Synthesis and Characterization of Doubly-Strapped Porphyrins

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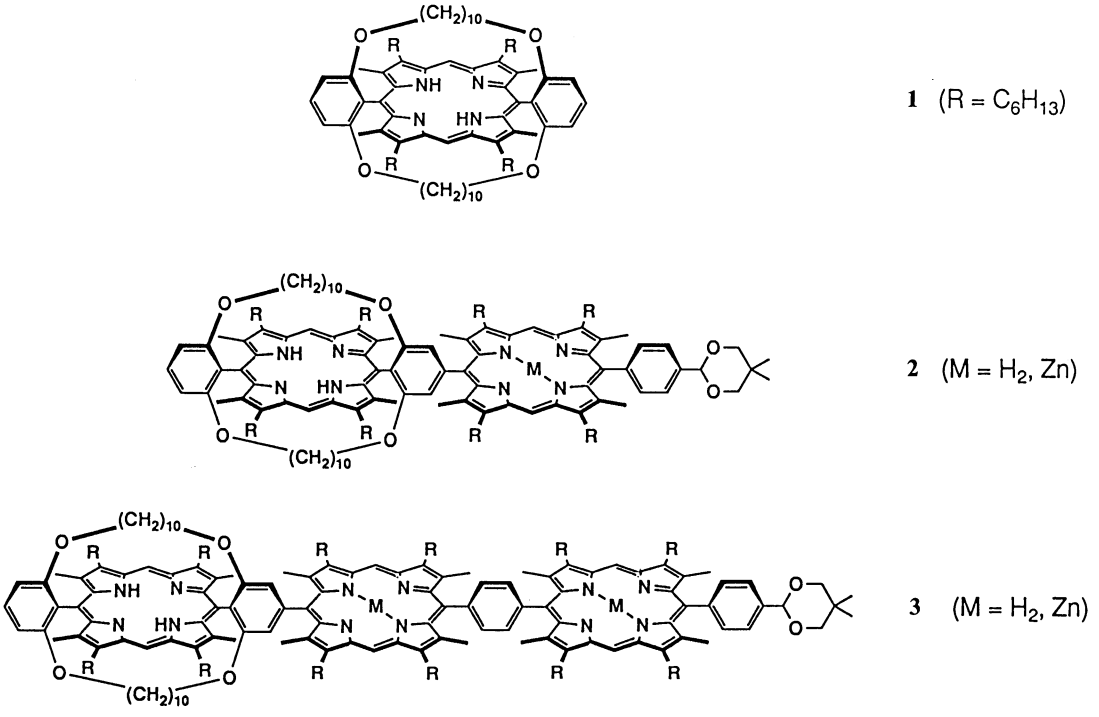
Synthesis of a "doubly-strapped" porphyrin is described, which has two $-O(CH_2)_{10}O-$ straps on both sides of the porphyrin ring. This porphyrin did not form the zinc complex when treated with zinc acetate, even under forcing conditions. Such inertness toward zinc insertion can be attributed to the steric hindrance of the $-O(CH_2)_{10}O-$ straps. Oligoporphyrins with one strapped ring were also synthesized. Reaction of these porphyrins with zinc acetate resulted in insertion of zinc into all non-strapped rings, while the strapped ring remained unchanged. These doubly-strapped porphyrins will be useful in constructing oligoporphyrins as photosynthetic model compounds, in which photochemical and electrochemical properties are controlled by selective metal insertion.

Since the determination of the three-dimensional structure of the photosynthetic bacterial reaction center,[1] efforts have been made to understand the primary charge separation process of photosynthesis on this structural basis.[2] Synthetic model compounds that are designed to mimic the arrangement of the natural photosynthetic pigments have been quite useful in studying dynamics of electron/energy transfer in multicomponent systems.[3,4] Porphyrins have been frequently used in such artificial model studies,[5] as they are very good synthetic analogs for natural chlorophylls. Recently several groups reported synthesis and characterization of oligoporphyrins with or without electron-accepting moiety (such as quinones) as photosynthetic model compounds.[3,4,6]

The bacterial reaction center contains six tetrapyrrolic pigments, two of which are metal-free and the remainder bind magnesium.[1] As the redox and photochemical properties of porphyrins vary significantly with the chelating metal,[7,8] site-selective metallation of oligoporphyrins will be quite promising in controlling properties of photosynthetic model compounds.[9]

In this paper, the author wishes to present a useful synthetic approach toward selectively metallated oligoporphyrins.[10] In the compounds **1**, **2**, and **3**, one porphyrin ring has two alkyl "straps" on both sides, which offer efficient protection of the ring against metallation. Those porphyrin rings that have no "straps" can be metallated, while the "strapped" ring remains metal-free. This approach allows one to prepare partially metallated oligoporphyrins with high site-selectivity.[11]



1 (R = C_6H_{13})

2 (M = H_2, Zn)

3 (M = H_2, Zn)

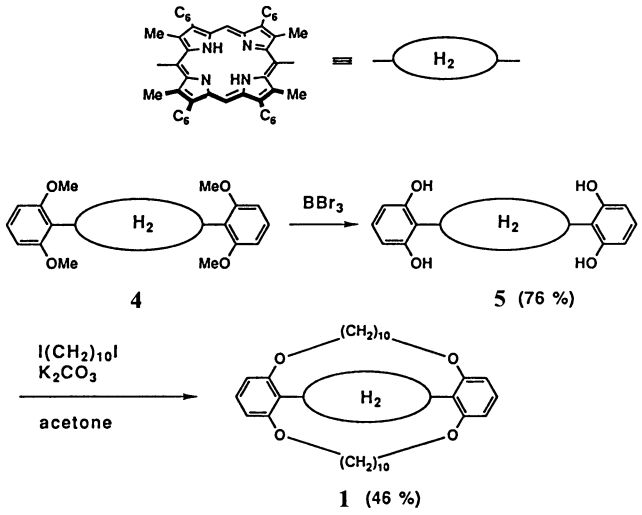
Chart 1.

