Synthesis of a 1,3,5-Triporphyrinylbenzene

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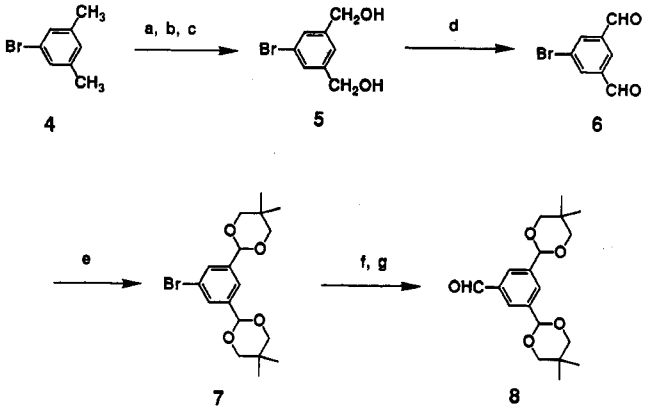
In recent years, a variety of porphyrin oligomers have been prepared as models for photosynthetic reaction centers and as four-electron oxygen-reduction catalysts. Increasing effort has been devoted to the synthesis of conformationally restricted models, since these models allow examination of the dynamics of electron and/or energy transfer events without the complication caused by conformational motions.[1,2] Among the conformationally restricted models, 5-aryloctaalkylporphyrins and 5,15-diaryloctaalkylporphyrins have often been used[3] because of their easy preparation, their high symmetry, and the thermal stability of their atropisomers. A 1,3-phenylene-bridged diporphyrin of this type was first prepared, albeit in low yield, by Sessler.[3b] However, we are not aware of any 1,3-phenylene-bridged porphyrins in which more than two porphyrins are connected to one benzene ring. Herein we describe an efficient synthesis of 1,3,5-triporphyrinylbenzene **3**, the first example of a porphyrin oligomer in which three porphyrins are attached to one benzene ring, in a constrained propeller-like geometry. The key transformation of this synthesis is the condensation of 3,5-di-*tert*-butylbenzaldehyde (**10**)[4] and diformyl-substituted porphyrin **11**–H_2 with bis(3-ethyl-4-methyl-2-pyrrolyl)methane (**9**)[5] under acidic conditions.

3,5-Bis(5,5-dimethyl-1,3-dioxan-2-yl)bromobenzene (**7**) was prepared in five steps from commercially available 5-bromo-*m*-xylene (**4**) (Scheme I): (1) bromination (2.5 equiv of NBS, CCl_4, reflux overnight in the presence of BPO); (2) acetolysis (excess of sodium acetate, AcOH, reflux overnight); (3) reduction ($LiAlH_4$, THF, 0 °C, 2 h); (4) oxidation (PCC, CH_2Cl_2, room temperature, 3 h); and (5) protection (neopentyl alcohol, TsOH, CH_2Cl_2, room temperature, overnight). The total yield of **7** from **4** was 45%. 3,5-Bis(5,5-dimethyl-1,3-dioxan-2-yl)benzaldehyde (**8**) was prepared in 83% yield from the reaction of **7** with magnesium and subsequent treatment of the Grignard intermediate with DMF.

