), 1090 (s), 885 (m), 750 (s), 470 (m), 340 (w, GaCl) cm^{-1}. Anal. Calcd for $C_{48}H_{24}ClGaN_8$: C, 70.49; H, 2.96; Cl, 4.33. Found: C, 70.40; H, 2.87; Cl, 4.44.

The compound is green and stable to heat (the sublimation residue is GaNcCl). It is insoluble in ethanol and toluene.

GaNcOH. A mixture of GaNcCl (7.5 g) and concentrated H_2SO_4 (200 mL) was stirred for 2 h, and the reaction product was poured over ice (500 g). The resulting mixture was filtered, and the solid was washed (H_2O). The washed solid was air-dried and mixed with concentrated NH_4OH (150 mL), and the mixture was refluxed for 1.5 h. After it cooled, the reaction product was filtered and the solid was washed (H_2O, acetone–H_2O solution), vacuum-dried (~100 °C), and weighed (6.7 g, 91%).

The product from this procedure readily hydrates in humid air. Thermogravimetric analysis data show that it loses its water of hydration below 110 °C at 1 atm.

GaNcOH·2H$_2$O. A mixture of recrystallized GaNcOSi(n-C_6H_{13})$_3$ (see below; 105 mg), H_2O (1 mL), and 3-picoline (20 mL) was refluxed for 3 h and cooled. The reaction product was filtered, and the solid was washed (pyridine, acetone), vacuum-dried (~100 °C), and weighed (72 mg, 89%): IR (Nujol) 3420 (m, br, OH), 1260 (w), 1085 (s), 890 (m), 755 (s), 640 (m, GaOH), 475 (m) cm^{-1}. Anal. Calcd for $C_{48}H_{29}GaN_8O_3$ (redried 110 °C, 1 Torr): C, 69.00; H, 3.50; Ga, 8.34; N, 13.41. Found: C, 69.31; H, 3.49; Ga, 8.21; N, 13.43.

The compound is green and is insoluble in acetone and toluene.

(n-C_6H_{13})$_3$SiOH. This preparation was patterned on work of Boksânyi, Liardon, and sz. Kováts.[22] A solution of (n-C_6H_{13})$_3$SiCl (40.3 g) in ether (30 mL) was added dropwise over 1 h to a cold (0 °C) mixture of H_2O (2.3 mL), triethylamine (20 mL), and ether (200 mL) that was being stirred. The resulting slurry was stirred for 1 h while being kept cool (0 °C) and then filtered. The filtrate was concentrated with a rotary evaporator (40 °C) to a cloudy suspension, and the suspension was mixed with hexanes (400 mL) and water (400 mL). After the organic layer of the mixture formed had been separated, it was dried ($MgSO_4$) and concentrated with a rotary evaporator (40 °C) to an oil. The oil was chromatographed (Al_2O_3-I, 5 × 5 cm, hexanes) and weighed (31.9 g). Analysis of the purified oil by gas chromatography showed that most of it (97%) was a single species (79% contained yield). The oil was colorless.

GaNcOSi(n-C_6H_{13})$_3$. A mixture of GaNcOH (6.7 g), (n-C_6H_{13})$_3$SiOH (12 mL), and toluene (5 mL) was gently heated (70–80 °C) for 2.5 h and cooled. The reaction product was diluted with petroleum ether (30 mL) and the resulting suspension was filtered. The solid was washed (petroleum ether), air-dried, and weighed (8.4 g, 93% assuming GaNcOH).

Part of the product was recrystallized (1,2,4-trimethylbenzene): IR (Nujol) 1262 (w), 1250 (w, $SiCH_2$), 1090 (s), 1000 (m, SiOGa), 892 (m), 758 (s), 472 (m) cm^{-1}. Anal. Calcd for $C_{66}H_{63}GaN_8OSi$: C, 73.26; H, 5.87; Ga, 6.44; Si, 2.60. Found: C, 72.88; H, 5.86; Ga, 6.12; Si, 2.29.

The compound is green and is slightly soluble in 1,2,4-trimethylbenzene. The treatment of GaNcOH·xH$_2$O with (n-C_6H_{13})$_3$SiCl in pyridine yields, not surprisingly, GaNcCl.

(GaNcF)$_n$. Recrystallized GaNcOSi(n-C_6H_{13})$_3$ (128 mg) was evaporated to dryness on a steam bath three times with aqueous HF (48%, 5 mL each time). The resulting solid was washed (H_2O, MeOH, toluene, petroleum ether), heated vigorously (300 °C) under vacuum ($<10^{-3}$ Torr) for 3 h, and weighed (76 mg, 80%): mp >540 °C (vacuum); IR (Nujol) 1262 (w), 1092 (s), 891 (m), 755 (s), 466 (s) cm^{-1}; powder XRD d (Å) (I/I_0) 15.3 (100), 6.72 (36), 3.74 (50). Anal. Calcd for $C_{48}H_{24}FGaN_8$: C, 71.93; H, 3.02; F, 2.37; Ga, 8.70. Found: C, 71.73; H, 3.31; F, 2.27; Ga, 8.47.

The compound is green and stable to heat (it does not decompose when heated to 540 °C under vacuum). It is insoluble in methanol and toluene.

SiNc(O-n-C_8H_{17})$_2$. A mixture of 1-octanol (50 mL) and NaOMe (589 mg) was partly distilled (6 mL of distillate). $SiNcCl_2$[20] (1.55 g) was added to the remainder, and the resulting suspension was refluxed for 50 min and cooled. The reaction product was filtered, and the solid was washed (MeOH), vacuum-dried (~90 °C), and weighed (1.57 g, 83%).

A like material prepared by the treatment of SiNc(OH)$_2$[20] with 1-octanol was recrystallized (1,2,4-trimethylbenzene and 1-octanol): mp

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(15) Schechtman, L. A.; Kenney, M. E. *Proc.—Electrochem. Soc.* **1983**, *83-3*, 340–358.

(16) Moyer, T. J.; Schechtman, L. A.; Kenney, M. E. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1984**, *25* (2), 234–235.

(17) Sounik, J. R.; Schechtman, L. A.; Kenney, M. E., In *Chemistry of Functional Dyes*; Yoshida, Z., Kitao, T., Eds.; Mita Press: Tokyo, 1989; pp 377–384.

(18) Sounik, J. R.; Schechtman, L. A.; Rihter, B. D.; Ford, W. E.; Rodgers, M. A. J.; Kenney, M. E. *Proc. SPIE-Int. Soc. Opt. Eng.* **1990**, *1203*, 224–232.

(19) Sounik, J. R.; Rihter, B. D.; Ford, W. E.; Rodgers, M. A. J.; Kenney, M. E. *Proc. SPIE-Int. Soc. Opt. Eng.* **1991**, *1426*, 340–349.

(20) Wheeler, B. L.; Nagasubramanian, G.; Bard, A. J.; Schechtman, L. A.; Dininny, D. R.; Kenney, M. E. *J. Am. Chem. Soc.* **1984**, *106*, 7404–7410.

(21) Mikhalenko, S. A.; Luk'yanets, E. A. *J. Gen. Chem. USSR* (*Engl. Transl.*) **1969**, *39*, 2495–2498; *Zh. Obshch. Khim.* **1969**, *39*, 2554–2558.

(22) Boksânyi, L.; Liardon, O.; sz. Kováts, E. *Helv. Chim. Acta* **1976**, *59*, 717–727.

>300 °C dec; NMR ($CDCl_3$) δ 10.06 (s, 5,36-Nc H), 8.62 (m, 1,4-Nc H), 7.94 (m, 2,3-Nc H), 0.69 (m, 7-CH_2), 0.48 (t, CH_3), 0.44 (m, 6-CH_2), 0.19 (m, 5-CH_2), –0.33 (m, 4-CH_2), –1.09 (m, 3-CH_2), –1.27 (m, 1,2-CH_2). Anal. Calcd for $C_{64}H_{58}N_8O_2Si$: C, 76.92; H, 5.85; Si, 2.81. Found: C, 76.74; H, 5.79; Si, 3.43.