Results and Discussion

Synthesis of Doubly-Strapped Porphyrins. Synthesis of the doubly-strapped porphyrin **1** is shown in Scheme 1. The ^{1}H NMR spectrum of **1** showed a set of signals in the high-field region (δ=0.8 to −2.6), which were assigned to the methylene signals of the $(CH_2)_{10}$ straps. This result indicates that the $(CH_2)_{10}$ straps in **1** are positioned right above (and below) the porphyrin ring.

There were reported several "strapped" porphyrins that suffered significant degree of ring distortion, which caused severe perturbation in their electronic structures.[11,12] In the present case, however, the compound **1** seemed to be free from such ring distortion. Indeed, the electronic absorption spectrum of **1** showed only minor changes from that of **4** (Table 1); the former showed a red shift by 1 to 3 nm, which is almost negligible. The fluorescence emission spectrum of **1** also showed a slight red shift. The quantum yield of fluorescence emission of **1** was almost equal to that of **4**. From these observation, it can be stated that **1** suffers no significant ring distortion, and that the electronic structure of **1** is quite similar to that of **4**.

Metallation of "Doubly-Strapped" Porphyrin. Reaction with zinc acetate (a metallation reagent) was investigated for the two compounds, **1** and 5,15-di(*p*-tolyl)-2,8,12,18-tetrahexyl-3,7,13,17-tetramethyl-21*H*,23*H*-porphine (**6**). Under the ordinary conditions (porphyrin 0.5 mmol dm^{-3}, zinc acetate 50 mmol dm^{-3}, in CH_2Cl_2–MeOH (10/1 by volume), at 20 °C, 45 min), **6** was quantitatively converted to the zinc complex, while **1** was recovered without any trace of the metallated product. Under more forcing conditions (in pyridine, 100 °C), **1** still resisted metallation. Such inertness of **1** toward metallation can be attributed to the steric hindrance of the $-O(CH_2)_{10}O-$ straps.



Scheme 1.

Table 1. UV-vis Absorption Maxima of **1** and **4**

Compound	λ_{max} (relative absorbance)
1	411 (1000) 507 (76) 541 (24) 576 (30) 630 (8)
4	410 (1000) 507 (77) 542 (27) 574 (33) 627 (9)

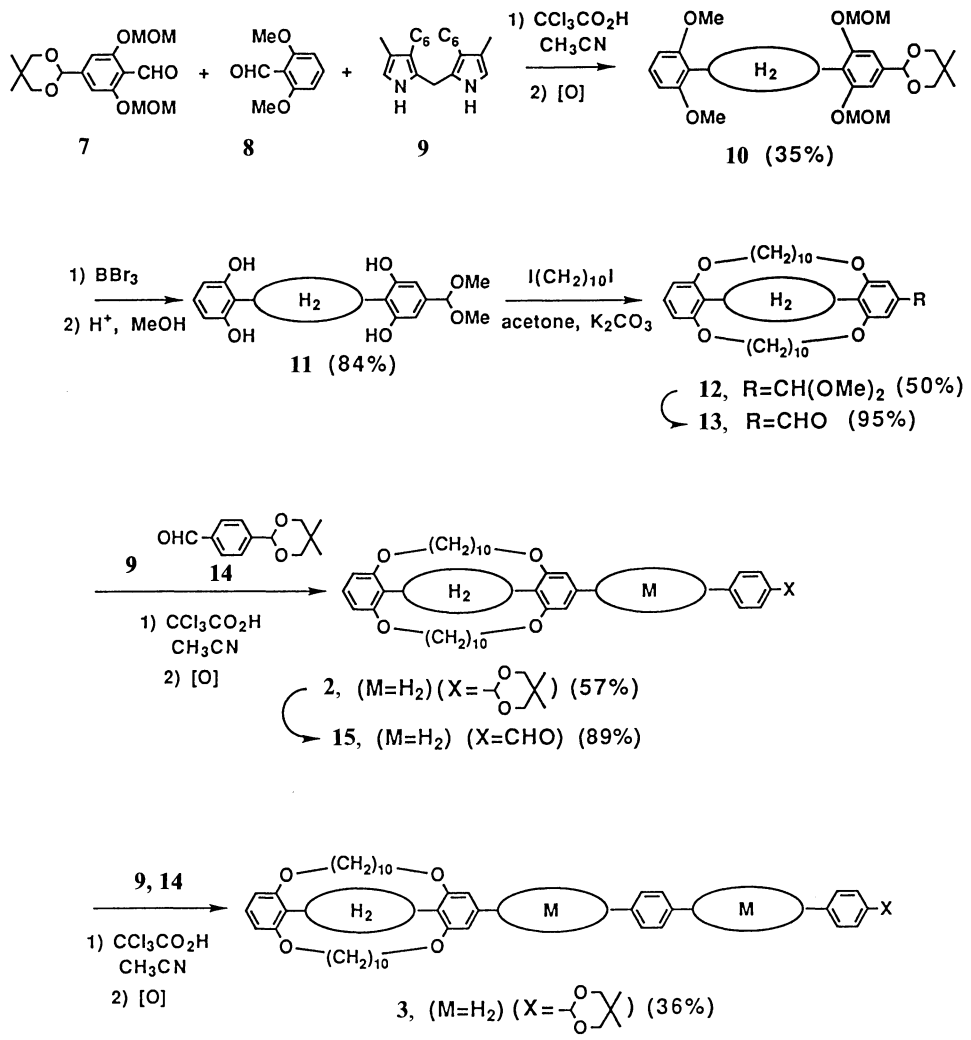
On the other hand, the effect of the straps on demetallation of the metalloporphyrin was also investigated. The zinc complex of **1** was prepared from the zinc complex of **5** and 1,10-diiododecane. When this zinc complex was dissolved in dichloromethane and treated with 4 mol dm^{-3} aqueous hydrochloric acid, complete demetallation took place within 10 min. Therefore, the straps do not protect the ring from depletion of the chelating metal.

