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One-Step Template-Directed Synthesis of a Macrocyclic Tetraarylporphyrin Hexamer Based on Supramolecular Interactions with a C_3-Symmetric Tetraarylporphyrin Trimer

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Abstract: Taking into consideration the model geometry of the macrocyclic hexaporphyrin **1** as a host molecule, the structure of a benzene-centered porphyrin trimer bearing pyridine rings at the apical positions has been designed with the aim to use the latter as a template for the synthesis of its own host. Indeed, in the presence of the porphyrin trimer **5**, the yield of the cyclization of a linear porphyrin hexamer, as a precursor of **1**, could be improved from 8 to 30% (variable yield) to 50% (reproducible yield). Even the condensation of equimolecular amounts of porphyrin monomers **20b** and **21b** in the presence of **5** led—probably through a loose preorganized complex between the latter and the Zn(II) chelate **20b**—to the formation of **1** in only five steps from **19**, as compared with 13 steps of the synthesis via linear porphyrin hexamer in the absence of template. As evidenced by ^{1}H NMR spectroscopic analysis of the supramolecular complex between **5** and an analogue of **1b** in which all H-atoms at the pyrrole rings have been replaced by deuterium, in the presence of unlabeled **1b**, a rapid dissociation and recombination of the host and guest molecules forming the supramolecular complex takes place even at low temperature (−40 °C). As at 55 °C all six Zn(II) porphyrinate rings of the complex **1b** + **5** become magnetically equivalent in the 500 MHz ^{1}H NMR time scale, approximate kinetic data for the ligand exchange process could be obtained.

Introduction

Control of molecular self-assembly to form supramolecular structures possessing characteristic functional properties is one of the primordial goals in modern preparative chemistry. Such kind of process, which is very common in molecular biology, has been until now rarely reproduced successfully in the laboratory. Thus, the synthesis of catalysts showing a specific substrate affinity[1] as well as the development of highly ordered networks using metal−ligand bonding,[2] hydrogen bonding,[3] and $\pi-\pi$ interactions[4] has been only recently exploited, thus opening new perspectives to the future development of chemistry.[5]

Characteristic for both a template[6] and a catalytic effect is a preorganization of the reacting molecules which reduces the entropy content of the transition state of the reaction. In contrast to a catalyst, however, a template possesses usually a higher affinity for the reaction product(s) than for the substrate, so that at least one equivalent of template has to be present in the reaction mixture in order to ensure the completion of the reaction. On the other hand, the interactions of a template with the substrate molecules are often more specific with respect to the geometry of the transition complex. Enzymes combine the advantages of a catalyst and a template in that they change their conformation after the transformation of the substrate into the product(s), thus diminishing the affinity of the latter for the enzyme.

Linstead's discovery that phthalocyanine synthesis takes place in the presence of metal ions[7] as well as Helberger's first synthesis of tetrabenzoporphyrin[8] belong to the earlier observed template effects in preparative organic chemistry. Even the role of metals in the biosynthesis of natural occurring tetrapyrrolic pigments was at that time a matter of speculation.[9] In the porphyrin series, Calvin and co-workers[10] reported in 1946 that the addition of zinc acetate to a reaction mixture of pyrrole and benzaldehyde doubled the yield from 4 to 5% to 10−11% of Rothemund's tetraphenylporphyrin synthesis.[11] Although at present *meso*-tetraarylporphyrins can be prepared in 30−40% yields without adding metal ions,[12] the favorable influence of

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metal ions, such as copper(I)[13] and cobalt(II),[14] on the synthesis of functionalized porphyrin derivatives, in general, is well documented in the literature.

More recently, the principle of ligand metal coordination has been extended by J. K. M. Sanders and co-workers[15] as well as in J. S. Lindsey's group[16] to the template syntheses of a series of macrocyclic porphyrin polymers (up to tetramers and hexamers, respectively) using the appropriate monomeric porphyrin metal chelates and pyridine-containing bi-, tri-, and tetradentate ligands as templates. In most cases, the template effect was determined by comparison of the yields obtained in absence and in the presence of the template, taking into account that cyclizations of linear precursors to yield macrocycles containing the same number of monomeric units are often promoted by the so-called "structure contribution",[16a] which is given by the yield of the cyclization obtained in the absence of template.

Template Synthesis of the Macrocyclic Porphyrin Hexamer 1. Within the scope of an ongoing research project on nanometer-sized polyporphyrin arrays, we reported not long ago the synthesis of a macrocyclic porphyrin hexamer (**1b**) by cyclization of the corresponding linear hexamer.[17] By this procedure, variable yields of the desired product between 8 and 30% were obtained. Later on, the synthesis of a supramolecular assembly between **1b** and a *niphaphyrin* (**2**)[18] composed of six 10-(pyridin-4-yl)porphyrin subunits attached to the C atoms of a benzene core through linkers consisting of collinear repetitive phenylethynyl units was achieved in our laboratory.[19] Owing to the high binding constant (3.5×10^9 mol^{-1}) of this complex, it became obvious to attempt a template synthesis of **1b** from the appropriate monomer in the presence of the above niphaphyrin. Unfortunately, however, no cyclic hexamer could be detected in the reaction mixture using the same conditions which served to cyclize the linear hexamer in absence of template.

At that point, a careful assessment of the molecular dimensions of both the final "host" molecule **1** and the most appropriate template was made using as segments (i) the diameter of the tetraphenylporphyrin molecule[20] and (ii) the distance between the C4 and C4′ atoms of tolane (9.65 Å)[21]—both known from X-ray diffraction studies—as well as (iii)

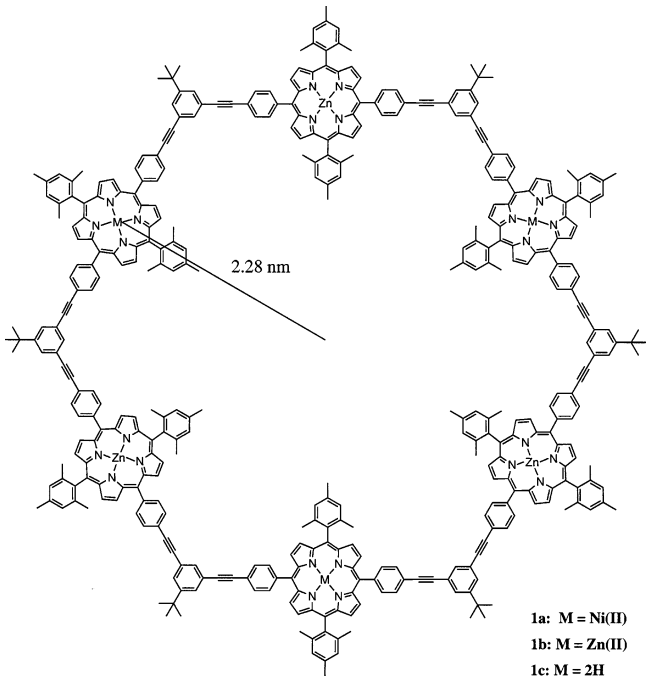

Figure 1. Different metal complexes of a toroid-like hexaporphyrin array with an internal diameter of the cavity of ca. 4.6 nm.

standard bond lengths for C−C bonds and the benzene ring. In the supramolecular complex, the length of the Zn−N(pyridine) bond is supposed to be 2.14 Å, corresponding to the value determined by X-ray diffraction analysis of pyridinato Zn(II) complexes of *meso*-substituted porphyrins.[22] Moreover, as the metal ion in porphyrin Zn(II) chelates can be pulled toward the ligand by about 0.33 Å on coordination with pyridine in an apical position,[22,23] this distance has to be added to the length of the Zn−N(pyridine) bond in order to estimate the distance between the N atom of the pyridine ring of the template, as the "guest", and the center of the plane of the porphyrin ring which complexes the Zn(II) ion in the host. The result from this estimate (2.47 Å) agrees with the corresponding distance (2.49 Å) in a tetrameric zinc porphyrin complex, as determined by X-ray diffraction analysis.[24] Thus, among the structurally related templates represented in Figure 2, templates **5** and **6**, with a radius of about 19 Å, should fit the best with the distance of 22.8 Å from the center of the cavity to the center of the porphyrin rings of **1** since 19 + 2.47 = 21.47 Å, whereas trimer **3** slightly exceeds the cavity dimensions (20.90 + 2.47 = 23.37 Å) and trimer **4** is too small to fit well inside the macrocycle (16.63 + 2.47 = 19.10 Å).

On the basis of the experience of other laboratories, pyridine rings were placed at the apical positions of the templates to provide the coordination sites for the central ions of the porphyrin rings of the macrocycle precursor. Accordingly, porphyrinato zinc(II) ligands were used owing to their property of forming stable five-coordinate 1:1 complexes with nitrogen-

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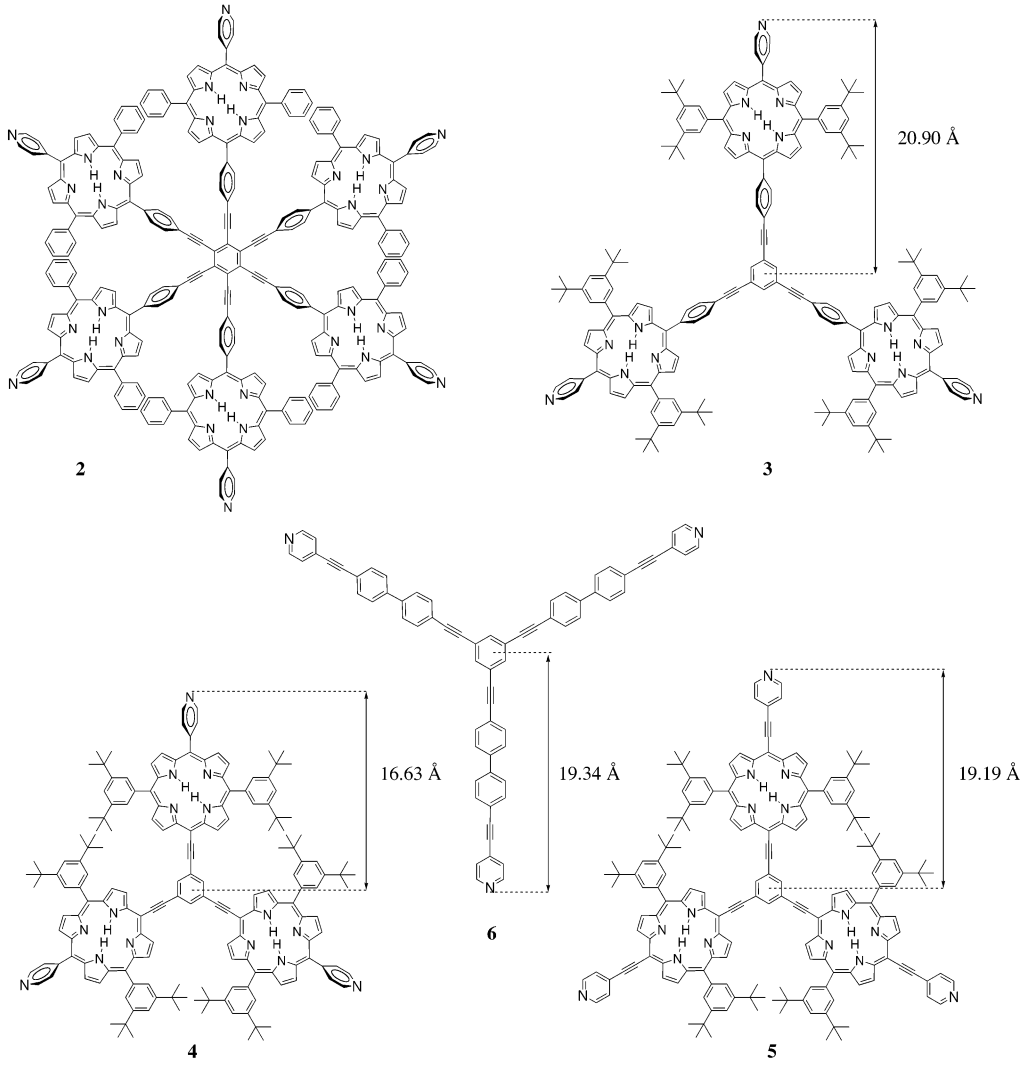

Figure 2. Ligands designed for the template-directed synthesis of macrocycles **1a**−**c**.

containing ligands. Other metal ions, such as Ru(II) and Mg(II), which also form five-coordinate complexes, seemed to be less appropriate. Actually, Ru(II) porphyrin complexes afford much more stable pyridine complexes than Zn(II), but they cannot be demetalated without destroying the porphyrin ring.[15g] Mg(II) complexes, on the other hand, which efficiently coordinate nitrogen-containing ligands,[25,26] are very sensitive to acids and are difficult to purify. Furthermore, using tridentate ligands as templates, no more than three (porphyrinato)zinc(II) rings can be ligated at once in the macrocycle precursor. Therefore, our first experiments were carried out with ligands in which Zn(II) porphyrin complexes alternate with their corresponding porphyrin free bases (e.g., **1c**) or with porphyrin Ni(II) complexes (e.g., **1a**), which coordinate nitrogen bases much less strongly than Zn(II).[27] In this way, the structure of the macrocycle precursor should be unequivocally predetermined before closing the macrocycle.

