Supramolecular Assemblies between Macrocyclic Porphyrin Hexamers and Star-Shaped Porphyrin Arrays†

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Received November 2, 2000

The syntheses of eight new star-shaped D_3-symmetric arrays in which three 15-(pyrid-4-yl)porphyrin subunits are attached to the 1, 3, and 5 positions of a benzene core through linkers consisting of collinear repetitive phenylethynyl units have been carried out using Pd(0)-catalyzed coupling reactions. By the same procedure, an analogous 10-(4-pyridin-yl)porphyrin hexamer in which all positions of the benzene core are substitued has been obtained. Likewise, the preparation of suitably sized cyclic porphyrin hexamers, in which all six or at least three alternate porphyrin rings are complexed with Zn(II) ions, is described in detail. In solution, such cyclic porphyrin hexamers form supramolecular assemblies with the star-shaped polyporphyrins in which the latter are held in the interior of the macrocycle through coordination of the apical pyridine rings with the Zn(II) ions. The suggested structures are supported by ^{1}H NMR spectroscopic and MALDI-TOF mass spectrometric measurements. They agree with the high values of the binding constants of the corresponding supramolecules, which range between $K = 1.1 \times 10^{10}$ and 1.4×10^9 M^{-1}.

Introduction

The study of intermolecular bonding, for which the term *supramolecular chemistry* was coined by Lehn in 1988,[1] has evolved in the past decade to a new, rapidly expanding research field, in which the future development of enzyme-mimetic catalysts,[2] optical switches,[3] molecular photonic wires,[4] light-harvesting arrays,[5] molecular devices,[6] and a wealth of further practical applications is rooted. In a recent paper,[7] we reported the synthesis of a macrocyclic porphyrin hexamer surrounding a cavity with a diameter of about 4.6 nm (Figure 1). As this value closely corresponds to the size of some star-shaped porphyrin trimers[8] and a porphyrin hexamer (niphaphyrin)[9] which have been synthesized also in our laboratory, it became obvious to investigate whether supramolecular assemblies between both kinds of porphyrin arrays could be accessible, in which the star-shaped polyporphyrins would be located inside the cavity of the doughnut-shaped porphyrin hexamer. For this purpose, however, the "guest" molecules had to be modified in order to ensure an intermolecular noncovalent bonding with the macrocyclic hexamer as the "host". Thus, the present work deals with the syntheses of eight new benzene-centered porphyrin trimers (**18**, **19a**−**f**, and **20**) and a porphyrin hexamer (**23**), all of them bearing pyridine rings instead of benzene rings at the apical positions. As, in general, replacement of pyrid-4-yl for phenyl at the apical positions brought about a loss of solubility of the porphyrin trimers, the introduction of alkyl chains instead of phenyl substituents at the vicinal meso C-atoms of the porphine rings proved to be advantageous for the purpose of the work. On the other hand, the syntheses of five macrocyclic porphyrin hexamers

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† Dedicated to Prof. Dr. Richard Neidlein (Pharmazeutisch-Chemisches Institut der Ruprecht-Karls-Universität Heidelberg) on the occasion of his 70th birthday.

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10.1021/jo0015523 CCC: $20.00
Published on Web 06/27/2001

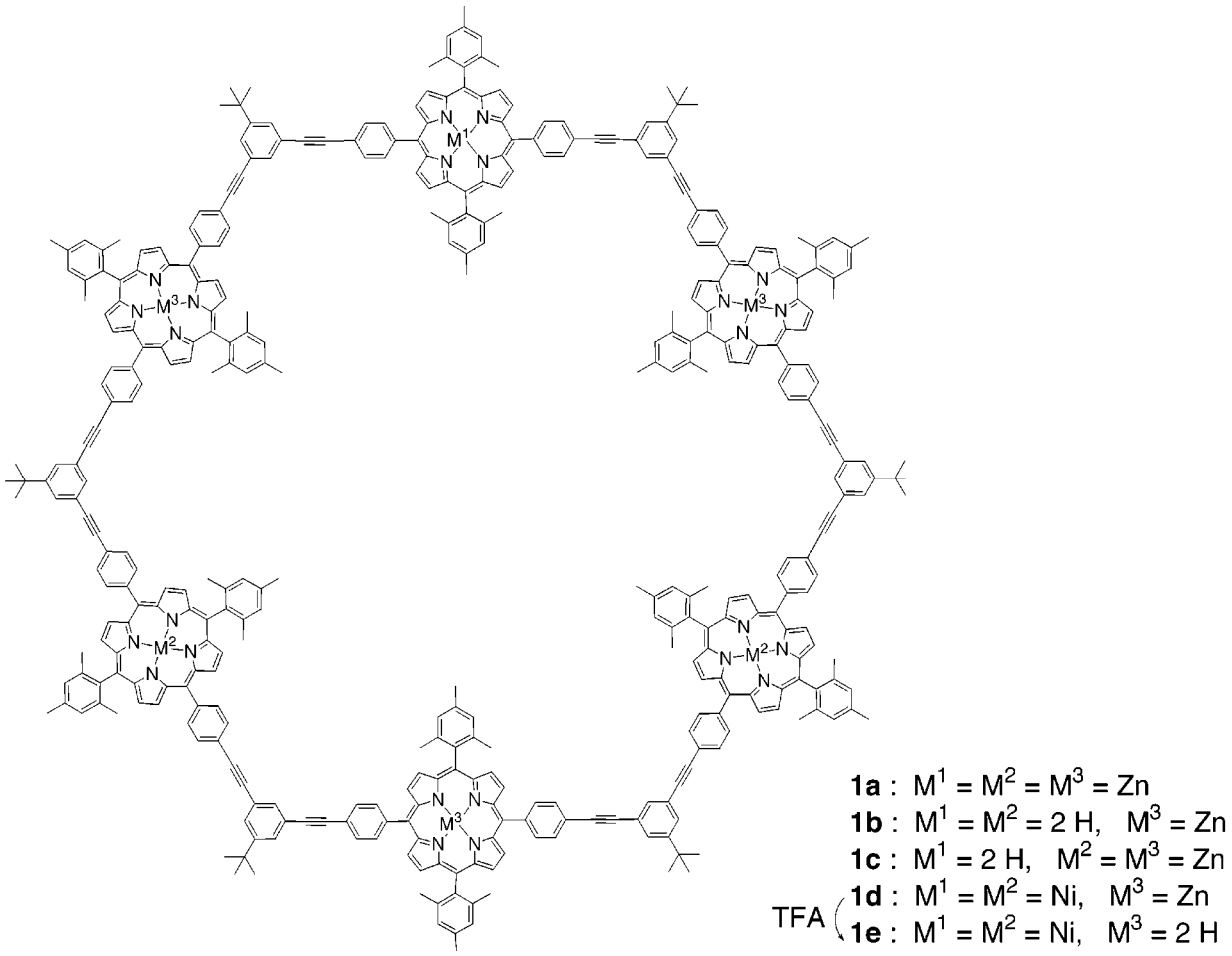

Figure 1. Toroid-like hexaporphyrin array with different metalated states and an internal diameter of the cavity amounting to ca. 4.6 nm.

(**1a**−**e**), similar to those described in a preliminary paper,[7] are described in detail in the Experimental Section. Moreover, the formation of supramolecular complexes of two porphyrin hexamers (**1a** and **1d**) with seven selected porphyrin trimers and the niphaphyrin **23** has been demonstrated by measurement of the corresponding binding constants as well as by ^{1}H NMR and mass spectrometry. A similar, but substantially smaller, supramolecular polyporphyrin array has been synthesized some years ago by Sanders et al.,[10] with a different purpose.

Results

Synthesis of Macrocyclic Porphyrin Hexamers (Scheme 1). Five macrocyclic porphyrin hexamers **(1a**−**e)** have been prepared from two building blocks, namely a diiodoporphyrin derivative (**2a**)[11] (as well as its metal chelates **2b**[8] and **2c**), and the cornerstone molecule **3**, which was obtained in 87% yield by treatment of the corresponding trimethylsilyl derivative with TBAF.[12]

Reaction of **2b** and **2c** with 1 equiv of **3** using palladium(0) as a catalyst gave **4a** and **4c**, respectively. The latter were reacted with trimethylsilylacetylene under palladium(II)-catalyzed conditions to afford **4b** and **4d**, in which two positions (i.e., a protected ethynyl group and a diethyltriazene-substituted phenyl C-atom) may be activated selectively. The used divergent/convergent strategy has been described previously for the synthesis of oligomers of phenylacetylene.[12,13] Thus, the iodo derivatives **5a** and **5c** were readily synthesized from **4b** and **4d** by treatment with methyl iodide, whereas treatment of **4b** with NaOH afforded the deprotected acetylene derivative **6**. Demetalation of **5a** with TFA, on the other hand, led to **5b**. Cross-coupling of **5a**−**c** with **6** in the presence of $Pd(PPh_3)_4$ yielded a set of three porphyrin dimers (**7a**−**c**), which differ only on their metalation state but contain at their ends the same functional groups as porphyrins **4b**,**d**.

The above three-step sequence was then repeated to prepare the porphyrin tetramers **10a**, **10c**, and **10e**, which were transformed by reaction with methyl iodide into **10b**, **10d**, and **10f**, respectively. Thereon, the linear porphyrin hexamers **11a**,**c**,**e**,**g** were obtained by reaction of tetramers **10b**,**d**,**f** with dimers **9a**−**c**. After subsequent activation of both terminal functional groups, the four hexamers were finally cyclized in the presence of pal-

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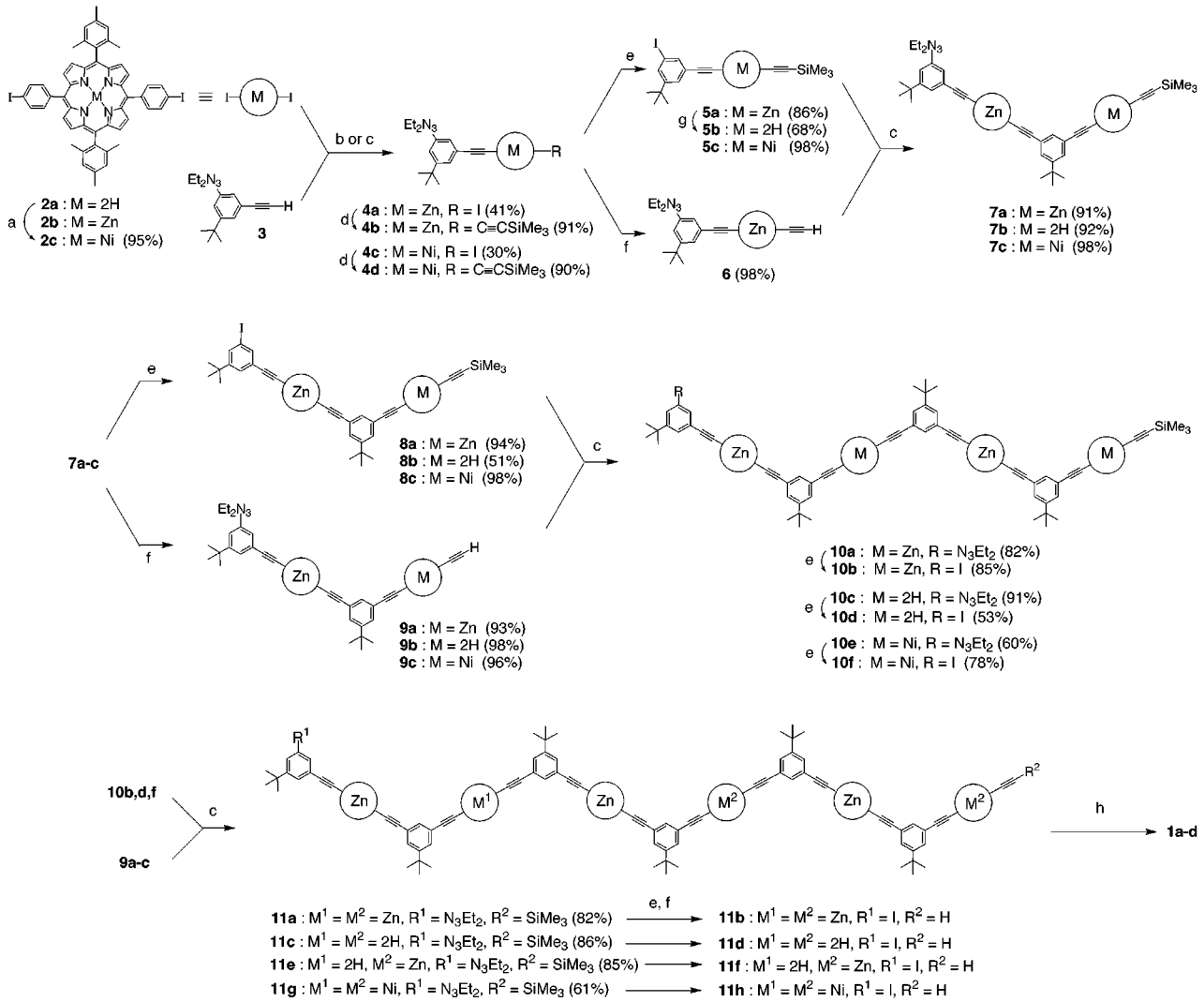
Scheme 1[a]



[a] Reagents and conditions: (a) $Ni(OAc)_2$, $4H_2O$, $CHCl_3$/AcOH, reflux, 48 h; (b) Pd_2dba_3, $AsPh_3$, DMF/Et_3N, 45 °C, 3 h; (c) $Pd(PPh_3)_4$, DMF/Et_3N, 40 °C, 14 h; (d) HC≡$CSiMe_3$, $Pd(PPh_3)_2Cl_2$, CuI, DMF/Et_3N, 35 °C, 14 h; (e) CH_3I, 135 °C, 2 h; (f) 1 M NaOH, THF, 20 °C; (g) TFA, $CHCl_3$, 20 °C; (h) substrate (2.5×10^{-4} M), $Pd(PPh_3)_4$ (1.25×10^{-3} M), DMF/Et_3N, 40 °C, 14 h.

ladium(0) in high-diluted solution, yielding **1a**−**d** (Scheme 1). The step-by-step method developed in this work enables the preparation of cyclic hexamers with different metalation states such as **1c**. Finally, a fifth macrocyclic hexamer (**1e**) was obtained by selective demetalation of **1d** with TFA.

Synthesis of Star-Shaped Porphyrin Trimers. The synthetic route to prepare stellular D_3-symmetric porphyrin trimers **18**−**20** is given in Scheme 2. The porphyrin trimers **19a**−**f** (with a diameter of 4.2 nm) were designed to accommodate the toroid-shaped macrocycles **1a**−**e**, the internal diameter of which amounts to 4.6 nm. The diameter of molecules **18** and **20** is smaller (3.3 nm) and larger (6.9 nm), respectively, than that of trimers **19a**−**f**.

meso-Phenyldipyrrylmethane (**12f**) was prepared according to a described procedure.[11] A series of *meso*-alkyldipyrrylmethanes **12a**−**e**, which were obtained in 32−40% yield as described for the *n*-pentyl homologue[14] by condensation of the corresponding alkyl aldehydes with pyrrole in CH_2Cl_2, using $BF_3{\cdot}OEt_2$ as a catalyst, was synthesized in order to improve the solubility of the star-shaped porphyrin trimers and their supramolecular complexes.

Attempts to prepare 10,20-dialkyl-5-(4-iodophenyl)-15-(pyrid-4-yl)porphines **14a**−**e** failed using procedures described in the literature for the preparation of *meso*-aryl-,[11,15] *meso*-alkyl-,[14] or *meso*-pyridylporphyrins.[16,17] On the contrary, mixed condensation of dipyrrylmethanes **12a**−**e** with 4-iodobenzaldehyde and 4-pyridinecarboxaldehyde in $CHCl_3$/EtOH, in the presence of TFA, followed by oxidation with DDQ, afforded in 10−13% overall yield the expected mixture of three porphyrins, namely 5,15-dialkyl-10,20-bis(4-iodophenyl)porphine (1−3%), 5,15-dialkyl-10,20-bis(pyrid-4-yl)porphine (4−6%), and the desired porphyrin **14** (3−6%), which were easily separated by chromatography. Under the same conditions, porphyrin **13** was obtained in 12% yield using trimeth-

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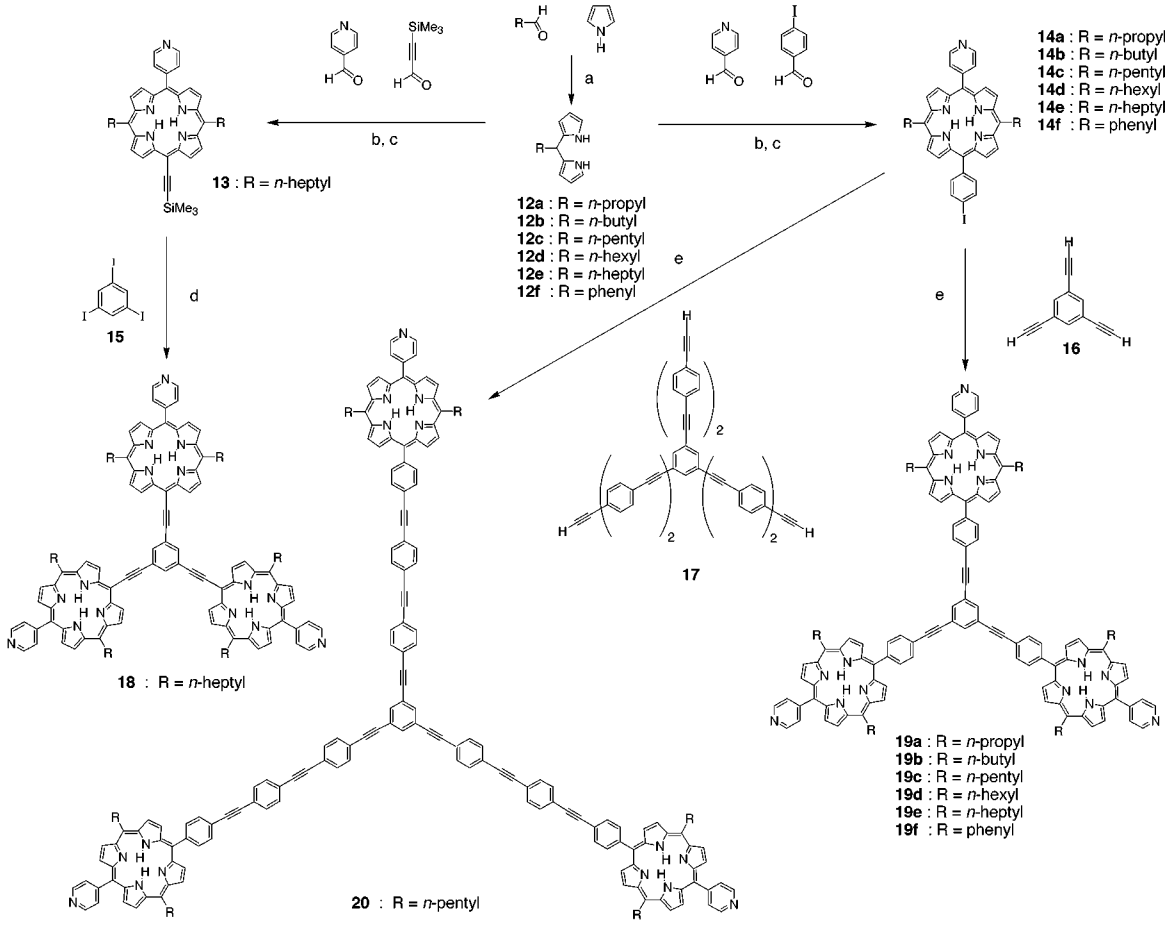
Scheme 2[a]



[a] Reagents and conditions: (a) $BF_3{\cdot}OEt_2$, CH_2Cl_2, 20 °C, 3 h; (b) TFA, $CHCl_3$/EtOH, 20 °C; (c) DDQ, 20 °C, 2 h; (d) $Pd(PPh_3)_4$, K_2CO_3, MeOH, THF/piperidine, 70 °C, 23 h; (e) Pd_2dba_3, $AsPh_3$, DMF/Et_3N, 35 °C.

ylsilylpropynal[18] instead of 4-iodobenzaldehyde. The presence of 5% ethanol in the reaction mixture seems to be critical, as with a lower content the yield of porphyrins decreases, whereas the presence of more than 5% ethanol improves the yield but favors the formation of byproducts as a consequence of scrambling reactions. The same is true for the concentration of TFA. The synthesis of 5,15-diphenylporphyrin **14f**, on the other hand, required more catalyst and a longer reaction time (24 h instead of 3 h) than those of the 5,15-dialkylporphyrins **14a**−**e**.

