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Synthesis of the First Phthalocyanine-Containing Dendrimer

George A. Kraus* and Steven Vander Louw

Department of Chemistry, Iowa State University,
Ames, Iowa 50011

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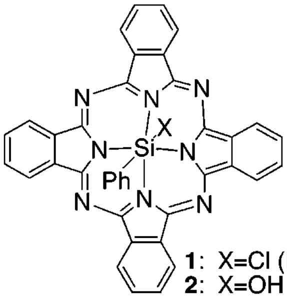
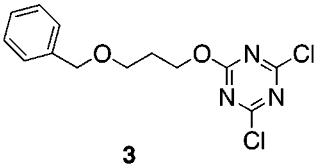
The primary event in photosynthesis is the capture of sunlight by the light-harvesting antennas. These antennas absorb the sunlight and transmit the resulting singlet electronic excitation to the photochemical reaction centers.[1,2] The antenna is an assembly of intensely absorbing pigments that are oriented in such a way as to permit efficient transfer of the singlet electron to the reaction center. Natural systems contain hundreds of pigments per reaction center. The time needed for the absorption of light and resultant excitation at the reaction center seldom exceeds the tens of picoseconds in green plants.[3−5] For the purposes of designing durable antennas, biodegradable pigments such as chlorophyll and bacteriochlorophyll are unattractive, since they are unstable outside of their protein hosts. However, phthalocyanines are extremely stable to heat, air, and light and mimic the spectral characteristics of chlorophyll *a*. Metalated phthalocyanines containing copper, zinc, cobalt, titanium, and gallium have been synthesized. The use of metallophthalocyanines containing silicon as the central atom avoids intersystem quenching of the excited state of the pigment. We envisioned the phthalocyanines being held at defined distances by connection as part of a dendrimer[6] framework.

Phthalocyanine **1** was synthesized by the method of Marks.[7] The reaction of phenyl trichlorosilane with 1,3-diiminoisoindoline generated phthalocyanine **1** in 39% yield. Compound **1** was reacted with excess sodium hydroxide in boiling pyridine following the procedure of Davison and Wynne[8] to generate the hydroxy compound **2** (abbreviated as PC−OH) in quantitative yield.

The synthesis of the dendrimer began by reacting the mono benzyl ether of propane-1,3-diol[9] with cyanuric chloride to produce **3** in 68% yield. With the monosubstituted triazine readily available, the next step was to attach the silicon phthalocyanines. Although the reaction of chlorotriazines with nucleophiles is well precedented, *there was no precedent for the use of silyloxy phthalocyanines as nucleophiles.*[10] Indeed, the reactions of compounds such as **2** seemed to be limited to silylation and acylation reactions. Interestingly, the substitution using the sodium salt of phthalocyanine **2** proceeded smoothly in chloroform using one equivalent of **2** and sodium hydride as a base to give the disubstituted triazine **4** in 71% yield. If another equivalent of the phthalocyanine anion was added to **4** and allowed to react over a four-day period in boiling chloroform, bis phthalocyanine adduct **5** was produced in 54% yield. The cleavage of the benzyl protecting group was readily accomplished with iodotrimethylsilane (TMSI) in chloroform at 25 °C over 30 min to afford the alcohol **6** in quantitative yield.[11]



1: X=Cl (PC-Cl)
2: X=OH (PC-OH)



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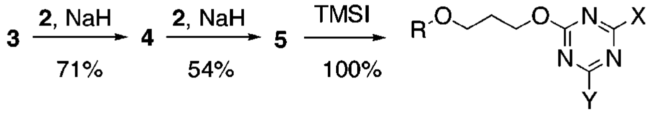

4: X=Cl, Y=OPC, R=Bn
5: X=Y=OPC, R=Bn
6: X=Y=OPC, R=H

A small dendrimer molecule would serve as a model system for the spectroscopy studies. To form this model system, compound **6** was treated with EDCI (1-(3-dimethylaminopropyl)-3-carbodiimide hydrochloride), (dimethylamino)pyridine (DMAP), and 1,3,5-benzenetricarboxylic acid (**7**) to form dendrimer **8** in 81% yield. Although some dendrimers containing porphyrins have recently been reported, phthalocyanine **8** is the first dendrimer with phthalocyanine units surrounding a central core.[12] Compound **8** will be useful for exploring energy transfer in photosynthetic systems.