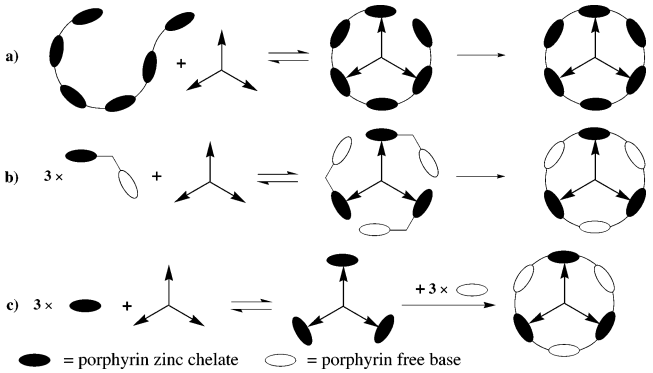

Figure 3. Different approaches to the template-directed synthesis of macrocycles **1**.

Strategies and Design. As tridentate ligands are used as templates, different strategies, three of them are represented in Figure 3, may be envisaged in order to carry out the template-directed synthesis of the macrocyclic hexamers **1**. The most obvious approach (Figure 3a) consists of the cyclization of the corresponding linear hexamers **23** (cf. Scheme 4) in the presence of the template, which by ligation to three (porphyrinato)zinc rings is supposed to hold the linear hexamer in a conformation favorable to the ring closure by intramolecular coupling, thus

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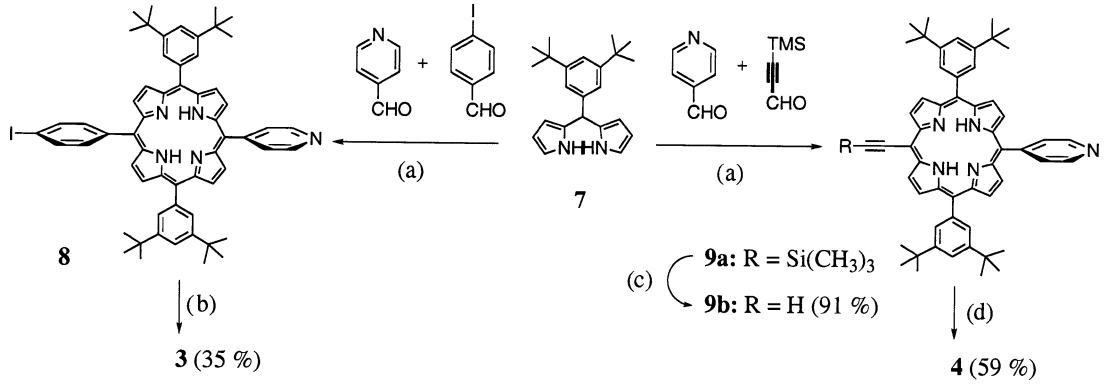
Scheme 1[a]



[a] Reagents and conditions: (a) TFA, CH_2Cl_2/EtOH (95:5), then DDQ; (b) 1,3,5-triethynylbenzene, in toluene/Et_3N (5:1), Pd_2dba_3/P(*o*-tol)$_3$, 35 °C; (c) CH_2Cl_2/Et_3N (1:1), TBAF, 25 °C; (d) same as (b) but with 1,3,5-triiodobenzene as reagent.

suppressing intermolecular reactions that presumably lead to chain-like products of high molecular weight. On the other hand, a more straightforward strategy consists in the coupling of three porphyrin rings (as free bases or Ni(II) chelates) with three (porphyrinato)zinc rings, which are held together in an appropriate arrangement by previous complexation with the template (Figure 3c). A modification of the latter approach is represented in Figure 3b, in which three identical angular building blocks, consisting of a (porphyrinato)zinc ring covalently bound to a porphyrin ring (as free base or Ni(II) chelate) through a *meta*-phenylene unit as cornerstone of the macrocycle, are linked together head-to-tail after coordination with the template. A further possibility of constructing the macrocycle, namely, a [3 + 3] coupling, was not taken into consideration because, using a tridentate ligand, two different complementary building blocks would be required.

Results and Discussion

Synthesis of the Templates. As a common starting material for the synthesis of templates **3**−**5**, dipyrrylmethane **7** was used, which was obtained in 82% yield through reaction of 3,5-di-*tert*-butylbenzaldehyde with excess pyrrole as described in the literature.[28,29] As usual, the *tert*-butyl substituents in the templates should prevent cofacial aggregation (i.e., $\pi-\pi$-stacking) of the porphyrin rings, thus improving the solubility of the corresponding polycyclic derivatives.

The benzene-centered trimers **3** and **4** were synthesized following procedures previously described[19] (cf. Scheme 1). As a precursor of **3**, porphyrin **8** was obtained in 6% yield by condensation of dipyrrylmethane **7** with an equimolecular mixture of 4-pyridinecarboxaldehyde and 4-iodobenzaldehyde,[30] in the presence of TFA, and subsequent oxidation with DDQ. As expected, the two corresponding symmetrically substituted porphyrins, [5,15-bis(3,5-di-*tert*-butylphenyl)-10,20-bis(4-iodophenyl)]porphine and [5,15-bis(3,5-di-*tert*-butylphenyl)-10,20-di(pyrid-4-yl)]porphine, were obtained as byproducts, which were separated by chromatography of the reaction mixture. Reaction of **8** with 1,3,5-triethynylbenzene[31,32] using the same conditions as those for the similar alkyl-substituted star-shaped trimers reported earlier[19] gave the expected trimer **3** in low yield (18%), probably due to the poor solubility of the starting porphyrin in DMF. Using toluene instead of DMF and the more active catalyst Pd[P(*o*-tol)$_3$]$_2$,[33] higher yields (35%) were obtained and no more attempts were made for optimizing the reaction, as the trimer **3** was a less efficient template for the synthesis of **1**.

Porphyrin **9a**, which was used as a building block for the synthesis of the smaller trimer **4**, was obtained under the same conditions as porphyrin **8** but after a shorter reaction time (5 instead of 12 h). Deprotection of **9a** with fluoride ions afforded porphyrin **9b** in high yield (91%), which was subsequently transformed into the trimer **4** (59%) by cross-coupling with triiodobenzene (cf. Scheme 1).

The synthetic pathway to the template molecule **5** is depicted in Scheme 2. Both the synthesis of 5,15-bisaryl-10,20-bisethynylporphyrins (such as **11**) and 5,10,15,20-tetraethynylporphyrins (which are known as chlorphyrins because of their green color)[34] deserve great interest due to their applications in the field of conjugated electronic materials with nonlinear optical properties.[35] Variable yields of these compounds are obtained by reacting propynals either with pyrrole itself[36,37] or with dipyrrylmethanes[29,36,38] (cf. **7** → **10**−**12**). Higher yields have been obtained by protection of the alkynal group with dicobalt octacarbonyl, prior to the porphyrin formation step, followed

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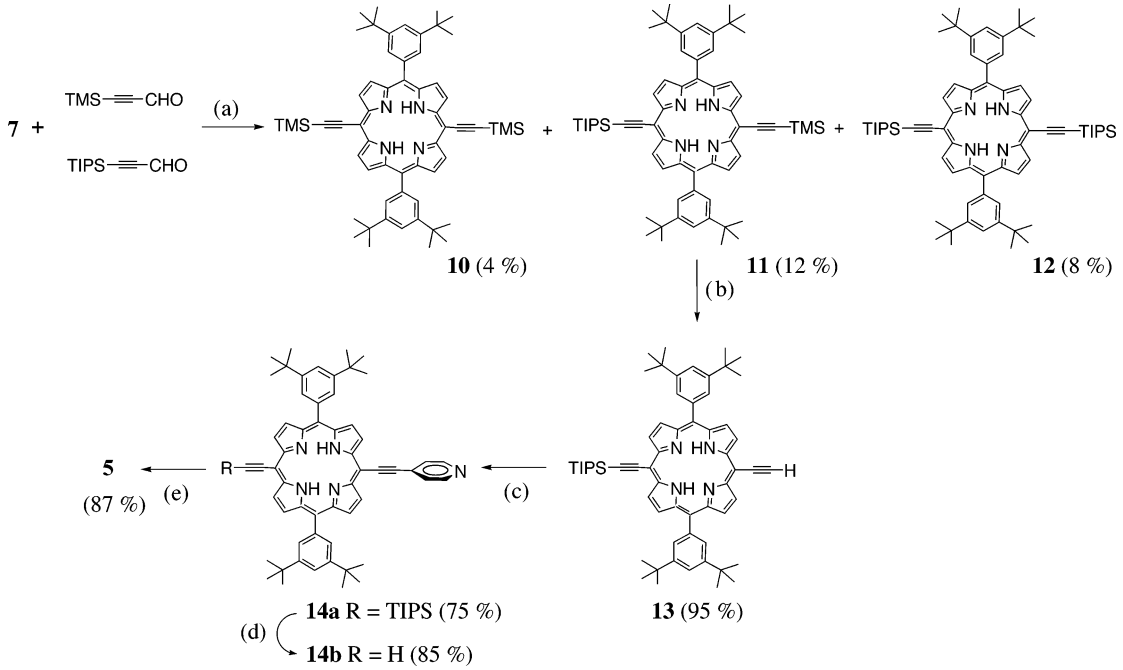
Scheme 2[a]



[a] Reagents and conditions: (a) TFA, $CHCl_3$/EtOH (95:5), 5 h, then DDQ; (b) NaOH (1 N), 2 h at 25 °C; (c) 4-iodopyridine in toluene/Et_3N (5:1), Pd_2dba_3/P(*o*-tol)$_3$, 60 °C; (d) CH_2Cl_2/Et_3N (1:1), TBAF; (e) 1,3,5-triiodobenzene in toluene/Et_3N (5:1), Pd_2dba_3/P(*o*-tol)$_3$, 35 °C.

by oxidative deprotection of the triple bond.[39] An alternative pathway is the coupling of *meso*-haloporphyrins with monosubstituted alkynes.[40,41] Thus, while this work was in progress, Plater et al.[42] reported the synthesis of **13** (as Zn chelate) *by* Sonogashira coupling of 5,15-dibromobis-10,20-(3,5-di-*tert*-butyl)porphine with trimethylsilylacetylene, subsequent deprotection of both ethynyl groups with fluoride ions, and selective reprotection of one ethynyl group with triisopropylsilyl chloride.

The procedure described in the present work afforded the desired porphyrin **11** in a one-pot, two-step reaction via mixed condensation of *meso*-(3,5-di-*tert*-butylphenyl)-2,2′-dipyrrylmethane (**7**) with 3-trimethylsilylprop-2-ynal[43] and 3-triisopropylsilylprop-2-ynal,[44] in the presence of trifluoroacetic acid, followed by oxidation of the porphyrinogen intermediate with DDQ (Scheme 2). As expected, the reaction mixture contained porphyrins **10** (4%) and **12** (8%) in addition to **11**, which was readily isolated by column chromatography as the main product (12%), despite the close resemblance of the two protecting groups (TMS and TIPS) used for the ethynyl functions. It is worth mentioning that no scrambling byproducts were detected, despite a long reaction time (5 h), though some side products resulting from acid-catalyzed rearrangements have been isolated in similar cases.[29,38a] Moreover, the reaction could be carried out on a larger scale, affording batches of more than 300 mg of porphyrin without affecting the yield. The above procedure was found to afford better yields than the alternative reaction of 3,5-di-*tert*-butylbenzaldehyde with the corresponding *meso*-alkynyldipyrrylmethanes, the latter being too electron-deficient to react efficiently with aromatic aldehydes.[38a]

The selective cleavage of the TMS protecting group of **11** was readily achieved with aqueous NaOH, affording the ethynylporphyrin **13** in 95% yield. At this point, two alternative routes to **5** are available starting from the same compound depending on whether step c in Scheme 2 precedes step e or vice versa. In our hands, however, only the pathway outlined in Scheme 2 proved to be successful. Thus, coupling of **13** with 4-iodopyridine[45] in the presence of Pd_2dba_3 and P(*o*-tol)$_3$ as catalyst afforded the ethynylpyridylporphyrin **14a** in 50% yield, which could be improved to 75% by adding a second portion of catalyst 6 h after the beginning of the reaction. Although 4-iodopyridine can be replaced by 4-bromopyridine hydrochloride, which is commercially available, the Pd-catalyzed coupling with the latter proved to not be reproducible, in our hands, as the yields fluctuated between 12 and 50%, compared with 75% in the case of 4-iodopyridine. Also, important amounts (up to 50%) of a porphyrin dimer formed by homocoupling of **13** were obtained when 4-bromopyridine hydrochloride was used, whereas only traces of homocoupling products could be isolated in the case of 4-iodopyridine. The fluctuating yields obtained with 4-bromopyridine hydrochloride are probably related to the low solubility and/or instability of the latter.[46]

Initial attempts to remove the triisopropylsilyl group of **14a** with TBAF failed to give any porphyrin. The decomposition of the product was avoided by carrying out the reaction in a mixture of CH_2Cl_2/Et_3N (1:1) instead of neat CH_2Cl_2, and quenching the reaction, after 10 min stirring at 25 °C by addition of $CaCl_2$. The deprotected porphyrin **14b** was thus isolated in fair yield (85%) and coupled further with 1,3,5-triiodobenzene

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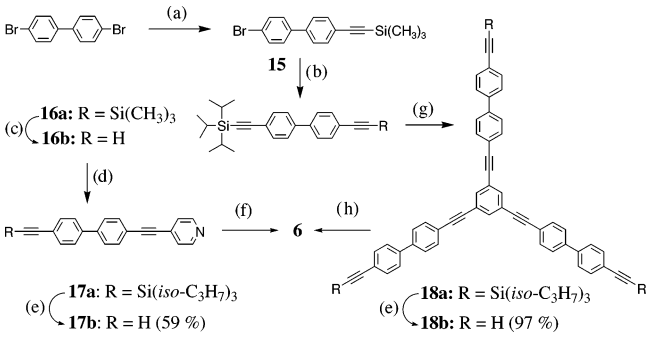
Scheme 3[a]



[a] Reagents and conditions: (a) TMSA in THF/*i*-Pr_2NH, $Pd(PPh_3)_2Cl_2$, CuI, 50 °C (33%); (b) same as in (a) but with TIPSA as reagent (62%); (c) 1 N NaOH in THF, 25 °C, 2 h (95%); (d) 4-iodopyridine in toluene/Et_3N (5:1), Pd_2dba_3/P(*o*-tol)$_3$, 80 °C (66%); (e) CH_2Cl_2/Et_3N (1:1), TBAF; (f) 1,3,5-triiodobenzene in DMF/*i*-Pr_2NEt (20:1), TBAI, CuI, Pd_2dba_3/tris(2,4,6-trimethylphenyl)phosphine 50 °C (59%); (g) same as (f) but at −20 °C (85%); (h) 4-iodopyridine in THF/Et_3N (5:1), $Pd(PPh_3)_2Cl_2$/PPh_3, 60 °C (56%).

in toluene at 35 °C using, as before, Pd_2dba_3 and P(*o*-tol)$_3$ as catalysts (cf. ref 32). The purification of the crude reaction mixture afforded, after chromatography on silica gel, some traces of homocoupling dimer as the first migrating component and trimer **5**, which was eluted as the second green fraction in 87% yield.