In a one-pot reaction, porphyrin **13** was deprotected with K_2CO_3 and EtOH, and the liberated alkyne was reacted in situ with triiodobenzene[19] in the presence of $Pd(PPh_3)_4$ (cf. ref 20), leading to the D_3-symmetric porphyrin trimer **18** in 72% yield. Reaction of **14a**−**f** with triethynylbenzene[8,21] in the presence of Pd(0) afforded the corresponding trimers **19a**−**f**. The yields of the reactions were improved using triphenylarsine instead of triphenylphosphine as the ligand for the palladium catalyst. Whereas pentyl-, hexyl-, heptyl-, and phenylporphyrin trimers **19c**−**f** were obtained in fair yields (46−51%), propyl and butyl trimers **19a**,**b** were obtained in only 9−10% yield. This might be due to their lower solubility, since the yield could be improved to 20% using toluene instead of DMF as a solvent.

Synthesis of the Star-Shaped Porphyrin Hexamer (Niphaphyrin) 23. Reaction of [(2,4,6-triethynyl-1,3,5-benzenetriyl)tri-2,1-ethynediyl]tris(trimethylsilane) (**21**)[22] with 5,15-diphenyl-10-(4-iodophenyl)-20-(pyrid-4-yl)-21*H*,23*H*-porphine (**14f**) in the presence of Pd_2dba_3 and triphenylarsine (cf. ref 23) led to the porphyrin trimer **22a**, the trimethylsilyl protecting groups of which were removed to afford **22b**. Coupling of the latter with a large excess of **14f**, using the same catalyst as above, afforded the niphaphyrin hexadentate ligand **23** (Scheme 3).

Binding Properties of the Macrocycles. The formation of supramolecular complexes between host macrocycles **1** and guest trimers **18**−**20** (Figure 2) was first investigated by UV/vis spectroscopy. Measurements at constant host concentration (∼10^{-8} M) were carried out in CH_2Cl_2 solutions at 20 °C. The obtained results show the formation of a 1:1 complex between **1a**,**d** and **18**,**19a**−**f**, the stability constants of which were determined experimentally from the titration curve by a nonlinear, least-squares curve-fitting algorithm[24] (Table 1). For all

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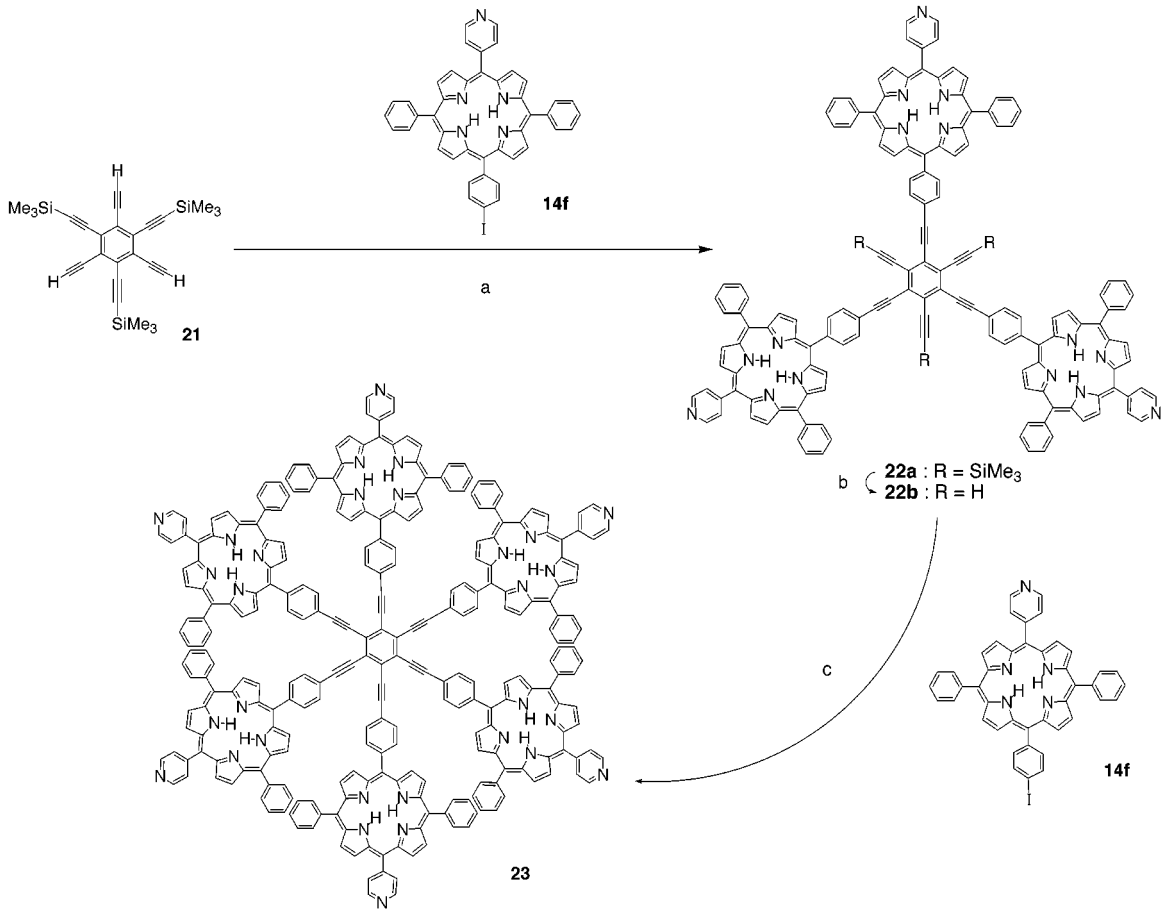
Scheme 3[a]



[a] Reagents and conditions: (a) **1** (1 equiv), **2** (6 equiv), Pd_2dba_3, $AsPh_3$, DMF/Et_3N, 40 °C, 6 h (37%); (b) 1 M NaOH, THF (73%); (c) **3b** (1 equiv), **2** (10 equiv), Pd_2dba_3, $AsPh_3$, DMF/Et_3N, 40 °C, 7 h (14%).

Table 1. Binding Constants (K) in CH_2Cl_2 at 20 °C between Porphyrin Hexamers and Star-Shaped Porphyrin Trimers

entry	host	guest	K (M^{-1})
1	**1a**	**19a**	2.6×10^9
2	**1a**	**19b**	2.0×10^9
3	**1a**	**19c**	4.3×10^9
4	**1a**	**19d**	3.8×10^9
5	**1a**	**19e**	2.2×10^9
6	**1a**	**19f**	5.3×10^9
7	**1d**	**19e**	1.1×10^{10}
8	**1d**	**18**	1.4×10^9
9	**11f**	**19e**	7.1×10^8
10	**1d**	**23**	3.5×10^9

the entries of Table 1, high values of stability constants are in good agreement with an effective three-center chelation. (cf. refs 10b and 25).

However, due to the high dilution used for the measurements, no complexation could be observed with macrocycle **1e** as the host, because chelation of nitrogen-containing ligands with Ni(II) is much less efficient than chelation with zinc.[26] All the binding constants between macrocycle **1a** and **19a**−**f** are in the range 2×10^9−5×10^9 M^{-1} (Table 1, entries 1−6), so that the alkyl or aryl substituents seem to have little influence on the binding properties of the macrocycle. The main significance of the long side chains is to improve the solubility of the complex, which is of major importance for NMR measurements (see below). Indeed, the concentrations required for NMR ($\sim 10^{-4}$ M) are several orders of magnitude higher than those used for the determination of stability constants by UV/vis spectroscopy. Ligand **19e** binds to macrocycle Zn_3Ni_3 (**1d**) about 5 times more strongly than to macrocycle Zn_6 (**1a**) (Table 1, entries 7 and 5). The fact that the binding constant of the same ligand **19e** with the linear hexamer **11f** (entry 9) is still high, although perceptibly lower than the stability constants of the cyclic supramolecules, agrees with a template effect of **19e** on the conformation adopted by **11f**. Such kinds of supramolecular polyporphyrin assemblies belong to the same type of complexes described by Sanders et al.[27] and, more recently, by Lindsey et al.[28] as intermediates of template-directed syntheses of hexameric wheel porphyrins. In our hands, however, attempts to synthesize macrocycles **1a**−**e** in the presence

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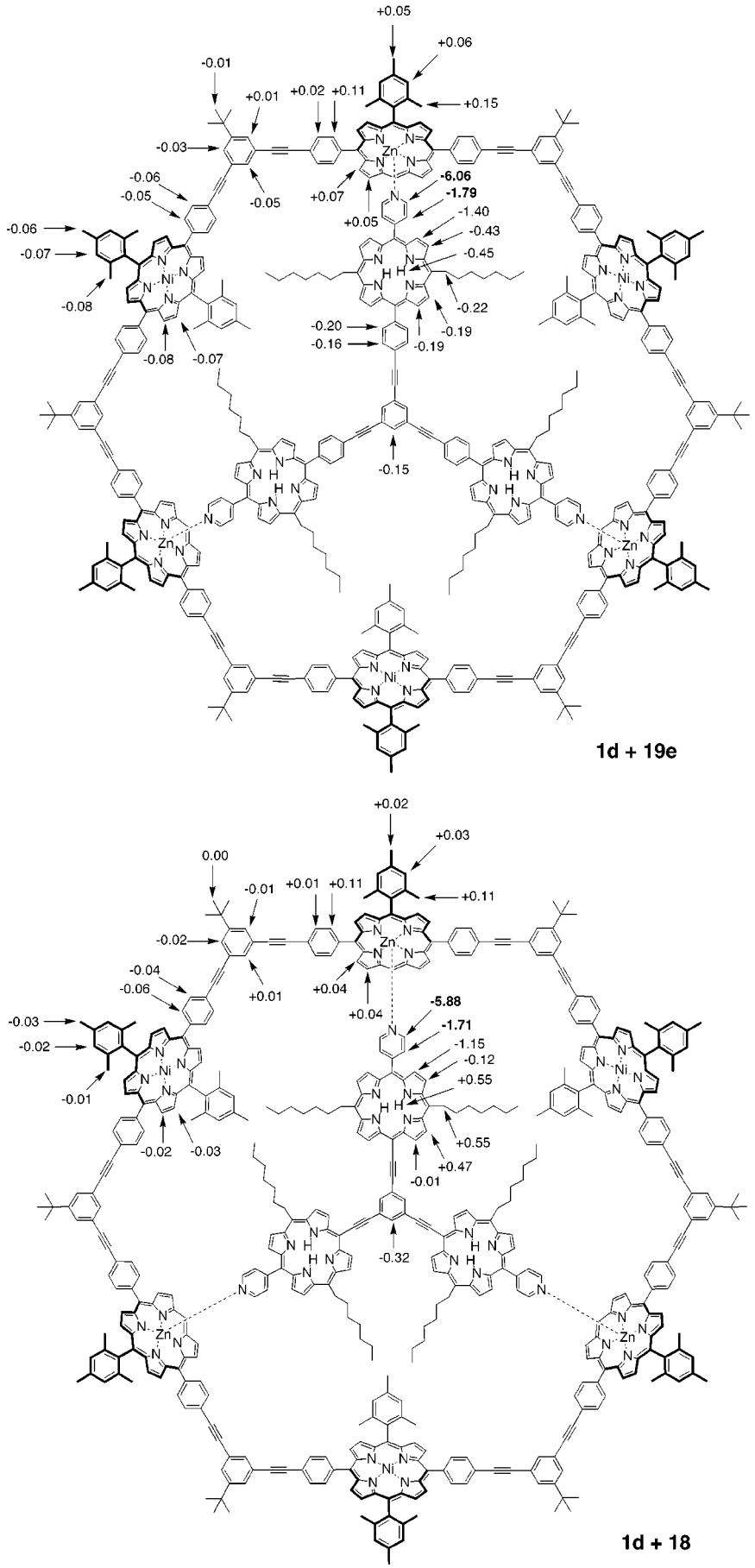

Figure 2. Complexes **1d** + **19e** and **1d** + **18** (mesityl groups at one of the meso positions on the zinc porphyrin rings of the macrocyclic host have been omitted for clarity). Changes in ^{1}H NMR chemical shifts on formation of the complexes are given ($\delta\Delta$ in ppm).

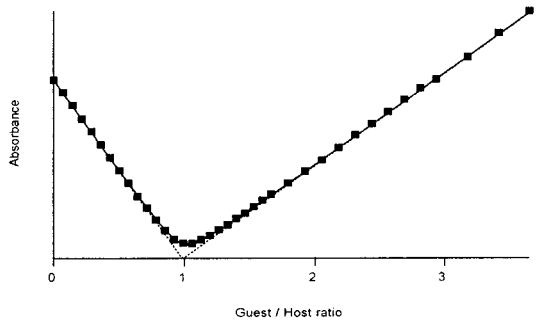

Figure 3. UV/vis binding curve for titration of **1d** with **19e** in CH_2Cl_2 at 20 °C. The plot shows the measured points (■), the calculated best fitting curve (—) for a binding constant of $K = 1.1 \times 10^{10}$ M^{-1}, and the infinite binding limit (- - -).

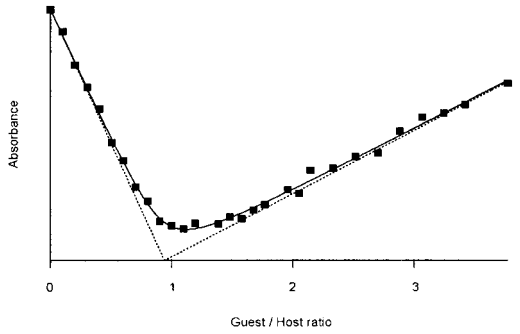

Figure 4. UV/vis binding curve for titration of **1d** with **18** in CH_2Cl_2 at 20 °C. The plot shows the measured points (■), the calculated best fitting curve (—) for a binding constant of $K = 1.4 \times 10^{9}$ M^{-1}, and the infinite binding limit (- - -).

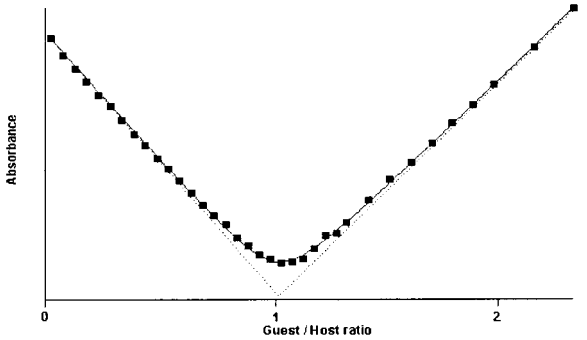

Figure 5. UV/vis binding curve for titration of **1e** with **24** in CH_2Cl_2 at 20 °C. The plot shows the measured points (■), the calculated best fitting curve (—) for a binding constant of $K = 3.5 \times 10^{9}$ M^{-1}, and the infinite binding limit (- - -).

of **19e** as a template led to the formation of a larger porphyrin oligomer (presumably a cyclic dodecamer) instead of the desired macrocyclic hexamer. The investigation of this puzzling result is presently underway.

Finally, the influence of the diameter of the guest on the stability of the supramolecular assemblies was investigated by measuring the constants of association between the macrocyclic hexamer **1d** and three ligands (**18**, **19e**, and **20**) of different sizes. As expected, the highest value of the stability constant was observed with trimer **19e**. A value ca. 10 times lower was measured for the smaller trimer **18**, thus suggesting that some distortion of the host molecule takes place in order to better accommodate the guest (Figures 3−5). With the third trimer **20**, the stoichiometry of the complex is not 1:1, thus confirming that **20** is too large to fit inside the cavity of **1d**.

Spectroscopic Characterization of the Supramolecular Assemblies. As mentioned above, no complexation could be observed with macrocycle **1e** as the host, either by UV/vis spectroscopy or by ^{1}H NMR spectroscopy. On the contrary, the complexation of macrocycle Zn_3Ni_3 (**1d)** with both **18** and **19e** could be investigated by ^{1}H NMR spectroscopy, which confirmed the 1:1 stoichiometry of the supramolecular assemblies. Measurements were performed at 298 K in $CDCl_3$, a solvent in which the complexes exhibited a good solubility. A full assignment of the resonance signals was made with the aid of COSY and NOE experiments, showing that the three pyridine rings of the star-shaped ligand bind to the three zinc ions of the macrocyclic host, whereas the three nickel ions remain uncomplexed.

The changes of the chemical shifts on formation of the complexes are quoted in Figure 2. The protons on the pyridine ring experience a large upfield shift ($\Delta\delta = -6.06$ ppm for the α-pyridine and −1.79 ppm for the β-pyridine protons in complex **1d** + **19e**) due to the ring-current of the porphyrin rings of the guest, which chelate Zn(II) ions. In complex **1d** + **19e**, the upfield shift is observed for all the protons of the guest, the intensity of this effect decreasing with their distance to the zinc ion. In agreement with the lower binding constant of complex **1d** + **18**, the upfield shifts of the protons on the pyridine of the latter are smaller ($\Delta\delta = -5.88$ for the α-pyridine and −1.71 ppm for the β-pyridine protons) and decrease more rapidly with distance than in complex **1d** + **19e**. According to the suggested structures of the supramolecular assemblies, only insignificant changes are observed in the chemical shifts of both the protons at the cornerstones and at the Ni-chelated porphyrin rings of the host, which are not involved in intermolecular bonding.

Strong support for the suggested structures of the above-described supramolecular complexes was obtained by mass spectrometric measurements. The MALDI-TOF spectrum (using dithranol as a matrix) of complex **1d** + **19e** revealed, in addition to the two peaks of the individual guest and host (m/z = 5623 and 2123, respectively), a smaller peak at m/z = 7747 for the supramolecular complex, which confirms its 1:1 stoichiometry. Similar results were obtained with the less strongly bound complex **1d** + **18** (m/z = 7519) (m/z = 5623 and 1896 for **1d** and **18**, respectively) and with the complex between **1a** and niphaphyrin **23** (m/z = 9547.3). All complexes were detected in positive mode as molecular ions. Recently, it has been shown that MALDI-MS is a suitable tool to study specific pseudorotaxane-like complexes where ionic hydrogen bonds form the dominant noncovalent interactions.[29] These findings are extended in the present work to complexes formed by multiple electrostatic donor/acceptor interactions. The use of the newly developed aprotic ET-matrix DCTB[30] was especially promising. For the complex **1a** + **23**, the result was an increase of almost 1 order of magnitude in signal intensity of the peak at m/z = 9547.3 compared to the result obtained in the protic dithranol matrix

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Experimental Section

General Methods. All air- or water-sensitive reactions were carried out under argon. Solvents were generally dried and distilled prior to use. Reactions were monitored by thin-layer chromatography (TLC) on Merck silica gel 60 F_{254} (0.2 mm) precoated aluminum foil. Flash chromatography (FC): Merck silica gel 60 (0.040−0.063 mm, 230−400 mesh), except otherwise noted. Melting points (mp) were determined with a hot stage apparatus (Thermovar, C. Reichert AG, Vienna) equipped with a digital thermometer. UV/vis spectra were recorded on a Hewlett-Packard 8452A diode-array or a Perkin-Elmer Lambda 40 spectrometer; λ_{max} (log ϵ) in nm. NMR: Varian Gemini 200 (^{1}H, 200.00 MHz; ^{13}C: 50.30 MHz), Bruker AM 360 (^{1}H, 360.14 MHz), or Bruker Avance DRX 500 (^{1}H: 500.13 MHz, ^{13}C: 125.76 MHz), in $CDCl_3$ solutions unless otherwise stated; ^{1}H and ^{13}C chemical shifts (δ) are given in ppm relative to Me_4Si as internal standard, J values in Hz. Mass spectra: Vacuum Generators Micromass 7070E instrument equipped with a data system DS 11−250, EI (electron ionization): acceleration voltage 70 eV, FAB (fast atom bombardment): in 3-nitrobenzyl alcohol with Ar at 8 kV; ES^+-MS (electrospray ionization, positive mode) and MALDI-MS-(Matrix Assisted Laser Desorption Ionization): FT mass spectrometer Bruker 4.7T BioAPEX II; MALDI-TOF: Bruker Reflex-II (delayed extraction, 20 kV acc. voltage, positive reflection mode) using dithranol (1,8,9-anthracenetriol) or DCTB (2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enyliden-e]malonitrile)[31] dissolved in $CHCl_3$ (0.05 M) as matrix (dried droplet method) and averaging 200−1100 shots. Tetrakis-(triphenylphosphine)palladium, tris(dibenzylideneacetone)di-palladium (Pd_2dba_3), triphenylarsine, and tetrabutylammonium fluoride (TBAF) were purchased from Aldrich Chemie (CH-9471 Buchs); dimethylformamide (DMF), trifluoroacetic acid (TFA), tetrahydrofuran (THF), trimethylsilylacetylene (TMSA), and other reagents from Fluka Chemie AG (CH-9471 Buchs). Porphyrins **2a**[13] and **2b**[9] were prepared according to described procedures.