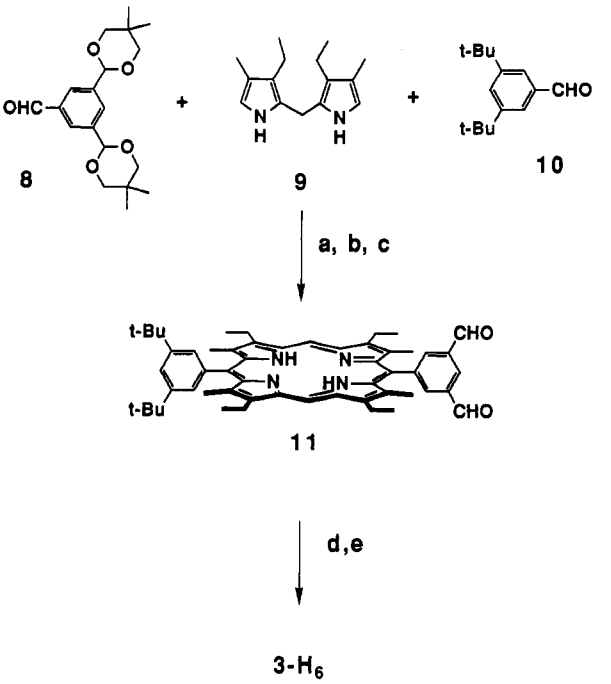
The synthetic route of **3** is outline in Scheme II. Aldehydes **8** and **10** were condensed with **9** in the presence of trichloroacetic acid in acetonitrile, and the resulting solution containing porphinogen compounds was oxidatively treated with *p*-chloranil.[6] After oxidized products were heated in an aqueous trifluoroacetic acid–CH_2Cl_2 mixture and metalated with $Zn(OAc)_2$, the porphyrin products were separated by flash column chromatography (silica gel, CH_2Cl_2) to give porphyrins **1**–Zn and **11**–Zn. Free-base porphyrins **1**–H_2 and **11**–H_2 were prepared by demetalation of the corresponding zinc prophyrins with aqueous HCl. Finally, **11**–H_2 was condensed with excesses of **9** and **10** under similar conditions. After oxidation and metalation, to our surprise, triporphyrin **3**–Zn_3 was obtained in 90% yield (based on the amount of **11**–H_2 used); the double porphyrin cyclization was effected in nearly quantitative yield in the one-pot reaction. We also attempted the preparation of diporphyrin **2**–Zn_2 from the similar condensation reaction of isophthaldehyde and **10** with **9**. The reaction proceeded well and gave **2**–Zn_2 in 60% yield after flash column chromatography. The simple ^{1}H-NMR spectrum of **3**–H_6 was consistent with its symmetric structure. It is interesting to note that the inner protons in the bridges of **2** and **3** (designated as H_a

Scheme I. Synthesis of 8[a]



[a] Key: (a) NBS (2.5 equiv), BPO, CCl_4, reflux, 24 h; (b) AcONa (large excess), AcOH, reflux, 24 h; (c) $LiAlH_4$, THF, 0 °C, 2 h; (d) PCC, CH_2Cl_2, rt, 3 h; (e) neopentyl alcohol, TsOH, CH_2Cl_2, rt, 24 h; (f) Mg, THF, reflux, 24 h; (g) DMF, THF, 0 °C.

Scheme II. Synthesis of 3–H_6[a]



[a] Key: (a) CCl_3CO_2H, CH_3CN, rt, 14 h; (b) *p*-chloranil, THF, rt, 3 h; (c) CF_3CO_2H, H_2O, CH_2Cl_2, reflux, 6 h; (d) **9** (10 equiv), **10** (8 equiv), CCl_3CO_2H, CH_3CN, rt, 20 h; (e) *p*-chloranil, THF, rt, 3 h.

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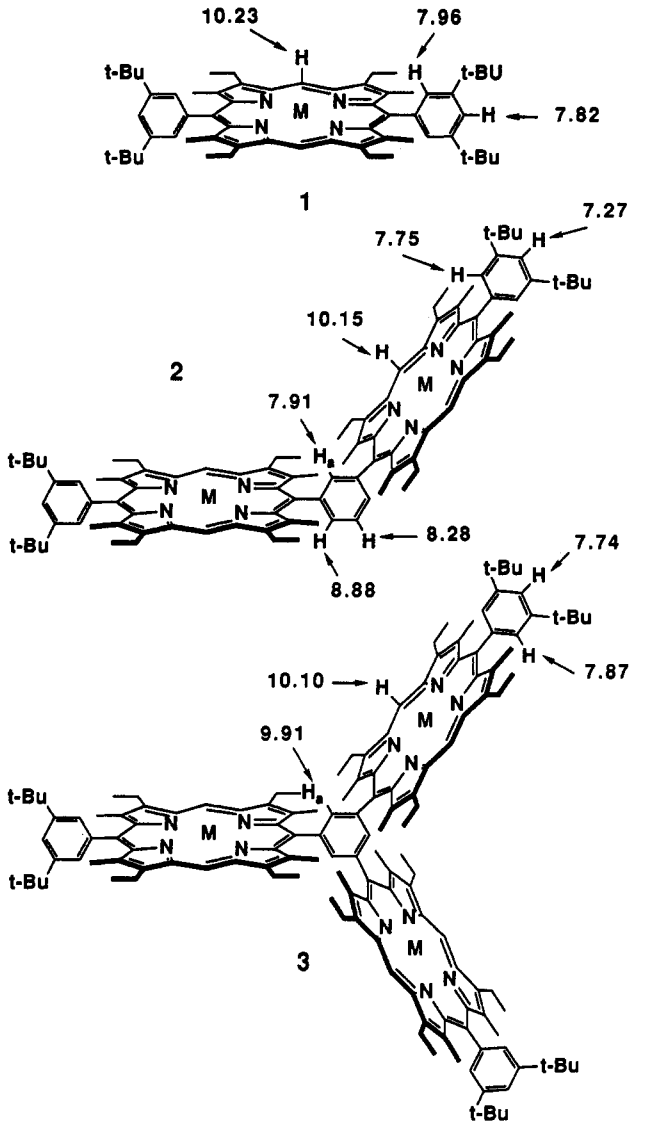