When compared with **5**, template **6** results from the replacement of three porphyrin rings by *p*,*p*′-biphenylene units, thus leaving the external diameter of the molecule almost unchanged. Trimer **6** was prepared from commercial 4,4′-dibromobiphenyl as starting material, following the pathway outlined in Scheme 3.

Intermediate **16a** was prepared either in one step by a mixed cross-coupling between 4,4′-dibromobiphenyl and an equimolecular mixture of trimethylsilylacetylene and triisopropylsilylacetylene or in two steps by reacting 4,4′-dibromobiphenyl first with trimethylsilylacetylene and then the obtained product **15** with triisopropylsilyl acetylene. The mixed coupling afforded **16a** in 16% yield along with 12% of 4-bromo-4′-(trimethylsilylethynyl)biphenyl (**15**), which, in its turn, was subsequently reacted with triisopropylsilylacetylene. On the other hand, the coupling of 4,4′-dibromobiphenyl with trimethylsilylacetylene led to a mixture of **15** (33%), starting material (14%), and small amounts of symmetrically 4,4′-disubstituted product, which were separated by column chromatography. The monosubstituted product **15** was reacted thereafter with triisopropylsilylacetylene to give **16a** in 62% yield. Thereon, the TMS protecting group of **16a** was cleaved under mild conditions (1 N aq NaOH) to afford the terminal alkyne intermediate **16b** in 95% yield. Alternative syntheses of intermediates **15**,[47] **16a**,[48] and **16b** [48] from 4-bromo-4′-iodobiphenyl as starting material have been previously reported in the literature.

Reaction of **16b** with an excess (2.5 equiv) of 4-iodopyridine under the conditions of the Sonogashira coupling, as described above for **14a**, afforded **17a** in 66% yield (cf. Scheme 3). Finally, removal of the remaining protecting group of **17a** with TBAF and reaction of the obtained product **17b** with triiodobenzene afforded the desired trimer **6** in 34% overall yield. An alternative synthesis of **6** involved the trimer **18a**, which was obtained in 85% yield through reaction of **16b** with triiodobenzene at −20 °C using Pd_2dba_3 in the presence of tris(2,4,6-trimethylphenyl)phosphine as catalyst.[49] Desilylation of **18a** with TBAF afforded the deprotected product **18b** (97%), which was subsequently reacted with an excess of 4-iodopyridine to gave the trimer **6** in 56% yield.

Preparation of the Substrates for the Template-Directed Synthesis of 1. As mentioned before, the template-directed synthesis of **1** was attempted using the porphyrin monomers **20b** and **21b** as well as the porphyrin dimer **22b** and the linear hexaporphyrin **23** as substrates (cf. Scheme 4). All of them were prepared from **19**[50] as the starting material. The deuterated derivative of the latter (**19**-d_8), containing 90% ^2H at all β-positions of the pyrrole rings, was synthesized from pyrrole-d_5 (98% ^2H)[51] via the corresponding *meso*-(mesityl)dipyrrylmethane-d_6 (cf. ref 50) following the procedure given in ref 52 (cf. Experimental Section). Transformation of **19** into **20a**, **22a**, and the linear porphyrin hexamer **23** has been reported elsewhere.[19] Deprotection of the ethynyl group of **22a** (M = 2H or Ni(II)) with aq NaOH (1 N) led to **22b** (M = 2H or Ni) in 84 and 97% yield, respectively. Intermediate **20a**, which had been previously obtained as a byproduct (30%) of the reaction of **19** with an equimolecular amount of 1-(3-*tert*-butyl-5-ethynylphenyl)-3,3-diethyltriaz-1-ene,[19] was obtained in 73% yield by reacting 2 equiv of the latter with **19** in the presence of $Pd(PPh_3)_2Cl_2$/CuI as a catalyst (cf. Experimental Section). Subsequent reaction of **20a** with iodomethane at 135 °C yielded **20b** almost quantitatively (98%). On the other hand, intermediate **21a** was obtained in 68% yield by reacting **19** with trimethylsilylacetylene in the presence of $Pd(PPh_3)_2Cl_2$/CuI as a catalyst. Thereafter, the Zn(II) ion was removed by treatment with TFA, and the triple bonds were deprotected by stirring with aq NaOH in THF to give **21b** (M = 2H). The total yield after purification by column chromatography amounts to 99%. Thereon, Ni(II) was inserted by reacting **21b** (M = 2H) with nickel acetate to afford **21b** (M = Ni) in 65% yield.

Template Synthesis Starting from the Linear Hexamer 23 (M = Ni). In our previous work, the macrocycle **1** was prepared by an iterative divergent−convergent approach involving 17 steps, the less satisfactory of which being the intramolecular cyclization of the linear hexamer intermediate **23**[17,19] (cf. Scheme 4). This stepwise procedure is cumbersome as it begins with a monomeric porphyrinic building block, which yields eventually the linear hexamer by successive functional group transformations. Moreover, the ring closure, which is the last step of the procedure, was not reproducible, as the yield obtained after laborious chromatographic purification varied in a large range (8−31%) without an apparent reason. As most attempts to optimize the cyclization step had been carried out with hexamer **23** in which Zn(II) and Ni(II) porphyrinate rings alternate (cf. Table 1), the effect of trimers **3**−**6** on the cyclization of this linear hexamer was investigated first.

It was observed in the course of these experiments that when Pd_2dba_3 together with P(*o*-tol)$_3$[32] was employed as the catalyst the hexameric macrocycle could be much more easily separated

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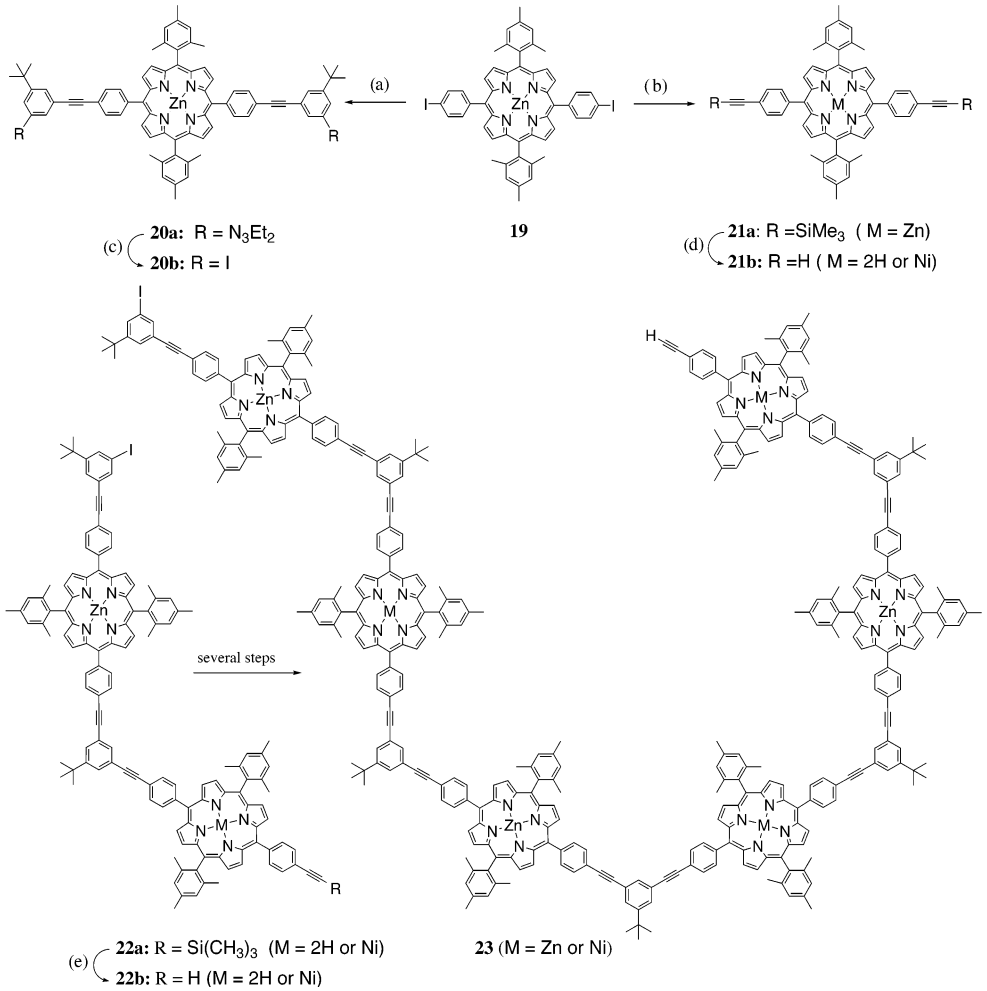
Scheme 4[a]



[a] Reagents and conditions: (a) 1-[3-(1,1-dimethylethyl)-5-ethynylphenyl]-3,3-diethyltriaz-1-ene in DMF/Et_3N (5:1), $Pd(PPh_3)_2Cl_2$/CuI, 35 °C, 14 h, (30%); (b) same as in (a) but with ethynyltrimethylsilane as a reagent (68%); (c) ICH_3, 135 °C, 2 h, (98%); (d) TFA in $CHCl_3$, 25 °C, 2 h, then aq. NaOH in THF, 25 °C, 3 h (100%); (e) 1 M aq. NaOH in THF, 25 °C, 3 h (84%).

Table 1. Dependence of the Yield of **1a**, Obtained by Cyclization of **23** in the Absence of Template, on the Reaction Conditions

entry	catalyst	solvent	yield (%)
1	$Pd(PPh_3)_4$	DMF/Et_3N	8−30[a]
2	$Pd(PPh_3)_4$	toluene/Et_3N	21
3	Pd_2dba_3/P(*o*-tol)$_3$	toluene/Et_3N	20−30
4	Pd_2dba_3/P(*o*-tol)$_3$	DMF/Et_3N	17

[a] From refs 17 and 19.

Table 2. Yield of Macrocycle **1a**, Obtained by Pd_2dba_3/P(*o*-tol)$_3$-Catalyzed Cyclization of **23** in Toluene/$(C_2H_3)_3N$ (5:1) as Solvent, in the Presence of Template

template	**3**	**4**	**5**	**5**[a]	**6**
yield (%)	45[b]	*c*	59[d]	41[b]	48

[a] In this run, only 30% Pd per I atom was added in two portions (cf. Experimental Section). [b] The isolated product was 95% pure. [c] No pure fraction could be isolated. [d] Maximal yield; mostly the yield varied between 52 and 55%.

from the reaction mixture. Therefore, the reaction in the presence of template was performed under the conditions specified in Table 2. Tetrahydrofuran cannot be used as a solvent because it competes with the pyridine ligands of the template for the porphyrin binding sites of the substrate. For the same reason, the concentration of triethylamine in the solvent (toluene) was reduced to 20% (v/v). The amine cannot be completely excluded, as the coupling reaction does not take place in the absence of base.

On the other hand, triethylamine was used instead of a secondary amine (e.g., diethylamine) in order to avoid side reactions such as addition to the acetylenic bonds (cf. ref 36). Also, high temperatures must be avoided in order to prevent dissociation of the kinetically labile substrate−template complex. These mild conditions also prevent the use of the copper reagents, afford coupling in dilute solution, and preserve the metalation state. Interestingly, although an excess of catalyst (60 mol % of Pd per I atom) was required to complete the reaction, the addition of a second batch of catalyst, a few hours after the beginning of the reaction, did not significantly increase the yield but facilitated substantially the separation of the cyclic hexamer by column chromatography. Presumably, some oligomers, which otherwise would be eluted closely to the cyclic hexamer, are converted in the presence of an excess of catalyst to less soluble compounds of high molecular weight.