The compound is blue-green. It is soluble in $CHCl_3$ and toluene. The treatment of $SiNcCl_2$ with a very large excess of NaO-*n*-C_8H_{17} in 1-octanol leads to H_2Nc upon workup. The $SiNcCl_2$ procedure is preferable to the $SiNc(OH)_2$ procedure because it is simpler ($SiNc(OH)_2$ is made from $SiNcCl_2$).

$SiNc[(OCH_2CH_2)_{\sim 17}OCH_3]_2$. A mixture of $SiNc(OH)_2$ (774 mg) and 1,2,4-trimethylbenzene (50 mL) was dried by distillation (~3 mL of distillate) and cooled. Poly(ethylene glycol) methyl ether (av MW 750, 3.9 g) was added to the dried mixture, and the resultant was refluxed for 7 h and cooled. The reaction product was subjected three times to a procedure in which it was mixed with toluene (100 mL) and a glycerol–water solution (5:95, 150 mL). The emulsion formed in this procedure was refluxed for 15 min and cooled, and the water layer that separated was isolated and rejected. After being dried ($MgSO_4$), the treated reaction product was chromatographed (Al_2O_3-I, 95:5 CH_2Cl_2:MeOH solution), and the resulting waxy solid was vacuum-dried (~60 °C) and weighed (561 mg, 25%): mp >250 °C; NMR (C_6D_6, 50 °C) δ 10.26 (s, 5.36-Nc H), 8.50 (m, 1,4-Nc H), 7.50 (m, 2,3-Nc H), 3.61 (m, 34- to 9-CH_2), 3.36 (m, 8-CH_2), 3.26 (m, 7-CH_2), 3.25 (s, CH_3), 3.05 (m, 6-CH_2), 2.85 (m, 5-CH_2), 2.61 (t, 4-CH_2), 2.05 (t, 3-CH_2), 1.02 (t, 2-CH_2), –0.64 (t, 1-CH_2). Anal. Calcd for $C_{118}H_{166}N_8O_{36}Si$: C, 61.60; H, 7.27; Si, 1.22. Found: C, 62.12; H, 7.18; Si, 1.39.

The compound is green. It is soluble in $CHCl_3$, toluene, and methanol and is insoluble in H_2O. *Caution*! Gloves should be worn when solutions of naphthalocyanines in polar solvents are handled, since some naphthalocyanines are strong sensitizers.

$SiNc[(OCH_2CH_2)_{\sim 43}OCH_3]_2$. A mixture of $SiNc(OH)_2$ (774 mg), poly(ethylene glycol) methyl ether (av MW 1900, 7.6 g), and 1,2,4-trimethylbenzene (80 mL) was refluxed for 6 h in an apparatus fitted with a Dean-Stark trap. The reaction product was concentrated with a rotary evaporator (~0.1 Torr, ~70 °C) and the concentrate was suspended in H_2O (250 mL). The suspension was filtered (diatomaceous earth filter aid), and the filtrate was extracted with toluene (350 mL) in a continuous extractor for 4 days. After the extract had been dehydrated ($MgSO_4$), it was evaporated to dryness with a rotary evaporator (~75 °C). The residue was chromatographed (Bio-Beads S-X1, 3 × 120 cm, toluene), and the resulting waxy solid was vacuum-dried (~50 °C) and weighed (601 mg, 13%): mp 139–141 °C; NMR (C_6D_6, 50 °C) δ 10.23 (s, 5,36-Nc H), 8.47 (m, 1,4-Nc H), 7.61 (m, 2,3-Nc H), 3.53 (m, 86- to 9-CH_2), 3.30 (m, 8-CH_2), 3.21 (m, 7-CH_2), 3.19 (s, CH_3), 3.01 (m, 6-CH_2), 2.81 (m, 5-CH_2), 2.56 (t, 4-CH_2), 2.05 (t, 3-CH_2), 1.00 (t, 2-CH_2), –0.64 (t, 1-CH_2); UV–vis (C_6H_6) λ_{max} (nm) (ϵ (M^{-1} cm^{-1})) 335 (7.4×10^4), 694 (4.4×10^4), 742 (4.1×10^4), 781 (2.7×10^5), (C_2H_5OH) 333 (7.5×10^4), 694 (4.0×10^4), 743 (3.9×10^4), 781 (2.3×10^5), (CH_3OH) 333 (7.6×10^4), 695 (3.9×10^4), 747 (sh) (3.9×10^4), 782 (2.3×10^5). Anal. Calcd for $C_{222}H_{374}N_8O_{88}Si$: C, 58.07; H, 8.21; Si, 0.61. Found: C, 57.49; H, 8.36; Si, 0.69.

The compound is green. It is soluble in $CHCl_3$, toluene, methanol, and H_2O (giving solutions that can be >0.02 M) and is insoluble in hexanes. Its H_2O solution is stable for at least 2 weeks.

$SiNc[4\text{-}(OCH_2CH_2)_{\sim 26}OC_6H_4C(CH_3)_2CH_2C(CH_3)_3]_2$. A mixture of $SiNc(OH)_2$ (774 mg), a solution of 4-$H(OCH_2CH_2)_{\sim 26}OC_6H_4C(CH_3)_2CH_2C(CH_3)_3$ and $H(OCH_2CH_2)_{\sim 26}OH$ (~95:5) in H_2O (70% phenoxypoly(ethylene glycol) and glycol, Triton X-305, Rohm and Haas (Philadelphia, PA) 6.92 g), and 1,2,4-trimethylbenzene (80 mL) was distilled slowly for 5 h (30 mL of distillate), cooled, and diluted with toluene (70 mL). The resulting solution was extracted three times with hot (~80 °C) water (100 mL each time), dried ($MgSO_4$), and evaporated to dryness with a rotary evaporator (~60 °C). The solid was chromatographed twice (Bio-Beads S-X1, 3 × 120 cm, toluene), vacuum-dried (~60 °C), and weighed (126 mg, 4% assuming 95:5 $SiNc[4\text{-}(OCH_2CH_2)_{26}OC_6H_4C(CH_3)_2CH_2C(CH_3)_3]_2$ and $SiNc[(OCH_2CH_2)_{26}OH]_2$): mp 183–186 °C; NMR ($C_6D_6$, 50 °C) δ 10.14 (s, 5,36-Nc H), 8.39 (m, 1,4-Nc H), 7.61 (m, 2,3-Nc H), 7.17 (d, 2,6-Ph H), 6.84 (d, 3,5-Ph H), 3.90 (t, 60-CH_2O), 3.61 (t, 59-CH_2O), 3.50 (58- to 9-CH_2O), 3.26 (m, 8-CH_2O), 3.17 (m, 7-CH_2O), 2.96 (m, 6-CH_2O), 2.81 (m, 5-CH_2O), 2.51 (t, 4-CH_2O), 1.98 (t, 3-CH_2O), 1.67 (s, CCH_2C), 1.30 (s, $C(CH_3)_2$), 0.97 (t, 2-CH_2O), 0.78 (s, $C(CH_3)_3$), –0.68 (t, 1-CH_2O). Anal. Calcd for $C_{179}H_{272}N_8O_{54}Si$: C, 62.71; H, 8.00; N, 3.27. Found: C, 62.44; H, 7.70; N, 3.10.

The compound is a waxy green solid. It is soluble in $CHCl_3$, toluene, and MeOH but is insoluble in H_2O.

$SiNc[4\text{-}OC_6H_4CO(OCH_2CH_2)_3OCH_3]_2$. A mixture of 4-$HOC_6H_4COOH$ (2.78 g), tris(ethylene glycol) monomethyl ether (10 mL), concentrated H_2SO_4 (1 drop), and toluene (80 mL) was refluxed for 12 h in an apparatus fitted with a Dean-Stark trap. After being cooled, the reaction product was washed three times with H_2O (75 mL each time), and the H_2O washings were combined. The combined washings were extracted three times with CH_2Cl_2 (50 mL each time), and the extracts and the water-washed reaction mixture were combined and dried ($MgSO_4$). The solution formed was concentrated with a rotary evaporator (~75 °C), and the resulting colorless oil, 4-$HOC_6H_4CO(OCH_2CH_2)_3OCH_3$, was weighed (4.35 g).