Synthesis of Partially Metallated Oligoporphyrins. In view of the results described above, the following is quite a reasonable synthetic approach toward a partially metallated oligoporphyrin; (1) to construct the oligoporphyrin skeleton with all the porphyrin rings metal-free, while introducing the "double straps" to those rings that are intended not to be metallated, and (2) to treat the whole molecule under the metallation conditions, in order to metallate all the "nonstrapped" rings. As the simplest examples, the compounds **2** and **3** were synthesized (Scheme 2).

When **2** was treated with zinc acetate in CH_2Cl_2–MeOH, **2** was quantitatively converted to the monozinc complex, which was characterized by ^{1}H NMR, MS and UV-vis spectroscopy. The ^{1}H NMR signals for the $(CH_2)_{10}$ straps of monozinc-**2** appeared at exactly the same positions as those of the free base of **2**; this indicates that the zinc metal was inserted exclusively to the "non-strapped" ring.

Similarly, the free base of **3** was treated with zinc acetate to give the dizinc complex quantitatively. Again, the zinc ions were inserted to the "non-strapped" rings.

There have been reported several "partially metallated" oligoporphyrins in literature.[3,4,9] Many of them were prepared by the reaction of metal-free oligoporphyrin with a limited amount of metal salt, followed by chromatographic separation of the mixture.[3,4] Limitation of this method is apparent; as the complexity of the oligoporphyrin grows up, the separation becomes extremely tedious. Partially metallated oligoporphyrins can be synthesized in a stepwise manner.[9a] The metal-free ring would be constructed after the other ring(s) had been constructed and metallated. This method too is of limited scope, however, because the metalloporphyrins may not be stable enough under the reaction conditions of porphyrin ring construction. Many workers synthesized partially metallated oligoporphyrins by coupling of a free base porphyrin and a metalloporphyrin through ester, ether, and amide linkages.[9b,c,f] Such compounds suffered undesirable conformational freedom that sometimes led to desparate complexity in their photophysical properties. Collman



Scheme 2.

et al. utilized silver(II) ion as a "protecting metal" in their synthesis of mixed-metal bisporphyrins.[9d] Although this is an interesting approach, it may not be compatible with our rather lengthy synthesis of oligoporphyrins.

The "double straps" will serve as a useful protecting group in synthesis of selectively metallated oligoporphyrins. The straps are linked by ether linkages which are stable under various conditions. They do not cause any significant change in the photophysical nature of the porphyrin ring they are attached to. Therefore, the "doubly-strapped" porphyrins will be convenient building blocks for construction of selectively metallated oligoporphyrins, and of sophisticated photosynthetic model compounds.

Experimental

General. Diethyl ether and tetrahydrofuran (THF) were refluxed over and distilled from sodium benzophenone ketyl. Dichloromethane was distilled from P_2O_5, acetonitrile from CaH_2, and acetone from $CaSO_4$. *N*,*N*-Dimethylformamide (DMF) was distilled under reduced pressure and stored over Molecular Sieves 4A. Other solvents and reagents were reagent grade. Melting points were measured on a Yanagimoto micro melting point apparatus and are uncorrected. Preparative separations were usually performed by flash column chromatography on silica gel (Merck, Kieselgel 60H, Art. 7739).

UV-visible spectra (in CH_2Cl_2) were obtained with a Shimadzu UV-3000 spectrometer. Steady-state fluorescence spectra were taken on a Shimadzu RF-502A spectrofluorimeter. ^{1}H NMR spectra were recorded on a JEOL GX-400 spectrometer (operating at 400 MHz), chemical shifts (in $CDCl_3$) being reported in the delta scale (ppm) relative to Me_4Si. Mass spectra were recorded on JEOL DX-300 and HX-110 spectrometers. For porphyrin compounds, the positive-FAB (fast atom bombardment) ionization method was used (accelerating voltage 1.5 kV and 10 kV, Xe atom as the primary ion source). The FAB matrix was 3-nitrobenzyl alcohol/chloroform. For measurements of high-resolution mass spectra of porphyrins, either polyethylene glycol (for m/z=800 to 1300) or caesium iodide (for higher m/z) was used as references.

Methyl 3,5-Bis(methoxymethoxy)benzoate (16). Sodium hydride (5.0 g of 60% oil dispersion, 125 mmol) was suspended

in DMF (10 ml) after being washed with hexane to remove mineral oil. This suspension was cooled with an ice bath under N_2, and a solution of methyl 3,5-dihydroxybenzoate (10.0 g, 59.5 mmol) in 20 ml of DMF was added dropwise over 30 min. The mixture was then heated to 60 °C for 2 h. At the end of this period evolution of gas ceased and a yellow cake was formed. The mixture was cooled to 0 °C again and a solution of chloromethyl methyl ether (10 ml, 132 mmol) in 8 ml of DMF was dropwise added (over 20 min), and the resulting suspension was stirred overnight. The reaction mixture was poured into water, extracted with CH_2Cl_2, washed thoroughly with water, dried over Na_2SO_4, and evaporated to give a yellow oil (12.5 g, 48.8 mmol, 82%). ^{1}H NMR δ=7.36 (2H, d, J=2.5 Hz), 6.91 (1H, t, J=2.2 Hz), 5.19 (4H, s), 3.90 (3H, s), 3.48 (6H, s). Found: m/z 340.1524. Calcd for $C_{12}H_{16}O_6$: M, 340.1515.

3,5-Bis(methoxymethoxy)benzaldehyde (17). This aldehyde was synthesized from **16** in two steps: (1) reduction to the primary alcohol by $LiAlH_4$ (in ether/THF, 0 °C to r.t., overnight, 94%), (2) oxidation to the aldehyde by pyridinium chlorochromate (1.28 equiv, with equimolar amount of sodium acetate, in CH_2Cl_2, r.t., 3.5 h, 68%). A yellow oil. ^{1}H NMR δ=9.91 (1H, s), 7.21 (2H, d, J=2.4 Hz), 6.98 (1H, t, J=2.3 Hz), 5.21 (4H, s), 3.49 (6H, s). Found: m/z 226.0814. Calcd for $C_{11}H_{14}O_5$: M, 226.0837.