After completion of the cyclization reaction, the usual procedure to remove the template from the host cavity consists in decomposition of the porphyrin zinc chelates by treatment

Table 3. Yields of Macrocycle **1c**, Obtained from Monomeric Porphyrins **20b** and **21b** (M = 2H), in the Presence of **5** as Template

run	1	2	3	4	5	6	7[a]
yield (%)	6.3	7.5	5.2	5.4	6.3	4.8	7.1

[a] In this run, macrocycle **1a** was synthesized from **20b** and **21b** (M = Ni).

with acid. In the present case, however, no additional demetalation step was necessary before separation of the reaction mixture by column chromatography since the complex between the cyclic hexamer and the trimer template dissociates on dissolving the crude product in THF before its isolation. Thus, the cyclic hexamer was eluted first with a $CHCl_3$/hexane mixture and purified further by preparative TLC. Thereon, about 50% of the template was retrieved eluting with a $CHCl_3$/MeOH mixture. The loss of the trimer template is probably related to the considerable precipitation observed during the template-directed syntheses, and it may be due to the inclusion of the template in the insoluble polymers formed as byproducts.

As expected, the best yields of macrocycle were obtained in the case of trimer **5**, whose dimensions fit the best into the inner cavity of the macrocycle (Table 2). The high yield obtained reflected a significant "template-directed" contribution to the ring closure reaction.

Trimer **3** proved to be a less efficient template. The lengths of its "arms" slightly exceed the cavity radius of **1b**, and even though the macrocycle is apparently flexible enough to accommodate the trimer, giving a very stable host−guest complex (the measured binding constant amounts to $K = 1.4 \times 10^9\ M^{-1}$), the reactive ends of the linear precursor complexed with **3** may be not close enough to favor intramolecular coupling against intermolecular reactions. Thus, polymers are presumably formed, which make the separation of the desired product more difficult. Actually, after repeated chromatographic separation, the purity of the macrocycle obtained in the presence of **3** as a template did not exceed 95%.

In the presence of the smaller trimer **4** as a template, only complex mixtures of products were obtained, and even if the presence of **1b** was detected, no pure fraction could be isolated. This was not surprising, as the arms of the trimer are too short to fit inside the cavity of the macrocyclic hexamer, so that probably not all three (porphyrinato)zinc(II) rings of the same linear precursor are complexed with one molecule of the template, thus disfavoring intramolecular coupling.

Trimer **6**, in which biphenyl moieties replace the porphyrin rings, has dimensions similar to those of **5**. Therefore, it forms a stable complex with **1b** (cf. Table 4) and serves also as an efficient template for the synthesis of the latter (cf. Tables 2 and 3).

The data collected along this work show that the template-directed synthesis of **1a** is reproducible under the employed conditions, the yields obtained in five runs ranging between 52 and 59% (Table 2). Not unexpectedly, the template-directed cyclization of the linear hexamer **23** (M = Zn) in the presence of **5** led to a very complex mixture of products, and no pure fraction could be isolated, even after repeated chromatography. This result may be explained by the circumstance that upon complexation of **23** (M = Zn) with the template there are still three unligated Zn−porphyrin rings, which are available for complexation with other molecules of the trimer, so that the geometry of the assembly, as a whole, is not anymore favorable to intramolecular coupling. In light of these experiments, we can conclude that the appropriate template for the linear **23** (M = Zn) hexamer should be a star-shaped hexamer (niphaphyrin) that bears the same arms as template **5**. Until now, unfortunately, our efforts to synthesize such a template were unsuccessful. Presently, a synthesis of a similar star-like hexamer whose arms are those used for the trimer **6** is underway.

Templated Synthesis Starting from Porphyrin Monomers. Encouraged by the above results, we attempted next the template-directed synthesis of **1a** using **5** as the template and porphyrins **20b** and **21b** (M = Ni) as the substrates (cf. Figure 3c). In this approach, the (porphyrinato)zinc(II) building blocks should ligate first to the pyridine rings at the apical positions of the template, thus forming a loose complex, in which three porphyrin rings are held in the appropriate positions to yield the macrocyclic porphyrin hexamer on reaction with **21b** (M = Ni) as the complementary building blocks. Thus, the cyclization step involves six coupling reactions, without isolation of any intermediate (cf. Figure 3c). Since pyridine ligands do not efficiently coordinate with the Ni(II) ions in porphyrin complexes,[27] they should not compete with the ligated (porphyrinato)zinc(II) rings for the apical positions in the above-mentioned loose complex. However, as suggested by Sanders and co-workers for a similar template-directed synthesis of a cyclic porphyrin tetramer,[15d,g] an alternative mechanism could consist in the trapping of linear intermediates by the template, while a preassembly of monomeric components around the ligand, before any chemical reaction takes place, is most likely if the porphyrin complexes (e.g., Ru(II) porphyrinates[15g] or Zn(II)−dioxoporphyrinates[53]) strongly bind the pyridine ligands. Actually, in the course of our experiments carried out to optimize the yield of the macrocyclic porphyrin hexamer **1a**, it was observed that if smaller amounts of catalyst than 2 × 30 mol % Pd per I atom were used, no pure macrocycle could be isolated. Instead, several fractions containing linear trimers to octamers were identified by ESI mass spectrometry. Evidently, therefore, linear polymerization of the building blocks **20b** and **21b** (M = Ni) compete with the reaction of the latter with a preorganized complex between **20b** and the template. Moreover, some components identified by ESI mass spectrometry lack the iodine atom, so that hydrodeiodination of the substrates,[54,55] which interrupts the polymerization process, seems to be an important side reaction under the employed conditions.

As templates normally bind too strongly to the product of the reaction to act catalytically, stoichiometric quantities of template and substrates are at least needed for an efficient cyclization. In the present case, the best results were obtained under these conditions. In our hands, no pure macrocycle could be isolated using a 1:1:1 ratio of reagents, although sometimes better yields have been reported using an excess of template.[15d] Replacement of the free base monomer **21b** (M = 2H) for the corresponding Ni(II) complex did not affect the outcome of the reaction (Table 3). The thus obtained macrocycle **1c** can be either transformed into the corresponding complex with six Zn(II) ions upon treatment with zinc acetate or completely

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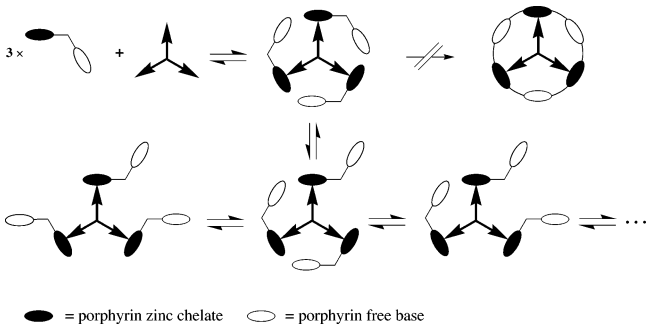

Figure 4. Unfavorable geometries of the substrate ligand complex may thwart the synthesis of macrocycles **1a**−**c** starting from porphyrin dimers.

demetalated by treatment with TFA. Subsequently, the metal-free macrocycle can be transformed into a complex with six metal ions of the same element, other than Zn(II). Despite its modest yield (~5%), the above-described templated synthesis starting from porphyrin monomers is more advantageous than the cyclization of the linear hexamer **23** (M = Zn) since the synthesis of the latter implies more than 13 time-consuming steps with an overall yield of only 1%.

Templated Synthesis Starting from Porphyrin Dimers. Should the mechanism of the above-described synthesis of **1a** imply the trapping of linear intermediates by the template, it would be conceivable that starting from a porphyrin dimer as the substrate the yield of the reaction could be improved since the cyclization process involves only three coupling reactions instead of six, as required in the one-pot synthesis starting from monomers (cf. Figure 3). Unexpectedly, however, attempted coupling of three molecules of **22b** in the presence of template **5** yielded a complex reaction mixture, from which no pure cyclic hexamer could be isolated. This result may reflect the higher disorder in a loose complex, in which three (porphyrinato)zinc-(II) rings are ligated to the apical pyridine residues, but the other three nonligated rings may adopt conformations which are unfavorable for intramolecular ring closing (cf. Figure 4).

Structure of the Supramolecular Complexes. The complexation behavior of the macrocyclic porphyrin hexamers **1a** and **1b** (as hosts) against the trimer templates **3**−**6** (as guests) was examined, and corresponding binding parameters were obtained by UV−vis spectroscopic titration experiments. Titrations were carried out at constant cyclic hexamer concentration in CH_2Cl_2 solutions at 20 °C.

The changes in absorption were monitored as a function of concentration of template in a range where maximum change in absorption was observed during the titration (cf. Figure 6). So, two sets of data were obtained: one for the decreasing absorption near λ_{max} of the free host and the second one for the rising absorption near λ_{max} of the newly formed complex (cf. ref 56). The simulation analysis of the resulting data was carried out by subtracting one data set from another using a least-squares curve-fitting program. The experimental points match well with a set of theoretical equations for a plain 1:1 complexation isotherm using the nonlinear least-squares optimization. Thus, values of binding constants for complexes between **1a** and **1b** and the star-shaped trimers **3**−**6** were obtained (Table 4), which are in agreement with an efficient three-point bonding[57] ranging between 10^8−10^9 mol dm^{-3} (cf. ref 19). It must be pointed out, however, that such values are at the limit of the accuracy of direct measurements from UV−vis titration curves,[56,58] so that the margin of error of the values quoted in Table 4 cannot be neglected.

Apparently, the macrocycle of hexamers **1a** and **1b** is flexible enough to accommodate the trimers **3**, **4**, and **5** without noticeable distortion of the molecule that obviously would result in lower values of the binding constant. Although trimer **6** is bound about 4 times less strongly than **5**, the supramolecular complex is stable enough for a template-directed synthesis. On the other hand, the guest affinity toward Zn porphyrinates is directly dependent on the ligand basicity,[59−61] that is, the more basic the ligands are, the stronger they bind. As the binding constants for all trimers are situated in the same range, their quality as templates depends rather on the geometry of the complex with the substrates which, in the end, is determined by the length of the arms of the template.

As in the case of previously described molecular complexes of **1a** with homologues of **5** (cf. ref 19), ^{1}H NMR spectroscopy proved to be a useful tool for the structure determination of the corresponding supramolecular assemblies. The assignment of the resonance signals of both the host and guest molecule in the complex was carried out by a combination of COSY and NOE experiments, which, in the case of complex **1a** + **5**, clearly show that the tridentate ligand binds inside the cavity of the hexaporphyrin macrocycle, the pyridine rings being bound to the Zn(II) ions and not to the Ni(II) ions, as a consequence of the low affinity of Ni(II) ions for nitrogen-containing ligands.[27] Accordingly, the ^{1}H NMR spectrum at 500 MHz of complex **1b** + **5** shows, at 20 °C, two sets of resonance signals corresponding to the Zn(II) porphyrinate rings which are bound to the pyridine moieties of the guest molecule and those in which the Zn(II) ions are devoid of axial ligands (cf. Figure 5). Interestingly, however, at 55 °C, all six Zn(II) porphyrinate rings become magnetically equivalent, as evidenced by the fact that only a set of signals is observed in the ^{1}H NMR spectrum of **1b** + **5** at this temperature (see below). As in the case of complex **1a** + **5**, the resonance signals at δ 2.79 and 6.10 ppm, assigned to the α- and β-H atoms, respectively, of the complexed pyridine rings are upfield shifted by $\Delta\delta = -6.06$ and -1.81 ppm, respectively, with respect to the corresponding signals of the free ligand. The observed upfield displacements are in the same range as those observed in similar complexes with tridentate ligands, thus confirming that all three pyridine ligands are bound simultaneously.[15g,62] Moreover, the structure of the molecular complex depicted in Figure 5 is consistent with the insignificant changes of chemical shift observed for the protons at the 1,3-phenylene rings serving as cornerstones of the macrocycle as well as the (porphyrinato)zinc(II) rings which are not involved in intermolecular bonding.