A mixture of $SiNc(O\text{-}n\text{-}C_8H_{17})_2$ (167 mg), some of the 4-$HOC_6H_4CO(OCH_2CH_2)_3OCH_3$ (516 mg), and 1,2,4-trimethylbenzene (25 mL) was slowly distilled for 5 h (10 mL of distillate) and then cooled. The reaction product was filtered, and the solid was washed (MeOH with sonication) and air-dried.

The dried solid was chromatographed (Al_2O_3-V, 9:1 CH_2Cl_2–MeOH solution). After being washed (MeOH), the solid obtained was vacuum-dried (~80 °C) and weighed (100 mg, 54% based on $SiNc(O\text{-}n\text{-}C_8H_{17})_2$): mp > 260 °C; NMR ($CDCl_3$) δ 10.08 (s, 5,36-Nc H), 8.67 (m, 1,4-Nc H), 7.96 (m, 2,3-Nc H), 6.60 (d, 3,5-Ph H), 3.93 (t, 1-CH_2), 3.37 (m, 6- to 2-CH_2), 3.21 (s, CH_3), 3.16 (d, 2,6-Ph H). MS-HRFAB exact mass, m/z: calcd for $C_{76}H_{62}N_8O_{12}Si$ (M^+), 1306.4256; found, 1306.4206, 1306.4234.

The compound is green and is soluble in $CHCl_3$.

$SiNc[OSi(n\text{-}C_4H_9)_2(n\text{-}C_{18}H_{37})]_2$. Crude *n*-$C_{18}H_{37}(n\text{-}C_4H_9)_2SiCl$ was made by treating *n*-$C_{18}H_{37}SiCl_3$ with *n*-BuMgCl in tetrahydrofuran at low temperature, working up the reaction mixture, and distilling the product. The fraction that was retained was colorless and was shown by gas chromatography to be largely (61%) *n*-$C_{18}H_{37}(n\text{-}C_4H_9)_2SiCl$.

With previously reported work as a guide,[20] $SiNc[OSi(n\text{-}C_4H_9)_2(n\text{-}C_{18}H_{37})]_2$ was made by treating $SiNc(OH)_2$ with the crude *n*-$C_{18}H_{37}(n\text{-}C_4H_9)_2SiCl$ in tri-*n*-butylamine and pyridine (65%).

The product was chromatographed (Al_2O_3-III, hexanes–toluene, 10:1): mp 138 °C; NMR (C_6D_6, 50 °C) δ 10.35 (s, 5,36-Nc H), 8.40 (m, 1,4-Nc H), 7.55 (m, 2,3-Nc H), 1.35 (m, 17- to 9-C_{18} CH_2), 1.24 (m, 8-C_{18} CH_2), 1.12 (m, 7-C_{18} CH_2), 0.92 (t, C_{18} CH_3), 0.86 (m, 6-C_{18} CH_2), 0.75 (m, 5-C_{18} CH_2), 0.44 (m, 4-C_{18} CH_2), 0.32 (m, 3-C_4 CH_2), 0.16 (t, C_4 CH_3), –0.58 (m, 2-C_{18} CH_2, 2-C_4 CH_2), –1.63 (m, 1-C_{18} CH_2, 1-C_4 CH_2) (3-C_{18} CH_2 obscured). Anal. Calcd for $C_{100}H_{134}N_8O_2Si_3$: C, 76.77; H, 8.63; Si, 5.39. Found: C, 76.66; H, 8.54; Si, 5.47.

The compound is a green solid. It is soluble in $CHCl_3$ and toluene.

$SiNc[OSi(i\text{-}C_4H_9)_2(n\text{-}C_{18}H_{37})]_2$, isoBOSINC. A solution of *i*-C_4H_9MgCl in ether (2.0 M, 90 mL) was added over a 3.5-h period to a cooled solution (ice bath) of *n*-$C_{18}H_{37}SiCl_3$ (18.4 mL) and tetrahydrofuran (250 mL) under Ar. The resulting mixture was stirred for 5 h with cooling (ice bath), allowed to stand for 12 h with cooling (0 °C), and then allowed to stand for 10 h without cooling. The reaction product was cooled (ice bath) and treated with cold (ice bath) dilute HCl (1 N, 200 mL). After the aqueous phase of the resulting mixture had been separated from the organic phase, it was extracted three times with ether (50 mL each time). The ether extracts and the organic phase were combined, and the resulting solution was washed three times with a saturated NaCl solution (50 mL each time), dried ($MgSO_4$), and evaporated to a waxy solid with a rotary evaporator (~60 °C). The solid was chromatographed (Al_2O_3-III, 1:1 hexanes–ether solution), and the resulting light yellow oil, *n*-$C_{18}H_{37}(i\text{-}C_4H_9)_2SiOH$, was weighed (9.0 g).

A mixture of $SiNc(O\text{-}n\text{-}C_8H_{17})_2$ (1.50 g) and 1,2,4-trimethylbenzene (120 mL) was dried by distillation (12 mL of distillate), and the solution formed was partly cooled (~90 °C). Some of the *n*-$C_{18}H_{37}(i\text{-}C_4H_9)_2SiOH$ (1.55 g) was added to this solution, and the mixture formed was refluxed for 5 h and cooled. The reaction product was diluted with MeOH (500 mL), and the resulting suspension was filtered. The solid was washed (MeOH), vacuum-dried (~80 °C), and weighed (1.74 g).

The solid was chromatographed (Al_2O_3-III, 9:1 hexanes–toluene solution) and weighed (859 mg, 37% based on $SiNc(O\text{-}n\text{-}C_8H_{17})_2$): mp 159–160 °C dec; NMR (C_6D_6, 65 °C) δ 10.35 (s, 5,36-Nc H); 8.48 (m, 1,4-Nc H), 7.62 (m, 2,3-Nc H), 1.42 (m, 17- to 8-C_{18} CH_2), 1.19 (m, 7-C_{18} CH_2), 0.96 (m, C_{18} CH_3), 0.88 (m, 5-C_{18} CH_2), 0.58 (m, 4-C_{18} CH_2), 0.43 (m, 3-C_{18} CH_2), –0.15 (s, C_4 CH_3), –0.45 (m, 2-C_138 CH_2), –1.59 (m, 1-C_{18} CH_2, 1-C_4 CH_2) (6-C_{18} CH_2, 2-C_4 CH obscured); UV–vis (C_6H_6) λ_{max} (nm) (ϵ (M^{-1} cm^{-1})) 336 (9.2×10^4), 690 (6.5×10^4), 737 (5.8×10^4), 776 (5.9×10^5), ($C_6H_5CH_3$) 333 (9.1×10^4), 690 (6.5×10^4), 736 (5.9×10^4), 776 (5.2×10^5). Anal. Calcd for $C_{100}H_{134}N_8O_2Si_3$: C, 76.77; H, 8.63; Si, 5.39. Found: C, 76.76; H, 8.89; Si, 5.23.

The compound is green and is soluble in $CHCl_3$, toluene, and hexanes (~10 mg/mL).

$SiNc[OSi(CH_3)_2(CH_2)_{10}COOCH_3]_2$. A mixture of $SiNc(OC_8H_{37})_2$ (490 mg), tri-*n*-butylamine (5 mL), and pyridine (50 mL) was partly distilled (10 mL of distillate) and cooled. $CH_3OOC(CH_2)_{10}Si(CH_3)_2Cl$ (0.50 mL) was added to the remainder, and the resulting solution was refluxed for 5 h and filtered. The filtrate was concentrated with a rotary evaporator (~70 °C), and the remainder (~5 mL) was diluted with MeOH (20 mL). The suspension formed was filtered, and the solid was washed with MeOH, vacuum-dried (~60 °C), and weighed (293 mg).

The product was recrystallized from a CH_2Cl_2–hexanes solution and weighed (260 mg, 41%): mp 237–238 °C; NMR (C_6D_6, 50 °C) δ 10.25 (s, 5,36-Nc H), 8.39 (m, 1,4-Nc H), 7.58 (m, 2,3-Nc H), 3.43 (s, OCH_3), 2.15 (t, J = 7.5 Hz, 10-CH_2), 1.54 (quint, J = 7.6 Hz, 9-CH_2), 1.08 (quint, J = 7.6 Hz, 8-CH_2), 0.91 (quint, J = 7.5 Hz, 7-CH_2), 0.72 (quint, J = 7.4 Hz, 6-CH_2), 0.59 (quint, J = 7.6 Hz, 5-CH_2), 0.34 (quint, J = 7.6 Hz, 4-CH_2), 0.07 (quint, J = 7.6 Hz, 3-CH_2), –0.68 (m, 2-CH_2), –1.62 (m, 1-CH_2), –2.13 (s, $SiCH_3$). MS-HRFAB exact mass, *m/z*: calcd for $C_{76}H_{82}N_8O_6Si_3$ $(M + H)^+$, 1287.5743; found, 1287.5697, 1287.5701.