Figure 1. Structures of porphyrin models 1–3. Chemical shifts (ppm) of selected protons are indicated for the respective free base porphyrins.

in Figure 1) appeared at considerably different chemical shifts: 7.91 and 9.91 ppm in 2–H_4 and 3–H_6, respectively.[7] This difference in the chemical shifts suggests that the spatial arrangement of the two porphyrins in 2–H_4 is not necessarily the same as that in 3–H_6. The synthetic strategy disclosed here will be widely applicable to the preparation of oligomeric porphyrins.

Aldehyde **10** has often been employed as a building block in porphyrin models,[8,9] presumably because 3,5-di-*tert*-butylphenyl substituents at a porphyrin meso position enhance the solubility of porphyrins in most of organic solvents by retarding porphyrin aggregation. This property seems to be important for the high yields of **2** and **3**. When *p*-tolualdehyde was used instead of **10** in the cyclization reaction under identical conditions, the diporphyrin yield dropped to ca. 30%.

(7) One of the reviewers suggested that the downfield shift of the inner proton of 3-H_6 may be attributed to a ring current effect of the adjacent porphyrin unit, in spite of some distortion.

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Table I. Absorption and Fluorescence Properties of 1–3[a]

	absorptn λ_{max} (nm)		fluorescence		
porphyrin	Soret	*Q* bands	λ_{max} (nm)	ϕ_{rel}[b]	τ_f[c] (ns)
1–H_2	407	505, 536, 576, 627	628, 694	1.00	12 (97)
2–H_4	416	509, 541, 580, 631	636, 704	0.90	9.0 (97)
3–H_6	425	516, 550, 583, 636	653, 710	0.44	7.1 (96)
1–Zn	416	546, 578	582, 636	1.00	1.5 (80)
2–Zn_2	413, 430	549, 581	602, 650	0.80	1.2 (86)
3–Zn_3	417, 432	556, 594	612, 657	0.48	<1[d]
1–Mg	418	554, 586	595, 648	1.00	7.2 (83)
2–Mg_2	419, 434	556, 599	613, 658	0.55	4.7 (87)
3–Mg_3	422, 435	563, 604	627, 675	0.28	3.4 (89)

[a] Measured in THF at rt. [b] Fluorescence quantum yield relative to that of the respective monomer. [c] Fluorescence lifetime measured by nanosecond time-correlated single-photon counting technique. Numbers in parentheses indicate the normalized preexponential factor in double exponential fit. [d] Shorter than the machine's response time.

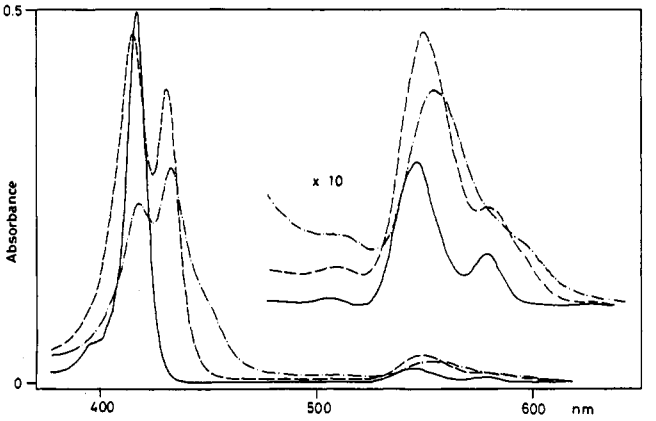

Figure 2. UV–vis absorption spectra of 1–Zn (—), dimer 2–Zn_2 (- -), and 3–Zn_3 (– · –) in THF. Concentrations are 1×10^{-6} M.