Additional support for the proposed structure of complexes **1a** + **5** and **1b** + **5** was supplied by the MALDI-TOF MS

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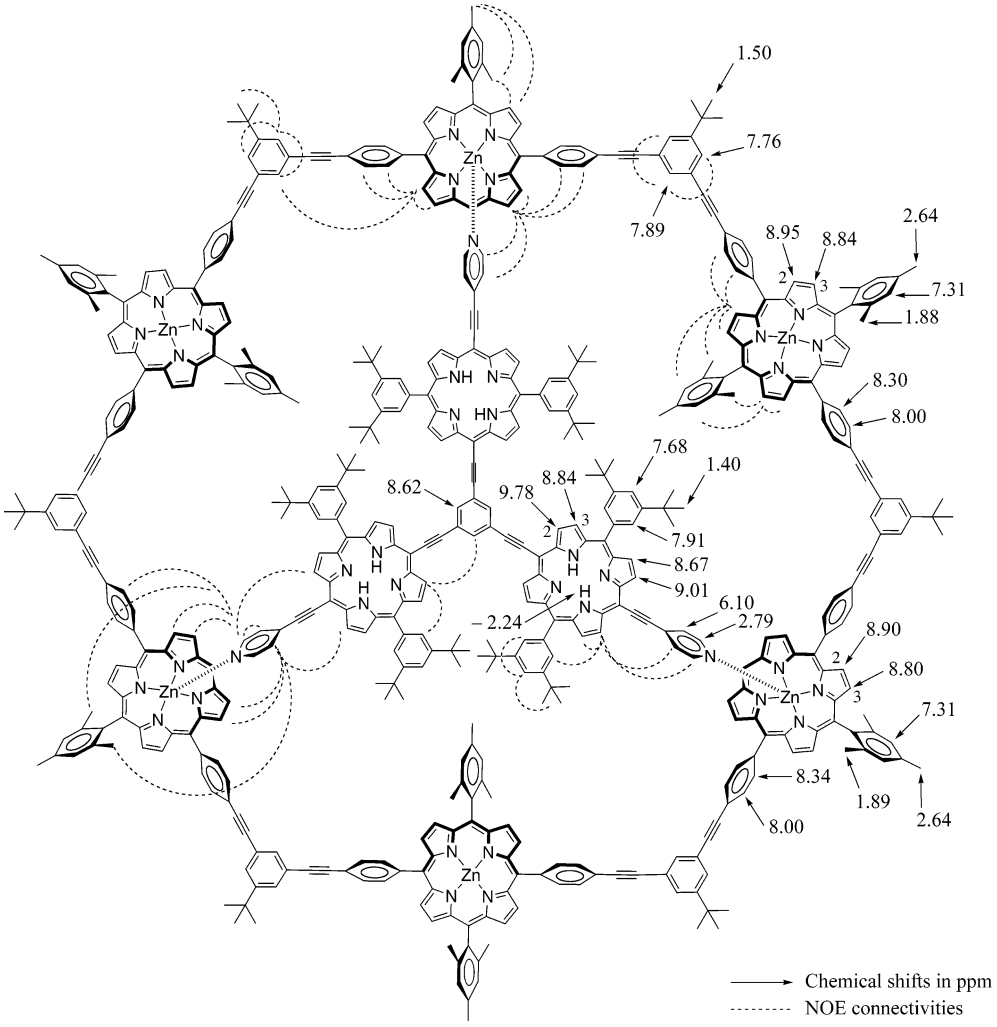

Figure 5. ^{1}H NMR resonance signals of the complex **1b** + **5** at 0 °C, as assigned by COSY and NOE experiments. Chemical shifts (in ppm) point to the corresponding atoms (→), and NOE connectivities are indicated by dashed lines (- - -). Mesityl groups at one of the *meso* positions of the (porphyrinato)zinc(II) rings have been omitted for clarity.

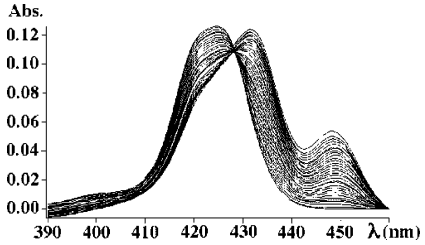

Figure 6. UV−vis titration spectra showing the decrease of the intensity of the Soret band of **1b** (5.19×10^{-8} M in CH_2Cl_2) and the increase of the intensity of the Soret band of the complex **1b** + **5** upon addition of ligand **5** (1.29×10^{-6} M in CH_2Cl_2).

Table 4. Binding Constants (K) in CH_2Cl_2 at 20 °C between Macrocycle **1a** and **1b** and Ligands **3**−**6**

macrocycle	ligand	K (M^{-1})
1a	3	1.4×10^9
1a	4	3.4×10^9
1a	5	2.8×10^9
1a	6	6.5×10^8
1b	5	2.7×10^9

technique that proved to be a valuable tool for analyzing complexes consisting of noncovalent interactions. The mass spectrum (DCTB matrix) of the complex **1a** + **5** revealed, besides the two peaks belonging to the individual ligand **5** (m/z = 2507.14) and cyclic hexamer **1a** (m/z = 5619.94), the expected molecular peak pattern of the corresponding supramolecular complex (m/z = 8126.06). Similar results were obtained for the complex **1b** + **5** (m/z = 8147.7) and its components **1b** (m/z = 5638.62) and **5**.

Dynamics of Supramolecular Assembly. A solution of the host macrocycle **1a** in $CDCl_3$ was titrated at 20 °C against the tridentate ligand **5**, and ^{1}H NMR spectra were recorded at 360 MHz. On adding **5**, the intensity of the sharp resonance signals of **1a** decreased, while new sharp signals belonging to the complex arose and gradually increased until only signals of the complex were present when 1 equiv of **5** had been added. Integration of the signal intensities reveals a guest/host ratio of 1:1 according to a structure analogous to those depicted in Figure 5. In the presence of an excess of **5**, the signals of the bound ligand broaden slightly, and broad signals of free **5** appear which are slightly shifted upfield. Presumably, they are broadened as a result of the weak binding to the external faces of the macrocycle via six-coordinate zinc(II) (cf. ref 15e).

On the other hand, when the host macrocycle **1b** was titrated against the same ligand (**5**) at 20 °C, slightly broadened resonance signals of both the complex and the host molecules

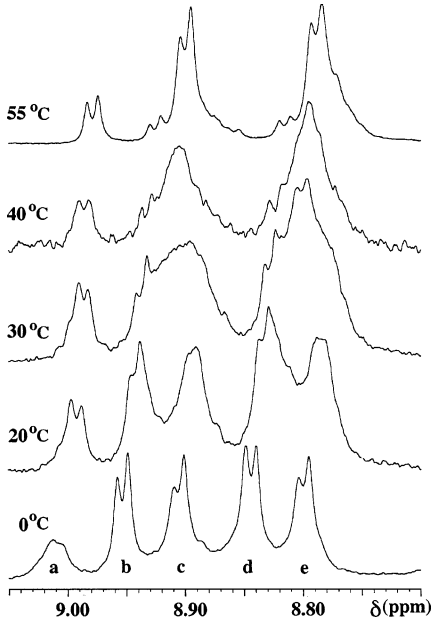

Figure 7. Detail of the 500 MHz ^{1}H NMR spectrum of complex **1b** + **5** in the δ = 8.70−9.05 ppm range showing the temperature dependence between 0 and +55 °C of the signals assigned to the H-atoms at (a) C8 and C12 of the porphyrin rings of the ligand; (b) even-numbered β-positions of the unligated Zn(II) porphyrinate rings of the macrocycle; (c) even-numbered β-positions of the ligated Zn(II) porphyrinate rings of the macrocycle; (d) odd-numbered β-positions of the unligated Zn(II) porphyrinate rings of the macrocycle; and (e) odd-numbered β-positions of the ligated Zn(II) porphyrinate rings of the macrocycle (cf. Figure 5).

were observed. Contrarily, progressive addition of the ligand to a solution of the host macrocycle at 0 °C allows one to clearly differentiate the resonance signals of the complex and the host macrocycle present in excess at the beginning (cf. Figure 5). Interestingly, the proton resonances of both the free and bound ligand are slightly broader at 0 °C than at 20 °C (cf. Figure 7), probably due to restricted rotation of the porphyrin rings around the axis of the acetylenic bonds.[63] Moreover, the resonance signals of both the complex and free host molecules do not broaden or shift until 1 equiv of ligand is added to the solution of the macrocycle, thus indicating that a distinct complex is formed,[61] since a dynamic equilibrium between a variety of complexes would result in broad, concentration-dependent signals (cf. refs 64 and 65). This is in agreement with the presence of a single isosbestic point at 428.2 nm for the family of curves obtained on progressive addition of ligand **5** to a solution of macrocycle **1b**, as monitored by UV−vis spectroscopy (cf. Figure 6). At 0 °C, addition of an excess of ligand **5** to the solution of the complex **1b** + **5** resulted in broadening of the resonance signals either as a result of ligation to the outer faces of the three Zn(II) porphyrinate rings, which are devoid of axial ligands inside the cavity of the macrocycle, or to exchange free and complexed ligand molecules, which is presumably accelerated in the presence of an excess of ligand by an associative S_N2-like mechanism via a six-coordinate Zn(II) intermediate[66] (cf. ref 67).

As mentioned before, at 55 °C, only a set of signals is observed for the six Zn(II) porphyrinate rings in the ^{1}H NMR spectrum of the complex **1b** + **5** (cf. Figure 7). When the host macrocycle **1b** was titrated against the ligand **5** at 55 °C, the ^{1}H resonance frequencies of both reactants at 500 MHz remained unchanged, and no shift or broadening of the resonance signals was observed until 1 equiv of ligand has been added. The intensity of the signals belonging to the newly formed complex increased progressively with the amount of trimer added, while the signals of the free host gradually disappeared. On addition of ligand to a solution of the complex **1b** + **5** at 55 °C, the resonance signals of the former became progressively broader and shifted gradually downfield on increasing the amount of ligand added.

In principle, the magnetic equivalence of all Zn(II) porphyrinate rings of complex **1b** + **5** can be explained either by intramolecular rotation of the ligand inside the cavity of the host molecule or by rapid dissociation and recombination of the host and guest molecules forming the complex. Actually, both mechanisms would agree with the observed broadening of the ^{1}H NMR signals at about 35 °C as the coalescence temperature (cf. Figure 7). Although the mechanism involving intramolecular ligand exchange, which drives the guest molecule to rapidly walk around the inside of the cavity, has been suggested by Sanders and co-workers in order to explain that only a set of porphyrin signals is seen, at room temperature, in the ^{1}H NMR spectrum of molecular complexes in which bidentate ligands are inside the cavity of a cyclic porphyrin trimer,[15c,56] an alternative mechanism involving the break of only one N−Zn bond followed by rotation of the (bidentate) ligand around the other N−Zn bond may also operate in their case (cf. ref 62b). In the case of **1b** + **5**, the interpretation of the ^{1}H NMR spectrum at 55 °C was hampered by the fact that, at this temperature, the resonance signals of the (uncomplexed) host macrocycle are shifted upfield by 0.026 ppm so that they largely overlap—even at 700 MHz—with the corresponding signals of the complex in the relevant range between δ 8.70 and 9.05 ppm.

Therefore, to get an insight into the kinetic stability of the complex **1b** + **5**, 1 equiv of the host molecule was added at −40 °C to a solution of the complex **1b**-d_{48} + **5**, in which the H-atoms at all β-positions of the porphyrin rings forming the macrocycle had been replaced by deuterium. Actually, if ligand exchange between labeled and unlabeled molecules of the host takes place slowly on the ^{1}H NMR time scale (at 500 MHz), the proton resonance signals corresponding to Zn(II) porphyrinate rings, which are ligated to the pyridine moieties of the ligand, should gradually appear on increasing the temperature. In an extreme case, ligand exchange does not take place at all, thus leading to the conclusion that the porphyrin rings of complex **1b** + **5** become equivalent at 55 °C as a result of intramolecular ligand exchange which drives the guest molecule to rapidly walk around inside the cavity. As a matter of fact, however, even after rapid addition of **1b** to the solution of the deuterated complex **1b**-d_{48} + **5** at −40 °C, the ^{1}H NMR spectrum of the mixture, which was recorded at −30 °C, reveals the presence of the resonance signals of the unlabeled complex (cf. Figure 8c). As the difference of chemical shifts of

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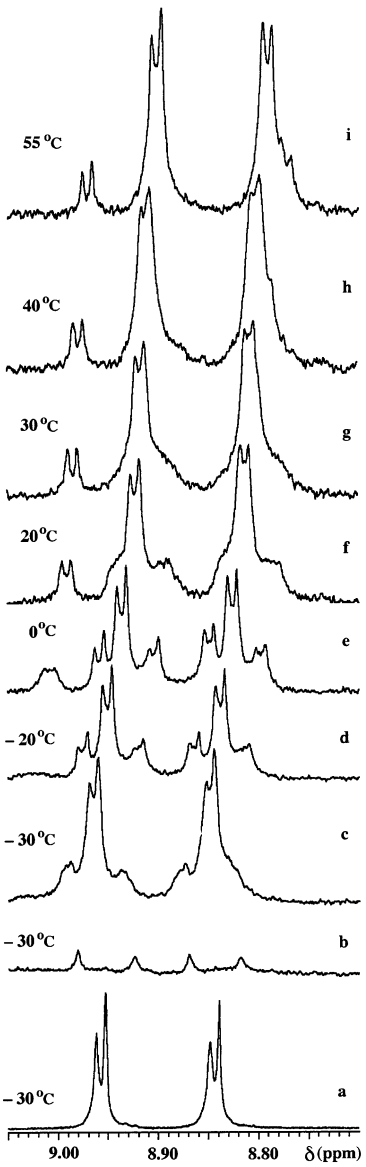

Figure 8. Detail from the ^{1}H NMR spectrum at −30 °C of (a) unlabeled **1b** and (b) complex **1b**-d_{48} + **5**, showing the signals of residual H-atoms at the β-positions of the porphyrin rings of **1b**-d_{48}. (c−i): Temperature dependence of the 500 MHz ^{1}H NMR spectrum of complex **1b**-d_{48} + **5** observed between −30 and +55 °C in the $\delta = 8.70-9.05$ ppm range, after addition of 1 equiv of unlabeled **1b** (for assignments, see Figures 5 and 7).