The compound is green and is soluble in $CHCl_3$ and toluene.

4-Chloro-1,2-bis(dibromomethyl)benzene. With the work of Kerfanto and Soyer[23] as a guide, Br_2 (64.2 mL) was added slowly (5 h) to hot (135–140 °C), illuminated (150-W flood lamp) 4-chloro-1,2-dimethylbenzene (44.1 g). The reaction product was subjected to vacuum (~60 Torr) for 12 h, and the resulting solid was ground, washed (hexanes), vacuum-dried (room temperature), and weighed (108 g, 75%): NMR ($CDCl_3$) δ 7.66 (s, 3-Ar H), 7.64 (d, 6-Ar H), 7.35 (d, 5-Ar H), 7.05 (s, 1- or 2-$CHBr_2$), 7.04 (s, 1- or 2-$CHBr_2$).

The product is white and is soluble in acetone and dimethyl sulfoxide.

6-Chloro-2,3-naphthalenedicarbonitrile. With the work of Kovshev, Puchnova, and Luk'yanets[24] as a guide, a mixture of 4-chloro-1,2-bis(dibromomethyl)benzene (80.1 g), fumaronitrile (15.0 g), NaI (52.7 g), and dry dimethylformamide (335 mL) was heated (80–82 °C) for 7 h and allowed to stand for 12 h. The reaction product and then $NaHSO_3$ (27.5 g) were added to H_2O (1 L) that was being stirred, and the resulting suspension was filtered. The solid was washed (H_2O, ether), vacuum-dried, (~90 °C), and weighed (25.0 g, 67%).

Some of the product was vacuum-sublimed twice (10^{-3} Torr, 170–180 °C): mp 241 °C; NMR ($(CD_3)_2SO$) δ 8.86 (s, 1- or 4-Ar H), 8.76 (s, 1- or 4-Ar H), 8.27 (s, 5-Ar H), 8.19 (d, 8-Ar H), 7.91 (d, 7-Ar H). Anal. Calcd for $C_{12}H_5ClN_2$: C, 67.78; H, 2.37; Cl, 16.67. Found: C, 67.61; H, 2.56; Cl, 16.86.

The compound is white and is soluble in acetone and dimethyl sulfoxide.

6-Chloro-1,3-diiminobenz[*f*]isoindoline. Anhydrous NH_3 was bubbled (2 mL/min) into a stirred mixture of 6-chloro-2,3-naphthalenedicarbonitrile (15.4 g), NaOMe (7.20 g), and MeOH (200 mL) for 1 h while the mixture was at room temperature and then for 3 h while it was at reflux. The reaction product was evaporated to a solid with a rotary evaporator (~40 °C), and the solid was washed (H_2O), vacuum-dried (~80 °C), and weighed (15.1 g, 91%): NMR ($(CD_3)_2SO$) δ 8.43 (s br, NH), 8.37 (s, 4- or 9-Ar H), 8.31 (s, 4- or 9-Ar H), 8.27 (s, 5-Ar H), 8.12 (d, 8-Ar H), 7.67 (d, 7-Ar H).

The product is yellow and is slightly soluble in acetone and dimethyl sulfoxide.

$SiNc(2/3\text{-}Cl)_4Cl_2$.[25] Under N_2, 6-chloro-1,3-diiminobenz[*f*]isoindoline (5.04 g) was added to a refluxing mixture of $SiCl_4$ (2.5 mL) and dry quinoline (40 mL) over 50 min. The resulting mixture was refluxed for 1.5 h. The reaction product was diluted with EtOH (75 mL), and the suspension was filtered. After the solid had been washed (MeOH), it was subjected to extraction (Soxhlet, pyridine), vacuum-dried (~90 °C), and weighed (4.66 g, 90%): IR (Nujol) 1263 (w), 1085 (s), 899 (m), 752 (m), 471 (m) cm^{-1}.

The product is blue-green and probably is relatively impure.

$SiNc(2/3\text{-}Cl)_4(O\text{-}n\text{-}C_8H_{17})_2$. A mixture of 1-octanol (50 mL) and NaOMe (721 mg) was partly distilled (15 mL of distillate), and the remaining solution was cooled slightly. $SiNc(2/3\text{-}Cl_4)_4Cl_2$ (2.47 g) was added to this solution, and the resulting mixture was refluxed for 2 h. The reaction product was cooled and filtered, and the solid was washed (MeOH), vacuum-dried (~90 °C), and weighed (2.53 g, 85% assuming $SiNc(2/3\text{-}Cl)_4Cl_2$ 100% pure).

Part of the product was recrystallized (1,2,4-trimethylbenzene): mp >300 °C; IR (Nujol) 1262 (w), 1087 (s), 898 (m), 757 (m), 469 (m) cm^{-1}. Anal. Calcd for $C_{64}H_{54}Cl_4N_8O_2Si$: C, 67.60; H, 4.79; Cl, 12.47; Si, 2.47. Found: C, 67.67; H, 4.90; Cl, 12.48; Si, 2.68.

The compound is blue-green and is slightly soluble in $CHCl_3$ and toluene.

$SiNc(2/3\text{-}Cl)_4[OSi(n\text{-}C_6H_{13})_3]_2$. A mixture of recrystallized $SiNc(2/3\text{-}Cl)_4(O\text{-}n\text{-}C_8H_{17})_2$ (185 mg), $(n\text{-}C_6H_{13})_3SiOH$ (972 mg), and dry 1,2,4-trimethylbenzene (19 mL) was refluxed for 7 h. The reaction product was concentrated with a rotary evaporator (~70 °C), and the concentrate was diluted with MeOH (30 mL). The resulting suspension was filtered, and the solid was washed (MeOH), vacuum-dried (~90 °C), and weighed (152 mg, 63%).

A portion of the product was chromatographed (Al_2O_3-III, hexanes–toluene, 1:1): mp 276 °C; NMR ($CDCl_3$) δ 10.07 (s, 5- or 36-Nc H), 10.00 (s, 5- or 36-Nc H), 8.64 (s, 1-Nc H), 8.60 (d, 4-Nc H), 7.87 (d, 3-Nc H), 0.62 (m, 5-CH_2), 0.44 (t, CH_3), 0.22 (m, 4-CH_2), 0.05 (m, 3-CH_2), –1.02 (m, 2-CH_2), –2.05 (m, 1-CH_2). Anal. Calcd for $C_{84}H_{98}Cl_4N_8O_2Si_3$: C, 68.27; H, 6.68; Cl, 9.60; Si, 5.70. Found: C, 68.11; H, 6.12; Cl, 9.97; Si, 5.61.

The compound is bright green. It is soluble in $CHCl_3$ and toluene and is insoluble in MeOH and acetone.

$SiNc(2/3\text{-}Cl)_4(OH)_2$. A mixture of recrystallized $SiNc(2/3\text{-}Cl)_4(O\text{-}n\text{-}C_8H_{17})_2$ (156 mg), concentrated HCl (0.5 mL), H_2O (1 mL), and toluene (35 mL) was refluxed for 5 h. The reaction product was cooled and filtered, and the solid was washed (dilute NH_4OH, MeOH), vacuum-dried (~80 °C), and weighed (113 mg, 90%): IR (Nujol) 3450 (w, br, OH), 1260 (w), 1083 (s), 900 (m), 834 (m, SiOH), 752 (m), 469 (m) cm^{-1}. Anal. Calcd for $C_{48}H_{22}Cl_4N_8O_2Si$: C, 63.17; H, 2.43; Cl, 15.54; Si, 3.08. Found: C, 62.81; H, 2.43; Cl, 15.58; Si, 3.23.