Experimental Section

Unless otherwise noted, materials were obtained from commercial suppliers and were used without purification. Acetonitrile was purified by distillation from calcium hydride. The purity of all title compounds was determined to be >95% by 300 MHz proton NMR and/or elemental analysis.

PcSi(Ph)(OH) (2). To a solution of **1** (1.00 g, 1.5 mmol) in 15 mL of boiling pyridine and 2 mL of water was added sodium hydroxide (0.245 g, 4 equiv). After

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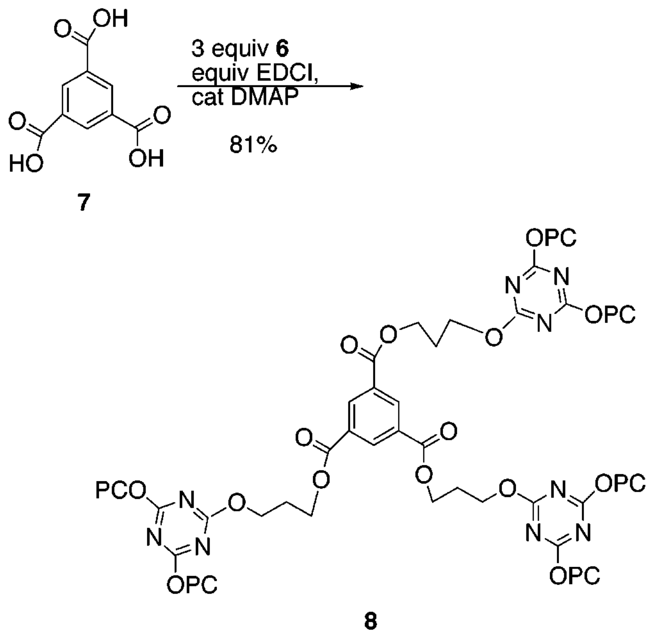

heating for 4 h, the reaction mixture was cooled to room temperature and filtered. The remaining solid was washed with refluxing methanol in a Soxlet extractor for 24 h. The solid was then dried under reduced pressure at 110 °C for 3 h to give 0.950 g (99%) of product as a green powder. ^{1}H NMR (CD_3OD) δ 6.81 (s, 5H), 8.37−8.42 (m, 8H), 9.63−9.69 (m, 8H). IR (Nujol) 1077, 1072, 916, 830, 794 cm^{-1}. Anal. calcd for $C_{38}H_{22}N_8OSi$: C, 71.91; H, 3.49; N, 17.65. Found: C, 72.04; H, 3.58; N, 17.77.

2,4-Dichloro-6-(3-benzyloxy-1-propanoxy)-1,3,5-triazine (3). To a solution of the monobenzyl ether of 1,3-propanediol (1.75 g, 11.0 mmol) in 22 mL of freshly distilled chloroform was added 0.463 g of sodium hydride (11.5 mmol, 1.1 equiv). In a separate flask, 1.93 g of cyanuric chloride (11.0 mmol, 1 equiv) was dissolved in 22 mL of freshly distilled chloroform and heated to 50 °C. The sodium hydride/alcohol solution was then added dropwise with stirring to the cyanuric chloride solution over a period of 1 h. After 4 h of stirring, 50 mL of water was added and the layers were separated. The aqueous layer was then extracted with methylene chloride and the combined organic layers dried over sodium sulfate. Removal of the solvent left 2.35 g of triazine ether **3** as a colorless oil. ^{1}H NMR ($CDCl_3$) δ 2.09−2.13 (m, 2H), 3.65 (t, J = 5 Hz, 2H), 4.53 (s, 2H), 4.61 (t, J = 5 Hz, 2H), 7.28 (s, 5H). IR (film) 3030, 2975, 1675, 1460, 1107 cm^{-1}. MS (CI, m/z) 318 ($M^+ + 4$), 316 ($M^+ + 2$), 314 (M^+), 166. HRMS m/z calculated for $C_{13}H_{13}O_2N_3Cl_2$, 313.0385, measured, 313.0389.