corresponding β-H-atoms at the Zn(II) porphyrinate rings, which are ligated to pyridine, and those which are devoid of the axial ligand amounts to 0.05 ppm (i.e., 25 Hz at 500 MHz), the first-order rate constant for the dissociation of the complex at a temperature of approximately 35 °C (308 K), at which the resonance signals of the H-atoms at the β-positions of the pyrrole rings of the unlabeled host molecule coalesce (cf. Figure 8g,h), may be estimated at $k_c = 56$ s^{-1} according to $k_c = (\pi/\sqrt{2})\Delta\nu$.[68] The corresponding free energy of activation can be calculated to be $\Delta G^{\ddagger}_{308} \approx 65.2$ kJ mol^{-1} using Eyring's equation. As the entropy of binding is unlikely to be greater than 130 J mol^{-1} K^{-1} (cf. ref 56), the activation enthalpy for the formation of the supramolecular complex will not exceed $\Delta H^{\ddagger} = 105$ kJ mol^{-1}. Accordingly, the free energy of activation for the dissociation of the complex at 20 °C (293 K) and at −30 °C (243 K) amounts to $\Delta G^{\ddagger} \approx 67$ and 74 kJ mol^{-1}, respectively. The corresponding rate constants for dissociation are $k_{293} = 6.5$ and $k_{243} = 7.4 \times 10^{-4}$ s^{-1}, respectively. The latter figure, which corresponds to a half-time of the reaction of about $\tau_{1/2} = 15$ min at 243 K, is in good agreement with the observation that even at low temperature exchange of the guest molecule of the complex was almost complete before measurements of the ^{1}H NMR spectrum could be started. On the other hand, a maximum rate constant for the dissociation of the supramolecular complex at 293 K can be calculated from the experimentally determined equilibrium constant $K = 2.7 \times 10^9$ (cf. Table 4), assuming that the maximum possible association rate constant is diffusion controlled, and therefore it cannot exceed the value 10^{10} M^{-1} s^{-1} (cf. refs 15f and 69). Therefore, as the equilibrium constant equals the quotient of this maximum on-rate divided by the off-rate, an upper limit of the latter should be $k = 3.7$ s^{-1}, a value which, within the margin of error, is close to the rate constant ($k_{293} = 6.5$ s^{-1}) derived from the kinetic experiment as explained above. Even though the large size and steric restrictions of the molecules involved in the formation of the complex may reduce the above diffusion limit, the above-mentioned inaccuracy of the experimental determination of the equilibrium constant, on the other hand, may result in a too high value for the latter, so that the correspondence between the rate constants estimated from the kinetic and thermodynamic data is quite satisfactory. Therefore, although intramolecular rotation of the guest molecule inside of the cavity of the host cannot be excluded unequivocally on the basis of the presently available data, these strongly suggest that intermolecular ligand exchange alone accounts for the equivalence of all porphyrin rings observed in the ^{1}H NMR spectrum of **1b** + **5** at 55 °C.

Conclusions

The template-directed synthesis of the macrocyclic hexaporphyrins **1a** and **1c** described in this work exemplifies a straightforward approach for the preparation of such macrocycles starting from monomeric porphyrin building blocks. The work emphasizes the importance of the molecular dimensions of both the host and guest molecules for the formation of a complex with the appropriate geometry required for the cyclization process. Unexpectedly, in contrast to the low dissociation constant ($K_{diss} \approx 10^{-9}$) of the supramolecular complex between the tridentate ligand **5** and the macrocycles **1a**−**c**, ^{1}H NMR spectroscopic analysis of the macrocyclic hexaporphyrin **1b** in the presence of its analogue, in which all H-atoms at the pyrrole rings have been replaced by deuterium, revealed that even at low temperature (−40 °C) a rapid dissociation and recombination of the host and guest molecules forming the supramolecular complex takes place.

Experimental Section

General. 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 foils. Reaction products were separated by flash chromatography (FC) on Merck silica gel 60 (0.040−0.063 mm, 230−400 mesh), except otherwise noted, and/or on preparative TLC plates (20 × 20 cm, silica gel 60 F_{254}, 1 mm). Melting

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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} (logϵ) in nm. NMR: Bruker Avance DPX360 (^{1}H, 360.14 MHz, ^{13}C, 90.56 MHz), or Bruker Avance DRX500 (^{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 parts per million relative to $Si(CH_3)_4$ as internal standard, and J values are in hertz. Assignments are based on homonuclear COSY-45, ^{1}H{^{1}H} NOE difference correlations, and/or chemical shifts. ^{13}C signal multiplicities were determined by attached proton test (APT) experiments. 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) using dithranol as matrix; FT mass spectrometer Bruker 4.7T BioAPEX II; MALDI-TOF, Bruker Reflex-II (delayed extraction, 20 kV acc. voltage, positive reflection mode) using DCTB (2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene] malonitrile)[19] dissolved in $CHCl_3$ (0.05 M) as matrix (dried droplet method) and averaging 200−1100 shots. Elemental analyses were carried out by Ilse Beetz Microanalytical Laboratory, Kronach, Germany.

Tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$) was purchased from Acros Organics (B-2440 Geel); tris(dibenzylideneacetone)dipalladium (Pd_2dba_3), tri-*o*-tolylphosphine (P(*o*-tol)$_3$), tetrabutylammonium fluoride (TBAF), tetrabutylammonium iodide (TBAI), dimethylformamide (DMF), and *N*,*N*-diisopropylethylamine (*iso*-Pr_2NEt) were purchased from Aldrich Chemie (CH-9471 Buchs); trifluoroacetic acid (TFA), tetrahydrofuran (THF), trimethylsilylacetylene (TMSA), triisopropylsilylacetylene (TIPSA), and other reagents were from Fluka Chemie AG (CH-9471 Buchs).

Macrocyclic Hexaporphyrin 1a from Linear Hexamer 23 (M = Ni) in the Absence of Template. A solution of **23** (M = Ni) (3 mg, 0.52 μmol) in 5 mL of toluene was purged of air by passing Ar for 5 min before triethylamine (1 mL) was added. Then, the mixture was degassed by three freezing/thaw cycles in vacuo before Pd_2dba_3 (0.14 mg, 0.156 μmol) and P(*o*-tol)$_3$ (0.38 mg, 1.248 μmol) were added at 25 °C under Ar. Thereon, the reaction mixture was stirred at 35 °C for 8 h under an Ar stream, protected from light, before a second portion of catalyst was added, and stirring was continued overnight. The solvent was removed under reduced pressure, and the solid residue was purified twice by FC, using $CHCl_3$/hexane (7:3) as eluant, to yield a main violet product which was washed with MeOH and *n*-hexane. The maximal yield of **1a** obtained by this procedure amounted to 0.6 mg (21%). Its analytical data were identical to those previously reported.[19]

Macrocyclic Hexaporphyrin 1a from Linear Hexamer 23 (M = Ni) in the Presence of Template. A mixture of **23** (M = Ni) (3 mg, 0.52 μmol) and **5** (1.3 mg, 0.52 μmol) was reacted under the same conditions as described above for the synthesis in the absence of template. FC of the reaction product afforded two main components: a violet band, which contained the desired product, was eluted first with $CHCl_3$/hexane (7:3), then the column was eluted successively with $CHCl_3$ and $CHCl_3$/MeOH (9:1) to afford a green fraction from which 0.6 mg (46%) of **5** was retrieved. Crude **1a** was dissolved in $CHCl_3$ and purified by TLC using *n*-hexane/$CHCl_3$/EtOAc (4:1:1) as eluant. Acyclic oligomers moved with the solvent front. The band with the lowest R_f was scraped off from the TCL plate, extracted with $CHCl_3$, and the solvent was evaporated under reduced pressure. The violet solid obtained was washed with MeOH and *n*-hexane and dried in vacuo to yield 1.6 mg (55%) of **1a**.

Macrocyclic Hexaporphyrin 1a from Monomers 20b and 21b (M = Ni) in the Presence of Template. A mixture of **20b** (14.1 mg, 10.6 μmol), **21b** (M = Ni) (8.5 mg, 10.6 μmol), and the template **5** (8.9 mg, 3.54 μmol) was dissolved in 20 mL of toluene/triethylamine (5:1) and reacted in the presence of Pd_2dba_3 (5.8 mg, 6.36 μmol) and P(*o*-tol)$_3$ (15.5 mg, 50.88 μmol) following the procedure described above for the synthesis in the absence of template. Separation of the reaction product by FC using successively $CHCl_3$/*n*-hexane (7:3), $CHCl_3$, and $CHCl_3$/MeOH (9:1) as eluants was followed by preparative TLC (*n*-hexane/$CHCl_3$/EtOAc 4:1:1), yielding 1.4 mg (7%) of **1a**, identical with the above samples.

Macrocyclic Hexaporphyrin 1c from Monomers 20b and 21b (M = 2H) in the Presence of Template. A mixture of **20b** (14.1 mg, 10.6 μmol), **21b** (M = 2H) (7.9 mg, 10.6 μmol), and **5** (8.9 mg, 3.54 μmol) was reacted as described above for **1a** to yield 1.0 mg (5%) of **1c**, as the component with the lowest R_f. Its analytical data are identical to those previously reported.[17]

Complex 1a + 5. The complex formation was monitored by ^{1}H NMR spectroscopy adding gradually 1 equiv of **5** (in concentrated $CDCl_3$ solution) to a solution of **1a** in $CDCl_3$ and recording a ^{1}H NMR spectrum after each addition. Signal integration indicates that a new species was formed between **1a** and **5** in a ratio of 1:1; the proton chemical shifts in the guest porphyrins are upfield shifted due to the ring currents of the porphyrin rings in the macrocycle. ^{1}H NMR (500.13 MHz): δ −2.16 (br, 6H, NH), 1.42 (s, 108H, *t*-Bu on **5**), 1.49 (s, 54H, *t*-Bu on **1a**), 1.84 (s, 36H, *o*-CH_3 on Ni porphyrinate), 1.88 (s, 36H, *o*-CH_3 on Zn porphyrinate), 2.58 (s, 18H, *p*-CH_3 on Ni porphyrinate), 2.63 (s, 18H, *p*-CH_3 on Zn porphyrinate), 2.76 and 6.06 (2 × apparent d, J = 5.99 Hz, 12H, C_6H_4N), 7.23 (s, 12H, phenyl-*m*-H on Ni porphyrinate), 7.29 (s, 12H, phenyl-*m*-H on Zn porphyrinate), 7.70 (t, J = 1.71 Hz, 6H, *p*-H on di-*t*-Bu-phenyl), 7.73 (app. s, 6H, *o*-H on *t*-Bu-phenyl), 7.66 (app. s, 6H, *o*-H on *t*-Bu-phenyl), 7.84 (app. s, 6H, *p*-H on *t*-Bu-phenyl), 7.89 (d, J = 1.71 Hz, 12H, *o*-H on di-*t*-Bu-phenyl), 7.92 and 8.10 (AA′XX′ apparent J = 8.07 Hz, 24H, phenylene on Ni porphyrinate), 7.98 and 8.33 (AA′XX′ apparent J = 8.07 Hz, 24H, phenylene on Zn porphyrinate), 8.62 (s, 3H, benzenetriyl), 8.63 and 9.00 (2 × d, J = 4.64 Hz, 12H, β-H on porphyrin trimer), 8.65 and 8.76 (2 × d, J = 4.9 Hz, 24H, β-H on Ni porphyrinate), 8.78 and 8.89 (2 × d, J = 4.64 Hz, 24H, β-H on Zn porphyrinate), 8.83 and 9.77 (2 × d, J = 4.64 Hz, 12H, β-H on porphyrin trimer). MALDI-TOF-MS (DCTB): 8126.063, 5619.941, 2507.143; calcd average mass for $C_{561}H_{471}N_{39}Ni_3Zn_3$ (complex **1a** + **5**), $C_{384}H_{300}N_{24}Ni_3Zn_3$ (**5**), and $C_{177}H_{171}N_{15}$ (**1a**) = 8131.50, 5622.99, and 2508.4, respectively.