The compound is bright green and is insoluble in $CHCl_3$ and toluene.

2/3-Tetrabromonaphthalocyanines. The procedures used for the precursors to the 2/3-tetrabromonaphthalocyanines and for the 2/3-tetrabromonaphthalocyanines themselves are similar to those used for the corresponding chloro compounds.

4-Bromo-1,2-bis(dibromomethyl)benzene:[23] yield 42%; NMR ($(CD_3)_2SO$) δ 7.92 (s, 6-Ar H), 7.77 (s, 3-Ar H), 7.73 (s, 5-Ar H), 7.68 (s, 1- or 2-$CHBr_2$), 7.67 (s, 1- or 2-$CHBr_2$). The product is a white solid and is soluble in acetone and dimethyl sulfoxide.

6-Bromo-2,3-naphthalenedicarbonitrile:[24] yield 69%, purified by vacuum sublimation; mp 250–251 °C (lit. 245–246 °C);[24] NMR ($(CD_3)_2SO$) δ 8.85 (s, 1- or 4-Ar H), 8.75 (s, 1- or 4-Ar H), 8.43 (s, 5-Ar H), 8.11 (d, 8-Ar H), 8.01 (d, 7-Ar H). Anal. Calcd for $C_{12}H_5BrN_2$: C, 56.06; H, 1.96; Br, 31.08. Found: C, 56.15; H, 2.08; Br, 31.23. The compound is a white solid and is soluble in acetone and dimethyl sulfoxide.

6-Bromo-1,3-diiminobenz[*f*]isoindoline: yield 87%; NMR ($(CD_3)_2SO$) δ 8.02 (s, 4- or 9-Ar H), 7.97 (s, 4- or 9-Ar H), 7.71 (d, 8-Ar H), 7.44 (d, 7-Ar H) (5-Ar H obscured). The product is a brown solid and is slightly soluble in acetone and dimethyl sulfoxide.

$SiNc(2/3\text{-}Br)_4Cl_2$: yield 79%; IR (Nujol) 2160 (w), 1086 (s), 901 (m), 762 (m), 475 (m, SiCl), 467 (sh) cm^{-1}. The product is a dull green solid and probably is relatively impure.

$SiNc(2/3\text{-}Br)_4(O\text{-}n\text{-}C_8H_{17})_2$: yield 85% (assuming $SiNc(2/3\text{-}Br)_4Cl_2$ 100% pure), purified by recrystallization (1,2,4-trimethylbenzene and 1-octanol); mp >300 °C dec; IR (Nujol) 1260 (w), 1086 (s), 899 (m), 757 (m), 468 (m) cm^{-1}. The product is a blue-green solid and is slightly soluble in $CHCl_3$ and toluene.

$SiNc(2/3\text{-}Br)_4[OSi(n\text{-}C_6H_{13})_3]_2$: yield 76%, purified by chromatography; mp 284 °C; NMR ($CDCl_3$) δ 10.06 (s, 5- or 36-Nc H), 10.00 (s, 5- or 36-Nc H), 8.82 (s, 1-Nc H), 8.54 (d, 4-Nc H), 7.99 (d, 3-Nc H), 0.61 (m, 5-CH_2), 0.44 (t, CH_3), 0.20 (m, 4-CH_2), 0.04 (m, 3-CH_2), –1.04 (m, 2-CH_2), –2.10 (m, 1-CH_2). Anal. Calcd for $C_{84}H_{98}Br_4N_8O_2Si_3$: C, 60.94; H, 5.97; Br, 19.30; Si, 5.09. Found: C, 61.32; H, 6.13; Br, 19.33; Si, 5.57. The compound is a bright green solid and is soluble in $CHCl_3$ and toluene and insoluble in MeOH and acetone.

$SiNc(2/3\text{-}Br)_4(OH)_2$: yield 95%; IR (mineral oil) 3450 (w, br, OH), 1260 (w), 1079 (s), 900 (m), 829 (m, SiOH), 751 (m), 475 (m) cm^{-1}. Anal. Calcd for $C_{48}H_{22}Br_4N_8O_2Si$: C, 52.87; H, 2.03; Br, 29.31; Si, 2.58. Found: C, 52.88; H, 2.47; Br, 28.98; Si, 2.51. The compound is a dark green solid and is insoluble in $CHCl_3$ and toluene.

$SnNcCl_2$. With a procedure of Mikhalenko and Luk'yanets[21] as a guide, a mixture of 2,3-naphthalenedicarbonitrile (2.85 g), $SnCl_2$ (1.77 g), and dry 1-chloronaphthalene (25 mL) was heated vigorously (~180 °C) for 1 h, heated more vigorously (~210 °C) for 1 h, and finally

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[23] Kerfanto, M.; Soyer, N. *Bull. Soc. Chim. Fr.* **1966**, 2966–2971.

[24] Kovshev, E. I.; Puchnova, V. A.; Luk'yanets, E. A. *J. Org. Chem. USSR* (*Engl. Transl.*) **1971**, *7*, 364–366; *Zh. Org. Khim.* **1971**, *7*, 369–371.

[25] $Nc(2/3\text{-}X)_4$ is an abbreviation for the mixture of all eight possible ring systems arising when each arm of the ring carries one halogen in either the 2 or the 3 position.

refluxed for 30 min. The reaction product was cooled and filtered, and the solid was washed (MeOH, pyridine, MeOH), vacuum-dried (~100 °C), and weighed (3.44 g, 95%): IR (Nujol) 1263 (w), 1097 (s), 893 (m), 753 (s), 472 (m), 269 (m, SnCl) cm^{-1}.

The product is a dull green-brown and is insoluble in $CHCl_3$ and toluene.

SnNc. A mixture of $SnNcCl_2$ (2.05 g), $NaBH_4$ (0.741 g), and pyridine (20 mL) was refluxed for 45 min and cooled slightly. Water (15 mL) was added to the reaction product, and the resultant was refluxed for 30 min. The suspension formed was cooled and filtered, and the solid was washed (MeOH), vacuum-dried (~100 °C), and weighed (1.77 g, 94%): IR (Nujol) 1260 (m), 1076 (s), 883 (m), 845 (s), 755 (s), 470 (s) cm^{-1}.

The product is green and is insoluble in $CHCl_3$ and toluene.

$SnNcI_2$. A mixture of SnNc (1.75 g), I_2 (1.41 g), and dry 1-chloronaphthalene (25 mL) was refluxed for 5 min and cooled. The reaction product was filtered, and the solid was washed ($CHCl_3$, pyridine, MeOH), vacuum-dried (~100 °C), and weighed (2.02 g, 88%): IR (Nujol) 1263 (w), 1074 (s), 891 (m), 749 (s), 474 (m) cm^{-1}.

The product is brown-green and is insoluble in $CHCl_3$ and toluene.

$SnNc(OH)_2$. Ammonia was bubbled slowly (~5 mL/min) into a refluxing mixture of $SnNcI_2$ (2.01 g), H_2O (2.0 mL), and pyridine (30 mL) for 4 h. The reaction product was cooled and filtered, and the solid was washed (pyridine), vacuum-dried (~100 °C), and weighed (1.54 g, 96%): IR (Nujol) 3480 (m, OH), 1261 (w), 1076 (s), 891 (m), 748 (s), 555 (m, SnOH), 472 (m) cm^{-1}.

The product is green and is insoluble in $CHCl_3$ and toluene.

$SnNc[OSi(n\text{-}C_6H_{13})_3]_2$. A mixture of $SnNc(OH)_2$ (374 mg), $(n\text{-}C_6H_{13})_3SiOH$ (1.01 g), and 1,2,4-trimethylbenzene (35 mL) was partly distilled (21 mL of distillate), and the remainder was refluxed for 5 h and cooled. The reaction product was diluted with MeOH (20 mL), and the resulting suspension was filtered. The solid was washed (MeOH), vacuum-dried (~90 °C), and weighed (520 mg, 84%).