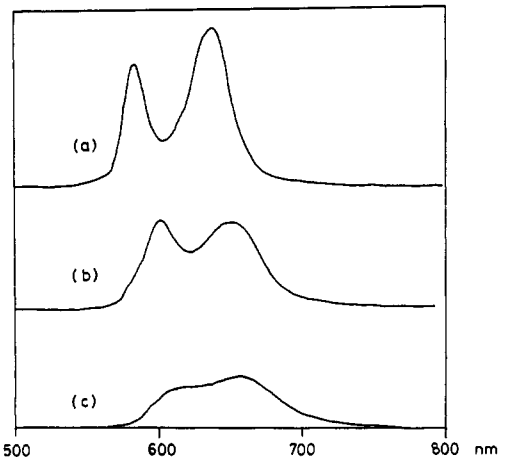

Figure 3. Fluorescence spectra of 1–Zn (a), dimer 2–Zn_2 (b), and 3–Zn_3 (c) in THF excited at their respective Soret maxima.

Magnesium complexes 1–Mg, 2–Mg_2, and 3–Mg_3 were prepared in good yields when the corresponding free-base porphyrins were heated with $Mg(ClO_4)_2$ in pyridine. The absorption and fluorescence properties of these porphyrin models in THF are summarized in Table I, and the absorption and fluorescence spectra of the zinc complexes are shown in Figures 2 and 3. A split Soret band due to exciton coupling was observed in the absorption spectrum of 2–Zn_2. Similar absorption spectra have been reported previously for 1,3-phenylene-bridged diporphyrins.[3b,c] A split Soret band was also observed for 3–Zn_3, but the

relative intensity of the absorption band at longer wavelength was larger than that at shorter wavelength. This spectral behavior is the opposite of that of 2–Zn_2. When the number of porphyrins increased, the fluorescence spectra became broader, the emission maximum was shifted to longer wavelength, the relative fluorescence quantum yields were decreased, and the fluorescence lifetimes became shorter. These changes caused by the increase in the number of porphyrins were even more prominent in the corresponding magnesium complexes.

Current efforts are being devoted to the preparation of hybrid metal complexes of the triporphyrin in order to study intramolecular electron and/or energy transfers in this topologically interesting molecule. Efforts are also being devoted to the extension of this methodology of double and/or multiple porphyrin cyclizations to other supramolecular systems.

Experimental Section

Melting points were measured on a Yanagimoto micro melting point apparatus and are uncorrected. UV–vis spectra were recorded on a Shimadzu and UV-3000 spectrometer. Steady-state fluorescence spectra were recorded on a Shimadzu RF-502A spectrofluorimeter. Fluorescence lifetimes were measured by the method of single photon counting on a HORIBA Model NAES 1100 nanosecond lifetime fluorimeter (2-ns pulse width). ^{1}H-NMR spectra were recorded on JMN-GX 400 and JMN-Alpha 500 spectrometers, and the isotope peaks in deuterated solvents were used as internal standards. Chemical shifts are reported on the δ scale (ppm) relative to tetramethylsilane. Mass spectra were recorded on a JEOL HX-110 spectrometer. Mass spectra of porphyrins were measured by the FAB method; the matrix was $CHCl_3$/*m*-nitrobenzyl alcohol unless otherwise stated. Infrared spectra were taken on a HORIBA FT-300 spectrometer. Preparative separations were usually performed by flash column chromatography on silica gel (Merck, Kieselgel 60H, Art. 7736).

For synthetic use, all reagents and solvents of the commercial reagent grade were used without further purification except where noted. Dry CH_3CN was obtained by reflux over and distillation from P_2O_5 and anhydrous K_2CO_3 and was stored over molecular sieves under nitrogen. Dry CH_2Cl_2 was distilled from P_2O_5.