Complex 1b + 5 was characterized as described above for the complex **1a** + **5**. ^{1}H NMR (500.13 MHz, 0 °C): δ −2.24 (br, 6H, NH), 1.42 (s, 108H, *t*-Bu on **5**), 1.50 (s, 54H, *t*-Bu on **1b**), 1.87 (*s*, 36H, *o*-CH_3 on unligated Zn porphyrinate), 1.89 (s, 36H, *o*-CH_3 on ligated Zn porphyrinate), 2.64 (s, 18H, *p*-CH_3 on ligated Zn porphyrinate), 2.65 (s, 18H, *p*-CH_3 on unligated Zn porphyrinate), 2.79 and 6.10 (2 × apparent d, J = 5.4 Hz, 12H, $-C_6H_4N$), 7.31 (s, 12H, *m*-H on ligated Zn porphyrinate), 7.32 (s, 12H, *m*-H on unligated Zn porphyrinate), 7.68 (app. s, 6H, *p*-Ph), 7.76 (app. s, 6H), 7.77 (app. s, 6H), 7.89 (app. s, 6H), 7.91 (app. s, 12H, *o*-Ph), 8.00 and 8.30 (AA′XX′ on unligated Zn porphyrinate, apparent J = 7.7 Hz, 24H), 8.00 and 8.34 (AA′XX′ on ligated Zn porphyrinate, apparent J = 7.7 Hz, 24H), 8.62 (s, 3H, benzenetriyl), 8.67 and 9.02 (2 × br, 12H, β-H on porphyrin trimer), 8.80 and 8.90 (2 × d, J = 4.3 Hz, 24H, β-H on ligated Zn porphyrinate), 8.84 and 8.95 (2 × d, J = 4.2 Hz, 24H, β-H on unligated Zn porphyrinate), 8.84 and 9.78 (2 × br, 12H, β-H on porphyrin trimer). NMR (500.13 MHz, 55 °C): δ −2.11 (br, 6H, NH), 1.39 (s, 108H, *t*-Bu on trimer), 1.50 (s, 54H, *t*-Bu on hexamer), 1.87 (s, 72H, *o*-CH_3 on Zn porphyrinate), 2.62 (s, 36H, *p*-CH_3 on Zn porphyrinate), 2.65 (s, 18H, *p*-CH_3 on unligated Zn porphyrinate), 2.82 and 6.04 (2 × br, 12H, $-C_6H_4N$), 7.28 (s, 24H, *m*-H on Zn porphyrinate), 7.68 (app. s, 6H, *p*-Ph), 7.74 (app. s, 12H), 7.87 (app. s, 18H), 7.97 and 8.29 (AA′XX′ on Zn porphyrinate, apparent J = 8.0 Hz, 48H), 8.58 (s, 3H, benzenetriyl), 8.60 and 8.98 (2 × d, J = 4.5 Hz, 12H, β-H on porphyrin trimer), 8.79 and 8.90 (2 × d, J = 4.4 Hz, 48H, β-H on Zn porphyrinate), 8.78 and 9.72 (2 × d, J = 4.3 Hz, 12H, β-H on porphyrin trimer). MALDI-TOF-MS: 8147.735, 5638.619, 2507.072; calcd

average mass for $C_{561}H_{471}N_{39}Zn_6$ (complex **1b** + **5**), $C_{384}H_{300}N_{24}Zn_6$ (**1b**), and $C_{177}H_{171}N_{15}$ (**5**) = 8151.6, 5643.2, and 2508.4, respectively.

5,5′,5″-[1,3,5-Benzenetriyltris(2,1-ethynediyl-4,1-phenylene)]tris-[10,20-bis(3,5-bis(1,1-dimethylethyl)phenyl)-15-(pyrid-4-yl)-21*H*,23*H*-porphine] (3). Air was removed from a solution of **8** (7 mg, 7.24 μmol) and 1,3,5-triethynylbenzene[31c] (0.27 mg, 1.81 μmol) in 7 mL of toluene/Et_3N (5:1) by blowing argon for 1 h. Then Pd_2dba_3 (0.7 mg, 0.8145 μmol) and P(*o*-tol)$_3$ (1.9 mg, 6.516 μmol) were added, and deaeration was continued for 10 min before heating at 35 °C for 5 h, when an aliquot of catalyst was added and stirring was continued overnight. FC of the reaction mixture yielded 1.7 mg pure product **3** (35%) and 1.6 mg (23%) of starting porphyrin **8**. UV/vis (CH_2Cl_2): 296 (4.99), 421 (6.08), 517 (4.72), 552 (4.48), 591 (4.24), 647 (4.19). ^{1}H NMR (360.14 MHz): δ −2.74 (br, 6H, NH), 1.54 (s, 108H, *t*-Bu), 7.82 (t, J = 1.8 Hz, 6H, *p*-Ph), 8.03 and 8.30 (AA′XX′, apparent J = 8.1 Hz, 12H, $-C_6H_4-$), 8.05 (s, 3H, benzenetriyl), 8.10 (d, J = 1.8 Hz, 12H, *o*-Ph), 8.19 and 9.02 (2 × apparent d, J = 5.5 Hz, 12H, $-C_6H_4N$), 8.80 and 8.95 (2 × d, J = 4.8 Hz, 12H, β-H on porphine), 8.92 and 8.96 (2 × d, J = 4.8 Hz, 12H, β-H on porphine). ES$^+$-MS (in THF/HCO_2H): 889.18 ([M + 3H]$^{3+}$); calcd average mass for $C_{189}H_{183}N_{15}$ = 2664.62. HRMS (ESI-MS): 888.50060; calcd for [M + 3H]$^{3+}$ = 888.49997.

5,5′,5″-[1,3,5-Benzenetriyltris(2,1-ethynediyl)]tris[10,20-bis(3,5-bis(1,1-dimethylethyl)phenyl)-15-(pyrid-4-yl)-21*H*,23*H*-porphine] (4). Deprotected porphyrin **9b** (7 mg, 8.88 μmol) and 1,3,5-triiodobenzene[70] (1.0 mg, 2.22 μmol) were dissolved in 7 mL of toluene/Et_3N (5:1), and the solution was deaerated by bubbling argon for 45 min. Then, Pd_2dba_3 (0.9 mg, 0.99 μmol) and P(*o*-tol)$_3$ (2.4 mg, 7.99 μmol) were added, and the mixture was flushed with argon for an additional 10 min before it was heated at 35 °C for 4 h, when an aliquot of catalyst was added and stirring was continued overnight. The product (3.2 mg, 59%) was isolated by FC on silica gel using successively $CHCl_3$ and $CHCl_3$/MeOH (9:1) as eluants. UV/vis (CH_2Cl_2): 302 (4.84), 439 (6.02), 535 (4.56), 580 (5.06), 610 (4.31), 670 (4.75). ^{1}H NMR (360.14 MHz): δ −2.24 (br, 6H, NH), 1.56 (s, 108H, *t*-Bu), 7.85 (app. s, 6H, *p*-Ph), 8.12 (d, J = 1.8 Hz, 12H, *o*-Ph), 8.18 and 9.04 (AA′XX′, apparent J = 5.4 Hz, 12H, $-C_6H_4N$), 8.75 and 8.90 (2 × d, J = 4.5 Hz, 12H, β-H on porphine), 8.81 (s, 3H, benzenetriyl), 9.10 and 10.01 (2 × d, J = 4.5 Hz, 12H, β-H on porphine). ES$^+$-MS (in THF/HCO_2H): 1219.04 ([M + 2H]$^{2+}$), 813.08 ([M + 3H]$^{3+}$); calcd average mass for $C_{171}H_{171}N_{15}$ = 2436.33. HRMS (ESI-MS): 812.46382; calcd for [M + 3H]$^{3+}$ = 812.46867.

5,5′,5″-[1,3,5-Benzenetriyltris(2,1-ethynediyl)]tris[10,20-bis(3,5-bis(1,1-dimethylethyl)phenyl)-15-[(pyrid-4-yl)ethynyl]-21*H*,23*H*-porphine] (5). A solution of **14b** (34 mg, 41.86 μmol) and 1,3,5-triiodobenzene[70] (4.77 mg, 10.46 μmol) in toluene (11.7 mL) was flushed with argon for 5 min before triethylamine (2.3 mL) was added. The mixture was deaerated by three freezing/thaw cycles in vacuo and then allowed to reach room temperature under Ar atmosphere before Pd_2dba_3 (4.3 mg, 4.7 μmol) and P(*o*-tol)$_3$ (11.5 mg, 37.65 μmol) were added. Thereon, the reaction mixture was stirred under an Ar stream, protected against light, at 35 °C for 8 h before an aliquot of catalyst was added and stirring was continued overnight. The solvent was removed under reduced pressure, and the crude product was purified by FC. A first fraction, which contained a porphyrin dimer formed by homocoupling of **14b**, was eluted with $CHCl_3$/EtOAc (5:1); the second green-colored fraction, which contained **5**, was eluted with $CHCl_3$/MeOH (9:1). The residue obtained after evaporation of the solvent was washed with MeOH and hexane to yield 22.8 mg (87%) of the product. UV/vis (CH_2Cl_2): 447 (5.97), 519 (4.31), 558 (4.38), 604 (4.11), 693 (4.95). ^{1}H NMR (500.13 MHz, 30 °C): δ −1.88 (br, 6H, NH), 1.59 (s, 108H, *t*-Bu), 7.86 (t, J = 1.8 Hz, 6H, *p*-Ph), 7.89 and 8.84 (AA′XX′, apparent J = 5.9 Hz, 12H, $-C_6H_4N$), 8.12 (d, J = 1.8 Hz, 12H, *o*-Ph), 8.79 (s, 3H, benzenetriyl), 8.98 and 9.70 (2 × d, J = 4.6 Hz, 12H, β-H on porphine), 9.03 and 9.94 (2 × d, J = 4.65 Hz, 12H, β-H on porphine). ES$^+$-MS (in THF/HCO_2H): 1255.28 ([M + 2H]$^{2+}$), 837.16 ([M + 3H]$^{3+}$); calcd average mass for $C_{177}H_{171}N_{15}$ = 2508.4. HRMS (ESI-MS): 836.46783; calcd for [M + 3H]$^{3+}$ = 836.46867.

4,4′,4″-[1,3,5-Benzenetriyltris(2,1-ethynediyl)]tris[[(4′-(pyrid-4-yl)ethynyl)]1,1′-biphenyl] (6). Method A: A mixture of **17b** (50 mg, 179 μmol), 1,3,5-triiodobenzene[70] (22 mg, 48.4 μmol), CuI (8.3 mg, 43.5 μmol), and TBAI (53.6 mg, 145 μmol) was deaerated flushing with argon for 30 min before DMF/^{i}Pr$_2$NEt (10.5 mL, 20:1) followed by Pd_2dba_3 (13.3 mg, 14.5 μmol) and tris(2,4,6-trimethylphenyl)-phosphine (11.3 mg, 29.0 μmol) were added. The mixture was deaerated for an additional 10 min and then heated at 50 °C overnight. The solvent was removed under reduced pressure, and the solid residue, dissolved in $CHCl_3$, was purified by FC using $CHCl_3$/MeOH (9:1) as eluant. The residue obtained from the main fraction, after evaporation of the solvent, was washed with MeOH to yield 28.3 mg (59%) of **6**. Mp 220 °C (dec), which was not soluble enough for recording a ^{13}C NMR spectrum. ^{1}H NMR (360.14 MHz): δ 7.41 and 8.63 (AA′XX′, apparent J = 5.9 Hz, 12H, $-C_6H_5N$), 7.65 (d, J = 3.2 Hz, 24H, phenylene), 7.72 (s, 3H, benzenetriyl). ES$^+$-MS (THF/HCO_2H): 909.99 ([M + H]$^+$), 456.10 ([M + 2H]$^{2+}$), 304.38 ([M + 3H]$^{3+}$); calcd average mass for $C_{69}H_{39}N_3$ = 910.10. HRMS (ESI-MS): 910.32138; calcd for [M + H]$^+$ = 910.32167.

Method B: A solution of **18b** (15 mg, 22 μmol) and 4-iodopyridine[45] (40.8 mg, 199 μmol) in 12 mL of THF/Et_3N (5:1) was deaerated by blowing argon for 45 min. Then, $Pd_2(PPh_3)_2Cl_2$ (7.0 mg, 9.94 μmol) and PPh_3 (5.2 mg, 19.88 μmol) were added, and deaeration was continued for 10 min before heating at 60 °C for 5 h, when an aliquot of catalyst was added and stirring was continued overnight. The solid residue obtained after evaporation of the solvent under reduced pressure was purified by FC using successively $CHCl_3$, $CHCl_3$/EtOAc (1:1), and $CHCl_3$/MeOH (1:1) as eluants to yield 11.2 mg (56%) of **6**.

5,15-Bis[3,5-bis(1,1-dimethylethyl)phenyl]-10-(4-iodophenyl)-20-(pyrid-4-yl)-21*H*,23*H*-porphine (8). To a deaerated solution of *meso*-(3,5-di-*tert*-butylphenyl)-2,2′-dipyrrylmethane (**7**)[29] (167 mg, 0.5 mmol) in 50 mL of CH_2Cl_2/EtOH (95:5) were successively added 4-iodobenzaldehyde[30] (116 mg, 0.5 mmol), 4-pyridine carboxaldehyde (48 μL, 0.5 mmol), and TFA (100 μL, 1.27 mmol). The solution was protected from light and stirred, under Ar, at 25 °C overnight. Thereafter, a saturated solution of DDQ (170 mg, 0.75 mmol) in THF was added, and stirring was continued for an additional 1 h. The solid residue obtained after removal of the solvent under reduced pressure was washed with methanol, then dissolved in CH_2Cl_2, and purified by FC. A first fraction consisting of 5,15-bis(4-iodophenyl)-10,20-bis(3,5-bis-(1,1-dimethylethyl)phenyl)porphyrin was eluted with CH_2Cl_2, then the column was eluted with CH_2Cl_2 /EtOAc (95:5) or, alternatively, CH_2Cl_2 /EtOH (97:3) to afford a second fraction which contained 14.7 mg (6%) of the desired product **8**. UV/vis (CH_2Cl_2): 419 (5.59), 516 (4.21), 551 (3.92), 591 (3.74), 646 (3.66). ^{1}H NMR (360.14 MHz): δ −2.78 (br, 2H, NH), 1.54 (s, 36H, *t*-Bu), 7.82 (t, J = 1.8 Hz, 2H, *p*-Ph), 7.96 and 8.10 (AA′XX′, apparent J = 7.7 Hz, 4H, $-C_6H_4I$), 8.08 (d, J = 1.5 Hz, 4H, *o*-Ph), 8.18 and 9.02 (AA′XX′, apparent J = 5.9 Hz, 4H, $-C_6H_4N$), 8.80 and 8.92 (2 × d, J = 4.8 Hz, 4H, β-H on porphine), 8.84 and 8.94 (2 × d, J = 4.8 Hz, 4H, β-H on porphine). ES$^+$-MS (in THF/HCO_2H): 967.10 ([M + H]$^+$), 483.98 ([M + 2H]$^{2+}$); calcd average mass for $C_{59}H_{60}N_5I$ = 966.10. HRMS (ESI-MS): 966.39599; calcd for [M + H]$^+$ = 966.39662. Anal. Calcd C 73.35, H 6.26, N 7.25; found C 73.34, H 6.21, N 7.18.