Part of the product was recrystallized (toluene): mp (evacuated, sealed capillary) 272–273 °C; NMR (C_6D_6) δ 10.22 (s, 5,36-Nc H), 8.30 (m, 1,4-Nc H), 7.54 (m, 2,3-Nc H), 0.73 (m, 5-CH_2), 0.49 (t, CH_3), 0.39 (m, 3- and 4-CH_2), –0.38 (m, 2-CH_2), –1.37 (m, 1-CH_2). Anal. Calcd for $C_{84}H_{102}N_8O_2Si_2Sn$: C, 70.52; H, 7.19; Sn, 8.30. Found: C, 70.15; H, 7.16; Sn, 8.46.

The compound is green. It is soluble in $CHCl_3$ and toluene and is insoluble in MeOH and acetone. It decomposes below 250 °C in an open capillary tube.

Characterization. The infrared spectra were taken with Perkin-Elmer IR 598 (Perkin-Elmer Corp., Norwalk, CT) and Mattson Cygnus 25 (Mattson Instruments, Inc., Madison, WI) spectrometers. A Varian XL-200 spectrometer (Varian Associates, Inc., Palo Alto, CA) was used to obtain the NMR spectra of all compounds for which spectra were obtained, except for $SiNc[OSi(n\text{-}C_4H_9)_2(n\text{-}C_{18}H_{37})]_2$ and $SiNc[OSi(CH_3)_2(CH_2)_{10}COOCH_3]_2$. For these compounds, a Bruker MSL-400 spectrometer (USA Bruker Instruments, Inc., Billerica, MA) was employed. The X-ray powder data were obtained by Molecular Structure Corp. (College Station, TX). A General Electric diffractometer equipped with a Cu source and interfaced to a California Systems L-11 software and automation package was used to obtain the X-ray data. The elemental analyses were carried out by Galbraith Laboratories, Inc. (Knoxville, TN), and the mass spectra were determined by the Midwest Center for Mass Spectrometry (Lincoln, NE).

Photoproperties. The instrumentation and techniques employed in the determination of the photophysical properties of the naphthalocyanines were the same as those described in earlier publications.[4,6,26] Benzophenone and protoporphyrin IX dimethyl ester were used as the standards in the procedure employed to determine the triplet-state quantum yields. 2,5-Dimethylfuran (0.04–0.08 M) was added as a singlet oxygen quencher to the naphthalocyanine solutions in some cases in order to make the determination of the rate constants for triplet quenching of O_2 more accurate.[4,26] This furan did not quench the triplet state of the naphthalocyanines under these conditions.

Results

Photoproperties of Various Metal Naphthalocyanines with Trihexylsiloxy Axial Ligands. The Q(0,0)-band absorption maxima, λ_Q, and four triplet-state properties of $SiNc[OSi(n\text{-}C_6H_{13})_3]_2$ and the five (trihexylsiloxy)metal naphthalocyanines described above when dissolved in benzene are presented in Table I. The triplet-state properties given are the quantum yield (Φ_T), the triplet-minus-ground-state extinction coefficient difference at 590 nm ($\Delta\epsilon_T$), the lifetime in the absence of O_2 (τ_T), and the bimolecular rate constant for quenching by O_2 (k_{ox}). The triplet-minus-ground-state absorption spectra of the compounds have maxima in the 580–600-nm range; the $\Delta\epsilon_T$ value for $SiNc[OSi(n\text{-}C_6H_{13})_3]_2$, 78 400 M^{-1} cm^{-1}, is 10% higher than the average value obtained when both protoporphyrin IX dimethyl ester and zinc tetraphenylporphyrin were used as sensitizers.[4] Within experimental error, the quantum yield for the photogeneration of O_2 ($^1\Delta_g$) in aerated benzene-d_6 is equal to Φ_T for the three silicon naphthalocyanines.

Table I. Photoproperties of Various Metal Naphthalocyanines with Trihexylsiloxy Axial Ligands in Benzene

	λ_Q (nm)	Φ_T	$\Delta\epsilon_T$[a] (M^{-1} cm^{-1})	τ_T (μs)	k_{ox} (10^8 M^{-1} s^{-1})
$AlNcOSi(n\text{-}C_6H_{13})_3$	796	0.04	55 000	120	0.30
$GaNcOSi(n\text{-}C_6H_{13})_3$	795	0.20	64 000	80	0.32
$SiNc[OSi(n\text{-}C_6H_{13})_3]_2$	775	0.21[b]	78 400[c]	290	1.9
$SiNc(2/3\text{-}Cl)_4[OSi(n\text{-}C_6H_{13})_3]_2$	774	0.23	80 000[d]	280	3.2
$SiNc(2/3\text{-}Br)_4[OSi(n\text{-}C_6H_{13})_3]_2$	775	0.25	82 500	105	3.0
$SnNc[OSi(n\text{-}C_6H_{13})_3]_2$	788	0.24	99 000	45	0.47
	±1	±20%	±15%	±10%	±10%

[a] Measured at 590 nm. [b] ±10%. [c] ±5%. [d] Assumed value.

Near-infrared emission measurements of the Al and Ga complexes in 2-methyltetrahydrofuran glass (77 K) revealed phosphorescence peaks at 1320 and 1335 nm, respectively. The phosphoresence from $SiNc[OSi(n\text{-}C_6H_{13})_3]_2$ occurs at 1330 nm.[4]

Photoproperties of Silicon Naphthalocyanines with Various Axial Ligands. Photoproperties for $SiNc[OSi(n\text{-}C_6H_{13})_3]_2$ and for four of the variously axially ligated Si naphthalocyanines described above when dissolved in various solvents are given in Table II. All of the compounds in Table II except $SiNc[4\text{-}OC_6H_4CO(OCH_2CH_2)_3CH_3]_2$ dissolve readily in benzene. The latter compound dissolves readily in CH_2Cl_2 and N,N-dimethylacetamide, so its photoproperties were measured with these two solvents instead of benzene.

The quantity Φ_T' in Table II is equal to $\Phi_T\Delta\epsilon_T/\Delta\epsilon_T'$, where $\Delta\epsilon_T'$ is the value of $\Delta\epsilon_T$ for $SiNc[OSi(n\text{-}C_6H_{13})_3]_2$ in benzene. This parameter is reported instead of Φ_T because the value of $\Delta\epsilon_T$ in solvents other than benzene could not be determined (the required energy-transfer standards do not exist). To the extent that the value of $\Delta\epsilon_T$ is constant throughout the series of compounds and solvents, the values of Φ_T' listed are approximately equal to the absolute values of Φ_T. For $SiNc[4\text{-}(OCH_2CH_2)_{\sim 26}OC_6H_4C(CH_3)_2CH_2C(CH_3)_3]_2$ and $SiNc[(OCH_2CH_2)_{\sim 43}OCH_3]_2$ in benzene, $\Delta\epsilon_T$ was measured and the values obtained were found to be nearly the same as the value of $\Delta\epsilon_T$ for $SiNc[OSi(n\text{-}C_6H_{13})_3]_2$ in benzene. As a result, instead of Φ_T' the absolute Φ_T values for these two sensitizer–solvent combinations are reported in Table II.

The solubility of O_2 in CH_2Cl_2 and in N,N-dimethylacetamide is not known, so that the values of k_{ox} are not reported in Table II for these solvents. Relative values of k_{ox} can be determined, however, by comparing the slopes of plots of triplet decay rate versus percent O_2 in the saturating gas. With CH_2Cl_2 as the solvent, the values of k_{ox} for $SiNc[4\text{-}(OCH_2CH_2)_{\sim 26}OC_6H_4C(CH_3)_2CH_2C(CH_3)_3]_2$ and $SiNc[4\text{-}OC_6H_4CO(OCH_2CH_2)_3OCH_3]_2$ relative to that for $SiNc[OSi(n\text{-}C_6H_{13})_3]_2$ are 0.30 and 0.12, respectively. With N,N-dimethylacetamide as the solvent, the k_{ox} values for these two compounds relative to that for $SiNc[OSi(n\text{-}C_6H_{13})_3]_2$ are 0.53 and 0.20, respectively.

The triplet-state characteristics of $SiNc[OSi(i\text{-}C_4H_9)_2(n\text{-}C_{18}H_{37})]_2$ in benzene are essentially the same as those of SiNc-

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[26] Rihter, B. D.; Kenney, M. E.; Ford, W. E.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1990**, *112*, 8064–8070.