1,3-Bis(5,5-dimethyl-1,3-dioxan-2-yl)-5-bromobenzene (7). Compound 7 was synthesized from 5-bromo-*m*-xylene (2.78 g, 15 mmol) in five steps as shown in Scheme I: (1) NBS (6.6 g, 37 mmol) bromination (CCl_4 (150 mL), reflux, overnight, in the presence of BPO (0.3 g)); (2) acetolysis with sodium acetate (AcONa (5 g) in AcOH (100 mL), reflux, overnight); (3) $LiAlH_4$ (1.14 g, 30 mmol) reduction in THF (200 mL); (4) PCC (8.62 g, 40 mmol) oxidation in CH_2Cl_2 (400 mL) for 3 h at rt; and (5) protection with neopentyl alcohol (neopentyl alcohol (3.12 g, 30 mmol), TsOH (100 mg), 150 mL of CH_2Cl_2 (150 mL), overnight, rt). Recrystallization from methanol gave colorless needles of 7 (2.60 g, 6.75 mmol, 45%): mp 130.0–130.5 °C; mass (EI) *m/z* 385 (M^+); ^{1}H-NMR ($CDCl_3$) 7.58 (2H, s, Ar-H), 7.47 (1H, s Ar-H), 5.28 (2H, s), 3.70 and 3.55 (8H, ABq, J = 10.4 Hz), 1.20 (6H, s, Me), and 0.70 (6H, s, Me); IR (KBr) 2958, 2931, 1577, 1468, 1377, 1163, 1105, 1028, and 987 cm^{-1}. Anal. Calcd for $C_{18}H_{25}O_4Br$: C, 56.11; H, 6.54; Br, 20.74. Found: C, 56.15; H, 6.50; Br, 20.77.

3,5-Bis(5,5-dimethyl-1,3-dioxan-2-yl)benzaldehyde (8). Magnesium turnings (84 mg, 3.5 mmol) were added to a three-necked flask and heated with stirring under N_2 for 4 h to activate the magnesium. Dry THF (1.5 mL) was added, and then a catalytic amount of I_2 was added in order to further activate the metal. Then, 7 (900 mg, 2.34 mmol) dissolved in 10 mL of dry THF was added slowly, and the resulting mixture was refluxed under N_2 overnight and then cooled to 0 °C. To the Grignard reagent thus prepared was added a mixture of dry DMF (1.5 mL) and dry THF (20 mL) slowly at 0 °C. After the mixture slowly warmed to rt, stirring was continued for another 1 h. The reaction mixture was poured into 3 N HCl (30 mL) and extracted with ether (3 × 100 mL). The organic layers were combined, successively washed with aqueous $NaHCO_3$, water, and brine, and dried over anhyd Na_2SO_4. After the evaporation of the solvent, separation by silica gel column chromatography (eluent, CH_2Cl_2/ether = 12/1) gave 8 as a colorless solid (650 mg, 1.95 mmol, 83%): mp 122.0–122.5 °C; mass (EI) *m/z* 344 (M^+); ^{1}H-NMR ($CDCl_3$) 10.15 (1H, s, CHO), 8.14 (2H, s, Ar-H), 8.04 (1H, s, Ar-H), 5.55 (2H, s), 3.92 and 3.76 (8H, ABq, J = 10.4 Hz), 1.36 (6H, s, Me), and 0.92 (6H, s, Me); IR (KBr) 2952, 2906, 1703, 1465, 1385, 1018, 978, and 802 cm^{-1}. Anal. Calcd for $C_{19}H_{28}O_5$: C, 68.24; H, 7.84. Found: C, 68.22; H, 7.90.