3,5-Bis(methoxymethoxy)-1-(5,5-dimethyl-1,3-dioxan-2-yl)benzene (18). The aldehyde **17** (3.88 g, 17.2 mmol), 2,2-dimethyl-1,3-propanediol (2.14 g, 20.1 mmol) was dissolved in 50 ml of CH_2Cl_2, p-toluenesulfonic acid monohydrate (0.38 g, 2 mmol) was added. The mixture was stirred for 45 min, poured into water, and the organic layer was separated, washed with dilute $NaHCO_3$ solution, dried over Na_2SO_4 and evaporated. Yellow oil, 5.30 g (17.0 mmol, 99%). ^{1}H NMR δ=6.85 (2H, d, J=2.1 Hz), 6.71 (1H, t, J=2.3 Hz), 5.31 (1H, s), 5.16 (4H, s), 3.75 (2H, d, J=11.3 Hz), 3.62 (2H, d, J=10.7 Hz), 3.46 (6H, s), 1.28 (3H, s), 0.79 (3H, s). found: m/z 312.1599. Calcd for $C_{16}H_{24}O_6$: M, 312.1566.

2,6-Bis(methoxymethoxy)-4-(5,5-dimethyl-1,3-dioxan-2-yl)benzaldehyde (7). To a solution of **18** (2.19 g, 7.0 mmol) and *N,N,N',N'*-tetramethylethylenediamine (4.88 g, 42 mmol) in dry ether, *n*-BuLi (1.6 mol dm^{-3} solution in hexane, 6.5 ml) was dropwise added over 10 min (r.t., under N_2). After 2 h, 1.1 g (15 mmol) of DMF was added. The reaction mixture was stirred overnight, poured into water, and extracted with ether. The extract was washed with water, dried over Na_2SO_4 and evaporated. The residual oil was a mixture of the aldehyde **7** and the starting material **18**. The aldehyde **7** was isolated by flash column chromatography (benzene–ether=95/5). Yellow oil, 1.59 g (4.7 mmol, 67%). ^{1}H NMR δ=10.51 (1H, s), 6.97 (2H, s), 5.32 (1H, s), 5.28 (4H, s), 3.77 (2H, d, J=10.0 Hz), 3.61 (2H, d, J=10.3 Hz), 3.50 (6H, s), 1.26 (3H, s), 0.79 (3H, s). Found: m/z 340.1524. Calcd for $C_{17}H_{24}O_7$: M, 340.1515.

5,15-Bis(2,6-dimethoxyphenyl)-2,8,12,18-tetrahexyl-3,7,13,17-tetramethyl-21*H*,23*H*-porphine (4) and 5-(2,6-Dimethoxyphenyl)-15-[4-(5,5-dimethyl-1,3-dioxan-2-yl)-2,6-bis(methoxymethoxy)phenyl]-2,8,12,18-tetrahexyl-3,7,13,17-tetramethyl-21*H*,23*H*-porphine (10). The aldehyde **7** (234 mg, 0.69 mmol), 2,6-dimethoxybenzaldehyde[13] (**8**, 229 mg, 1.38 mmol), and bis(3-hexyl-4-methyl-2-pyrrolyl)methane (**9**, 709 mg, 2.07 mmol) were dissolved in 25 ml of CH_3CN, trichloroacetic acid (68 mg, 0.41 mmol) was added, and the mixture was stirred for 5 h. (protected from light, under N_2, r.t.). p-Chloranil (763 mg, 3.1 mmol) dissolved in THF was added, and the mixture was stirred overnight. The solvent was evaporated under reduced pressure, and the residue was dissolved in CH_2Cl_2, washed with saturated $NaHCO_3$ solution (twice) and water, and dried over Na_2SO_4. To this solution, a saturated solution of zinc acetate in methanol (5 ml) was added, and the mixture was stirred for 1 h, washed with water, dried, and evaporated. The products were separated by two successive flash column chromatography: first, CH_2Cl_2 as eluent, to remove polymeric by-products; second, benzene as eluent, to separate the two major products **4** (first fraction) and **10** (second fraction). Both **4** and **10** were isolated as zinc complexes. Yield: **4**, 381 mg (0.367 mmol, 35% based on **9**), **10**, 420 mg (0.346 mmol, 33%). To obtain the free base porphyrin, a CH_2Cl_2 solution of **4** (or **10**) was shaken twice with 4 mol dm^{-3} aqueous HCl, washed with water and saturated $NaHCO_3$ solution (twice), dried over Na_2SO_4 and evaporated to give the free base of **4** (or **10**) in quantitative yield.

Compound data of **4**: Mp>300 °C. ^{1}H NMR δ=10.12 (2H, s, meso), 7.73 (2H, t, J=8.3 Hz, Ph), 6.99 (4H, d, J=8.3 Hz, Ph), 3.98 (8H, t, hex-1), 3.54 (12H, s, MeO), 2.61 (12H, s, Me), 2.19 (8H, quint, hex-2), 1.72 (8H, quint, hex-3), 1.46 (8H, quint, hex-4), 1.35 (8H, sext, hex-5), 0.89 (12H, t, hex-6), −2.21 (2H, s, NH). UV-vis, see Table 1. Found: m/z 975.664. Calcd for $C_{64}H_{86}N_4O_4$: M+H, 975.671.