Table II. Photoproperties of Silicon Naphthalocyanines with Various Axial Ligands

axial ligand	solvent	λ_Q (nm)	Φ_T'	τ_T (μs)	k_{ox} (10^8 M^{-1} s^{-1})
$OSi(n\text{-}C_6H_{13})_3$	C_6H_6	775	0.21^a	290	1.9
	CH_2Cl_2	773	0.21	270	
	$CH_3CON(CH_3)_2$	777	0.21	260	
$4\text{-}(OCH_2CH_2)_{\sim 26}OC_6H_4C(CH_3)_2CH_2C(CH_3)_3$	C_6H_6	781	0.15^b	190	0.95
	CH_2Cl_2	782	0.13	150	
	$CH_3CON(CH_3)_2$	782	0.15	205	
	CH_3OH	781	0.08	130	0.38
$(OCH_2CH_2)_{\sim 17}OCH_3$	C_6H_6	782	0.15	225	0.88
$(OCH_2CH_2)_{\sim 43}OCH_3$	C_6H_6	781	0.14^c	230	0.89
	CH_3CH_2OH	781	0.11	150	0.44
	CH_3OH	782	0.09	170	0.39
	H_2O	805	0.01	130	0.35
$4\text{-}OC_6H_4CO(OCH_2CH_2)_3OCH_3$	CH_2Cl_2	799	0.11	135	
	$CH_3CON(CH_3)_2$	800	0.11	145	
		±1	±15%	±10%	±10%

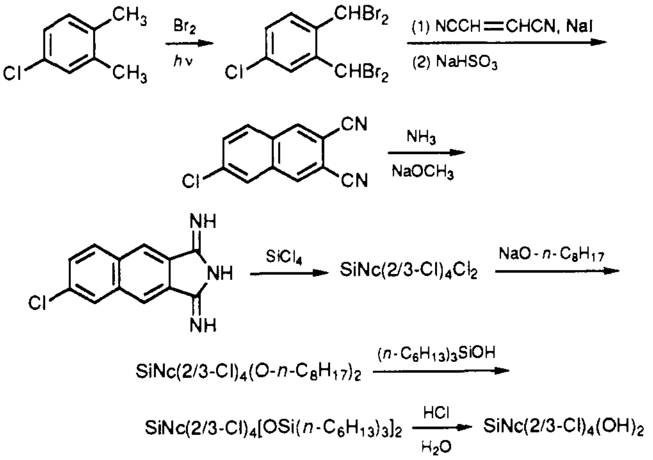
[a] Absolute Φ_T; $\Delta\epsilon_T$ at 590 nm = 78 400 M^{-1} cm^{-1} (±5%). [b] Absolute Φ_T; $\Delta\epsilon_T$ at 590 nm = 76 500 M^{-1} cm^{-1} (±5%). [c] Absolute Φ_T; $\Delta\epsilon_T$ at 590 nm = 76 300 M^{-1} cm^{-1} (±5%).

$[OSi(n\text{-}C_6H_{13})_3]_2$ in benzene, so this compound has not been included in Table II.

For $SiNc[4\text{-}(OCH_2CH_2)_{\sim 26}OC_6H_4C(CH_3)_2CH_2C(CH_3)_3]_2$ in 2-methyltetrahydrofuran glass at 77 K, no phosphorescence is observed under conditions for which it is readily observed for $SiNc[OSi(n\text{-}C_6H_{13})_3]_2$.

Discussion

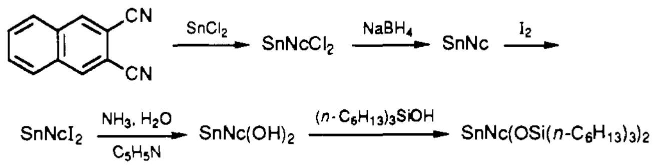
Syntheses. The set of transformations used in the preparation of the silicon tetrachloronaphthalocyanine isomer mixtures is



As is seen, the preparation of the $SiNc(2/3\text{-}Cl)_4Cl_2$ isomer mixture involves five reactions, a free-radical bromination, a 4 + 2 cycloaddition, an aromatization, a nitrile ammonolysis, and a template cyclization. The template cyclization reaction leads to an $SiNc(2/3\text{-}Cl)_4Cl_2$ isomer mixture rather than a single $SiNc(2/3\text{-}Cl)_4Cl_2$ isomer because each of the four diiminoisoindoline molecules that enters into the formation of a naphthalocyanine ring can enter in one of two ways. Presumably, this mixture and each of the other isomer mixtures derived from it contain all eight possible isomers.

The isomer mixtures $SiNc(2/3\text{-}Cl)_4(O\text{-}n\text{-}C_8H_{17})_2$ and $SiNc(2/3\text{-}Br)_4(O\text{-}n\text{-}C_8H_{17})_2$ and the compound $SiNc(O\text{-}n\text{-}C_8H_{17})_2$ are particularly convenient for use as ligand-exchange substrates because they have easily displaceable ligands and, in addition, are readily accessible, soluble in warm organic solvents, and easily recrystallizable. The demetalation of $SiNcCl_2$ which occurs when it is treated with excess $NaO\text{-}n\text{-}C_8H_{17}$ is noteworthy because no other reagent is known that demetalates a Si naphthalocyanine. Probably this demetalation involves nucleophilic attack on the Si by the octoxide ion and can be induced by other alkoxide ions.

The set of transformations used in the preparation of the Sn naphthalocyanines is



The ring cyclization step used in this set of transformations differs from the cyclization step used in the set of transformations for the silicon tetrachloronaphthalene isomer mixtures in that the metal involved undergoes an oxidation. Since this oxidation is a two-electron oxidation, it is possible that it, rather than an external oxidation (e.g., a solvent oxidation), supplies the two electrons required by the cyclization. The means by which the chloro ligands of the macrocycle are exchanged for other ligands in this set of transformations also differs. Here, first the chloro ligands are eliminated in a step involving reductive elimination, and then the new ligands are added in a separate step involving oxidative addition. While this procedure does result in the exchange of the difficulty displaceable chloro ligands, probably simpler procedures can be found.

The reaction sequences used for the synthesis of the Al and Ga naphthalocyanines involve reactions that are the same as or are closely related to those used to prepare the Si naphthalocyanines described here and earlier.[20] The polymer $(AlNcF_x)_n$ of the Al sequence might be better formulated as $(AlNcFO_x)_n$, i.e., as a fractionally air-oxidized (air doped) polymer similar to $(AlPcFI_x)_n$, because of its significant conductivity.[15,27]

Structure and Physical Properties. It is probable that the Sn in SnNc is substantially out of the plane of the macrocycle because of the relatively large radius of Sn(II). This conclusion is supported by the out-of-plane position of the Sn in SnPc.[28]

Earlier it has been concluded that both $(AlNcF)_n$ and $(GaNcF)_n$ are polymers with linear backbones.[15,29,30] On the basis of the powder X-ray data given in this paper and the interpretations given to the X-ray data for related phthalocyanines, it is apparent that the ring–ring spacings in $(AlNcF)_n$ and $(GaNcF)_n$ are 3.62 and 3.74 Å. These spacings are smaller than those in $(AlPcF)_n$ and $(GaPcF)_n$, 3.66 and 3.86 Å.[31] The smaller size of the spacing in $(AlNcF)_n$ relative to that in $(AlPcF)_n$ and of the spacing in $(GaNcF)_n$ relative to that in $(GaPcF)_n$ could be caused by larger nonbonding attractive forces between the faces of the rings. These could arise because of the larger size of the rings.

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(27) Shimura, Y.; Hoshi, M.; Shimura, M. *J. Electrochem. Soc.* **1986**, *133*, 239–240.
(28) Friedel, M. K.; Hoskins, B. F.; Martin, R. L.; Mason, S. A. *J. Chem. Soc. D* **1970**, 400–401.
(29) Shimura, M. *Mem. Fac. Technol., Tokyo Metrop. Univ.* **1986**, *36*, 3761–3766.
(30) Shimura, M.; Sakagami, M.; Shimura, Y. *Mem. Fac. Technol., Tokyo Metrop. Univ.* **1987**, *37*, 3861–3870.
(31) Linsky, J. P.; Paul, T. R.; Nohr, R. S.; Kenney, M. E. *Inorg. Chem.* **1980**, *19*, 3131–3135.