Synthesis of Porphyrin Monomers 1 and 11. Aldehydes 8 (668 mg, 2 mmol) and 10 (872 mg, 4 mmol) were dissolved in dry CH_3CN (40 mL). Then, dipyrrylmethane 9 (1368 mg, 6 mmol) dissolved in CH_3CN (5 mL) was added. After the resulting solution was stirred for 2–3 min, trichloroacetic acid (60 mg, 0.37 mmol) in dry CH_3CN (3 mL) was added. The mixture was stirred at rt for 14 h under N_2 in the dark. A solution of *p*-chloranil (2.1 g, 8.57 mmol) in dry THF (60 mL) was added, and stirring was continued for another 3 h. The resulting reaction mixture was poured into 6 N HCl solution and extracted with $CHCl_3$ until the extract was colorless. The $CHCl_3$ layers were combined, washed with aqueous $NaHCO_3$ and water, and dried over anhyd Na_2SO_4. A saturated solution of $Zn(OAc)_2$ in MeOH (30 mL) was added. The solution was heated at reflux for 1 h, poured into water, and dried over anhyd Na_2SO_4. After evaporation of the solvent, the fraction containing zinc porphyrin products was separated on a short silica gel column. After evaporation of the solvent, the residue was dissolved in a mixture of CH_2Cl_2 (100 mL), trifluoroacetic acid (100 mL), and water (20 mL). After refluxing for 6 h, the resulting mixture was poured into ice–water and extracted with $CHCl_3$ (3 × 100 mL). The $CHCl_3$ layers were combined, successively washed with aqueous $NaHCO_3$ and water, and dried over anhyd Na_2SO_4. A saturated solution of $Zn(OAc)_2$ in MeOH (40 mL) was added, and the resulting mixture was heated at reflux for 1 h and poured into water. The organic layer was separated and dried over anhyd Na_2SO_4. After evaporation of the solvent, separation on silica gel flash column chromatography with CH_2Cl_2 as the eluent gave 1–Zn (the first fraction, 1374 mg, 50% yield based on the amount of 9 used) and 11–Zn (the second fraction, 690 mg, 40% yield based on the amount of 8 used). Free base 1–H_2 was obtained by acidic demetalation of 1–Zn, which was transformed into magnesium complex 1–Mg under the usual conditions.[10] 1–H_2: mp >300 °C; mass (FAB) *m/z* 855 (M^+) ^{1}H-NMR ($CDCl_3$) 10.23 (2H, s, meso), 7.96 (4H, s, Ar-H), 7.82 (2H, s, Ar-H), 4.05 (8H, m, $-CH_2CH_3$), 2.50 (12H, s, Me), 1.82 (12H, t, $-CH_2CH_3$), 1.60 (36H, s, t~Bu), and −2.35 (2H, broad, NH); 2960, 2929, 1593, 1466, 1446, 1365, 1254, 1057, 849, and 771 cm^{-1}. Anal. Calcd for $C_{80}H_{78}N_4$: C, 84.26; H, 9.19; N, 6.55. Found: C, 84.21; H, 9.24; N, 6.51. 1–Zn: mp >300 °C; mass (FAB) *m/z* 916 (M^+ − 1). 1–Mg: mp >300 °C; mass (FAB) *m/z* 877 (M^+).

11–H_2: mp >300 °C; mass (FAB) *m/z* 800 (M^+ + 1); ^{1}H-NMR ($CDCl_3$) 10.05 (2H, s, meso), 9.91 (2H, s, CHO), 8.55 (2H, s, Ar-H), 8.50 (1H, s, Ar-H), 7.56 (2H, s, Ar-H), 7.48 (1H, s, Ar-H), 3.70 (8H, m, $-CH_2CH_3$), 2.18 (6H, s, Me), 2.10 (6H, s, Me), 1.48 (12H, m, $-CH_2CH_3$), 1.25 (18H, s, t-Bu), and −2.68 (2H, broad, NH); IR (KBr) 2960, 2927, 1703, 1593, 1464, 1387, 1369, 1107, and 769 cm^{-1}. Anal. Calcd for $C_{54}H_{62}N_4O_2$: C, 81.16; H, 7.82; N, 7.01. Found: C, 81.10; H, 7.76; N, 6.97.

Synthesis of Porphyrin Trimer 3. Triporphyrin 3 was synthesized from 11–H_2 in a single step. Thus, 11–H_2 (130 mg, 0.16 mmol), 10 (280 mg, 1.28 mmol), and 9 (364 mg, 1.6 mmol) were dissolved in a mixture of dry CH_3CN (15 mL) and dry CH_2Cl_2 (5 mL). After the solution was stirred for about 3 min, trichloroacetic acid (115 mg, 0.7 mmol) was added. The resulting mixture was stirred in the dark under N_2 for 20 h. A solution of *p*-chloranil (315 mg, 1.27 mmol) in THF (35 mL) was added, and the resulting solution was stirred for another 3 h. Then the solution was poured into 6 N HCl (250 mL) and extracted with $CHCl_3$ until the extract was colorless. The $CHCl_3$ layers were combined, neutralized by shaking with aqueous $NaHCO_3$, and washed with water. A saturated solution of $Zn(OAc)_2$ in MeOH (20 mL) was added, and the resulting mixture was heated at reflux for 1 h. The solution was poured into water, and the organic