10: Mp 82—86 °C. ^{1}H NMR δ=10.13 (2H, s, meso), 7.73 (1H, t, J=8.6 Hz, arom-H), 7.37 (2H, s, arom-H), 7.00 (2H, d, J=8.3 Hz, arom-H), 5.69 (1H, s, acetal-H), 4.89 (4H, s, OCH_2OCH_3), 3.98 (10H, m, hex-1 and acetal-CH_2), 3.82 (2H, d, J=10.8 Hz, acetal-CH_2), 3.54 (6H, s, MeO), 2.68 (12H, 2 singlets, Me), 2.61 (6H, s, OCH_2OCH_3), 2.17 (8H, m, hex-2), 1.69 (8H, m, hex-3), 1.45 (m, hex-4 and acetal-Me), 1.33 (m, hex-5), 0.88 (15H, m, hex-6 and acetal-Me), −2.24 (2H, broad, NH). UV-vis, λ_{max} (relative Abs.) 409 (1000), 507 (73), 541 (23), 574 (30), 627 (8), 655 (2). Found: m/z 1149.766. Calcd for $C_{72}H_{100}N_4O_8$: M+H, 1149.759.

5,15-Bis(2,6-dihydroxyophenyl)-2,8,12,18-tetrahexyl-3,7,13,17-tetramethyl-21*H*,23*H*-porphine (5). A solution of **4** (150 mg, 0.154 mmol) in dry CH_2Cl_2 (30 ml) was cooled to −78 °C under N_2, and a solution of BBr_3 (1.2 ml, 4.6 mmol) in CH_2Cl_2 (10 ml) was added dropwise over 45 min.[14] After stirring overnight, the reaction mixture was poured into water. Ethyl acetate was added until all organic substance dissolved, and the organic phase was separated, washed twice with aqueous $NaHCO_3$, dried and evaporated. The product was purified by reprecipitation from CH_2Cl_2–hexane. Yield: 107 mg (0.116 mmol, 76%). Mp 220—223 °C. ^{1}H NMR δ=10.32 (2H, s), 7.64 (2H, t, J=8.3 Hz), 7.00 (4H, d, J=8.3 Hz), 4.65 (broad), 4.01 (8H, t), 2.78 (12H, s), 2.20 (8H, quint), 1.75 (8H, quint), 1.5 (m), 1.37 (8H, sext), 0.91 (12H, t), −2.3 (very broad). UV-vis, λ_{max} (relative Abs.) 405 (1000), 507 (75), 542 (55), 572 (37), 626 (31). Found: m/z 919.606. Calcd for $C_{60}H_{78}N_4O_4$: M+H, 919.608.

Strapped Porphyrin 1. The compound **5** (18 mg, 0.02 mmol) and 1,10-diiododecane (16 mg, 0.04 mmol) were dissolved in 60 ml of dry acetone. Anhydrous K_2CO_3 (44 mg, 0.32 mmol) was added, and the mixture was heated to reflux under N_2. Heating was continued for two days, during which period 1,10-diiododecane (64 mg) and K_2CO_3 (176 mg) were added in three portions. The reaction mixture was poured into water and extracted with CH_2Cl_2. The extract was washed with water, dried over Na_2SO_4, and evaporated. The product **1** was separated by flash column chromatography

(CH_2Cl_2), and purified by reprecipitation from CH_2Cl_2 and hexane. The solid **1** was washed with MeOH and dried. Yield: 11 mg (0.009 mmol, 46%). Mp 231—233 °C. ^{1}H NMR δ=10.08 (2H, s, meso), 7.67 (2H, t, J=8.3 Hz, Ph), 7.07 (4H, d, J=8.3 Hz, Ph), 3.99 (8H, t, J=7.6 Hz, hex-1), 3.79 (8H, t, J=5.2 Hz, strap-1), 2.64 (12H, s, Me), 2.21 (8H, quint, J=7.6 Hz, hex-2), 1.73 (8H, quint, J=8.1 Hz, hex-3), 1.46 (8H, quint, J=7.8 Hz, hex-4), 1.35 (8H, sext, J=7.5 Hz, hex-5), 0.88 (12H, t, J=7.3 Hz, hex-6), 0.62 (8H, quint, J=5.6 Hz, strap-2), −1.18 (8H, m, strap-3), −1.52 (8H, m, strap-4), −2.27 (2H, s, NH), −2.50 (8H, m, strap-5). UV-vis, see Table 1. Found: m/z 1195.888. Calcd for $C_{80}H_{114}N_4O_4$: M+H, 1195.889.

Zinc Complex of 1. The zinc complex of **5** (36 mg, 0.037 mmol; synthesized from the free base of **5** by the action of zinc acetate in CH_2Cl_2–MeOH) was treated in acetone (100 ml) with three portions of 1,10-diiododecane (29 mg×3) and K_2CO_3 (83 mg×3), in a similar manner as in the free base **1**. After four days, the reaction mixture was worked up, and the product was purified by repeated column chromatography and reprecipitation from hot CH_2Cl_2 and EtOH. Yield: 16 mg (0.012 mmol, 34%). Mp 240—242 °C. ^{1}H NMR δ=10.09 (2H, s, meso), 7.68 (2H, t, J=8.3 Hz, Ph), 7.05 (4H, d, J=8.3 Hz, Ph), 3.99 (8H, t, J=8.2 Hz, hex-1), 3.80 (8H, t, J=5.4 Hz, strap-1), 2.63 (12H, s, Me), 2.21 (8H, quint, J=7.5 Hz, hex-2), 1.74 (8H, quint, J=7.6 Hz, hex-3), 1.48 (8H, quint, J=7.8 Hz, hex-4), 1.36 (8H, sext, J=7.3 Hz, hex-5), 0.90 (12H, t, J=7.3 Hz, hex-6), 0.63 (8H, quint, J=6.1 Hz, strap-2), −1.16 (8H, m, strap-3), −1.34 (8H, m, strap-4), −2.36 (8H, m, strap-5). UV-vis, λ_{max} (relative Abs.) 412 (1000), 537 (38), 570 (21), 578 (24). Found: m/z 1256.782. Calcd for $C_{80}H_{112}N_4O_4Zn$: M, 1256.795.