Macrocyclic Porphyrin Hexamer 1a. Air was removed from a solution of **11b** (6.2 mg, 1.07 μmol) in 4.28 mL of DMF/Et_3N (5:1) by passing argon through it for 30 min. $Pd(PPh_3)_4$ (6.2 mg, 5.36 μmol) was added, deaeration was continued for 10 min, and then the mixture was heated at 40 °C for 6 h. The solvent was subsequently removed under reduced pressure, and the crude product was purified by 2-fold FC ($CHCl_3$/hexane, gradient from 60:40 to 80:20) and finally by MPLC using a Lobar column (Lichroprep Si60, 40−63 μm, Merck), provided 1.80 mg (30%) of **1a**: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 1.49 (s, 54H), 1.84 (s, 72H), 2.64 (s, 36H), 7.29 (s, 24H), 7.75 (d, J = 1.4, 12H), 7.86 (t, J = 1.4, 6H), 7.97 and 8.27 (AA′XX′, J_{AX} = 8.3, 48H), 8.81 and 8.92 (2 × d, J = 4.6, 48H); UV/vis (CH_2Cl_2) 292, 425, 550, 590; UV/vis (benzene) 289, 427, 551, 592; MALDI-MS (dithranol) m/z 5644.1 ([M + H]$^+$) (calcd average mass for $C_{384}H_{300}N_{24}Zn_6$ 5643.03); ES^+-MS ($CHCl_3$/MeOH/HCOOH) m/z 1755.2 ([M − 6Zn + 15H]$^{3+}$), 1316.6 ([M − 6Zn + 16H]$^{4+}$), 1053.5 ([M − 6Zn + 17H]$^{5+}$), 878.1 ([M − 6Zn + 18H]$^{6+}$).

Macrocyclic Porphyrin Hexamer 1b. Reaction of **11d** (6.3 mg, 1.13 μmol), as described for **1a**, afforded 0.95 mg (15%) of **1b**: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ −2.61 (s, 6H), 1.49 (s, 54H), 1.84 and 1.85 (2 × s, 72H), 2.63 (s, 36H), 7.29 (s, 24H), 7.75 (d, J = 1.4, 12H), 7.86 (t, J = 1.4, 6H), 7.97 and 8.25 (AA′XX′, J_{AX} = 8.1, 24H), 7.97 and 8.27 (AA′XX′, J_{AX} = 8.1, 24H), 8.73 and 8.84 (2 × d, J = 4.4, 24H), 8.81 and 8.92 (2 × d, J = 4.8, 24H); UV/vis (CH_2Cl_2) 292, 423, 516, 550, 592, 648; UV/vis (benzene) 289, 425, 516, 551, 593, 650; MALDI-MS (dithranol) m/z 5453.9 ([M + H]$^+$) (calcd average mass for $C_{384}H_{306}N_{24}Zn_3$ 5452.94); ES^+-MS (THF) m/z 2727.4 [M + 2H]$^{2+}$, 1818.6 [M + 3H]$^{3+}$.

Macrocyclic Porphyrin Hexamer 1c. Reaction of **11f** (5.0 mg, 0.876 μmol), as described for **1a**, afforded 0.39 mg (8%) of pure **1c**: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ −2.61 (s, 2H), 1.49 (s, 54H), 1.84 and 1.85 (2 × s, 72H), 2.64 (s, 36H), 7.29 (s, 24H), 7.75 (d, J = 1.4, 12H), 7.86 (t, J = 1.4, 6H), 7.97 and 8.25 (AA′XX′, J_{AX} = 8.1, 8H), 7.97 and 8.27 (AA′XX′, J_{AX} = 8.1, 40H), 8.73 and 8.83 (2 × d, J = 4.4, 8H), 8.81 and 8.93 (2 × d, J = 4.8, 40H); UV/vis (CH_2Cl_2) 292, 424, 515, 550, 590, 647; UV/vis (benzene) 289, 427, 516, 551, 592, 648; MALDI-MS (dithranol) m/z 5580.7 ([M + H]$^+$) (calcd average mass for $C_{384}H_{302}N_{24}Zn_5$ 5579.67).

Macrocyclic porphyrin hexamer 1d was obtained from **11h** (5.0 mg, 0.869 μmol), as described for **1a**. In different batches the yield oscillated between 0.73 and 1.51 mg (15−31%): ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 1.48 (s, 54H), 1.82 (s, 36H), 1.84 (s, 36H), 2.58 (s, 18H), 2.63 (s, 18H), 7.22 (s, 12H), 7.29 (s, 12H), 7.72 (t, J = 1.5, 6H), 7.74 (t, J = 1.5, 6H), 7.82 (t, J = 1.4, 6H), 7.90 and 8.07 (AA′XX′, J_{AX} = 8.2, 24H), 7.96 and 8.26 (AA′XX′, J_{AX} = 8.2, 24H), 8.63 and 8.74 (2 × d, J = 4.8, 24H), 8.81 and 8.91 (2 × d, J = 4.8, 24H); UV/vis (CH_2Cl_2) 290, 423, 533, 548, 590; MALDI-MS (dithranol) m/z 5623.3 ([M + H]$^+$) (calcd average mass for $C_{384}H_{300}N_{24}Ni_3Zn_3$ 5622.99); ES^+-MS (THF/HCOOH) m/z 1359.1 [M − 3Zn + 10H]$^{4+}$, 1087.5 [M − 3Zn + 11H]$^{5+}$.

Macrocyclic Porphyrin Hexamer 1e. To a solution of **1d** (1.14 mg, 0.203 μmol) in $CHCl_3$ (2 mL) was added TFA (200 μL), and the mixture was stirred at 20 °C for 2 h. The mixture was diluted with $CHCl_3$ (10 mL), and then saturated aqueous $NaHCO_3$ was added. The organic layer was separated, washed with water, and dried ($MgSO_4$) before the solvent was evaporated. The residue was purified by FC ($CHCl_3$/hexane 60:40) to yield 0.84 mg (76%) of **1e**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ −2.61 (s, 6H), 1.48 (s, 54H), 1.82 (s, 36H), 1.85 (s, 36H), 2.58 (s, 18H), 2.63 (s, 18H), 7.22 (s, 12H), 7.29 (s, 12H), 7.73 (2 × t, J = 1.5, 12H), 7.82 (t, J = 1.5, 6H), 7.90 and 8.07 (AA′XX′, J_{AX} = 8.2, 24H), 7.96 and 8.24 (AA′XX′, J_{AX} = 8.2, 24H), 8.63 and 8.74 (2 × d, J = 4.8, 24H), 8.72 and 8.83 (2 × d, J = 4.8, 24H); UV/vis (CH_2Cl_2) 289, 421, 521, 550, 591, 647; MALDI-MS (dithranol) m/z 5433.3 ([M + H]$^+$) (calcd average mass for $C_{384}H_{306}N_{24}Ni_3$ 5432.90).

[5,15-Bis(4-iodophenyl)-10,20-bis(mesityl)porphinato-(2−)]nickel (2c). To a solution of 5,15-bis(4-iodophenyl)-10,-20-bis(mesityl)porphine (**2a**)[11] (620 mg, 0.652 mmol) in 62 mL of $CHCl_3$/AcOH (9:1) was added nickel acetate tetrahydrate (2.92 g, 11.7 mmol), and the mixture was refluxed for 48 h. Thereafter, $CHCl_3$ (200 mL) and water (200 mL) were added. The organic layer was separated, washed with water, and dried ($MgSO_4$). The residue obtained after removal of the solvent was purified by FC ($CHCl_3$/hexane 35:65) to yield 624 mg (95%) of **2c**: ^{1}H NMR (360.14 MHz) δ 1.79 (s, 12H), 2.58 (s, 6H), 7.21 (s, 4H), 7.77 and 8.01 (AA′XX′, J_{AX} = 8.1, 8H), 8.60 (d, J = 4.8, 4H), 8.67 (d, J = 4.8, 4H); UV/vis (CH_2Cl_2) 295 (3.78), 414 (5.36), 528 (4.19); ES^+-MS (THF/MeOH) m/z 1007.64 (M$^+$) Anal. Calcd for $C_{50}H_{38}I_2N_4Ni$ (1007.39): C, 59.61; H, 3.80; N, 5.56. Found: C, 59.40; H, 3.96; N, 5.64.

1-[3-(1,1-Dimethylethyl)-5-ethynylphenyl]-3,3-diethyl-1-triazene (3). To a solution of 1-[3-(1,1-dimethylethyl)-5-[(trimethylsilyl)ethynyl]phenyl]-3,3-diethyl-1-triazene[12] (111.6 mg, 0.339 mmol) in 11 mL of THF was added TBAF (1M in THF, 0.35 mL, 0.35 mmol), and the mixture was stirred for 10 min at 20 °C. A few grains of $CaCl_2$ were added to remove any excess of fluoride, and the solvent was evaporated. The crude product was purified by FC (CH_2Cl_2/hexane 1:4) to yield 75.9 mg (87%) of **3** as a white solid: mp 45−46 °C; ^{1}H NMR (360.14 MHz, $CDCl_3$) δ 1.27 (br s, 6H), 1.33 (s, 9H), 3.02 (s, 1H), 3.76 (q, J = 7.0, 4H), 7.29 (t, J = 1.8, 1H), 7.39 (t, J = 1.8, 1H), 7.42 (t, J = 1.8, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 12.7, 12.8, 31.2, 34.7, 44.0, 75.8, 84.6, 119.5, 120.45, 121.8, 125.9, 151.0, 151.9; EI-MS m/z 257 (M$^+$). Anal. Calcd for $C_{16}H_{23}N_3$ (257.38): C, 74.67; H, 9.01; N, 16.33. Found: C, 74.97; H, 9.28; N, 16.01.

[5-[4-[[3-(3,3-Diethyl-1-triazenyl)-5-(1,1-dimethylethyl)-phenyl]ethynyl]phenyl]-15-(4-iodophenyl)-10,20-bis(2,4,6-trimethylphenyl)porphinato(2−)]zinc (4a). Air was removed from a solution of **2b**[8] (1.70 g, 1.68 mmol) and **3** (0.432 g, 1.68 mmol) in 378 mL of DMF/Et_3N (5:1) by blowing argon for 30 min. Then, $Pd(PPh_3)_4$ (193.7 mg, 0.168 mmol) was added, and deaeration was continued for 10 min. Thereafter, the

(31) Yellow crystals of DCTB (mp 124 °C) were a gift from H. Luftmann (cf. ref 30).

mixture was heated at 40 °C for 14 h. The solvent was removed under reduced pressure, and the crude product was purified by FC. Three fractions were obtained: unreacted **2b** (0.370 g; 22%), **4a** (0.796 g; 41%), and 5,15-bis[4-[[3-(3,3-diethyl-1-triazenyl)-5-(1,1-dimethylethyl)phenyl]ethynyl]phenyl]-10,20-bis(mesityl)porphinato(2−)]zinc (0.640 g; 30%), which were successively eluted using $CHCl_3$/hexane/Et_3N (gradient from 50:50:0.2 to 65:35:0.2). **4a**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ 1.32 (t, J = 7.3, 6H), 1.42 (s, 9H), 1.82 (s, 12H), 2.63 (s, 6H), 3.82 (q, J = 7.3, 4H), 7.29 (s, 4H), 7.49 (d, J = 1.8, 2H), 7.58 (t, J = 1.8, 1H), 7.93 and 8.07 (AA′XX′, J_{AX} = 8.2, 4H), 7.97 and 8.22 (AA′XX′, J_{AX} = 8.6, 4H), 8.79 and 8.86 (2 × d, J = 4.9, 4H), 8.79 and 8.90 (2 × d, J = 4.9, 4H); UV/vis (CH_2Cl_2) 296 (4.71), 422 (5.75), 550 (4.38), 584 (3.67), 592 (3.66); FAB-MS m/z 1143.1. Anal. Calcd for $C_{66}H_{60}IN_7Zn$ (1143.53): C, 69.32; H, 5.29; N, 8.57. Found: C, 69.54; H, 5.48; N, 8.44.

[5-[4-[[3-(3,3-Diethyl-1-triazenyl)-5-(1,1-dimethylethyl)-phenyl]ethynyl]phenyl]-10,20-bis(2,4,6-trimethylphenyl)-15-[4-[(trimethylsilyl)ethynyl]phenyl]porphinato-(2−)]zinc (4b). Air was removed from a solution of **4a** (0.796 g, 0.696 mmol) in 144 mL of DMF/Et_3N (5:1) by blowing argon for 20 min. Then, $Pd(PPh_3)_2Cl_2$ (48.9 mg, 69.6 μmol), CuI (26.5 mg, 139.2 μmol), and trimethylsilylacetylene (289 μL, 2.09 mmol) were added. Thereafter, the mixture was heated at 35 °C for 14 h. The solvent was removed under reduced pressure, and the crude product was purified by FC ($CHCl_3$/hexane/Et_3N 50:50:0.2 then 65:35:0.2) to yield 0.708 g (91%) of **4b**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ 0.37 (s, 9H), 1.32 (t, J = 7.3, 6H), 1.42 (s, 9H), 1.82 (s, 12H), 2.63 (s, 6H), 3.83 (q, J = 7.3, 4H), 7.28 (s, 4H), 7.49 (d, J = 1.6, 2H), 7.58 (t, J = 1.6, 1H), 7.85 and 8.18 (AA′XX′, J_{AX} = 7.6, 4H), 7.93 and 8.22 (AA′XX′, J_{AX} = 7.6, 4H), 8.78 and 8.85 (2 × d, J = 4.7, 4H), 8.78 and 8.90 (2 × d, J = 4.7, 4H); UV/vis (CH_2Cl_2) 298 (4.57), 422 (5.64), 550 (4.29), 584 (3.72); FAB-MS m/z 1114.5. Anal. Calcd for $C_{71}H_{69}N_7SiZn$ (1113.84): C, 76.56; H, 6.24; N, 8.80. Found: C, 75.97; H, 6.39; N, 8.96.

[5-[4-[[3-(3,3-Diethyl-1-triazenyl)-5-(1,1-dimethylethyl)-phenyl]ethynyl]phenyl]-15-(4-iodophenyl)-10,20-bis(2,4,6-trimethylphenyl)porphinato(2−)]nickel (4c). Reaction of **2c** (575 mg, 0.571 mmol) with **3** (146.9 mg, 0.571 mmol) in the presence of $Pd(PPh_3)_4$ (65.9 mg, 57.1 μmol) in 132 mL of DMF/Et_3N, as described for **4a**, with subsequent purification by FC, afforded three fractions: unreacted **2c** (278 mg; 48%), **4c** (196 mg; 30%), and 5,15-bis-[4-[[3-(3,3-diethyl-1-triazenyl)-5-(1,1-dimethylethyl)phenyl]ethynyl]phenyl]-10,20-bis(mesityl)-porphinato(2−)]nickel (110 mg; 15%), which were successively eluted using $CHCl_3$/hexane/Et_3N (gradient from 35:65:0.2 to 50:50:0.2). **4c**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ 1.31 (t, J = 7.3, 6H), 1.40 (s, 9H), 1.80 (s, 12H), 2.57 (s, 6H), 3.81 (q, J = 7.3, 4H), 7.21 (s, 4H), 7.46 (t, J = 1.7, 1H), 7.48 (t, J = 1.7, 1H), 7.55 (t, J = 1.7, 1H), 7.78 and 8.01 (AA′XX′, J_{AX} = 8.2, 4H), 7.85 and 8.02 (AA′XX′, J_{AX} = 8.2, 4H), 8.60 and 8.67 (2 × d, J = 4.8, 4H), 8.60 and 8.71 (2 × d, J = 4.8, 4H); UV/vis (CH_2Cl_2) 292 (4.66), 415 (5.38), 527 (4.25); ES$^+$-MS (THF/HCOOH) m/z 1137.62 ([M + H]$^+$), 1037.6 ([M − N_3Et_2 + H]$^+$). Anal. Calcd for $C_{66}H_{60}IN_7Ni$ (1136.85).: C, 69.73; H, 5.32; N, 8.62. Found: C, 69.56; H, 5.55; N, 8.72.

[5-[4-[[3-(3,3-Diethyl-1-triazenyl)-5-(1,1-dimethylethyl)-phenyl]ethynyl]phenyl]-10,20-bis(2,4,6-trimethylphenyl)-15-[4-[(trimethylsilyl)ethynyl]phenyl]porphinato(2−)]-nickel (4d). Reaction of **4c** (234 mg, 0.206 mmol) with TMSA (86.6 μL, 0.625 mmol) in the presence of $Pd(PPh_3)_4$ (14.6 mg, 20.9 μmol) and CuI (7.9 mg, 41.7 μmol) in 42 mL of DMF/Et_3N, as described for **4b**, with subsequent purification by FC ($CHCl_3$/hexane/Et_3N 50:50:0.2 then 65:35:0.2), afforded 205 mg (90%) of **4d**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ 0.35 (s, 9H), 1.31 (t, J = 7.3, 6H), 1.40 (s, 9H), 1.80 (s, 12H), 2.57 (s, 6H), 3.81 (q, J = 7.3, 4H), 7.21 (s, 4H), 7.46 (t, J = 1.7, 1H), 7.48 (t, J = 1.7, 1H), 7.55 (t, J = 1.7, 1H), 7.78 and 7.98 (AA′XX′, J_{AX} = 8.5, 4H), 7.85 and 8.02 (AA′XX′, J_{AX} = 8.5, 4H), 8.60 and 8.66 (2 × d, J = 4.9, 4H), 8.60 and 8.71 (2 × d, J = 4.9, 4H); UV/vis (CH_2Cl_2) 292 (4.68), 416 (5.38), 528 (4.27); ES$^+$-MS (THF/HCOOH) m/z 1108.0 ([M + H]$^+$), 1007.9 ([M − N_3Et_2 + H]$^+$). Anal. Calcd for $C_{71}H_{69}N_7NiSi$ (1107.16): C, 77.02; H, 6.28; N, 8.86. Found: C, 76.95; H, 6.03; N, 8.93.

[5-[4-[[3-(1,1-Dimethylethyl)-5-iodophenyl]ethynyl]-phenyl]-10,20-bis(2,4,6-trimethylphenyl)-15-[4-[(trimethylsilyl)ethynyl]phenyl]-21*H*,23*H*-porphinato(2−)]zinc (5a). To a thick-walled screw cap tube was added a solution of **4b** (210 mg, 0.188 mmol) in iodomethane (21 mL). The tube was flushed with argon and then screwed and heated to 135 °C for 2 h. The reaction mixture was cooled to room temperature, and the solvent was removed under reduced pressure. The crude product was purified by FC ($CHCl_3$/hexane/Et_3N 50:50:0.1) to yield 211 mg (98%) of **5a**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ 0.38 (s, 9H), 1.38 (s, 9H), 1.83 (s, 12H), 2.63 (s, 6H), 7.28 (s, 4H), 7.65 (t, J = 1.5, 1H), 7.74 (t, J = 1.5, 1H), 7.85 (t, J = 1.5, 1H), 7.86 and 8.18 (AA′XX′, J_{AX} = 7.9, 4H), 7.91 and 8.23 (AA′XX′, J_{AX} = 7.9, 4H), 8.78 and 8.85 (2 × d, J = 4.6, 4H), 8.78 and 8.89 (2 × d, J = 4.6, 4H); UV/vis (CH_2Cl_2) 292 (4.34), 422 (5.52), 550 (4.17), 590 (3.52); FAB-MS m/z 1141.1. Anal. Calcd for $C_{67}H_{59}IN_4SiZn$ (1140.60): C, 70.55; H, 5.21; N, 4.91. Found: C, 70.96; H, 5.12; N, 5.06.