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layer was separated and dried over anhyd Na_2SO_4. After evaporation of the solvent, the zinc porphyrin complexes were separated by silica gel flash column chromatography with $CHCl_3$ as the eluent to give **3**–Zn_3 (400 mg, 90% based on the amount of **11**–H_2 used) as a red-purple solid. Free base **3**–H_6, obtained by acidic demetalation of **3**–Zn_3, was transformed into magnesium complex **3**–Mg_3 under the usual conditions. **3**–H_6: mp >300 °C; mass (FAB) *m/z* 2074 (M^+ + 1); ^{1}H-NMR ($CDCl_3$) 10.10 (6H, s, meso), 9.91 (3H, s, Ar-H), 7.87 (6H, s, Ar-H), 7.74 (3H, s, Ar-H), 3.88 (12H, q, $-CH_2CH_3$), 3.75 (12H, q, $-CH_2CH_3$), 3.27 (18H, s, Me), 2.37 (18H, s, Me), 1.65 (18H, t, $-CH_2CH_3$), 1.50 (18H, t, $-CH_2CH_3$), 1.43 (54H, s, t-Bu), and −1.78 (6H, broad, NH); IR (KBr) 2960, 2927, 1702, 1621, 1450, 1365, 1255, 999, 954, 840, and 775 cm^{-1}. Anal. Calcd for $C_{144}H_{174}N_{12}$: C, 83.43; H, 8.46; N, 8.11. Found: C, 83.36; H, 8.50; N, 8.07. **3**–Zn_3: mp >300 °C; mass (FAB) *m/z* 2263 (M^+). **3**–Mg_3: mp >300 °C; mass (FAB) *m/z* 2140 (M^+).

Synthesis of Porphyrin Dimer 2. A 1,3-phenylene-bridged diporphyrin was synthesized from commercially available isophthalaldehyde in a single step. Thus, isophthalaldehyde (26.8 mg, 0.2 mmol), **10** (350 mg, 1.6 mmol), and **9** (448 mg, 2.0 mmol) were dissolved in a mixture of dry CH_3CN (15 mL) and CH_2Cl_2 (5 mL). After the solution stirred for about 2–3 min, trichloroacetic acid (100 mg, 61 mmol) was added, and the resulting mixture was stirred in the dark under N_2 for 20 h. A solution of *p*-chloranil (400 mg, 1.61 mmol) in THF (40 mL) was added, and the resulting solution was stirred for another 2 h. The reaction mixture was poured into 6 N HCl and extracted with $CHCl_3$ until the extract was colorless. The organic layers were combined and neutralized with aqueous $NaHCO_3$. A saturated solution of $Zn(OAc)_2$ in MeOH (40 mL) was added, and the resulting mixture was heated at reflux for 1 h. The solution was poured into water again, and the organic layer was separated and dried over anhyd Na_2SO_4. After evaporation of the solvent, the zinc porphyrin complexes were separated by silica gel flash column chromatography with $CHCl_3$ as the eluent to give **2**–Zn_2 as a red-purple solid (184 mg, 60% yield based on the amount of isophthalaldehyde used). Free base **2**–H_4, obtained by acidic demetalation of **2**–Zn_2, was transformed into magnesium complex **2**–Mg_2 under the usual conditions. **2**–H_4: mp >300 °C; mass (FAB) *m/z* 1409 (M^+ + 1); ^{1}H-NMR ($CDCl_3$) 10.15 (4H, s, meso), 8.88 (2H, d, *J* = 7.7 Hz, Ar-H), 8.28 (1H, t, *J* = 7.7 Hz, Ar-H), 7.91 (1H, broad, Ar-H), 7.75 (4H, s, Ar-H), 7.27 (2H, s, Ar-H), 3.99 (8H, q, $-CH_2CH_3$), 3.95 (8H, q, $-CH_2CH_3$), 3.08 (12H, s, Me), 2.35 (12H, s, Me), 1.70 (24H, m, $-CH_2CH_3$), 1.52 (36H, s, t-Bu), and −2.13 (4H, broad, NH); IR (KBr) 2960, 2927, 1625, 1448, 1365, 1253, 1134, 1059, 953, 843, and 768 cm^{-1}. Anal. Calcd for $C_{98}H_{118}N_8$: C, 83.60; H, 8.44; N, 7.96. Found: C, 83.63; H, 8.40; N, 8.02. **2**–Zn_2: mp >300 °C; mass (FAB) *m/z* 1534 (M^+). **2**–Mg_2: mp >300 °C; mass (FAB) *m/z* 1453 (M^+ + 1).

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Supplementary Material Available: ^{1}H NMR spectra of **1**–H_2, **2**–H_4, **3**–H_6, **7**, **8**, and **11**–H_2 (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.