Attempted Metallation of Free Base 1 and 6. The free base porphyrin (2 μmol) was dissolved in CH_2Cl_2 (4 ml), a solution of zinc acetate in MeOH (0.5 mol dm^{-3}, 0.4 ml) was added, and the mixture was stirred for 45 min at room temperature. The reaction mixture was washed twice with water, dried over Na_2SO_4, and evaporated. The product was characterized by ^{1}H NMR, UV, and MS spectroscopy. Reaction of **1** resulted in complete recovery of the free base porphyrin. Reaction of **6** gave the zinc complex quantitatively.

5-(2,6-Dihydroxyphenyl)-15-[4-(dimethoxymethyl)-2,6-dihydroxyphenyl]-2,8,12,18-tetrahexyl-3,7,13,17-tetramethyl-21*H*,23*H*-porphine (11). The compound **10** (free base; prepared from 203 mg=0.167 mmol of the zinc complex) was dissolved in 20 ml of dry CH_2Cl_2, and the solution was cooled to −78 °C under N_2. Boron tribromide (1.9 g, 7.6 mmol) in 15 ml of CH_2Cl_2 was added dropwise over 40 min. The mixture was then allowed to warm slowly to room temperature overnight, when it was poured into water and washed twice with water. The solvent was evaporated, and the residue was dissolved in a mixture of 40 ml of methanol and 10 ml of 4 mol dm^{-3} aqueous HCl, and the solution was heated to gentle reflux for 4 h. The mixture was poured into water, extracted with CH_2Cl_2, washed with water, dried, and evaporated. Finally, this material was dissolved in MeOH (40 ml) containing *p*-toluenesulfonic acid (200 mg), and the solution was heated to reflux for 4 h. The mixture was poured into water, extracted with CH_2Cl_2, washed with $NaHCO_3$ solution and water, dried, and evaporated. The product was reprecipitated with CH_2Cl_2–hexane, and washed with hexane. Yield: 140 mg (0.141 mmol, 84%). Mp 109—116 °C. ^{1}H NMR δ=10.31 (2H, s, meso), 7.64 (1H, t, J=8.3 Hz, arom), 7.09 (2H, s, arom), 6.99 (2H, d, J=8.3 Hz, arom), 5.68 (1H, s, acetal), 4.62 (4H, broad, OH), 4.01 (8H, m, hex-1), 3.55 (6H, s, OMe), 2.77 (12H, 2 singlets, Me), 2.19 (8H, m, hex-2), 1.74 (8H, m, hex-3), 1.48 (m, hex-4), 1.38 (8H, m, hex-5), 0.90 (12H, m, hex-6), −2.37 (2H, broad, NH). UV-vis, λ_{max} (relative Abs.) 404 (1000), 507 (81), 542 (53), 573 (38), 625 (32). Found: m/z 993.637. Calcd for $C_{63}H_{84}N_4O_6$: M+H, 993.645.

Strapped Porphyrin 12. The porphyrin **11** (88 mg, 0.089 mmol) and 1,10-diiododecane (209 mg, 0.53 mmol) were dissolved in 250 ml of dry acetone, anhydrous K_2CO_3 (335 mg, 4 mmol) was added, and the mixture was heated to reflux for 2 d. Most of inorganic substance was removed by decantation, and the solution was concentrated with a rotary evaporator. Ethanol was added, and the mixture was filtered to obtain the solid material (**12** and inorganic salt), which was dissolved in CH_2Cl_2, washed with water, dried and evaporated. The product was reprecipitated from CH_2Cl_2 and washed with EtOH. Yield: 57 mg (0.045 mmol, 50%). Mp 158—161 °C. ^{1}H NMR δ=10.08 (2H, s, meso), 3.98 (8H, t, hex-1), 2.64 (12H, 2 singlets, Me), 2.21 (8H, quint, hex-2), 1.72 (8H, quint, hex-3), 1.46 (8H, quint, hex-5), 1.34 (8H, sext, hex-5), 0.88 (12H, t, hex-6), −2.28 (2H, s, NH); 5,15-substituents: 7.67 (1H, t), 7.19 (2H, s), 7.09 (2H, d), 5.74 (1H, s, acetal-H), 3.56 (6H, s, OMe); strap CH_2's: 3.82 (4H, t), 3.78 (4H, t), 0.62 (8H, m), −1.13 (4H, m), −1.22 (4H, m), −1.53 (8H, m), −2.51 (8H, m). UV-vis, λ_{max} (relative Abs.) 412 (1000), 507 (74), 541 (22), 577 (29), 630 (8). Found: m/z 1269.911. Calcd for $C_{83}H_{120}N_4O_6$: M+H, 1269.927.

Strapped Porphyrin 13. The porphyrin **12** (55 mg, 0.043 mmol) was dissolved in a mixture of concentrated HCl (7 ml), THF (15 ml) and acetic acid (10 ml). The resulting solution was stirred overnight, poured into water, and extracted with CH_2Cl_2. The aqueous phase was made slightly alkaline with 30% aqueous NaOH and extracted again with CH_2Cl_2. The combined organic phase was washed with aqueous $NaHCO_3$ and water, dried over Na_2SO_4, and evaporated. The residue was reprecipitated from CH_2Cl_2–MeOH and dried. Yield: 50 mg (0.041 mmol, 95%). Mp 189—193 °C. ^{1}H NMR δ=10.09 (2H, s, meso), 3.99 (8H, t, hex-1), 2.64 (6H, s, Me), 2.61 (6H, s, Me), 2.21 (8H, quint, hex-2), 1.73 (8H, quint, hex-3), 1.47 (8H, quint, hex-4), 1.85 (8H, m, hex-5), 0.89 (12H, 2 triplets, hex-6), −2.28 (2H, s, NH); 5,15-substituents: 10.25 (1H, s, CHO), 7.68 (1H, t, J=8.3 Hz), 7.57 (2H, s), 7.08 (2H, d, J=8.3 Hz); strap CH_2"s: 3.89 (4H, t, J=5.4 Hz), 3.78 (4H, t, J=5.4 Hz), 0.70 (4H, quint), 0.60 (4H, quint), −1.01 (4H, m), −1.26 (4H, m), −1.50 (8H, m), −2.39 (4H, m), −2.60 (4H, m). UV-vis, λ_{max} (relative Abs.) 413 (1000), 508 (82), 542 (26), 577 (32), 631 (10). Found: m/z 1223.887. Calcd for $C_{81}H_{114}N_4O_5$: M+H, 1223.884.