5-[4-[[3-(1,1-Dimethylethyl)-5-iodophenyl]ethynyl]-phenyl]-10,20-bis(2,4,6-trimethylphenyl)-15-[4-[(trimethylsilyl)ethynyl]phenyl]-21*H*,23*H*-porphine (5b). To a solution of **5a** (212 mg, 0.186 mmol) in $CHCl_3$ (66 mL) was added TFA (6.6 mL), and the mixture was stirred at 20 °C for 2 h. The mixture was diluted with $CHCl_3$ (80 mL), and then saturated aqueous $NaHCO_3$ was added. The organic layer was separated, washed with water, and dried ($MgSO_4$) before the solvent was evaporated. The residue was purified by FC ($CHCl_3$/hexane 50:50) to yield 137 mg (68%) of **5b**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ −2.64 (s, 2H), 0.37 (s, 9H), 1.38 (s, 9H), 1.83 (s, 12H), 2.63 (s, 6H), 7.28 (s, 4H), 7.65 (t, J = 1.7, 1H), 7.74 (t, J = 1.7, 1H), 7.85 (t, J = 1.7, 1H), 7.86 and 8.16 (AA′XX′, J_{AX} = 8.4, 4H), 7.91 and 8.21 (AA′XX′, J_{AX} = 8.4, 4H), 8.70 and 8.75 (2 × d, J = 4.8, 4H), 8.71 and 8.80 (2 × d, J = 4.8, 4H); UV/vis (CH_2Cl_2) 288 (4.54), 420 (5.64), 516 (4.29), 550 (4.03), 590 (3.86), 646 (3.72); ES$^+$-MS ($CHCl_3$/MeOH) m/z 1078.1 ([M + H]$^+$).

[5-[4-[[3-(1,1-Dimethylethyl)-5-iodophenyl]ethynyl]-phenyl]-10,20-bis(2,4,6-trimethylphenyl)-15-[4-[(trimethylsilyl)ethynyl]phenyl]-21*H*,23*H*-porphinato(2−)]nickel (5c). Reaction of **4d** (205 mg, 0.185 mmol) in CH_3I (20.5 mL), as described for **5a**, with subsequent purification by FC ($CHCl_3$/hexane/Et_3N 40:60:0.1), afforded 206 mg (98%) of **5c**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ 0.35 (s, 9H), 1.36 (s, 9H), 1.80 (s, 12H), 2.57 (s, 6H), 7.21 (s, 4H), 7.62 (t, J = 1.5, 1H), 7.73 (t, J = 1.5, 1H), 7.78 and 7.98 (AA′XX′, J_{AX} = 8.5, 4H), 7.83 (t, J = 1.5, 1H), 7.84 and 8.04 (AA′XX′, J_{AX} = 8.5, 4H), 8.60 and 8.66 (2 × d, J = 4.9, 4H), 8.60 and 8.70 (2 × d, J = 4.9, 4H); UV/vis (CH_2Cl_2) 289 (4.55), 416 (5.37), 528 (4.26); ES$^+$-MS (THF/HCOOH) m/z 1133.9 (M$^+$). Anal. Calcd for $C_{67}H_{59}IN_4NiSi$ (1133.92): C, 70.97; H, 5.24; N, 4.94. Found: C, 71.24; H, 4.97; N, 4.87.

[5-[4-[[3-(3,3-Diethyl-1-triazenyl)-5-(1,1-dimethylethyl)-phenyl]ethynyl]phe nyl]-15-(4-ethynylphenyl)-10,20-bis-(2,4,6-trimethylphenyl)-21*H*,23*H*-porphinato(2−)]zinc (6). To a solution of **4b** (270 mg, 0.242 mmol) in THF (40 mL) was added aqueous NaOH (1 M, 22.5 mL), and the mixture was stirred vigorously at 20 °C for 3 h. After evaporation of the THF, CH_2Cl_2 (60 mL) and water (60 mL) were added. The organic layer was separated, washed with water, and dried ($MgSO_4$). The residue obtained after removal of the solvent was purified by FC ($CHCl_3$/hexane/Et_3N 55:45:0.2) to yield 248 mg (98%) of **6**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ 1.32 (t, J = 7.0, 6H), 1.42 (s, 9H), 1.82 (s, 12H), 2.63 (s, 6H), 3.30 (s, 1H), 3.83 (q, J = 7.0, 4H), 7.28 (s, 4H), 7.49 (d J = 1.5, 2H), 7.58 (t, J = 1.5, 1H), 7.87 and 8.20 (AA′XX′, J_{AX} = 7.6, 4H), 7.93 and 8.22 (AA′XX′, J_{AX} = 7.9, 4H), 8.78 and 8.85 (2 × d, J = 4.6, 4H), 8.78 and 8.90 (2 × d, J = 4.6, 4H); UV/vis (CH_2Cl_2) 296 (4.66), 422 (5.70), 550 (4.33), 590 (3.67); FAB-MS m/z 1042.9. Anal. Calcd for $C_{68}H_{61}N_7Zn$ (1041.66): C, 78.40; H, 5.90; N, 9.41. Found: C, 78.22; H, 6.12; N, 9.36.

[μ-[5-[4-[[3-[[4-[10,20-Bis(2,4,6-trimethylphenyl)-15-[4-[(trimethylsilyl)ethynyl]phenyl]-21*H*,23*H*-porphin-5-yl-*N*^{21},*N*^{22},*N*^{23},*N*^{24}]phenyl]ethynyl]-5-(1,1-dimethylethyl)-phenyl]ethynyl]phenyl]-15-[4-[[3-(3,3-diethyl-1-triazenyl)-5-(1,1-dimethylethyl)phenyl]ethynyl]phenyl]-10,20-bis-

(2,4,6-trimethylphenyl)-21*H*,23*H*-porphinato (4-)-*N*^{21},*N*^{22},*N*^{23},*N*^{24}]]dizinc (7a). Air was removed from a solution of **5a** (0.357 g, 0.313 mmol) and **6** (0.335 g, 0.322 mmol) in 144 mL of DMF/Et_3N (5:1) by passing argon through it for 30 min. $Pd(PPh_3)_4$ (54.3 mg, 0.047 mmol) was added, deaeration was continued for 10 min, and then the mixture was heated at 40 °C for 14 h. The solvent was subsequently removed under reduced pressure, and the crude product was purified by FC ($CHCl_3$/hexane/Et_3N 60:40:0.2) to yield 0.588 g (91%) of **7a**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ 0.38 (s, 9H), 1.32 (t, J = 7.1, 6H), 1.42 (s, 9H), 1.49 (s, 9H), 1.84 (s, 24H), 2.64 (s, 12H), 3.82 (q, J = 7.1, 4H), 7.29 (s, 8H), 7.49 (d J = 1.5, 2H), 7.59 (t, J = 1.5, 1H), 7.75 (d, J = 1.5, 2H), 7.84 (t, J = 1.5, 1H), 7.86 and 8.19 (AA′XX′, J_{AX} = 8.4, 4H), 7.93 and 8.23 (AA′XX′, J_{AX} = 8.2, 4H), 7.98 and 8.26 (AA′XX′, J_{AX} = 8.2, 4H), 7.98 and 8.27 (AA′XX′, J_{AX} = 8.2, 4H), 8.79 and 8.85 (2 × d, J = 4.6, 4H), 8.80 and 8.91 (2 × d, J = 4.6, 4H), 8.81 (2 × d, J = 4.6, 2 × 2H), 8.92 (2 × d, J = 4.6, 2 × 2H); UV/vis (CH_2Cl_2) 294 (5.00), 422 (5.93), 512 (4.06), 550 (4.67), 590 (4.13); ES$^+$-MS ($CHCl_3$/MeOH) m/z 1027.2 (M^{2+}) (calcd average mass for $C_{135}H_{119}N_{11}SiZn_2$ 2054.34).

[5-[4-[[3-[[4-[10,20-Bis(2,4,6-trimethylphenyl)-15-[4-[(trimethylsilyl)ethynyl]phenyl]-21*H*,23*H*-porphin-5-yl]-phenyl]ethynyl]- 5-(1,1-dimethylethyl)phenyl]ethynyl]-phenyl]-15-[4-[[3-(3,3-diethyl-1-triazenyl)-5-(1,1-dimethylethyl)phenyl]ethynyl]phenyl]-10,20-bis(2,4,6-trimethylphenyl)-21*H*,23*H*-porphinato(2−)-*N*^{21},*N*^{22},*N*^{23},*N*^{24}]zinc (7b). Reaction of **5b** (0.306 g, 0.284 mmol) with **6** (0.304 g, 0.292 mmol) in the presence of $Pd(PPh_3)_4$ (31.5 mg, 0.027 mmol) in 90 mL of DMF/Et_3N, as described for **7a**, with subsequent purification by FC ($CHCl_3$/hexane/Et_3N 60:40:0.2), afforded 0.370 g (92%) of **7b**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ −2.63 (s, 2H), 0.37 (s, 9H), 1.32 (t, J = 7.3, 6H), 1.42 (s, 9H), 1.49 (s, 9H), 1.84 (s, 24H), 2.64 (s, 12H), 3.80 (q, J = 7.3, 4H), 7.29 (s, 8H), 7.49 (d J = 1.8, 2H), 7.58 (t, J = 1.8, 1H), 7.75 (dd, J = 1.5, 2H), 7.84 (t, J = 1.5, 1H), 7.86 and 8.16 (AA′XX′, J_{AX} = 8.5, 4H), 7.93 and 8.22 (AA′XX′, J_{AX} = 8.5, 4H), 7.97 and 8.25 (AA′XX′, J_{AX} = 8.5, 4H), 7.97 and 8.27 (AA′XX′, J_{AX} = 8.5, 4H), 8.70 and 8.76 (2 × d, J = 4.8, 4H), 8.73 and 8.83 (2 × d, J = 4.8, 4H), 8.80 and 8.91 (2 × d, J = 4.4, 4H), 8.81 and 8.92 (2 × d, J = 4.4, 4H); UV/vis (CH_2Cl_2) 292 (5.02), 422 (5.95), 516 (4.45), 550 (4.59), 590 (4.19), 650 (3.95); ES$^+$-MS ($CHCl_3$/MeOH) m/z 1991.9 ([M + H]$^+$), 996.2 ([M + 2H]$^{2+}$) (calcd average mass for $C_{135}H_{121}N_{11}SiZn$ 1990.98).

[μ-[5-[4-[[3-[[4-[10,20-Bis(2,4,6-trimethylphenyl)-15-[4-[(trimethylsilyl)ethynyl]phenyl]-21*H*,23*H*-porphin-5-yl-*N*^{21},*N*^{22},*N*^{23},*N*^{24}]phenyl]ethynyl]-5-(1,1-dimethyl-ethyl)-phenyl]ethynyl]phenyl]-15-[4-[[3-(3,3-diethyl-1-triazenyl)-5-(1,1-dimethylethyl)phenyl]ethynyl]phenyl]-10,20-bis(2,4,6-trimethylphenyl)-21*H*,23*H*-porphinato(4−)-*N*^{21},*N*^{22},*N*^{23},*N*^{24}]](zinc)nickel (7c). Reaction of **5c** (0.206 g, 0.182 mmol) with **6** (0.195 g, 0.187 mmol) in the presence of $Pd(PPh_3)_4$ (42.6 mg, 0.043 mmol) in 132 mL of DMF/Et_3N, as described for **7a**, with subsequent purification by FC ($CHCl_3$/hexane/Et_3N 70:30:0.2), afforded 0.366 g (98%) of **7c**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ 0.35 (s, 9H), 1.32 (t, J = 7.4, 6H), 1.42 (s, 9H), 1.47 (s, 9H), 1.81 (s, 12H), 1.84 (s, 12H), 2.58 (s, 6H), 2.64 (s, 6H), 3.82 (q, J = 7.4, 4H), 7.22 (s, 4H), 7.29 (s, 4H), 7.49 (d J = 1.5, 2H), 7.59 (t, J = 1.5, 1H), 7.74 (t, J = 1.5, 1H), 7.79 and 7.99 (AA′XX′, J_{AX} = 8.5, 4H), 7.81 (t, J = 1.5, 1H), 7.90 and 8.07 (AA′XX′, J_{AX} = 8.5, 4H), 7.93 and 8.22 (AA′XX′, J_{AX} = 8.5, 4H), 7.97 and 8.26 (AA′XX′, J_{AX} = 8.5, 4H), 8.60 and 8.67 (2 × d, J = 4.8, 4H), 8.62 and 8.74 (2 × d, J = 4.8, 4H), 8.80 and 8.91 (2 × d, J = 4.6, 4H), 8.81 and 8.92 (2 × d, J = 4.6, 4H); UV/vis (CH_2Cl_2) 292 (5.00), 422 (5.81), 531 (4.40), 548 (4.45), 590 (3.87); ES$^+$-MS (THF/HCOOH) m/z 1024.6 ([M + 2H]$^{2+}$) (calcd average mass for $C_{135}H_{119}N_{11}NiSiZn$ 2047.66).

[μ-[5-[4-[[3-[[4-[10,20-Bis(2,4,6-trimethylphenyl)-15-[4-[(trimethylsilyl)ethynyl]phenyl]-21*H*,23*H*-porphin-5-yl-*N*^{21},*N*^{22},*N*^{23},*N*^{24}]phenyl]ethynyl]-5-(1,1-dimethylethyl)-phenyl]ethynyl]phenyl]-15-[4-[[3-(1,1-dimethylethyl)-5-iodophenyl]ethynyl]phenyl]-10,20-bis(2,4,6-trimethylphenyl)-21*H*,23*H*-porphinato(4−)-*N*^{21},*N*^{22},*N*^{23}, *N*^{24}]]dizinc (8a). Reaction of **7a** (189 mg, 0.092 mmol), as described for **5a**, with subsequent purification by FC ($CHCl_3$/hexane/Et_3N 55:45:0.1), afforded 180 mg (94%) of **8a**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ 0.38 (s, 9H), 1.38 (s, 9H), 1.49 (s, 9H), 1.83 (s, 12H), 1.84 (s, 12H), 2.64 (s, 12H), 7.29 (s, 8H), 7.66 (t J = 1.5, 1H), 7.74 (t, J = 1.5, 1H), 7.75 (d, J = 1.5, 2H), 7.84 (t, J = 1.5, 1H), 7.86 (t, J = 1.5, 1H), 7.86 and 8.18 (AA′XX′, J_{AX} = 8.4, 4H), 7.92 and 8.24 (AA′XX′, J_{AX} = 8.2, 4H), 7.98 and 8.26 (AA′XX′, J_{AX} = 8.1, 8H), 8.78 and 8.85 (2 × d, J = 4.7, 4H), 8.80 and 8.89 (2 × d, J = 4.7, 4H), 8.81 and 8.92 (2 × d, J = 4.6, 4H), 8.81 and 8.93 (2 × d, J = 4.6, 4H); UV/vis (CH_2Cl_2) 290 (4.90), 422 (5.93), 550 (4.64), 590 (4.03); ES$^+$-MS ($CHCl_3$/MeOH) m/z 1040.3 (M^{2+}) (calcd average mass for $C_{131}H_{109}IN_8SiZn_2$ 2081.11).

[5-[4-[[3-[[4-[10,20-Bis(2,4,6-trimethylphenyl)-15-[4-[(trimethylsilyl)ethynyl]phenyl]-21*H*,23*H*-porphin-5-yl]-phenyl]ethynyl]-5-(1,1-dimethylethyl)phenyl]ethynyl]-phenyl]-15-[4-[[3-(1,1-dimethylethyl)-5-iodophenyl]ethynyl]-phenyl]-10,20-bis(2,4,6-trimethylphenyl)-21*H*,23*H*-porphinato(2−)-*N*^{21},*N*^{22},*N*^{23},*N*^{24}]zinc (8b). Reaction of **7b** (114.5 mg, 57.5 μmol), as described for **5a**, with subsequent purification by 2-fold FC ($CHCl_3$/hexane/Et_3N 50:50:0.1), afforded 58.9 mg (51%) of **8b**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ −2.63 (s, 2H), 0.37 (s, 9H), 1.38 (s, 9H), 1.49 (s, 9H), 1.84 (s, 24H), 2.64 (s, 12H), 7.29 (s, 8H), 7.66 (t J = 1.4, 1H), 7.75 (m, 3H), 7.84 (t, J = 1.4, 1H), 7.86 (t, J = 1.4, 1H), 7.86 and 8.17 (AA′XX′, J_{AX} = 8.1, 4H), 7.92 and 8.24 (AA′XX′, J_{AX} = 8.1, 4H), 7.98 and 8.25 (AA′XX′, J_{AX} = 8.1, 4H), 7.98 and 8.27 (AA′XX′, J_{AX} = 8.1, 4H), 8.71 and 8.76 (2 × d, J = 4.8, 4H), 8.73 and 8.84 (2 × d, J = 4.8, 4H), 8.81 and 8.90 (2 × d, J = 4.6, 4H), 8.82 and 8.93 (2 × d, J = 4.6, 4H); UV/vis (CH_2Cl_2) 288 (4.95), 422 (5.84), 516 (4.37), 548 (4.49), 588 (4.23), 644 (3.99); ES$^+$-MS ($CHCl_3$/MeOH) m/z 2018.6 ([M + H]$^+$), 1009.4 ([M + 2H]$^{2+}$), 978.2 ([M − Zn + 4H]$^{2+}$) (calcd average mass for $C_{131}H_{111}IN_8SiZn$ 2017.74).

[μ-[5-[4-[[3-[[4-[10,20-Bis(2,4,6-trimethylphenyl)-15-[4-[(trimethylsilyl)ethynyl]phenyl]-21*H*,23*H*-porphin-5-yl-*N*^{21},*N*^{22},*N*^{23},*N*^{24}]phenyl]ethynyl]-5-(1,1-dimethylethyl)-phenyl]ethynyl]phenyl]-15-[4-[[3-(1,1-dimethylethyl)-5-iodophenyl]ethynyl]phenyl]-10,20-bis(2,4,6-trimethylphenyl)-21*H*,23*H*-porphinato(4−)-*N*^{21},*N*^{22},*N*^{23}, *N*^{24}]](zinc)-nickel (8c). Reaction of **7c** (210 mg, 102.6 μmol), as described for **5a**, with subsequent purification by FC ($CHCl_3$/hexane/Et_3N 50:50:0.1), afforded 208 mg (98%) of **8c**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ 0.35 (s, 9H), 1.38 (s, 9H), 1.47 (s, 9H), 1.81 (s, 12H), 1.84 (s, 12H), 2.58 (s, 6H), 2.64 (s, 6H), 7.21 (s, 4H), 7.29 (s, 4H), 7.66 (t J = 1.5, 1H), 7.72 (t, J = 1.5, 1H), 7.74 (t, J = 1.5, 1H), 7.75 (t, J = 1.5, 1H), 7.79 and 7.99 (AA′XX′, J_{AX} = 8.2, 4H), 7.81 (t, J = 1.5, 1H), 7.86 (t, J = 1.5, 1H), 7.91 and 8.07 (AA′XX′, J_{AX} = 8.2, 4H), 7.92 and 8.24 (AA′XX′, J_{AX} = 8.2, 4H), 7.97 and 8.26 (AA′XX′, J_{AX} = 8.2, 4H), 8.60 and 8.66 (2 × d, J = 4.8, 4H), 8.62 and 8.73 (2 × d, J = 4.8, 4H), 8.80 and 8.89 (2 × d, J = 4.8, 4H), 8.81 and 8.92 (2 × d, J = 4.8, 4H); UV/vis (CH_2Cl_2) 291 (4.96), 422 (5.84), 531 (4.40), 548 (4.49), 590 (3.86); MALDI-MS (dithranol) m/z 2074.4 (M^+) (calcd average mass for $C_{131}H_{109}IN_8NiSiZn$ 2074.43).

[μ-[5-[4-[[5-(1,1-Dimethylethyl)-3-[[4-[15-[4-[[3-(3,3-diethyl-1-triazenyl)-5-(1,1-dimethylethyl)phenyl]ethynyl]-phenyl]-10,20-bis(2,4,6-trimethylphenyl)-21*H*,23*H*-porphin-5-yl-*N*^{21},*N*^{22},*N*^{23},*N*^{24}]phenyl]ethynyl]phenyl]ethynyl]-phenyl]-15-(4 -ethynylphenyl)-10,20-bis(2,4,6-trimethylphenyl)-21*H*,23*H*-porphinato(4−)-*N*^{21}, *N*^{22},*N*^{23},*N*^{24}]]dizinc (9a). Reaction of **7a** (348 mg, 0.169 mmol), as described for **6**, with subsequent purification by FC ($CHCl_3$/hexane/Et_3N 60:40:0.1), afforded 311 mg (93%) of **9a**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ 1.32 (t, J = 7.1, 6H), 1.42 (s, 9H), 1.49 (s, 9H), 1.84 (2 × s, 2 × 12H), 2.64 (s, 12H), 3.30 (s, 1H), 3.82 (q, J = 7.1, 4H), 7.29 (s, 8H), 7.49 (d J = 1.5, 2H), 7.59 (t, J = 1.5, 1H), 7.75 (d, J = 1.5, 2H), 7.84 (t, J = 1.5, 1H), 7.88 and 8.21 (AA′XX′, J_{AX} = 8.2, 4H), 7.93 and 8.22 (AA′XX′, J_{AX} = 8.2, 4H), 7.98 and 8.26 (AA′XX′, J_{AX} = 8.2, 4H), 7.98 and 8.27 (AA′XX′, J_{AX} = 8.2, 4H), 8.78 and 8.85 (2 × d, J = 4.6, 4H), 8.79 and 8.90 (2 × d, J = 4.6, 4H), 8.80 and 8.91 (2 × d, J = 4.6, 4H), 8.81 and 8.91 (2 × d, J = 4.6, 4H); UV/vis (CH_2Cl_2) 294 (5.00), 422 (5.96), 550 (4.64), 590 (3.88); ES$^+$-MS ($CHCl_3$/MeOH) m/z

991.0 (M^{2+}), 940.9 ([M − N_3Et_2 + H]$^{2+}$) (calcd average mass for $C_{132}H_{111}N_{11}Zn_2$ 1982.16).