Triazine Phthalocyanine ether (4). To a solution of **2** (0.100 g, 0.16 mmol) in 20 mL of freshly distilled chloroform was added 6.8 mg of sodium hydride (0.17 mmol, 1.1 equiv). In a separate flask, 54.0 mg of **3** (0.17 mmol, 1.1 equiv) was dissolved in 10 mL of freshly distilled chloroform and heated to 50 °C. The sodium hydride/alcohol solution was then added dropwise with stirring to the triazine solution over a period of 1 h. After stirring overnight, 50 mL of water was added and the solution filtered. The solid was washed with hexane and methanol until the filtrate was colorless and then dried in vacuo to afford 0.103 g (71%) of **4** as a green powder. ^{1}H NMR ($CDCl_3$) δ 2.09−2.24 (m, 2H), 3.68 (t, J = 5.0 Hz, 2H), 4.59 (s, 2H), 4.64 (t, J = 5.0 Hz, 2H), 6.81 (s, 5H), 7.28 (s, 5H), 8.37−8.52 (m, 8H), 9.65−9.82 (m, 8H). Anal. calcd for $C_{51}H_{34}N_{11}ClO_3Si$: C, 67.14; H, 3.76; N, 16.88. Found: C, 67.01; H, 3.82; N, 16.96.

Triazine Bisphthalocyanine Ether (5). To a solution of **2** (63.5 mg, 0.10 mmol) in 20 mL of freshly distilled chloroform was added 4.4 mg of sodium hydride (0.11 mmol, 1.1 equiv). In a separate flask, 0.100 g of **4** (0.11 mmol, 1.1 equiv) was dissolved in 20 mL of freshly distilled chloroform and heated to 50 °C. The sodium hydride/alcohol solution was then added dropwise with stirring to the triazine solution over a period of 1 h. After 4 days of stirring, 50 mL of water was added and the solution filtered. The solid was washed with hexane and methanol until the filtrate was colorless and then dried in vacuo to afford 81.5 mg (54%) of **5** as a deep green powder.^{1}H NMR ($CDCl_3$) δ 2.09−2.24 (m, 2H), 3.68 (t, J = 5.1 Hz, 2H), 4.59 (s, 2H), 4.64 (t, J = 5.1 Hz, 2H), 6.81 (s, 10H), 7.28 (s, 5H), 8.37−8.52 (m, 16H), 9.65−9.82 (m, 16H). Anal. calcd for $C_{89}H_{55}N_{19}O_4Si_2$: C, 70.77; H, 3.67; N, 17.61. Found: C, 70.85; H, 3.60; N, 17.48.

Triazine Bisphthalocyanine Alcohol (6). To a solution of **5** (0.100 mg, 0.066 mmol) in 15 mL of freshly distilled chloroform was added 12.2 μL of iodotrimethylsilane (0.086 mmol, 1.3 equiv). After 30 min of stirring, 15 mL of methanol was added and the solution filtered. The solid was washed with hexane and methanol until the filtrate was colorless and then dried in vacuo to afford 99.6 mg (quant) of **6** as a deep green powder. ^{1}H NMR ($CDCl_3$) δ 2.07−2.28 (m, 2H), 3.67 (t, J = 5.1 Hz, 2H), 4.68 (t, J = 5.1 Hz, 2H), 6.81 (s, 10H), 8.37−8.52 (m, 16H), 9.65−9.82 (m, 16H). Anal. calcd for $C_{82}H_{49}N_{19}O_4Si_2$: C, 69.33; H, 3.47; N, 18.72. Found: C, 69.19; H, 3.40; N, 18.60.

Phthalocyanine Dendrimer (8). To a solution of 1,3,5-tribenzoic acid (48.9 mg, 0.023 mmol) in 22 mL of freshly distilled chloroform was added 13.4 mg of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (0.07 mmol, 3.1 equiv) and 1.4 mg of 4-(dimethylamino)-pyridine (0.012 mmol, 0.5 equiv). After stirring for 10 min, 0.100 g of **6** (0.07 mmol, 3 equiv) was added to the solution. After stirring for 2 days, the reaction was quenched with water and filtered. The remaining green powder was washed with water and acetone until the filtrate was colorless. The solid was then extracted in a Soxlet extractor for 48 h using acetone as the solvent. Drying of the solid in vacuo afforded 0.254 g (81%) of **8** as a green powder. ^{1}H NMR ($CDCl_3$) δ 2.07−2.28 (m, 6H), 3.67 (t, J = 5.1 Hz, 6H), 4.68 (t, J = 5.1 Hz, 6H), 6.81 (s, 30H), 7.45 (s, 3H), 8.37−8.52 (m, 48H), 9.65−9.82 (m, 48H). UV (MeCN) 281, 355, 440 nm. Anal. calcd for $C_{255}H_{147}N_{57}O_{18}Si_6$: C, 68.59; H, 3.32; N, 17.87. Found: C, 68.47; H, 3.23; N 17.70.

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