Bisporphyrin 2. The formyl porphyrin **13** (45 mg, 0.037 mmol), the dipyrrolylmethane **9** (76 mg, 0.22 mmol) and the aldehyde **14** (41 mg, 0.18 mmol) were dissolved in a mixture of CH_3CN and CH_2Cl_2 containing CCl_3CO_2H (19 mg, 0.12 mmol), and the solution was stirred for 13 h (dark, under N_2). *p*-Chloranil (82 mg, 0.33 mmol) dissolved in THF was added. After 4 h the reaction mixture was poured into water, extracted with CH_2Cl_2, washed with aqueous $NaHCO_3$ and water, dried, and evaporated. The residue was separated by repeated flash column chromatography (CH_2Cl_2+Et_2O, 1—5%). Two major products were obtained, and the second fraction was the bisporphyrin **2** (44 mg, 0.021 mmol, 57% based on **13**). Mp 218—220 °C. ^{1}H NMR δ=10.34 (2H, s, meso), 10.22 (2H, s, meso), 4.17 (8H, m, hex-1), 4.0 (14H, m, hex-1, one acetal-CH_2 and one strap-OCH_2), 3.38 (12H, 2

singlets, Me), 2.69 (6H, s, Me), 2.52 (6H, s, Me), 2.3 (16H, m, hex-2), 1.88 (8H, m, hex-3), 1.77 (8H, m, hex-3), 1.6—1.4 (m, hex-4, hex-5 and one acetal-Me), 1.0—0.9 (27H, m, hex-6 and one acetal-Me), −1.69 (1H, s, NH), −1.89 (2H, singlet+broad signal, NH), −2.0 (1H, br, NH); strap-CH_2's: 3.82 (4H, t, one OCH_2), 0.76 (4H, m), 0.64 (4H, m), −0.94 (4H, m), −1.20 (4H, m), −1.49 (8H, m), −2.36 (4H, m), −2.54 (4H, m); others: 8.13 (2H, d), 7.94 (2H, s), 7.92 (2H, d), 7.70 (1H, t), 7.11 (2H, d), 5.78 (1H, s, acetal), 3.88 (2H, d, one acetal-CH_2). UV-vis, λ_{max} (relative Abs.) 418 (1000), 510 (86), 543 (26), 577 (33), 630 (7). Found: m/z 2086.573. Calcd for $C_{140}H_{196}N_8O_6$: M+H, 2086.531.

Bisporphyrin 15. The bisporphyrin **2** (35 mg, 0.017 mmol) was dissolved in a mixture of acetic acid (8 ml), trifluoroacetic acid (1 ml), 5% aqueous H_2SO_4 (1 ml) and heated to gentle reflux for 3 h. The mixture was poured into water, extracted with CH_2Cl_2, washed with water and $NaHCO_3$ solution, dried over Na_2SO_4 and evaporated. The product was reprecipitated from CH_2Cl_2–MeOH to give 30 mg (0.015 mmol, 89%) of **15**. Mp 262—266 °C. ^{1}H NMR δ=10.37 (2H, s, meso), 10.23 (2H, s, meso), 4.18 (8H, m, hex-1), 4.05 (8H, m, hex-1), 3.40 (6H, s, Me), 3.39 (6H, s, Me), 2.70 (6H, s, Me), 2.50 (6H, s, Me), 2.37 (8H, m, hex-2), 2.27 (8H, m, hex-2), 1.89 (8H, m, hex-3), 1.79 (8H, m, hex-3), 1.59 (m, hex-4), 1.52 (m, hex-4), 1.4 (m, hex-5), 1.0 (m, hex-6), −1.65 (1H, s, NH), −1.87 (3H, singlet+broad signal, NH); strap-CH_2's: 4.00 (4H, t), 3.82 (4H, t), 0.77 (4H, quint), 0.65 (4H, quint), −0.92 (4H, m), −1.18 (4H, m), −1.44 (8H, m) −2.34 (4H, m), −2.52 (4H, m); others: 10.42 (1H, s, CHO), 8.32 (4H, AB quartet), 7.95 (2H, s), 7.70 (1H, t), 7.11 (2H, d). UV-vis, λ_{max} (relative Abs.) 418 (1000), 510 (50), 540 (57), 577 (38), 631 (7). Found: m/z 2000.449. Calcd for $C_{135}H_{186}N_8O_5$: M+H, 2000.458.