[5-[4-[[5-(1,1-Dimethylethyl)-3-[[4-[15-[4-[[3-(3,3-diethyl-1-triazenyl)-5-(1,1-dimethylethyl)phenyl]ethynyl]phenyl]-10,20-bis(2,4,6-trimethylphenyl)-21*H*,23*H*-porphin-5-yl-*N*^{21},*N*^{22},*N*^{23},*N*^{24}]phenyl]ethynyl]phenyl]ethynyl]phenyl]-15-(4-ethynylphenyl)-10,20-bis(2,4,6-trimethylphenyl)-21*H*,23*H*-porphinato(2−)]zinc (9b). Reaction of **7b** (231 mg, 0.116 mmol), as described for **6**, with subsequent purification by FC ($CHCl_3$/hexane/Et_3N 60:40:0.2), afforded 219 mg (98%) of **9b**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ −2.63 (s, 2H), 1.32 (t, J = 7.3, 6H), 1.42 (s, 9H), 1.49 (s, 9H), 1.84 (s, 24H), 2.64 (s, 12H), 3.32 (s, 1H), 3.82 (q, J = 7.3, 4H), 7.29 (s, 8H), 7.49 (d J = 1.5, 2H), 7.59 (t, J = 1.5, 1H), 7.75 (d, J = 1.5, 2H), 7.84 (t, J = 1.5, 1H), 7.88 and 8.19 (AA′XX′, J_{AX} = 8.5, 4H), 7.93 and 8.23 (AA′XX′, J_{AX} = 8.5, 4H), 7.97 and 8.25 (AA′XX′, J_{AX} = 8.5, 4H), 7.97 and 8.27 (AA′XX′, J_{AX} = 8.5, 4H), 8.71 and 8.77 (2 × d, J = 4.8, 4H), 8.73 and 8.83 (2 × d, J = 4.8, 4H), 8.80 and 8.91 (2 × d, J = 4.4, 4H), 8.81 and 8.92 (2 × d, J = 4.4, 4H); UV/vis (CH_2Cl_2) 292 (4.95), 422 (5.92), 516 (4.34), 550 (4.52), 590 (4.10), 646 (3.74); ES$^+$-MS ($CHCl_3$/MeOH) m/z 1919.5 ([M + H]$^+$), 956.0 ([M + 2H]$^{2+}$) (calcd average mass for $C_{132}H_{113}N_{11}Zn$ 1918.80).

[μ-[5-[4-[[5-(1,1-Dimethylethyl)-3-[[4-[15-[4-[[3-(3,3-diethyl-1-triazenyl)-5-(1,1-dimethylethyl)phenyl]ethynyl]-phenyl]-10,20-bis(2,4,6-trimethylphenyl)-21*H*,23*H*-porphin-5-yl-*N*^{21},*N*^{22},*N*^{23},*N*^{24}]phenyl]ethynyl]phenyl]ethynyl]-phenyl]-15-(4-ethynylphenyl)-10,20-bis(2,4,6-trimethylphenyl)-21*H*,23*H*-porphinato(4−)-*N*^{21},*N*^{22}, *N*^{23},*N*^{24}]](zinc)-nickel (9c). Reaction of **7c** (350 mg, 170.9 μmol), as described for **6**, with subsequent purification by FC ($CHCl_3$/hexane/Et_3N 50:50:0.2), afforded 324 mg (96%) of **9c**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ 1.32 (t, J = 7.4, 6H), 1.42 (s, 9H), 1.47 (s, 9H), 1.81 (s, 12H), 1.84 (s, 12H), 2.58 (s, 6H), 2.64 (s, 6H), 3.28 (s, 1H), 3.82 (q, J = 7.4, 4H), 7.22 (s, 4H), 7.29 (s, 4H), 7.49 (d J = 1.5, 2H), 7.59 (t, J = 1.5, 1H), 7.72 (t, J = 1.5, 1H), 7.74 (t, J = 1.5, 1H), 7.81 (t, J = 1.5, 1H), 7.81 and 8.01 (AA′XX′, J_{AX} = 8.5, 4H), 7.90 and 8.07 (AA′XX′, J_{AX} = 8.5, 4H), 7.93 and 8.23 (AA′XX′, J_{AX} = 8.5, 4H), 7.97 and 8.26 (AA′XX′, J_{AX} = 8.5, 4H), 8.60 and 8.68 (2 × d, J = 4.8, 4H), 8.62 and 8.74 (2 × d, J = 4.8, 4H), 8.80 and 8.91 (2 × d, J = 4.8, 4H), 8.81 and 8.92 (2 × d, J = 4.8, 4H); UV/vis (CH_2Cl_2) 292 (4.99), 422 (5.80), 530 (4.39), 548 (4.45), 590 (3.87); MALDI-MS (dithranol) m/z 1876.2 ([M − N_3Et_2]$^+$) (calcd average mass for $C_{132}H_{111}N_{11}NiZn$ 1975.48).

Porphyrin Tetramer 10a. Reaction of **8a** (58.8 mg, 28.3 μmol) with **9a** (54.2 mg, 27.3 μmol) in the presence of Pd(PPh_3)$_4$ (4.8 mg, 4.15 μmol) in 13.2 mL of DMF/Et_3N, as described for **7a**, with subsequent purification by FC ($CHCl_3$/hexane/Et_3N 60:40:0.2), afforded 88.4 mg (82%) of **10a**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ 0.38 (s, 9H), 1.32 (t, J = 7.2, 6H), 1.42 (s, 9H), 1.49 (s, 27H), 1.84 (2 × s, 24H), 1.85 (s, 24H), 2.64 (s, 12H), 2.65 (s, 12H), 3.80 (q, J = 7.2, 4H), 7.29 (s, 8H), 7.30 (s, 8H), 7.49 (d, J = 1.6, 2H), 7.59 (t, J = 1.6, 1H), 7.76 (m, 6H), 7.84 (m, 3H), 7.86 and 8.18 (AA′XX′, J_{AX} = 8.2, 4H), 7.93 and 8.23 (AA′XX′, J_{AX} = 8.2, 4H), 7.98 and 8.26 (AA′XX′, J_{AX} = 8.1, 4H), 7.98 and 8.27 (AA′XX′, J_{AX} = 8.1, 4H), 7.98 and 8.28 (AA′XX′, J_{AX} = 8.2, 16H), 8.79 and 8.85 (2 × d, J = 4.6, 4H), 8.80 and 8.91 (2 × d, J = 4.6, 4H), 8.80 and 8.92 (2 × d, J = 4.6, 4H), 8.81 and 8.92 (2 × d, J = 4.6, 4H), 8.82 and 8.93 (2 × d, J = 4.8, 16H); UV/vis (CH_2Cl_2) 294 (5.13), 422 (6.19), 550 (4.95), 584 (4.76); ES$^+$-MS ($CHCl_3$/MeOH) m/z 1311.6 (M^{3+}), 983.6 (M^{4+}) (calcd average mass for $C_{263}H_{219}N_{19}SiZn_4$ 3935.36).

Porphyrin tetramer 10b. Reaction of **10a** (40.5 mg, 10.3 μmol), as described for **5a**, with subsequent purification by FC ($CHCl_3$/hexane/Et_3N, gradient from 55:45:0.1 to 70:30:0.1), afforded 34.8 mg (85%) of **10b**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ 0.38 (s, 9H), 1.38 (s, 9H), 1.49 (s, 27H), 1.84 (2 × s, 24H), 1.85 (s, 24H), 2.64 (s, 12H), 2.65 (s, 12H), 7.29 (s, 8H), 7.30 (s, 8H), 7.66 (t, J = 1.5, 1H), 7.75 (t, J = 1.5, 1H), 7.76 (m, 6H), 7.84 (m, 3H), 7.86 (t, J = 1.5, 1H), 7.86 and 8.18 (AA′XX′, J_{AX} = 8.2, 4H), 7.92 and 8.24 (AA′XX′, J_{AX} = 8.3, 4H), 7.98 (apparent d, J = 8.1, 12H), 8.27 (m, 12H), 8.78 and 8.85 (2 × d, J = 4.6, 4H), 8.80 and 8.89 (2 × d, J = 4.7, 4H), 8.80 and 8.92 (2 × d, J = 4.6, 4H), 8.81 and 8.93 (2 × d, J = 4.6, 4H), 8.82 and 8.93 (2 × d, J = 4.8, 16H); UV/vis (CH_2Cl_2) 290 (5.31), 422 (6.22), 550 (4.98), 592 (4.36); ES$^+$-MS ($CHCl_3$/MeOH) m/z 1320.4 (M^{3+}), 990.4 (M^{4+}) (calcd average mass for $C_{259}H_{209}IN_{16}SiZn_4$ 3962.12).

Porphyrin Tetramer 10c. Reaction of **8b** (37.2 mg, 18.44 μmol) with **9b** (34.4 mg, 17.9 μmol) in the presence of Pd(PPh_3)$_4$ (3.1 mg, 2.68 μmol) in 9 mL of DMF/Et_3N, as described for **7a**, with subsequent purification by FC ($CHCl_3$/hexane/Et_3N 60:40:0.2), afforded 62.4 mg (91%) of **10c**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ −2.63 (s, 2H), −2.60 (s, 2H), 0.37 (s, 9H), 1.32 (t, J = 7.4, 6H), 1.42 (s, 9H), 1.49 (s, 27H), 1.85 (m, 48H), 2.64 (s, 24H), 3.82 (q, J = 7.4, 4H), 7.29 (s, 8H), 7.30 (s, 8H), 7.49 (d, J = 1.7, 2H), 7.59 (t, J = 1.7, 1H), 7.76 (d, J = 1.7, 6H), 7.85 (m, 3H), 7.86 and 8.17 (AA′XX′, J_{AX} = 8.3, 4H), 7.93 and 8.23 (AA′XX′, J_{AX} = 8.3, 4H), 7.98 and 8.26 (AA′XX′, J_{AX} = 8.3, 12H), 7.98 and 8.27 (AA′XX′, J_{AX} = 8.3, 12H), 8.71 and 8.76 (2 × d, J = 4.8, 4H), 8.72 and 8.85 (2 × d, J = 4.8, 4H), 8.74 and 8.85 (2 × d, J = 4.8, 8H), 8.81 and 8.91 (2 × d, J = 4.8, 4H), 8.82 and 8.93 (2 × d, J = 4.8, 4H), 8.83 and 8.93 (2 × d, J = 4.8, 8H); UV/vis (CH_2Cl_2) 292 (5.18), 422 (6.18), 516 (4.63), 550 (4.81), 592 (4.41), 648 (4.25); ES$^+$-MS ($CHCl_3$/MeOH) m/z 1269.9 (M^{3+}), 1236.8 ([M − N_3Et_2 + H]$^{3+}$), 952.4 (M^{4+}) (calcd average mass for $C_{263}H_{223}N_{19}SiZn_2$ 3808.63).

Porphyrin Tetramer 10d. Reaction of **10c** (57.9 mg, 15.2 μmol), as described for **5a**, with subsequent purification by FC ($CHCl_3$/hexane/Et_3N 60:40:0.1), afforded 30.7 mg (53%) of **10d**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ −2.63 (s, 2H), −2.60 (s, 2H), 0.37 (s, 9H), 1.38 (s, 9H), 1.49 (s, 27H), 1.85 (m, 48H), 2.64 (s, 24H), 7.30 (2 × s, 16H), 7.66 (t, J = 1.4, 1H), 7.75 (t, J = 1.4, 1H), 7.76 (d, J = 1.4, 6H), 7.85 (m, 3H), 7.86 (t, J = 1.4, 1H), 7.86 and 8.17 (AA′XX′, J_{AX} = 8.2, 4H), 7.92 and 8.24 (AA′XX′, J_{AX} = 8.2, 4H), 7.98 (apparent d, J = 8.4, 12H), 8.26 (m, 6H), 8.27 (m, 6H), 8.71 and 8.76 (2 × d, J = 4.8, 4H), 8.72 and 8.85 (2 × d, J = 4.8, 4H), 8.74 and 8.85 (2 × d, J = 4.8, 8H), 8.81 and 8.90 (2 × d, J = 4.8, 4H), 8.818 and 8.929 (2 × d, J = 4.8, 4H), 8.824 and 8.933 (2 × d, J = 4.8, 8H); UV/vis (CH_2Cl_2) 292 (5.14), 422 (6.15), 516 (4.62), 550 (4.76), 592 (4.32), 648 (4.10); ES$^+$-MS ($CHCl_3$/MeOH/HCOOH) m/z 1918.1 ([M + 2H]$^{2+}$), 1279.2 ([M + 3H]$^{3+}$), 1258.2 ([M − Zn + 5H]$^{3+}$), 1237.1 ([M − 2Zn + 7H]$^{3+}$), 959.6 ([M + 4H]$^{4+}$), 943.9 ([M − Zn + 6H]$^{4+}$), 928.2 ([M − 2Zn + 8H]$^{4+}$), 755.4 ([M − Zn + 7H]$^{5+}$), 742.6 ([M − 2Zn + 9H]$^{5+}$) (calcd average mass for $C_{259}H_{213}IN_{16}SiZn_2$ 3835.39).

Porphyrin Tetramer 10e. Reaction of **8c** (180 mg, 86.8 μmol) with **9c** (176.6 mg, 89.4 μmol) in the presence of Pd(PPh_3)$_4$ (15 mg, 13 μmol) in 45 mL of DMF/Et_3N, as described for **7a**, with subsequent purification by 2-fold FC ($CHCl_3$/hexane/Et_3N 60:40:0.2), afforded 204 mg (60%) of **10e**: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 0.35 (s, 9H), 1.32 (t, J = 7.4, 6H), 1.42 (s, 9H), 1.47 (s, 27H), 1.81 (s, 12H), 1.83 (s, 12H), 1.85 (s, 24H), 2.58 (2 × s, 2 × 6H), 2.64 (s, 12H), 3.82 (q, J = 7.4, 4H), 7.21 (s, 4H), 7.23 (s, 4H), 7.29 (s, 8H), 7.49 (d, J = 1.5, 2H), 7.59 (t, J = 1.5, 1H), 7.72 (m, 3H), 7.74 (m, 3H), 7.78 and 7.99 (AA′XX′, J_{AX} = 8.2, 4H), 7.81 (m, 3H), 7.90 and 8.07 (AA′XX′, J_{AX} = 8.2, 4H), 7.91 and 8.08 (AA′XX′, J_{AX} = 8.2, 8H), 7.93 and 8.23 (AA′XX′, J_{AX} = 8.2, 4H), 7.97 and 8.26 (AA′XX′, J_{AX} = 8.5, 12H), 8.60 and 8.66 (2 × d, J = 4.8, 4H), 8.62 and 8.73 (2 × d, J = 4.8, 4H), 8.63 and 8.74 (2 × d, J = 4.8, 8H), 8.80 and 8.91 (2 × d, J = 4.8, 4H), 8.81 and 8.92 (2 × d, J = 4.8, 4H), 8.82 and 8.92 (2 × d, J = 4.8, 8H); UV/vis (CH_2Cl_2) 291 (5.48), 422 (6.29), 533 (4.87), 548 (4.94), 590 (4.30); MALDI-MS (dithranol) m/z 3822.4 ([M − N_3Et_2]$^+$) (calcd average mass for $C_{263}H_{219}N_{19}Ni_2SiZn_2$ 3922.00).

Porphyrin Tetramer 10f. Reaction of **10e** (204 mg, 52 μmol), as described for **5a**, with subsequent purification by FC ($CHCl_3$/hexane/Et_3N, gradient from 60:40:0.1 to 70:30:0.1), afforded 161 mg (78%) of **10f**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ 0.35 (s, 9H), 1.38 (s, 9H), 1.47 (s, 27H), 1.81 (s, 12H), 1.83 (s, 12H), 1.84 (s, 12H), 1.85 (s, 12H), 2.58 (2 × s, 2 × 6H), 2.64 (s, 12H), 7.21 (s, 4H), 7.23 (s, 4H), 7.29 (s, 8H), 7.66 (t, J = 1.5, 1H), 7.73 (m, 3H), 7.74 (t, J = 1.5, 1H), 7.74 (m, 3H), 7.78 and 7.99 (AA′XX′, J_{AX} = 8.2, 4H), 7.81 (m, 3H), 7.86 (t, J = 1.5, 1H), 7.90 and 8.07 (AA′XX′, J_{AX} = 8.2, 4H), 7.91 and 8.08 (AA′XX′, J_{AX} = 8.2, 8H), 7.92 and 8.24 (AA′XX′, J_{AX} = 8.2, 4H),

7.97 and 8.26 (AA′XX′, J_{AX} = 8.2, 12H), 8.60 and 8.66 (2 × d, J = 4.8, 4H), 8.62 and 8.73 (2 × d, J = 4.8, 4H), 8.63 and 8.74 (2 × d, J = 4.8, 8H), 8.80 and 8.89 (2 × d, J = 4.8, 4H), 8.81 and 8.92 (2 × d, J = 4.8, 4H), 8.82 and 8.92 (2 × d, J = 4.8, 8H); UV/vis (CH_2Cl_2) 290 (5.32), 422 (6.16), 532 (4.74), 549 (4.82), 591 (4.21); MALDI-MS (dithranol) m/z 3948.6 (M^+) (calcd average mass for $C_{259}H_{209}IN_{16}Ni_2SiZn_2$ 3948.76).

Linear Porphyrin Hexamer 11a. Reaction of **10b** (33.0 mg, 8.33 μmol) with **9a** (16.0 mg, 8.07 μmol) in the presence of $Pd(PPh_3)_4$ (1.44 mg, 1.25 μmol) in 4.08 mL of DMF/Et_3N, as described for **7a**, with subsequent purification by FC ($CHCl_3$/hexane/Et_3N, gradient from 60:40:0.2 to 70:30:0.2), afforded 38.3 mg (82%) of **11a**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ 0.38 (s, 9H), 1.32 (t, J = 7.2, 6H), 1.42 (s, 9H), 1.49 (s, 45H), 1.83, 1.84 and 1.85 (3 × s, 12H, 12H and 48H), 2.63 (s, 12H), 2.64 (s, 24H), 3.81 (q, J = 7.2, 4H), 7.29 (s, 8H), 7.30 (s, 16H), 7.49 (d, J = 1.5, 2H), 7.59 (t, J = 1.5, 1H), 7.76 (d, J = 1.5, 10H), 7.85 (t, J = 1.5, 5H), 7.86 and 8.18 (AA′XX′, J_{AX} = 8.4, 4H), 7.93 and 8.23 (AA′XX′, J_{AX} = 8.3, 4H), 7.97−7.99 (m, 20H), 8.26, 8.27 and 8.28 (3 × apparent d, J = 8.3, 2H, 2H and 16H), 8.79 and 8.85 (2 × d, J = 4.6, 4H), 8.80 and 8.91 (2 × d, J = 4.6, 4H), 8.81 and 8.92 (2 × d, J = 4.6, 4H), 8.82 and 8.93 (2 × d, J = 4.6, 4H), 8.82 and 8.94 (2 × d, J = 4.7, 32H); UV/vis (CH_2Cl_2) 294 (5.37), 422 (6.29), 550 (5.04), 590 (4.44); ES$^+$-MS ($CHCl_3$/MeOH/HCOOH) 1335.2 ([M − 6Zn − N_3Et_2 + 17H]$^{4+}$), 1068.2 ([M − 6Zn − N_3Et_2 + 18H]$^{5+}$), 890.5 ([M − 6Zn − N_3Et_2 + 19H]$^{6+}$), 763.3 ([M − 6Zn − N_3Et_2 + 20H]$^{7+}$) (calcd average mass for $C_{391}H_{319}N_{27}SiZn_6$ 5816.37).