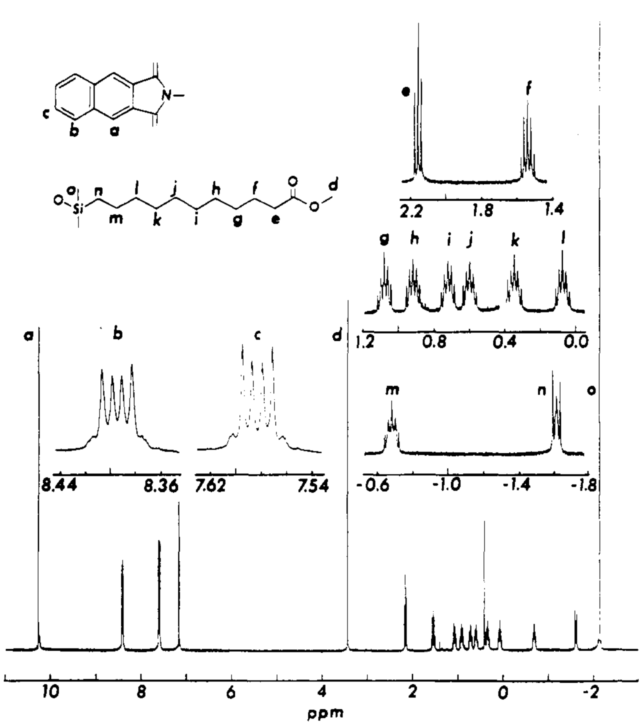

Figure 2. NMR spectrum of $SiNc[(OSi(CH_3)_2(CH_2)_{10}COOCH_3)]_2$ (400 MHz, C_6H_6, 50 °C).

The smaller ring–ring spacing in $(AlNcF)_n$ relative to that in $(GaNcF)_n$ should reduce the negative oxidation potential for it. Thus, this smaller spacing could be the cause of the greater susceptibility of $(AlPcF)_n$ to fractional air oxidation.

The materials properties of the naphthalocyanines, e.g., the low melting point and hexanes solubility of $SiNc[OSi(i\text{-}C_4H_9)_2(n\text{-}C_{18}H_{37})]$ and the low melting point and water solubility of $SiNc[(OCH_2CH_2)_{\sim 43}OCH_3]_2$, can be understood in terms of the size, flexibility, polarity, and degree of branching of the axial ligands.

NMR and Infrared Spectra. The NMR spectra of naphthalocyanines, as is already known, show large ring current effects.[20] A particularly striking example of this is offered by the 400-MHz spectrum of $SiNc[OSi(CH_3)_2(CH_2)_{10}COOCH_3]_2$. In it, Figure 2, separated multiplets for all 15 types of protons are present. The non-first-order character of the α-CH_2 and β-CH_2 multiplets is attributed to restrictions on the rotation of the α-CH_2 group about the bond between it and the Si.

The pattern of the infrared bands associated with the naphthalocyanine ring is fairly simple because of the high symmetry of the ring. Among the characteristic bands are those at ~1260, 1080, 890, 760, and 470 cm^{-1}.

Photoproperties of Various Metal Naphthalocyanines with Trihexylsiloxy Axial Ligands. From Table I it is seen that for the unhalogenated Si, the chloro Si, and the bromo Si compounds, λ_Q is independent of the kinds of atoms in the 2 and 3 positions of the macrocycle. This is consistent with earlier observations.[32] More substantial shifts in λ_Q can be obtained by changing the central metal.

The heavy-atom effect on intersystem crossing in porphyrins is well-known, but less information is available regarding such effects in phthalocyanines and naphthalocyanines.[26,33-36] The data in Table I indicate that Φ_T in naphthalocyanines is not very sensitive to heavy-atom effects, since the replacement of Si ($Z = 14$) by Sn ($Z = 50$) results in an increase in Φ_T of only 15%, although there is a significant reduction in τ_T. Likewise, the replacement of four peripheral hydrogen atoms of the naphthalocyanine ring system by bromine atoms ($Z = 35$) results in an increase in Φ_T of only 20% with a concomitant decrease in τ_T.

The λ_Q and k_{ox} values for the unhalogenated Si and the Sn compounds in Table I are inversely related. This inverse relationship reflects the proximity of the energy level of the T_1 state of the naphthalocyanine ring to that of the $^1\Delta_g$ state of O_2.[6]

Effect of Axial Ligands on Photoproperties of Silicon Naphthalocyanines. The results in Table II clearly show that the nature of the axial ligands of a Si naphthalocyanine can have a significant effect on its photoproperties. For the siloxide, first alkoxide, and phenoxide in a common solvent, λ_Q is smaller for the siloxide than for the alkoxide and still smaller than for the phenoxide. For this same trio, the values of Φ_T' and τ_T for the siloxide are larger than those for the alkoxide and still larger than those for the phenoxide. The inverse relationship between λ_Q and k_{ox} for the siloxide and the alkoxides again reflects the energy of the T_1 state of the naphthalocyanine ring relative to that of the $^1\Delta_g$ state of O_2.

Of the naphthalocyanines prepared, $SiNc[(OCH_2CH_2)_{\sim 43}OCH_3]_2$ is remarkable in that it dissolves readily in a wide variety of solvents, including water (giving solutions with water that can be, as noted above, >0.02 M). The Q-band absorption maximum of the compound in water is significantly red-shifted and broadened compared to its maximum in organic solvents, and Φ_T' is much smaller (Table II). These results indicate that the compound is extensively self-aggregated in water even at concentrations below 10 μM because it is known that the self-aggregation of dyes, including tetrapyrroles, generally broadens and shifts their absorption maxima and quenches their excited states.[37-42]

Conclusions. The materials properties of axially ligated naphthalocyanines of the type studied are greatly dependent on the size, flexibility, polarity, and degree of branching of the axial ligands. Specific photoproperties of such naphthalocyanines are from slightly to greatly dependent on the nature of the ligands, kinds of atoms in the 2 and 3 positions of the ring, atomic numbers of the atoms in the center and in the 2 and 3 positions of the ring, and the type of solvent used. Taking into account the information provided by this and previous studies, it is clear that naphthalocyanines with specifially chosen and widely varying sets of materials and photochemical properties can be designed and prepared. Some of the potentially available compounds along with at least one of those described in this paper, i.e., $SiNc[OSi(i\text{-}C_4H_9)_2(n\text{-}C_{18}H_{37})]_2$, have property sets of interest for photodynamic therapy.

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(32) Kovshev, E. I.; Luk'yanets, E. A. *J. Gen. Chem. USSR (Engl. Transl.)* **1972**, *42*, 1584–1587; *Zh. Obshch. Khim.* **1972**, *42*, 1593–1597.

(33) Becker, R. S. *Theory and Interpretation of Fluorescence and Phosphorescence*; Wiley Interscience: New York, 1969; pp 190–199.

(34) Gouterman, M. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. III, Part A, pp 1–165.

(35) Ferraudi, G. In *Phthalocyanines: Properties and Applications*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH Publishers: New York, 1989; pp 291–340.

(36) Serpone, N.; Jamieson, M. A. *Coord. Chem. Rev.* **1989**, *93*, 87–153.

(37) Kalyanasundaram, K.; Neumann-Spallart, M. *J. Phys. Chem.* **1982**, *86*, 5163–5169.

(38) Seely, G. R.; Senthilathipan, V. *J. Phys. Chem.* **1983**, *87*, 373–375.

(39) Rodgers, M. A. J. In *Photodynamic Therapy of Tumors and Other Diseases*; Jori, G., Perria, C., Eds.; Libreria Progetto: Padova, Italy, 1985; pp 21–35.

(40) Sundstron, V.; Gillbro, T. *J. Chem. Phys.* **1985**, *83*, 2733–2743.

(41) Lambert, C. R.; Reddi, E.; Spikes, J. D.; Rodgers, M. A. J.; Jori, G. *Photochem. Photobiol.* **1986**, *44*, 595–601.

(42) Krasnovsky, A. A., Jr.; Egorov, S. Yu.; Nasarova, O. V.; Yartsev, E. I.; Panomarev, G. V. *Stud. Biophys.* **1988**, *124*, 123–142.