Trisporphyrin 3. The bisporphyrin **15** (23 mg, 0.012 mmol), **9** (24 mg, 0.070 mmol), **14** (13 mg, 0.059 mmol) and CCl_3CO_2H (10 mg, 0.060 mmol) were dissolved in CH_2Cl_2–CH_3CN (4 ml+6 ml) and the mixture was stirred for 15.5 h. *p*-Chloranil (26 mg) dissolved in THF was added, and 5 ml of CH_2Cl_2 was added to dissolve the precipitates. After being stirred for 3.5 h, the mixture was poured into water, extracted with CH_2Cl_2, washed with aqueous $NaHCO_3$ and water, dried and evaporated. The residue was dissolved in CH_2Cl_2 and treated with zinc acetate (3 ml of saturated solution in MeOH) for 30 min (r.t.), washed with water and dilute aqueous $NaHCO_3$, dried and evaporated. The mixture was separated by flash column chromatography. After the by-product (5,15-bis[4-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl]porphyrin) was removed (R_f=1.0 for CH_2Cl_2), the product **3** and the unchanged **2** was separated by repeated chromatography (CH_2Cl_2+Et_2O, 5%; **3** eluted faster than **2**). The trisporphyrin **3** was obtained as dizinc complex (13 mg, 0.004 mmol, 36% based on **2**). The metal-free **3** was obtained by treatment of the CH_2Cl_2 solution with hydrochloric acid. Mp 275—285 °C. ^{1}H NMR δ=10.46 (2H, s, meso), 10.36 (2H, s, meso), 10.24 (2H, s, meso), 4.20 (16H, m, hex-1), 4.02 (14H, m, hex-1, strap-OCH_2 and acetal-CH_2), 3.43 (6H, s, Me), 3.41 (6H, s, Me), 3.24 (6H, s, Me), 3.22 (6H, s, Me), 2.70 (6H, s, Me), 2.53 (6H, s, Me), 2.40—2.24 (24H, m, hex-2), 1.90 (16H, m, hex-3), 1.77 (8H, m, hex-3), 1.6—1.4 (m, hex-4, hex-5 and one acetal-Me), 1.2—0.9 (m, hex-6 and one acetal-Me), −1.50 (10H, m, strap-CH_2 and NH), −1.68 (1H, s, NH), −1.89 (2H, s, NH), −2.02 (1H, s, NH); strap-CH_2's: 3.83 (4H, t, J=5.2 Hz), 0.88 (4H, m), 0.66 (4H, m), −0.92 (4H, m), −1.19 (4H, m), −2.34 (4H, m), −2.52 (4H, m); others: 8.61 (4H, s, *p*-C_6H_4), 8.14 (2H, d, J=7.8 Hz, *p*-C_6H_4), 7.98 (2H, s), 7.93 (2H, d, J=7.8 Hz, *p*-C_6H_4), 7.71 (1H, t), 7.12 (2H, d, J=8.3 Hz), 5.78 (1H, s, acetal), 3.89 (2H, d, J=10.7 Hz, one acetal-CH_2). UV-vis, λ_{max} (relative Abs.) 423 (1000), 511 (107), 543 (32), 577 (41), 630 (9). MS m/z 2862.

Metallation of 2 and 3. Metal-free porphyrin (1.3 μmol) in 5 ml of CH_2Cl_2 was treated with zinc acetate (36 μmol) in MeOH (1 ml) for 30 min (r.t.). The reaction mixture was washed with water and dilute aqueous $NaHCO_3$, dried over Na_2SO_4, and evaporated. The product was checked by ^{1}H NMR, UV-vis and MS spectroscopy. The bisporphyrin **2** gave a monozinc complex, and the trisporphyrin **3** gave a dizinc complex.

Compound Data of Monozinc-2. ^{1}H NMR δ=10.27 (2H, s, meso), 10.22 (2H, s, meso), 4.15 (8H, m, hex-1), 4.05 (4H, m, hex-1), 3.99 (10H, m, hex-1, one strap-OCH_2 and one acetal-CH_2), 3.41 (6H, s, Me), 3.39 (6H, s, Me), 2.69 (6H, s, Me), 2.49 (6H, s, Me), 2.39—2.17 (16H, m, hex-2), 1.88 (8H, m, hex-3), 1.77 (8H, m, hex-3), 1.6—1.3 (m, hex-4, hex-5 and one acetal-Me), 0.99—0.85 (m, hex-6 and one acetal-Me), −1.60 (1H, s, NH), −1.83 (1H, s, NH); strap CH_2's: 3.82 (4H, t, J=5.4 Hz), 0.78 (4H, m), 0.65 (4H, m), −0.93 (4H, m), −1.20 (4H, m), −1.46 (8H, m), −2.34 (4H, m), −2.54 (4H, m); others: 8.14 (2H, d, J=7.8 Hz, *p*-C_6H_4), 7.97 (2H, s), 7.92 (2H, d, J=7.7 Hz, *p*-C_6H_4), 7.70 (1H, t), 7.12 (2H, d, J=8.3 Hz), 5.80 (1H, s, acetal), 3.89 (2H, d, J=10.7 Hz, one acetal-CH_2). UV-vis, λ_{max} (relative Abs.) 420 (1000), 510 (86), 543 (26), 577 (33), 630 (7). MS m/z 2150.

Dizinc-3: ^{1}H NMR δ=10.34 (2H, s, meso), 10.26 (2H, s, meso), 10.24 (2H, s, meso), 4.18—4.00 (30H, m, hex-1, one strap-OCH_2 and one acetal-CH_2), 3.44 (6H, s, Me), 3.42 (6H, s, Me), 3.23 (6H, s, Me), 3.22 (6H, s, Me), 2.70 (6H, s, Me), 2.50 (6H, s, Me), 2.40—2.21 (24H, m, hex-2), 1.90 (16H, m, hex-3), 1.78 (8H, m, hex-3), 1.65—1.37 (m, hex-4, hex-5 and one acetal-Me), 1.03—0.92 (m, hex-6 and one acetal-Me), −1.58 (1H, s, NH), −1.81 (1H, s, NH); strap-CH_2's: 3.83 (4H, t, J=10.3 Hz), 0.80 (4H, m), 0.66 (4H, m), −0.90 (4H, m), −1.18 (4H, m), −1.46 (8H, m), −2.32 (4H, m), −2.51 (4H, m); others: 8.63 (4H, s, *p*-C_6H_4), 8.15 (2H, d, J=7.7 Hz, *p*-C_6H_4), 8.01 (2H, s), 7.93 (2H, d, J=7.7 Hz, *p*-C_6H_4), 8.01 (2H, s), 7.93 (2H, d, J=7.7 Hz, *p*-C_6H_4), 7.71 (1H, t), 7.12 (2H, d, J=8.3 Hz), 5.80 (1H, s, acetal), 3.89 (2H, d, J=10.7 Hz, one acetal-CH_2). UV-vis, λ_{max} (relative Abs.) 412 (751), 428 (1000), 510 (48), 543 (78), 578 (40), 631 (6). MS m/z 2983—2995.

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