Linear Porphyrin Hexamer 11b. Reaction of **11a** (37.5 mg, 6.45 μmol) with CH_3I, as described for **5a** (72%), followed by treatment with NaOH, as described for **6** (88%), afforded 23.6 mg of **11b**: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 1.38 (s, 9H), 1.49 (s, 45H), 1.84 (2 s, 24H), 1.85 (s, 48H), 2.64 (s, 12H), 2.65 (s, 24H), 3.31 (s, 1H), 7.29 (s, 8H), 7.30 (s, 16H), 7.66 (t, J = 1.5, 1H), 7.75 (t, J = 1.6, 1H), 7.76 (d, J = 1.5, 10H), 7.85 (m, 5H), 7.86 (t, J = 1.5, 1H), 7.88 and 8.21 (AA′XX′, J_{AX} = 8.3, 4H), 7.92 and 8.24 (AA′XX′, J_{AX} = 8.3, 4H), 7.97−7.99 (m, 20H), 8.26, 8.27 and 8.28 (3 × apparent d, J = 8.3, 2H, 2H and 16H), 8.79 and 8.86 (2 × d, J = 4.6, 4H), 8.80 and 8.90 (2 × d, J = 4.6, 4H), 8.81 and 8.92 (2 × d, J = 4.7, 4H), 8.81 and 8.93 (2 × d, J = 4.7, 4H), 8.82 and 8.94 (2 × d, J = 4.6, 32H); UV/vis (CH_2Cl_2) 290 (5.38), 422 (6.38), 550 (5.09), 590 (4.30); ES$^+$-MS ($CHCl_3$/MeOH/HCOOH) m/z 1348.7 ([M − 6Zn + 16H]$^{4+}$), 1079.1 ([M − 6Zn + 17H]$^{5+}$), 899.5 ([M − 6Zn + 18H]$^{6+}$), 771.1 ([M − 6Zn + 19H]$^{7+}$) (calcd average mass for $C_{384}H_{301}IN_{24}Zn_6$ 5770.95).

Linear Porphyrin Hexamer 11c. Reaction of **10d** (81.2 mg, 21.2 μmol) with **9b** (41.8 mg, 21.8 μmol) in the presence of $Pd(PPh_3)_4$ (3.7 mg, 3.2 μmol) in 9.0 mL of DMF/Et_3N, as described for **7a**, with subsequent purification by FC ($CHCl_3$/hexane/Et_3N 60:40:0.2), afforded 102.9 mg (86%) of **11c**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ −2.63 (s, 2H), −2.60 (s, 4H), 0.38 (s, 9H), 1.32 (t, J = 7.0, 6H), 1.42 (s, 9H), 1.49 (s, 45H), 1.84, 1.85 and 1.86 (3 × s, 72H), 2.64 (s, 36H), 3.82 (q, J = 7.0, 4H), 7.30 (s, 24H), 7.49 (d, J = 1.4, 2H), 7.59 (m, 1H), 7.76 (m, 10H), 7.85 (m, 5H), 7.86 and 8.17 (AA′XX′, J_{AX} = 8.5, 4H), 7.93 and 8.23 (AA′XX′, J_{AX} = 8.5, 4H), 7.98 (apparent d, J = 8.5, 20H), 8.26 (m, 20H), 8.71 and 8.76 (2 × d, J = 4.8, 4H), 8.72 and 8.85 (2 × d, J = 4.8, 4H), 8.74 and 8.85 (2 × d, J = 4.8, 16H), 8.80 and 8.91 (2 × d, J = 4.6, 4H), 8.82 and 8.92 (2 × d, J = 4.6, 4H), 8.82 and 8.93 (2 × d, J = 4.7, 16H); UV/vis (CH_2Cl_2) 294 (5.44), 422 (6.42), 516 (4.88), 550 (5.04), 590 (4.58), 646 (4.26); ES$^+$-MS ($CHCl_3$/MeOH) m/z 1842.3 ([M − N_3Et_2 + H]$^{3+}$), 1381.8 ([M − N_3Et_2 + H]$^{4+}$) (calcd average mass for $C_{391}H_{325}N_{27}SiZn_3$ 5626.27).

Linear Porphyrin Hexamer 11d. Reaction of **11c** (48.8 mg, 8.67 μmol) with CH_3I, as described for **5a** (43%), followed by treatment with NaOH, as described for **6** (77%), afforded 21.1 mg of **11d**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ −2.63 (s, 2H), −2.60 (s, 4H), 1.38 (s, 9H), 1.49 (s, 45H), 1.84, 1.85 and 1.86 (3 × s, 72H), 2.64 (s, 36H), 3.31 (s, 1H), 7.30 (2 × s, 24H), 7.66 (t, J = 1.4, 1H), 7.75 (t, J = 1.4, 1H), 7.76 (d, J = 1.4, 10H), 7.85 (d, J = 1.4, 5H), 7.86 (t, J = 1.4, 1H), 7.90 and 8.20 (AA′XX′, J_{AX} = 8.4, 4H), 7.94 and 8.24 (AA′XX′, J_{AX} = 8.5, 4H), 7.98 (apparent d, J = 8.1, 20H), 8.27 (m, 20H), 8.71 and 8.78 (2 × d, J = 4.8, 4H), 8.73 and 8.85 (2 × d, J = 4.8, 4H), 8.74 and 8.85 (2 × d, J = 4.8, 16H), 8.81 and 8.89 (2 × d, J = 4.6, 4H), 8.82 and 8.92 (2 × d, J = 4.8, 4H), 8.82 and 8.93 (2 × d, J = 4.8, 16H); UV/vis (CH_2Cl_2) 292 (5.32), 422 (6.31), 516 (4.76), 550 (4.92), 590 (4.47), 646 (4.14); ES$^+$-MS (THF/HCOOH) m/z 1396.1 ([M + 4H]$^{4+}$), 1380.4 ([M − Zn + 6H]$^{4+}$), 1117.1 ([M + 5H]$^{5+}$), 1104.5 ([M − Zn + 7H]$^{5+}$) (calcd average mass for $C_{384}H_{307}IN_{24}Zn_3$ 5580.85).

Linear Porphyrin Hexamer 11e. Reaction of **10b** (23.3 mg, 5.88 μmol) with **9b** (11.7 mg, 6.10 μmol) in the presence of $Pd(PPh_3)_4$ (1.0 mg, 0.88 μmol) in 2.7 mL of DMF/Et_3N, as described for **7a**, with subsequent purification by FC ($CHCl_3$/hexane/Et_3N 60:40:0.2 then 70:30:0.2), afforded 28.8 mg (85%) of **11e**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ −2.60 (s, 2H), 0.37 (s, 9H), 1.32 (t, J = 7.0, 6H), 1.42 (s, 9H), 1.49 (s, 45H), 1.84−1.86 (m, 72H), 2.64 (s, 36H), 3.82 (q, J = 7.0, 4H), 7.30 (s, 24H), 7.50 (d, J = 1.8, 2H), 7.59 (t, J = 1.8, 1H), 7.76 (m, 10H), 7.85 (m, 5H), 7.86 and 8.18 (AA′XX′, J_{AX} = 8.3, 4H), 7.93 and 8.23 (AA′XX′, J_{AX} = 8.3, 4H), 7.98 and 8.27 (2 × AA′XX′, J_{AX} = 8.3, 8H), 7.98 and 8.28 (AA′XX′, J_{AX} = 8.3, 32H), 8.74 and 8.85 (2 × d, J = 4.8, 8H), 8.79 and 8.86 (2 × d, J = 4.8, 4H), 8.81 and 8.91 (2 × d, J = 4.4, 4H), 8.81 and 8.92 (2 × d, J = 4.4, 4H), 8.82 and 8.92 (2 × d, J = 4.4, 4H), 8.82 and 8.93 (2 × d, J = 4.8, 24H); UV/vis (CH_2Cl_2) 290 (5.58), 422 (6.42), 516 (4.79), 550 (5.19), 592 (4.72), 648 (4.39); ES$^+$-MS ($CHCl_3$/MeOH) m/z 1884.4 ([M − N_3Et_2 + H]$^{3+}$), 1413.6 ([M − N_3Et_2 + H]$^{4+}$) (calcd average mass for $C_{391}H_{321}N_{27}SiZn_5$ 5753.00).

Linear Porphyrin Hexamer 11f. Reaction of **11e** (14.5 mg, 2.52 μmol) with CH_3I, as described for **5a** (62%), followed by treatment with NaOH, as described for **6** (75%), afforded 6.7 mg of **11f**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ −2.60 (s, 2H), 1.38 (s, 9H), 1.49 (s, 45H), 1.84 and 1.85 (2 × s, 72H), 2.64 (s, 36H), 3.31 (s, 1H), 7.30 (s, 24H), 7.66 (t, J = 1.4, 1H), 7.76 (m, 11H), 7.85 (m, 5H), 7.87 (t, J = 1.4, 1H), 7.88 and 8.20 (AA′XX′, J_{AX} = 8.1, 4H), 7.92 and 8.24 (AA′XX′, J_{AX} = 8.1, 4H), 7.98 (apparent d, J = 8.1, 20H), 8.28 (m, 20H), 8.74 and 8.85 (2 × d, J = 4.8, 8H), 8.80 and 8.86 (2 × d, J = 4.8, 4H), 8.81 and 8.90 (2 × d, J = 4.4, 4H), 8.81 and 8.93 (2 × d, J = 4.4, 8H), 8.82 and 8.93 (2 × d, J = 4.4, 24H); UV/vis (CH_2Cl_2) 294 (5.42), 422 (6.38), 516 (4.59), 550 (5.08), 588 (4.58), 650 (4.21); ES$^+$-MS ($CHCl_3$/MeOH/HCOOH) m/z 1797.9 ([M − 5Zn + 13H]$^{3+}$), 1348.7 ([M − 5Zn + 14H]$^{4+}$), 1079.1 ([M − 5Zn + 15H]$^{5+}$), 899.4 ([M − 5Zn + 16H]$^{6+}$) (calcd average mass for $C_{384}H_{303}IN_{24}Zn_5$ 5707.58).

Linear Porphyrin Hexamer 11g. Reaction of **10f** (160 mg, 40.5 μmol) with **9c** (83.0 mg, 42 μmol) in the presence of $Pd(PPh_3)_4$ (7.1 mg, 6.1 μmol) in 18.6 mL of DMF/Et_3N, as described for **7a**, with subsequent purification by 2-fold FC ($CHCl_3$/hexane/Et_3N, gradient from 50:50:0.2 to 70:30:0.2), afforded 143 mg (61%) of **11g**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ 0.35 (s, 9H), 1.32 (t, J = 7.4, 6H), 1.42 (s, 9H), 1.47 (s, 45H), 1.81 and 1.83 (2 × s, 36H), 1.84 and 1.85 (2 × s, 36H), 2.57 and 2.58 (2 × s, 18H), 2.64 (s, 18H), 3.82 (q, J = 7.4, 4H), 7.21 (s, 4H), 7.22 (s, 8H), 7.29 (s, 12H), 7.49 (d, J = 1.5, 2H), 7.59 (t, J = 1.5, 1H), 7.73 (t, J = 1.5, 5H), 7.74 (t, J = 1.5, 5H), 7.78 and 7.99 (AA′XX′, J_{AX} = 8.2, 4H), 7.82 (m, 5H), 7.91 and 8.07 (AA′XX′, J_{AX} = 8.2, 4H), 7.91 and 8.08 (2 × AA′XX′, J_{AX} = 8.2, 16H), 7.93 and 8.23 (AA′XX′, J_{AX} = 8.2, 4H), 7.97 and 8.26 (AA′XX′, J_{AX} = 8.2, 20H), 8.60 and 8.66 (2 × d, J = 4.8, 4H), 8.62 and 8.73 (2 × d, J = 4.8, 4H), 8.63 and 8.74 (2 × d, J = 4.8, 16H), 8.80 and 8.91 (2 × d, J = 4.8, 4H), 8.81 and 8.92 (2 × d, J = 4.8, 4H), 8.82 and 8.92 (2 × d, J = 4.8, 16H); UV/vis (CH_2Cl_2) 291 (5.59), 423 (6.39), 533 (4.97), 548 (5.05), 590 (4.43); MALDI-MS (dithranol) m/z 5696.0 ([M − N_3Et_2]$^+$), 5918.1 ([M − N_3Et_2 + dithranol]$^+$) (calcd average mass for $C_{391}H_{319}N_{27}Ni_3SiZn_3$ 5796.33); ES$^+$-MS ($CHCl_3$/HCOOH) m/z 1836.2 ([M − N_3Et_2 − 3Zn + 9H]$^{3+}$), 1377.2 ([M − N_3Et_2 − 3Zn + 10H]$^{4+}$), 1102.0 ([M − N_3Et_2 − 3Zn + 11H]$^{5+}$).

Linear Porphyrin Hexamer 11h. Reaction of **11g** (142 mg, 24.5 μmol) with CH_3I, as described for **5a** (93%), followed by treatment with NaOH, as described for **6** (94%), afforded 123.4 mg of **11h**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ 1.38 (s, 9H), 1.49 (s, 45H), 1.81 and 1.83 (2 × s, 36H), 1.84 and 1.85 (2 × s, 36H), 2.57 and 2.58 (2 × s, 18H), 2.63 (s, 18H), 3.26 (s, 1H), 7.21 (s, 4H), 7.22 (s, 8H), 7.29 (s, 12H), 7.66 (t, J = 1.5, 1H),

7.73 (m, 5H), 7.74 (m, 6H), 7.81 and 8.01 (AA′XX′, J_{AX} = 8.2, 4H), 7.82 (m, 5H), 7.86 (t, J = 1.5, 1H), 7.91 and 8.07 (AA′XX′, J_{AX} = 8.2, 4H), 7.91 and 8.08 (AA′XX′, J_{AX} = 8.2, 16H), 7.92 and 8.24 (AA′XX′, J_{AX} = 8.2, 4H), 7.97 and 8.26 (2 × AA′XX′, J_{AX} = 8.2, 20H), 8.60 and 8.68 (2 × d, J = 4.8, 4H), 8.62 and 8.74 (2 × d, J = 4.8, 4H), 8.63 and 8.75 (2 × d, J = 4.8, 16H), 8.80 and 8.90 (2 × d, J = 4.8, 4H), 8.81 and 8.93 (2 × d, J = 4.8, 4H), 8.82 and 8.93 (2 × d, J = 4.8, 16H); UV/vis (CH_2Cl_2) 290 (5.47), 423 (6.32), 534 (4.87), 548 (4.96), 590 (4.27); MALDI-MS (dithranol) m/z 5751.1 (M^+) (calcd average mass for $C_{384}H_{301}IN_{24}Ni_3Zn_3$ 5750.91).

General Procedure for the Synthesis of *meso*-Alkyl-2,2′-dipyrrylmethanes 12a−e. To a solution of pyrrole (200 mmol) and alkyl aldehyde (20 mmol) in CH_2Cl_2 (300 mL) was added dropwise a 8 M solution of $BF_3{\cdot}OEt_2$ in CH_2Cl_2 (0.45 mL, 3.6 mmol), and the reaction mixture was allowed to stir at 20 °C for 3 h. Triethylamine (2 mL) was then added, and the solvent was removed under reduced pressure. The crude product was purified by FC (CH_2Cl_2/hexane/Et_3N 2:1:0.01), affording the corresponding dipyrrylmethane as a yellow oil, which was used without further purification for the synthesis of the corresponding porphyrins.

***meso*-Propyl-2,2′-dipyrrylmethane (12a):** 40%; ^{1}H NMR (360.14 MHz, $CDCl_3$) δ 0.92 (t, J = 7.3, 3H, CH_3), 1.31 (m, 2H, CH_2), 1.92 (m, 2H, CH_2), 4.00 (t, J = 7.6, 1H, CH), 6.06 (m, 2H, H-5,5′), 6.13 (m, 2H, H-4, 4′), 6.63 (m, 2H, H-3,3′), 7.82 (br s, 2H, NH).

***meso*-Butyl-2,2′-dipyrrylmethane (12b):** 35%; ^{1}H NMR (360.14 MHz, $CDCl_3$) δ 0.87 (t, J = 7.0, 3H, CH_3), 1.30 (m, 4H, CH_2), 1.93 (m, 2H, CH_2), 3.96 (t, J = 7.6, 1H, CH), 6.06 (m, 2H, H-5, 5′), 6.13 (m, 2H, H-4, 4′), 6.62 (m, 2H, H-3,3′), 7.75 (br s, 2H, NH).

***meso*-Pentyl-2,2′-dipyrrylmethane (12c):**[11,14] 44%; ^{1}H NMR (360.14 MHz, $CDCl_3$) δ 0.86 (t, J = 7.0, 3H, CH_3), 1.29 (m, 6H, CH_2), 1.93 (m, 2H, CH_2), 3.97 (t, J = 7.6, 1H, CH), 6.05 (m, 2H, H-5,5′), 6.14 (m, 2H, H-4, 4′), 6.63 (m, 2H, H-3,3′), 7.77 (br s, 2H, NH).

***meso*-Hexyl-2,2′-dipyrrylmethane (12d):** 32%; ^{1}H NMR (360.14 MHz, $CDCl_3$) δ 0.86 (t, J = 7.0, 3H, CH_3), 1.29 (m, 8H, CH_2), 1.93 (m, 2H, CH_2), 3.94 (t, J = 7.6, 1H, CH), 6.05 (m, 2H, H-5, 5′), 6.14 (m, 2H, H-4, 4′), 6.62 (m, 2H, H-3,3′), 7.75 (br s, 2H, NH).

***meso*-Heptyl-2,2′-dipyrrylmethane (12e):** 38%; ^{1}H NMR (360.14 MHz, $CDCl_3$) δ 0.86 (t, J = 7.0, 3H, CH_3), 1.28 (m, 10H, CH_2), 1.93 (m, 2H, CH_2), 3.98 (t, J = 7.6, 1H, CH), 6.06 (m, 2H, H-5, 5′), 6.14 (m, 2H, H-4, 4′), 6.64 (m, 2H, H-3,3′), 7.81 (br s, 2H, NH).

General Procedure for the Synthesis of 5,15-Diheptyl-10-(pyrid-4-yl)-20-[(trimethylsilyl)ethynyl]-21*H*,23*H*-porphine (13) and 5,15-Dialkyl-10-(4-iodophenyl)-20-(pyrid-4-yl)-21*H*,23*H*-porphines (14a−e). To a degassed solution (50 mL) of the dipyrrylmethane (1 mmol) in $CHCl_3$/EtOH (95:5) were successively added 4-iodobenzaldehyde (1 mmol), TFA (1.52 mmol), and 4-pyridinecarboxaldehyde (1 mmol). The solution was protected from light and stirred under argon at 20 °C for 2.5 h. Then DDQ (340 mg, 1.5 mmol, dissolved in minimal amount of THF) was added, and the stirring was continued for an additional 2 h. The reaction mixture was filtered through an alumina and silica gel pad and washed with $CHCl_3$ until the filtrate was colorless. The solvent was removed under reduced pressure, and the crude product was purified by FC (CH_2Cl_2 then CH_2Cl_2 /EtOAc 95:5 or CH_2Cl_2 /EtOH 97:3). The first fraction was the 5,15-dialkyl-10,20-bis-(4-iodophenyl)-21*H*,23*H*-porphine, the second the desired porphyrin (**14a**−**e**), and the third the 5,15-dialkyl-10,20-bis(pyrid-4-yl)-21*H*,23*H*-porphine. Further purification was achieved by a second FC (CH_2Cl_2) or by repeated recrystallizations from a solution of $CHCl_3$ by layered addition of methanol. At the end, the dark violet solid obtained was washed with hexane and methanol and dried.

5,15-Diheptyl-10-(pyrid-4-yl)-20-[(trimethylsilyl)ethynyl]-21*H*,23*H*-porphine(13) was obtained in 12% yield by reacting *meso*-heptyl-2,2′-dipyrrylmethane **(12e)**[14] (244 mg, 1 mmol) with trimethylsilylpropynal[18] (126 mg, 1 mmol) and 4-pyridinecarboxaldehyde (96 μL, 1 mmol) in the presence of TFA (120 μL, 1.52 mmol), according to the general procedure: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ −2.44 (br s, 2H, NH), 0.64 (s, 9H, $-(CH_3)_3$), 0.88 (t, J = 6.8, 6H, $-CH_3$), 1.32 (m, 8H, $-CH_2$-$CH_2CH_2CH_2CH_2CH_2CH_3$), 1.49 (m, 4H, $-CH_2CH_2CH_2CH_2CH_2$-CH_2CH_3), 1.75 (m, 4H, $-CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 2.46 (m, 4H, $-CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 4.86 (t, J = 8.0, 4H, $-CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 8.08 and 9.01 (AA′XX′, J_{AX} = 5.9, 4H, $-C_6H_4N$), 8.70 and 9.34 (2 × d, J = 5.0, 4H, β-H on porphine), 9.44 and 9.72 (2 × d, J = 5.0, 4H, β-H on porphine); UV/vis (CH_2Cl_2) 426 (5.59), 529 (4.09), 568 (4.32), 608 (3.65), 667 (4.05); ES$^+$-MS (THF/HCOOH) m/z 681.00 ([M + H]$^+$). Anal. Calcd for $C_{44}H_{53}N_5Si$ (680.02): C, 77.71; H, 7.86; N, 10.30. Found: C, 77.54; H, 8.01; N, 10.23.

5,15-Dipropyl-10-(4-iodophenyl)-20-(pyrid-4-yl)-21*H*,23*H*-porphine (14a) was obtained in 6% yield by reacting **12a** (188 mg, 1 mmol) with 4-iodobenzaldehyde[32] (232 mg, 1 mmol) and 4-pyridinecarbaldehyde (96 μL, 1 mmol), according to the general procedure: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ −2.76 (br s, 2H, NH), 1.30 (t, J = 7.3, 6H, $-CH_3$), 2.53 (m, 4H, $-CH_2CH_2$-CH_3), 4.92 (t, J = 7.3, 4H, $-CH_2CH_2CH_3$), 7.91 and 8.09 (AA′XX′, J_{AX} = 8.0, 4H, $-C_6H_4I$), 8.13 and 9.02 (AA′XX′, J_{AX} = 4.0, 4H, $-C_6H_4N$), 8.79 and 9.45 (2 × d, J = 4.8, 4H, β-H on porphine), 8.84 and 9.43 (2 × d, 4H, β-H on porphine); UV/vis (CH_2Cl_2) 301 (4.15), 418 (5.54), 516 (4.21), 551 (3.90), 594 (3.66), 650 (3.72); ES$^+$-MS ($CHCl_3$/HCOOH) m/z 674.51 ([M + H]$^+$), 337.7 ([M + 2H]$^{2+}$). Anal. Calcd for $C_{37}H_{32}N_5I$ (673.59): C, 65.97; H, 4.79; N, 10.40. Found: C, 66.10; H, 4.55; N, 10.24.

5,15-Dibutyl-10-(4-iodophenyl)-20-(pyrid-4-yl)-21*H*,23*H*-porphine (14b) was obtained in 4% yield after purification by FC (CH_2Cl_2), reacting **12b** (202 mg, 1 mmol) with 4-iodobenzaldehyde[32] (232 mg, 1 mmol) and 4-pyridinecarbaldehyde (96 μL, 1 mmol), according to the general procedure: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ −2.75 (br s, 2H, NH), 1.11 (t, J = 7.7, 6H, $-CH_3$), 1.79 (m, 4H, $-CH_2CH_2CH_2CH_3$), 2.49 (m, 4H, $-CH_2CH_2CH_2CH_3$), 4.97 (t, J = 7.7, 4H, $-CH_2CH_2CH_2CH_3$), 7.92 and 8.10 (AA′XX′, J_{AX} = 8.1, 4H, $-C_6H_4I$), 8.15 and 9.03 (AA′XX′, J_{AX} = 5.9, 4H, $-C_6H_4N$), 8.80 and 9.46 (2 × d, J = 4.8, 4H, β-H on porphine), 8.85 and 9.44 (2 × d, J = 4.8, 4H, β-H on porphine); UV/vis (CH_2Cl_2) 303 (4.18), 418 (5.49), 516 (4.17), 551 (3.88), 594 (3.59), 651 (3.66); ES$^+$-MS ($CHCl_3$/HCOOH) m/z 702.60 ([M + H]$^+$), 351.79 ([M + 2H]$^{2+}$). Anal. Calcd for $C_{39}H_{36}N_5I$ (701.65): C, 66.76; H, 5.17; N, 9.98. Found: C, 66.54; H, 5.12; N, 10.12.

5,15-Dipentyl-10-(4-iodophenyl)-20-(pyrid-4-yl)-21*H*,23*H*-porphine (14c) was obtained in 5% yield by reacting **12c** (216 mg, 1 mmol) with 4-iodobenzaldehyde[32] (232 mg, 1 mmol) and 4-pyridinecarbaldehyde (96 μL, 1 mmol), according to the general procedure: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ −2.75 (br s, 2H, NH), 0.95 (t, J = 8.0, 6H, $-CH_3$), 1.51 (m, 4H, $-CH_2$-$CH_2CH_2CH_2CH_3$), 1.75 (m, 4H, $-CH_2CH_2CH_2CH_2CH_3$), 2.50 (m, 4H, $-CH_2CH_2CH_2CH_2CH_3$), 4.94 (t, J = 8.1, 4H, $-CH_2$-$CH_2CH_2CH_2CH_3$), 7.91 and 8.09 (AA′XX′, J_{AX} = 8.4, 4H, $-C_6H_4I$), 8.13 and 9.03 (AA′XX′, J_{AX} = 5.9, 4H, $-C_6H_4N$), 8.79 and 9.45 (2 × d, J = 4.8, 4H, β-H on porphine), 8.84 and 9.42 (2 × d, J = 5.1, 4H, β-H on porphine); UV/vis (CH_2Cl_2) 306 (3.89), 418 (5.44), 517 (4.09), 552 (3.78), 594 (3.51), 651 (3.61); ES$^+$-MS ($CHCl_3$/MeOH) m/z 730.80 ([M + H]$^+$). Anal. Calcd for $C_{41}H_{40}N_5I$ (729.70): C, 67.49; H, 5.53; N, 9.60. Found: C, 67.41; H, 5.53; N, 9.44.

5,15-Dihexyl-10-(4-iodophenyl)-20-(pyrid-4-yl)-21*H*,23*H*-porphine (14d) was obtained in 5% yield, after purification by two recrystallizations from a $CHCl_3$ solution by layered addition of MeOH, reacting **12d** (230 mg, 1 mmol) with 4-iodobenzaldehyde[32] (232 mg, 1 mmol) and 4-pyridinecarbaldehyde (96 μL, 1 mmol), according to the general procedure: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ −2.75 (br s, 2H, NH), 0.91 (t, J = 7.3, 6H, $-CH_3$), 1.36 (m, 4H, $-CH_2CH_2CH_2CH_2CH_2CH_3$), 1.49 (m, 4H, $-CH_2CH_2CH_2CH_2CH_2CH_3$), 1.78 (m, 4H, $-CH_2$-$CH_2CH_2CH_2CH_2CH_3$), 2.49 (m, 4H, $-CH_2CH_2CH_2CH_2CH_2$-CH_3), 4.94 (t, J = 8.0, 4H, $-CH_2CH_2CH_2CH_2CH_2CH_3$), 7.92 and 8.09 (AA′XX′, J_{AX} = 8.1, 4H, $-C_6H_4I$), 8.14 and 9.03

(32) Paciorek, K. J. L.; Masuda, S. R.; Shih, J. G.; Nakahara, J. H. *J. Fluorine Chem.* **1991**, *53*, 233−248.

(AA′XX′, J_{AX} = 5.9, 4H, $-C_6H_4N$), 8.79 and 9.45 (2 × d, J = 4.8, 4H, β-H on porphine), 8.84 and 9.43 (2 × d, J = 4.8, 4H, β-H on porphine); UV/vis (CH_2Cl_2) 304 (3.93), 418 (5.32), 516 (3.99), 552 (3.73), 594 (3.49), 651 3.56); ES$^+$-MS ($CHCl_3$/MeOH) m/z 758.79 ([M + H]$^+$). Anal. Calcd for $C_{43}H_{44}N_5I$ (757.75): C, 68.16; H, 5.85; N, 9.24. Found: C, 68.03; H, 5.98; N, 9.13.

5,15-Diheptyl-10-(4-iodophenyl)-20-(pyrid-4-yl)-21*H*,23*H*-porphine (14e) was obained in 3% yield, after purification by two recrystallizations from a $CHCl_3$ solution by layered addition of MeOH, reacting **12e** (244 mg, 1 mmol) with 4-iodobenzaldehyde[32](232 mg, 1 mmol) and 4-pyridinecarbaldehyde (96 μL, 1 mmol), according to the general procedure: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ −2.76 (br s, 2H, NH), 0.89 (t, J = 7.3, 6H, $-CH_3$),1.31 (m, 8H, $-CH_2CH_2CH_2CH_2CH_2CH_2$-$CH_3$), 1.49 (m, 4H, $-CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 1.75 (m, 4H, $-CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 2.48 (m, 4H, $-CH_2CH_2$-$CH_2CH_2CH_2CH_2CH_3$), 4.92 (t, J = 7.7, 4H, $-CH_2CH_2CH_2CH_2$-$CH_2CH_2CH_3$), 7.90 and 8.08 (AA′XX′, J_{AX} = 8.4, 4H, $-C_6H_4I$), 8.12 and 9.02 (AA′XX′, J_{AX} = 5.5, 4H, $-C_6H_4N$), 8.78 and 9.43 (2 × d, J = 4.8, 4H, β-H on porphine), 8.83 and 9.41 (2 × d, J = 4.8, 4H, β-H on porphine); UV/vis (CH_2Cl_2) 302 (4.06), 418 (5.41), 517 (4.09), 552 (3.83), 594 (3.59), 651 (3.66); ES$^+$-MS ($CHCl_3$/HCOOH) m/z 786.77 ([M + H]$^+$), 393.89 ([M + 2H]$^{2+}$). Anal. Calcd for $C_{45}H_{48}N_5I$ (785.81): C, 68.78; H, 6.16; N, 8.91. Found: C, 68.65; H, 6.03; N, 9.07.

5,15-Diphenyl-10-(4-iodophenyl)-20-(pyrid-4-yl)-21*H*,23*H*-porphine (14f). To a degassed solution of *meso*-phenyl-2,2′-dipyrrylmethane[11] (**12f**) (111 mg, 0.5 mmol) in CH_2Cl_2/EtOH 95:5 (50 mL) were successively added 4-iodobenzaldehyde[32] (116 mg, 0.5 mmol), TFA (1.27 mmol), and 4-pyridinecarboxaldehyde (48 μL, 0.5 mmol). The solution was protected from light and stirred under argon at 20 °C for 24 h. Then DDQ (170 mg, 0.75 mmol, dissolved in minimal amount of THF) was added, and the stirring was continued for additional 2 h. The reaction mixture was filtered through an alumina and silica gel pad and washed with $CHCl_3$ until the filtrate was colorless. The solvent was removed under reduced pressure, and the crude product was purified by FC (CH_2Cl_2, then CH_2Cl_2/EtOAc 1/1, then EtOAc). The first fraction was 5,15-diphenyl-10,20-bis(4-iodophenyl)-21*H*,23*H*-porphine, the second the desired porphyrin **14f,** and the third 5,15-diphenyl-10,20-bis(pyrid-4-yl)-21*H*,23*H*-porphine. The solids obtained were washed with methanol and hexane and dried. Porphyrin **14f** was obtained in 6% yield: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ −2.84 (br s, 2H, NH), 7.73−7.79 (m, 6H, m-, *p*-phenyl), 8.19−8.21 (m, 4H, *o*-phenyl), 7.94 and 8.09 (AA′XX′, J_{AX} = 8.1, 4H, $-C_6H_4-I$), 8.16 and 9.02 (AA′XX′, J_{AX} = 5.9, 4H, $-C_6H_4N$), 8.79 and 8.89 (2 × d, J = 4.8, 4H, β-H on porphine), 8.84 and 8.87 (2 × d, J = 4.8, 4H, β-H on porphine); UV−vis (CH_2Cl_2) 417 (5.49), 514 (4.09), 549 (3.69), 589 (3.56), 644 (3.39); ES$^+$-MS ($CHCl_3$/MeOH) m/z 742.61 ([M + H]$^+$). Anal. Calcd for $C_{43}H_{28}N_5I$ (741.63): C, 69.64; H, 3.80; N, 9.44. Found: C, 69.33; H, 3.97; N, 9.46.

5,5′,5″-[1,3,5-Benzenetriyltris(2,1-ethynediyl)]tris[10,20-diheptyl-15-(pyrid-4-yl)-21*H*,23*H*-porphine] (18). The protected porphyrin **13** (5 mg, 7.35 μmol), 1,3,5-triiodobenzene[19] (**15**) (0.866 mg, 1.9 μmol), and K_2CO_3 (2.3 mg, 16.8 μmol) were dissolved in THF (3 mL). The solution was degassed by bubbling argon for 30 min, and then piperidine (0.2 mL), methanol (0.2 mL), and $Pd(PPh_3)_4$ (1 mg) were added. The mixture was flushed with argon for an additional 10 min and then heated at 70 °C for 23 h. The solvents were removed under reduced pressure, and the crude product was purified by FC (CH_2Cl_2/Et_3N 97:3, then $CHCl_3$, then $CHCl_3$/EtOH 97:3) to yield 2.50 mg (72%) of **18**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ −3.29 (br s, 6H, NH), 0.90 (t, J = 6.8, 18H, $-CH_3$), 1.33 (m, 24H, $-CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 1.45 (m, 12H, $-CH_2CH_2$-$CH_2CH_2CH_2CH_2CH_3$), 1.66 (m, 12H, $-CH_2CH_2CH_2CH_2CH_2$-$CH_2CH_2CH_3$), 2.28 (m, 12H, $-CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 4.11 (t, J = 7.7, 12H, $-CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 8.05 and 8.99 (AA′XX′, 2 × d, J_{AX} = 5.0, 12H, $-C_6H_4N$), 8.96 (s, 3H, benzenetriyl), 8.53 and 9.07 (2 × d, J = 5.0, 12H, β-H on porphine), 8.93 and 9.85 (2 × d, J = 4.5, 12H, β-H on porphine); UV/vis (CH_2Cl_2) 301 (4.63), 440 (5.78), 534 (4.39), 581 (4.91), 676 (4.70); ES$^+$-MS (THF/HCOOH) m/z 632.77 ([M + 3H]$^{3+}$), 948.77 ([M + 2H]$^{2+}$) (calcd average mass for $C_{129}H_{135}N_{15}$ 1895.58).

5,5′,5″-[1,3,5-Benzenetriyltris(2,1-ethynediyl-4,1-phenylene)]tris[10,20-dipropyl-15-(pyrid-4-yl)-21*H*,23*H*-porphine] (19a). Air was removed from a solution of **14a** (33.7 mg, 50 μmol) and 1,3,5-triethynylbenzene[8,21] (**16**) (1.87 mg, 12.44 μmol) in 10 mL of DMF/Et_3N (5:1) by blowing argon for 1 h. Then, Pd_2dba_3 (2.54 mg, 2.78 μmol) and $AsPh_3$ (6.86 mg, 22.4 μmol) were added, and deaeration was continued 10 min, before the solution was heated at 35 °C for 5 h. Then, the same amounts of catalyst were added again, and stirring was continued for an additional 2 h. The solvent was removed under reduced pressure, and the crude product was purified by FC (CH_2Cl_2) to yield 13.6 mg (40%) of the unreacted porphyrin **14a** (13.6 mg, 40%) and 2.2 mg (10%) of the expected trimer **19a**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ −2.71 (br s, 6H, NH), 1.33 (t, J = 7.3, 18H, $-CH_3$), 2.57 (m, 12H, $-CH_2CH_2$-CH_3), 4.98 (t, J = 7.7, 12H, $-CH_2CH_2CH_3$), 8.06 and 8.28 (AA′XX′, J_{AX} = 8.1, 12H, $-C_6H_4-$), 8.11 (s, 3H, benzenetriyl), 8.15 and 8.98 (AA′XX′, J_{AX} = 5.1, 12H, $-C_6H_4N$), 8.81 and 9.49 (2 × d, J = 4.8, 12H, β-H on porphine), 8.95 and 9.50 (2 × d, J = 4.8, 12H, β-H on porphine); UV/vis (CH_2Cl_2) 296 (4.93), 422 (5.91), 516 (4.66), 552 (4.45), 593 (4.20), 651 (4.28); ES$^+$-MS (THF/HCOOH) m/z 596.77 ([M + 3H]$^{3+}$), 894.58 ([M + 2H]$^{2+}$) (calcd average mass for $C_{123}H_{99}N_{15}$ 1787.24).

5,5′,5″-[1,3,5-Benzenetriyltris(2,1-ethynediyl-4,1-phenylene)]tris[10,20-dibutyl-15-(pyrid-4-yl)-21*H*,23*H*-porphine] (19b). Reaction, as described for **19a**, of **14b** (35.1 mg, 50 μmol) with **16** (1.85 mg, 12.35 μmol) in the presence of Pd_2dba_3 (2.54 mg, 2.78 μmol) and $AsPh_3$ (6.81 mg, 22.24 μmol) for 4 h, and additional 15 h, with subsequent purification by FC (CH_2Cl_2), afforded 18.1 mg (52%) of the unreacted porphyrin **14b** and 2.0 mg (9%) of the expected trimer **19b**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ −2.69 (br s, 6H, NH), 1.28 (t, J = 7.3, 18H, $-CH_3$), 1.81 (m, 12H, $-CH_2CH_2CH_2CH_3$), 2.52 (m, 12H, $-CH_2CH_2$-CH_2CH_3), 4.99 (t, J = 7.7, 12H, $-CH_2CH_2CH_2CH_3$), 8.06 and 8.28 (AA′XX′, J_{AX} = 8.1, 12H, $-C_6H_4-$), 8.11 (s, 3H, benzenetriyl), 8.16 and 9.04 (AA′XX′, J_{AX} = 5.9, 12H, $-C_6H_4N$), 8.82 and 9.48 (2 × d, J = 4.8, 12H, β-H on porphine), 8.95 and 9.49 (2 × d, J = 4.8, 12H, β-H on porphine); UV/vis (CH_2Cl_2) 297 (4.86), 423 (5.95), 517 (4.57), 553 (4.30), 595 (3.77), 652 (4.05); ES$^+$-MS (THF/HCOOH) m/z 624.80 ([M + 3H]$^{3+}$), 936.73 ([M + 2H]$^{2+}$) (calcd average mass for $C_{129}H_{111}N_{15}$ 1871.40).

5,5′,5″-[1,3,5-Benzenetriyltris(2,1-ethynediyl-4,1-phenylene)]tris[10,20-dipentyl-15-(pyrid-4-yl)-21*H*,23*H*-porphine] (19c). Air was removed from a solution of **14c** (36.5 mg, 50 μmol) and 1,3,5-triethynylbenzene[8,21] (**16**) (1.88 mg, 12.52 μmol) in 10 mL of DMF/Et_3N (5:1) by blowing argon for 1 h. Then, Pd_2dba_3 (2.58 mg, 2.82 μmol) and $AsPh_3$ (6.90 mg, 22.54 μmol) were added, and deaeration was continued 10 min before the mixture was heated at 35 °C for 4 h. The solvent was removed under reduced pressure, and the crude product was purified by FC (CH_2Cl_2), to yield 12.2 mg (50%) of **19c**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ −2.71 (br s, 6H, NH), 0.96 (t, J = 7.3, 18H, $-CH_3$), 1.52 (m, 12H, $-CH_2CH_2CH_2CH_2CH_3$), 1.76 (m, 12H, $-CH_2CH_2CH_2CH_2CH_3$), 2.51 (m, 12H, $-CH_2CH_2CH_2$-CH_2CH_3), 4.93 (t, J = 7.3, 12H, $-CH_2CH_2CH_2CH_2CH_3$), 8.05 and 8.26 (AA′XX′, J_{AX} = 8.4, 12H, $-C_6H_4-$), 8.13 and 9.02 (AA′XX′, J_{AX} = 5.8, 12H, $-C_6H_4N$), 8.11 (s, 3H, benzenetriyl), 8.79 and 9.44 (2 × d, J = 4.8, 12H, β-H on porphine), 8.93 and 9.45 (2 × d, J = 4.8, 12H, β-H on porphine); UV/vis (CH_2Cl_2) 297 (4.89), 423 (5.93), 517 (4.64), 553 (4.43), 595 (4.12), 652 (4.25); ES$^+$-MS (THF/HCOOH) m/z 652.87 ([M + 3H]$^{3+}$), 978.76 ([M + 2H]$^{2+}$). Anal. Calcd for $C_{135}H_{123}N_{15}$ (1955.55): C, 82.92; H, 6.34; N, 10.74. Found: C, 82.44; H, 6.52; N, 10.43

5,5′,5″-[1,3,5-Benzenetriyltris(2,1-ethynediyl-4,1-phenylene)]tris[10,20-dihexyl-15-(pyrid-4-yl)-21*H*,23*H*-porphine] (19d). Reaction of **14d** (37.9 mg, 50 μmol) with **16** (1.85 mg, 12.32 μmol), as described for **19c**, afforded 12.6 mg (50%) of **19d**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ −2.70 (br s, 6H, NH), 0.92 (t, J = 7.3, 18H, $-CH_3$), 1.37 (m, 12H, $-CH_2CH_2CH_2$-$CH_2CH_2CH_3$), 1.49 (m, 12H, $-CH_2CH_2CH_2CH_2CH_2CH_3$), 1.78 (m, 12H, $-CH_2CH_2CH_2CH_2CH_2CH_3$), 2.51 (m, 12H, $-CH_2CH_2$-$CH_2CH_2CH_2CH_2CH_3$), 4.95 (t, J = 7.7, 12H, $-CH_2CH_2CH_2CH_2CH_2$

$-CH_3$), 8.05 and 8.27 (AA′XX′, J_{AX} = 8.4, 12H, $-C_6H_4-$), 8.14 and 9.03 (AA′XX′, J_{AX} = 6.2, 12H, $-C_6H_4N$), 8.11 (s, 3H, benzenetriyl), 8.80 and 9.45 (2 × d, J = 4.8, 12H, β-H on porphine), 8.93 and 9.46 (2 × d, J = 4.8, 12H, β-H on porphine); UV/vis (CH_2Cl_2) 297 (4.80), 423 (5.91), 517 (4.55), 553 (4.31), 595 (3.87), 652 (4.11); ES$^+$MS (THF/HCOOH) m/z 680.93 ([M + 3H]$^{3+}$), 1020.90 ([M + 2H]$^{2+}$) (calcd average mass for $C_{141}H_{135}N_{15}$ 2039.72).

5,5′,5″-[1,3,5-Benzenetriyltris(2,1-ethynediyl-4,1-phenylene)]tris[10,20-diheptyl-15-(pyrid-4-yl)-*21H*,*23H*-porphine] (19e). Reaction of **14e** (39.3 mg, 50 μmol) with **16** (1.88 mg, 12.54 μmol), as described for **19c**, afforded 13.5 mg (51%) of **19e**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ −2.70 (br s, 6H, NH), 0.89 (t, J = 7.3, 18H, $-CH_3$), 1.33 (m, 24H, $-CH_2CH_2CH_2$-$CH_2CH_2CH_2CH_3$), 1.51 (m, 12H, $-CH_2CH_2CH_2CH_2CH_2CH_2$-$CH_3$), 1.79 (m, 12H, $-CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 2.52 (m, 12H, $-CH_2CH_2CH_2CH_2CH_2CH_2-CH_3$), 4.97 (t, J = 7.7, 12H, -$CH_2CH_2CH_2CH_2CH_2CH_3$), 8.06 and 8.28 (AA′XX′, J_{AX} = 8.1, 12H, $-C_6H_4$-), 8.15 and 9.03 (AA′XX′, J_{AX} = 5.5, 12H, $-C_6H_4N$), 8.11 (s, 3H, benzenetriyl), 8.81 and 9.47 (2 × d, J = 4.8, 12H, β-H on porphine), 8.95 and 9.48 (2 × d, J = 4.8, 12H, β-H on porphine); UV/vis (CH_2Cl_2) 296 (4.92), 423 (5.96), 517 (4.64), 553 (4.42), 595 (4.05), 652 (4.22); ES$^+$-MS (THF/HCOOH) m/z 708.99 ([M + 3H]$^{3+}$), 1062.94 ([M + 2H]$^{2+}$) (calcd average mass for $C_{147}H_{147}N_{15}$ 2123.88).

5,5′,5″-[1,3,5-Benzenetriyltris(2,1-ethynediyl-4,1-phenylene)]tris[10,20-diphenyl-15-(pyrid-4-yl)-21*H*,23*H*-porphine] (19f). Reaction of **14f** (29.3 mg, 39.5 μmol) with **16** (1.48 mg, 9.87 μmol) in the presence of Pd_2dba_3 (1.98 mg, 2.16 μmol) and $AsPh_3$ (5.3 mg, 17.3 μmol), as described for **19c**, afforded 8.8 mg (46%) of **19f**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ −2.79 (br s, 6H, NH), 7.75−7.83 (m, 18H, m-, p−C_6H_5), 8.21−8.24 (m, 12H; o−C_6H_5), 8.02 and 8.28 (AA′XX′, J_{AX} = 8.5, 12H, $-C_6H_4$-), 8.17 and 9.02 (AA′XX′, J_{AX} = 5.9, 12H, $-C_6H_4N$), 8.04 (s, 3H, benzenetriyl), 8.80 and 8.90 (2 × d, J = 4.8, 12H, β-H on porphine), 8.92 (apparent s, 12H, β-H on porphine); UV/vis (CH_2Cl_2) 286 (5.03), 419 (5.99), 515 (4.68), 550 (4.41), 589 (4.22), 646 (4.11); ES$^+$-MS (THF/HCOOH) m/z 664.77 ([M + 3H]$^{3+}$), 996.62 ([M + 2H]$^{2+}$) (calcd average mass for $C_{141}H_{87}N_{15}$ 1991.34). Anal. Calcd for $C_{141}H_{87}N_{15}$ (1991.34): C, 85.05; H, 4.40; N, 10.55. Found: C, 80.13; H, 4.79; N, 9.97.

5,5′,5″-[1,3,5-Benzenetriyltris(2,1-ethynediyl-4,1-phenylene-2,1-ethynediyl-4,1-phenylene-2,1-ethynediyl-1,4-phenylene)]tris[10,20-diphenyl-15-(pyrid-4-yl)-21*H*,23*H*-porphine] (20). Reaction of **14c** (14.3 mg, 19.6 μmol) with **17**[8] (3.7 mg, 4.9 μmol) in the presence of Pd_2dba_3 (1.0 mg, 1.1 μmol) and $AsPh_3$ (2.7 mg, 8.82 μmol), as described for **19c**, afforded 5.2 mg (42%) of **20**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ −2.71 (br s, 6H, NH), 0.96 (t, J = 7.3, 18H, $-CH_3$), 1.50−1.55 (m, 12H, $-CH_2CH_2CH_2CH_2CH_3$), 1.77 (m, 12H, $-CH_2CH_2CH_2CH_2CH_3$), 2.52 (m, 12H, $-CH_2CH_2CH_2CH_2CH_3$), 4.97 (t, J = 7.0, 12H, $-CH_2CH_2CH_2CH_2CH_3$), 7.58 and 7.60 (AA′BB′, J_{AB} = 8.6, 12H), 7.64 and 7.71 (AA′XX′, J_{AX} = 8.3, 12H), 7.72 (s, 3H, benzenetriyl) 7.96 and 8.21 (AA′XX′, J_{AX} = 8.0, 12H) 8.15 and 9.03 (AA′XX′, J_{AX} = 5.8, 12H, $-C_6H_4N$), 8.81 and 9.45 (2 × d, J = 4.8, 12H, β-H on porphine), 8.89 and 9.47 (2 × d, J = 4.8, 12H, β-H on porphine); UV/vis (CH_2Cl_2) 361 (5.25), 421 (5.94), 517 (4.56), 553 (4.34), 595 (3.93), 651 (4.13); ES$^+$-MS (THF/HCOOH) m/z 853.08 ([M + 3H]$^{3+}$), 1278.94 ([M + 2H]$^{2+}$) (calcd average mass for $C_{183}H_{147}N_{15}$ 2556.27).

5,5′,5″-[[2,4,6-Tris[(trimethylsilyl)ethynyl]-1,3,5-benzenetriyl]tris(2,1-ethynediyl-4,1-phenylene)]tris[10,20-diphenyl-15-(pyrid-4-yl)-21*H*,23*H*-porphine] (22a). Air was removed from a solution of 5,15-diphenyl-10-(4-iodophenyl)-20-(pyrid-4-yl)-21*H*,23*H*-porphine (**14f**) (22.2 mg, 30 μmol) and [(2,4,6-triethynyl-1,3,5-benzenetriyl)tri-2,1-ethynediyl]tris(trimehylsilane) (**21**)[22] (2.19 mg, 5.0 μmol) in 6.5 mL of DMF/Et_3N (5:1) by blowing argon for 30 min. Then, Pd_2dba_3 (1.37 mg, 1.5 μmol) and $AsPh_3$ (3.7 mg, 12 μmol) were added, and deaeration was continued for 10 min before the mixture was heated at 40 °C for 6 h. The solvent was removed under reduced pressure, and the crude product was purified by two successive FC ($CHCl_3$/MeOH: gradient from 100:0 to 98:2), to yield 4.2 mg (37%) of **22a**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ −2.79 (s, 6 H, NH), 0.51 (s, 27 H, $SiMe_3$), 7.74−7.83 (m, 18 H, phenyl *m*- and *p*-H), 8.08 and 8.30 (AA′XX′, J_{AX} = 8.2 Hz, 12 H, phenylene H), 8.18 and 9.04 (AA′XX′, J_{AX}=5.9 Hz, 12 H, pyridine H), 8.20−8.24 (m, 12 H, phenyl *o*-H), 8.81 and 8.91 (2 × d, J = 4.5 Hz, 12 H, β-H on porphine outside), 8.93 (s, 12 H, β-H on porphine inside); UV/vis (CH_2Cl_2) 352 (4.69), 420 (5.85), 515 (4.49), 551 (4.15), 590 (3.81), 646 (3.67); ES$^+$-MS (THF/HCOOH) m/z 1140.8 ([M + 2H]$^{2+}$), 760.9 ([M + 3H]$^{3+}$) (calcd average mass for $C_{156}H_{111}N_{15}Si_3$ 2279.95).

5,5′,5″-[(2,4,6-Triethynyl-1,3,5-benzenetriyl)tris(2,1-ethynediyl-4,1-phenylene)]tris[10,20-diphenyl-15-(pyrid-4-yl)-21*H*,23*H*-porphine] (22b). To a solution of **22a** (4.2 mg, 1.84 μmol) in THF (4.8 mL) was added aqueous NaOH (1 M, 2.4 mL), and the mixture was stirred vigorously at 20 °C for 4 h. After evaporation of the THF, CH_2Cl_2 was added. The organic layer was separated, washed with water, and dried ($MgSO_4$). The residue obtained after removal of the solvent was washed thoroughly with MeOH and then with pentane, yielding 2.8 mg (73%) of **22b**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ −2.79 (s, 6 H, NH), 4.09 (s, 3 H, C≡CH), 7.74−7.83 (m, 18 H, phenyl *m*- and *p*-H), 8.12 and 8.30 (AA′XX′, J_{AX} = 8.2 Hz, 12 H, phenylene H), 8.18 and 9.03 (AA′XX′, J_{AX} = 5.0 Hz, 12 H, pyridine H), 8.20−8.24 (m, 12 H, phenyl *o*-H), 8.81 and 8.91 (2 × d, J = 4.6 Hz, 12 H, β-H on porphine outside), 8.92 (s, 12 H, β-H on porphine inside); UV/vis (CH_2Cl_2) 349 (5.00), 420 (5.90), 515 (4.75), 551 (4.55), 590 (4.38), 646 (4.28); MALDI-MS (dithranol) m/z 2063.3 (M$^+$) (calcd average mass for $C_{147}H_{87}N_{15}$ 2063.40).

5,5′,5″,5‴,5⁗,5⁗′-[1,2,3,4,5,6-Benzenehexaylhexakis-(2,1-ethynediyl-4,1-phenylene)]hexakis[10,20-diphenyl-15-(pyrid-4-yl)]-21*H*,23*H*-porphine (23). Air was removed from a solution of **14f** (10.1 mg, 13.6 μmol) and **22b** (2.8 mg, 1.36 μmol) in 7.7 mL of DMF/Et_3N (5:1) by blowing argon for 45 min. Then, Pd_2dba_3 (0.37 mg, 0.40 μmol) and $AsPh_3$ (1.0 mg, 3.26 μmol) were added, and deaeration was continued for 10 min, before the mixture was heated at 40 °C for 5 h. Then, the same amounts of Pd_2dba_3 and $AsPh_3$ were added again, and stirring was continued for 2 h. The solvent was removed under reduced pressure, and the crude product was purified by two successive FC ($CHCl_3$/MeOH: gradient from 100:0 to 97:3), to yield 0.74 mg (14%) of **23**: ^{1}H NMR (360.14 MHz, $CDCl_3$) δ −2.92 (s, 12 H, NH), 7.41 (m, 24 H, 10,20-phenyl *m*-H), 7.48 (m, 12 H, 10,20-phenyl *p*-H), 7.91 (m, 24 H, 10,-20-phenyl *o*-H), 8.08 and 8.97 (AA′XX′, J_{AX} = 4.5 Hz, 24 H, pyridine H), 8.40 and 8.45 (AA′XX′, J_{AX} = 8.2 Hz, 24 H, 5-phenylene H), 8.68 (d, J = 4.9 Hz, 12 H, H-2 and H-8), 8.70 (d, J = 4.9 Hz, 12 H, H-12 and H-18), 8.74 (d, J = 4.9 Hz, 12 H, H-13 and H-17), 8.92 (d, J = 4.9 Hz, 12 H, H-3 and H-7); UV/vis (CH_2Cl_2) 420 (6.08), 515 (4.85), 551 (4.58), 590 (4.49), 646 (4.23); ES$^+$-MS (THF/HCOOH) m/z 1302.5 ([M + 3H]$^{3+}$), 977.1 ([M + 4H]$^{4+}$) (calcd average mass for $C_{276}H_{168}N_{30}$ 3904.56).

Complex between Host Macrocycle 1d and Guest Trimer 19e. The complex formation was monitored by ^{1}H NMR spectroscopy. To a $CDCl_3$ solution of host macrocycle **1d** was added gradually 1 equiv of guest trimer **19e** (in concentrated $CDCl_3$ solution), a proton spectrum being registered each time. The integration indicates that a new species was formed with a 1:1 ratio between guest and host. The chemical shifts of the protons corresponding to the guest porphyrin are upfield shifted due to the ring current of the three zinc porphyrins of the host macrocycle. ^{1}H NMR (500.13 MHz, $CDCl_3$) assignments established with COSY and NOE experiments: δ −3.15 (br s, 6H, NH), 0.88 (m, 18H, $-CH_3$), 1.25 (m, 24H, $-CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 1.38 (m, 12H, $-CH_2CH_2$-$CH_2CH_2CH_2CH_2CH_3$), 1.47 (s, 54H, *t*-Bu), 1.61 (m, 12H, $-CH_2$-$CH_2CH_2CH_2CH_2CH_2CH_3$), 1.74 (s, 36H, *o*-CH_3 on Ni-porphine) 1.99 (s, 36H, *o*-CH_3 on Zn-porphine), 2.30 (m, 12H, $-CH_2CH_2$-$CH_2CH_2CH_2CH_2CH_3$), 2.52 (s, 18H, *p*-CH_3 on Ni-porphine), 2.68 (s, 18H, *p*-CH_3 on Zn-porphine), 2.92 and 6.35 (2 × apparent d, J = 5.7, 12H, $-C_6H_4N$), 4.76 (m, 12H, $-CH_2CH_2$-$CH_2CH_2CH_2CH_2CH_3$), 7.15 (s, 12H, *m*-H on Ni-porphine), 7.35 (s, 12H, *m*-H on Zn-porphine), 7.40 and 9.04 (2 × d, J = 4.5, 12H, β-H on trimer porphine), 7.69 (app. s, 6H), 7.75 (app. s, 6H), 7.77 (app. s, 6H), 7.84 and 8.02 (AA′XX′, J_{AX} = 8.0, 24H, phenylene on Ni porphine), 7.90 and 8.08 (AA′XX′, J_{AX} = 8.0,

12H, phenylene on trimer porphine), 7.96 (s, 3H, benzenetriyl) 7.98 and 8.37 (AA′XX′, J_{AX} = 6.9, 24H, phenylene on Zn porphine), 8.56 and 8.66 (2 × d, J = 4.8, 24H, β-H on Ni porphine), 8.75 and 9.29 (2 × d, J = 4.5, 12H, β-H on trimer porphine), 8.86 and 8.98 (2 × d, J = 4.5, 24H, β-H on Zn porphine); MALDI-TOF-MS (dithranol) m/z 7746.7 (complex **1d** + **19e**) (calcd average mass for $C_{531}H_{447}N_{39}Ni_3Zn_3$ 7746.87), 5622.6 (host **1d**), 2123.0 (guest **19e**).

Complex between host macrocycle 1d and guest trimer 18 was obtained as described previously for the complex **1d** + **19e**: ^{1}H NMR (500.13 MHz, $CDCl_3$) assignments established with COSY and NOE experiments δ −2.74 (br s, 6H, NH), 0.74 (m, 18H, $-CH_3$), 1.17 (m, 24H, $-CH_2CH_2CH_2$-$CH_2CH_2CH_2CH_3$), 1.34 (m, 12H, $-CH_2CH_2CH_2CH_2CH_2CH_2$-$CH_3$), 1.48 (s, 54H, *t*-Bu), 1.61 (m, 12H, $-CH_2CH_2CH_2CH_2CH_2CH_2$-$CH_2CH_2CH_3$), 1.81 (s, 36H, *o*-$CH_3$ on Ni-porphine) 1.95 (s, 36H, *o*-CH_3 on Zn-porphine), 2.27 (m, 12H, $-CH_2CH_2CH_2CH_2CH_2$-CH_2CH_3), 2.55 (s, 18H, *p*-CH_3 on Ni-porphine), 2.65 (s, 18H, *p*-CH_3 on Zn-porphine), 3.11 and 6.34 (2 × apparent d, J = 5.0, 12H, $-C_6H_4N$), 4.70 (m, 12H, $-CH_2CH_2CH_2CH_2CH_2CH_2$-$CH_3$), 7.20 (s, 12H, *m*-H on Ni-porphine), 7.32 (s, 12H, *m*-H on Zn-porphine), 7.38 and 8.95 (2 × d, J = 4.5, 12H, β-H on trimer porphine), 7.70 (app s, 6H), 7.73 (app s, 6H), 7.83 (app s, 6H), 7.86 and 8.01 (AA′XX′, J_{AX} = 8.2, 24H, phenylene on Ni porphine), 7.97 and 8.37 (AA′XX′, J_{AX} = 8.8, 24H, phenylene on Zn porphine), 8.60 and 8.72 (2 × d, J = 4.9, 24H, β-H on Ni porphine), 8.64 (s, 3H, benzenetriyl), 8.85 and 8.95 (2 × d, J = 4.5, 24H, β-H on Zn porphine), 9.40 and 9.84 (2 × d, J = 4.5, 12H, β-H on trimer porphine); MALDI-TOF-MS (dithranol) m/z 7519.1 (complex **1d** + **18**) (calcd average mass for $C_{513}H_{435}N_{39}Ni_3Zn_3$ 7518.57), 5622.8 (host **1d**), 1896.2 (guest **18**).

Complex between Host Macrocycle 1a and Guest Hexamer 23. To a $CDCl_3$ solution of macrocycle **1a** was added 1 equiv of star hexamer **23** ($CDCl_3$ solution): NMR (500.13 MHz) δ −3.53 (br s, 12H, NH), 1.46 (s, 54H, t-Bu), 1.87 (s, 72H, *o*-CH_3 on Zn-porphine), 2.63 (s, 36H, p-CH_3 on Zn-porphine), 2.74 and 6.20 (2 × apparent d, J = 6.3, 24H, $-C_6H_4N$), 7.20 (s, 24H, *m*-H on Zn-porphine), 7.21 and 8.25 (2 × d, J = 4.5, 24H, β-H on star porphine,), 7.42 (t, J = 7.3, 24H, *m*-phenyl, star porphine), 7.52 (t, J = 7.3, 12H, *p*-phenyl on star porphine,), 7.66 (app s, 6H), 7.71 (app s, 12H), 7.73 (m, 24H, *o*,*o*′-phenyl on star porphine), 7.85 and 8.26 (m, 48H, on Zn porphine), 8.10 and 8.21 (AA′XX′ J_{AX} = 8.0, 24H, on star porphine), 8.48 and 8.62 (2 × d, J = 4.5, 24H, β-H on star porphine), 8.77 and 8.87 (2 × d, J = 4.5, 48H, β-H on Zn porphine); MALDI-TOF-MS (ET-matrix DCTB) m/z 9547.3 (complex **1a** + **23**) (calcd average mass for $C_{660}H_{468}N_{54}Zn_6$ 9547.59), 5643.7 (host **1a**), 3905.9 (guest **23**).

Acknowledgment. This work was supported in part by the Swiss National Science Foundation (Project No. 2000-056881.99). NMR spectra on a Bruker Avance DRX 500 instrument were performed by F. Fehr, mass spectra by F. Nydegger and I. Müller. Some MALDI mass spectra were measured by Dr G. Baykut (Bruker, Bremen). MALDI-TOF mass spectra of complexes **1d** + **19e**, **1d** + **18,** and **1e** + **23** were measured by H.-U. Hediger (ETH Zürich).

Supporting Information Available: Copies of ^{1}H NMR for all new compounds, ^{13}C NMR for compound **3**, EI-MS, ESI-MS, MALDI-MS, MALDI-TOF, and UV−vis spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0015523