5,15-Bis[3,5-bis(1,1-dimethylethyl)phenyl]-10-(pyrid-4-yl)-20-[(trimethylsilyl)ethynyl]-21*H*,23*H*-porphine (9a). A solution of *meso*-(3,5-di-*tert*-butylphenyl)-2,2′-dipyrrylmethane (**7**)[29] (334.5 mg, 1 mmol), 3-trimethylsilylprop-2-ynal[43] (126 mg, 1 mmol), and 4-pyridinecarboxaldehyde (96 μL, 1 mmol) in CH_2Cl_2/EtOH (100 mL, 95:5) was deaerated by bubbling Ar for 30 min. Then, TFA (120 μL, 1.52 mmol) was added, and the reaction mixture was stirred for 4 h at room

(70) Ozasa, S.; Fujiota, Y.; Hashino, H.; Kimura, N.; Ibuki, *E. Chem. Pharm. Bull.* **1983**, *31*, 2313−2320.

temperature, protected from light. Thereafter, a saturated solution of DDQ (340 mg, 1.5 mmol) in THF was added, and stirring was continued for an additional 1 h. The reaction mixture was filtered through a silica and alumina pad, which was subsequently washed with $CHCl_3$ until the filtrate was colorless. The solvent was removed under reduced pressure, and the solid residue was dissolved in CH_2Cl_2/hexane (1:1) and purified by FC, eluting successively with CH_2Cl_2/hexane (1:1), CH_2Cl_2, $CHCl_3$, and $CHCl_3$/EtOAc (9:1). The first eluted fraction contained 5,15-bis(3,5-bis(1,1-dimethylethyl)phenyl)-10,20-bis[(trimethylsilyl)ethynyl)]porphyrin (33.4 mg, 8%) followed by the desired product **9a** (22.7 mg, 5%). UV/vis (CH_2Cl_2): 428 (5.57), 529 (4.17), 566 (4.31), 605 (3.76), 662 (3.94). ^{1}H NMR (360.14 MHz): δ −2.43 (br, 2H, NH), 0.61 (s, 9H, TMS), 1.54 (s, 36H, *t*-Bu), 7.82 (t, J = 1.8 Hz, 2H, *p*-Ph), 8.06 (d, J = 1.8 Hz, 4H, *o*-Ph), 8.14 and 9.02 (AA′XX′, apparent J = 5.9 Hz, 4H, $-C_6H_4N$), 8.71 and 8.86 (2 × d, J = 4.5 Hz, 4H, β-H on porphine), 8.95 and 9.69 (2 × d, J = 5.0 Hz, 4H, β-H on porphine). ES$^+$-MS (in THF/HCO_2H): 861.03 ([M + H]$^+$), 430.76 ([M + 2H]$^{2+}$); calcd average mass for $C_{58}H_{65}N_5Si$ = 860.30. HRMS (ESI-MS): 860.50820; calcd for [M + H]$^+$ = 860.50820. Anal. Calcd C 80.98, H 7.62, N 8.14; found C 80.94, H 7.69, N 8.09.

5-Ethynyl-10,20-bis[3,5-bis(1,1-dimethylethyl)phenyl]-15-(pyrid-4-yl)-21*H*,23*H*-porphine (9b). To a solution of **9a** (12.7 mg, 14.76 μmol) in 30 mL of CH_2Cl_2/Et_3N (1:1) was added TBAF (15 μL soln. 1 M in THF, 15.00 μmol), and the mixture was stirred for 10 min at 25 °C. The reaction was quenched by adding ca. 1 g of $CaCl_2$. The solvent was removed under reduced pressure, and the solid residue was purified by FC with $CHCl_3$ containing 2% Et_3N as eluant to yield 10.6 mg (91%) of **9b**. UV/vis (CH_2Cl_2): 425 (5.56), 524 (4.21), 561 (4.15), 601 (3.73), 658 (3.78). ^{1}H NMR (360.14 MHz): δ −2.49 (br, 2H, NH), 1.54 (s, 36H, *t*-Bu), 4.21 (s, 1H, ethynyl), 7.83 (t, J = 1.8 Hz, 2H, *p*-Ph), 8.06 (d, J = 1.8 Hz, 4H, *o*-Ph), 8.14 and 9.02 (AA′XX′, apparent J = 5.9 Hz, 4H, $-C_6H_4N$), 8.73 and 8.98 (2 × d, J = 4.5 Hz, 4H, β-H on porphine), 8.87 and 9.72 (2 × d, J = 4.5 Hz, 4H, β-H on porphine). ES$^+$-MS (in THF/HCO_2H): 789.01 ([M + H]$^+$), 394.74 ([M + 2H]$^{2+}$); calcd average mass for $C_{55}H_{57}N_5$ = 788.10. HRMS (ESI-MS): 788.46892; calcd for [M + H]$^+$ = 788.46867. Anal. Calcd C 83.82, H 7.29, N 8.89; found C 83.74, H 7.32, N 8.79.

5,15-Bis-[3,5-bis(1,1-dimethylethyl)phenyl]-10-[(triisopropylsilyl)-ethynyl]-20-[(trimethyl silyl)ethynyl]-21*H*, 23*H*-porphine (11). A solution of *meso*-(3,5-di-*tert*-butylphenyl)-2,2′-dipyrrylmethane (**7**)[29] (2.0 g, 6 mmol), 3-trimethylsilylprop-2-ynal[43] (756 mg, 6 mmol), and 3-triisopropylsilylprop-2-ynal[44] (1.27 g, 6 mmol) in 600 mL of $CHCl_3$/EtOH (95:5) was purged of air by bubbling Ar for 25 min. Then, TFA (720 μL, 9.12 mmol) was added, and the reaction mixture was stirred under Ar at 25 °C for 5 h, protected from light. Thereafter, a saturated solution of DDQ (2.0 g, 8.8 mmol) in THF was added, and stirring was continued for an additional 1 h. The reaction mixture was filtered through a silica gel and alumina pad, which was subsequently washed with CH_2Cl_2 until the filtrate became colorless. Chromatography of the solid residue obtained after evaporation of the solvent under reduced pressure on silica gel using successively a 1:4 and 3:2 mixture of CH_2Cl_2/*n*-hexane, as eluant, afforded three fractions. The first and third eluted violet−green bands containing **12** (260.6 mg, 8%) and **10** (100 mg, 4%), respectively, whose analytical data agree with those reported in ref 37e and refs 25b and 34a, respectively. After evaporation of the solvent, the component of the second violet−green band was washed with cold methanol and dried in vacuo to yield 352.4 mg (12%) of the desired product **11**. UV/vis (CH_2Cl_2): 433 (5.51), 543 (4.06), 584 (4.64), 620 (3.74), 680 (4.28). ^{1}H NMR (360.14 MHz): δ −2.12 (br, 2H, NH), 0.59 (s, 9H, TMS), 1.43 (m, 21H, TIPS), 1.54 (s, 36H, *t*-Bu), 7.80 (t, J = 1.8 Hz, 2H, *p*-Ph), 8.03 (d, J = 1.8 Hz, 4H, *o*-Ph), 8.86 and 9.61 (2 × d, J = 4.5 Hz, 4H, β-H on porphine), 8.87 and 9.66 (2 × d, J = 4.5 Hz, 4H, β-H on porphine). ES$^+$-MS (in THF/HCO_2H): 964.09 ([M + H]$^+$), 321.33 ([M + 3H]$^{3+}$), 642.87 ([2M + 3H]$^{3+}$); calcd average mass for $C_{64}H_{82}N_4Si_2$ = 963.60. HRMS (ESI-MS): 963.61641; calcd for [M + H]$^+$ = 963.61508.

5-Ethynyl-10,20-bis[3,5-bis(1,1-dimethylethyl)phenyl]-15-[(triisopropylsilyl)ethynyl] −21*H*,23*H*-porphine (13). To a solution of **11** (143.6 mg, 149 μmol) in 20 mL of THF was added 5 mL of 1 N aq. NaOH, and the mixture was stirred for 2 h at 25 °C. Thereon, the solid residue obtained after evaporation of the solvent under reduced pressure was dissolved in CH_2Cl_2/*n*-hexane (4:1) and purified by column chromatography on silica gel using CH_2Cl_2/*n*-hexane (4:1) as eluant to afford 126 mg (95%) of **13**. UV/vis (CH_2Cl_2): 430 (5.47), 538 (4.12), 579 (4.50), 616 (3.77), 676 (4.15). ^{1}H NMR (360.14 MHz): δ −2.18 (br, 2H, NH), 1.43 (m, 21H, (*i*-Pr)$_3$Si, 1.55 (s, 36H, *t*-Bu), 4.18 (s, 1H), 7.82 (t, J = 1.8 Hz, 2H, *p*-Ph), 8.03 (d, J = 1.8 Hz, 4H, *o*-Ph), 8.89 and 9.66 (2 × d, J = 4.5 Hz, 4H, β-H on porphine), 8.89 and 9.67 (2 × d, J = 4.5 Hz, 4H, β-H on porphine). ES$^+$-MS (in THF/HCO_2H): 892.07 ([M + H]$^+$), 446.31 ([M + 2H]$^{2+}$), 297.3 ([M + 3H]$^{3+}$), 594.45 ([2M + 3H]$^{3+}$); calcd average mass for $C_{61}H_{74}N_4Si$ = 891.40. HRMS (ESI-MS): 891.57574; calcd for [M + H]$^+$ = 891.57555.

5,15-Bis[3,5-bis(1,1-dimethylethyl)phenyl]-10-[(triisopropylsilyl)-ethynyl]-20-[(pyrid-4-yl)ethynyl)]-21*H*, 23*H*-porphine (14a). A solution of **13** (60 mg, 67.3 μmol) and 4-iodopyridine[45] (34.5 mg, 168.25 μmol) in 15 mL of toluene/Et_3N (5:1) was purged of air by blowing Ar for 45 min before Pd_2dba_3 (9.2 mg, 10.09 μmol) and P(*o*-tol)$_3$ (24.6 mg, 80.76 μmol) were added. Deaeration was continued for 10 min, and then the solution was heated at 60 °C for 6 h. Thereon, the same amounts of catalyst were added, and stirring was continued overnight. The crude product obtained after evaporation of the solvent under reduced pressure was purified by FC. A first fraction, which contained very small amounts of a porphyrin dimer formed by homocoupling of **13**, was eluted with CH_2Cl_2, then the column was eluted successively with $CHCl_3$ and $CHCl_3$/EtOAc (5:1) to afford a second fraction containing the desired product. The solid residue obtained after evaporation of the eluant was washed with methanol and dried in vacuo to yield 49.1 mg (75%) of **14a**. UV/vis (CH_2Cl_2): 438 (5.57), 549 (4.05), 592 (4.73), 624 (3.85), 685 (4.45). ^{1}H NMR (360.14 MHz): δ −2.03 (br, 2H, NH), 1.43 (m, 21H, (*i*-Pr)$_3$Si), 1.56 (s, 36H, *t*-Bu), 7.83 (t, 2H, J = 1.8 Hz, *p*-Ph), 7.86 and 8.81 (AA′XX′, apparent J = 5.9 Hz, 4H, $-C_6H_4N$), 8.04 (d, J = 1.8 Hz, 4H, *o*-Ph), 8.89 and 9.67 (2 × d, J = 4.5 Hz, 4H, β-H on porphine), 8.92 and 9.66 (2 × d, J = 4.5 Hz, 4H, β-H on porphine). ES$^+$-MS (in THF/HCO_2H): 969.42 ([M + H]$^+$), 484.81 ([M + 2H]$^{2+}$); calcd average mass for $C_{66}H_{77}N_5Si$ = 968.50. HRMS (ESI-MS): 968.60557; calcd for [M + H]$^+$ = 968.60210.

5-Ethynyl-10,20-bis[3,5-bis(1,1-dimethylethyl)phenyl]-15-[(pyrid-4-yl)ethynyl]-21*H*,23*H*-porphine (14b). To a solution of **14a** (51.4 mg, 53.07 μmol) in 16 mL of CH_2Cl_2/Et_3N (1:1) was added 63.7 μL of TBAF solution (1 M in THF), and the mixture was stirred for 10 min at 25 °C. Then, the reaction was quenched by addition of ca. 1 g of $CaCl_2$, and the solid residue obtained after evaporation of the solvent under reduced pressure was chromatographed on a silica gel column using CH_2Cl_2 as eluant to afford 36.7 mg (85%) of **14b**. UV/vis (CH_2Cl_2): 436 (5.54), 543 (4.09), 586 (4.62), 620 (3.85), 680 (4.32). ^{1}H NMR (360.14 MHz): δ −2.12 (br, 2H, NH), 1.56 (s, 36H, *t*-Bu), 4.21 (s, 1H), 7.85 (t, J = 1.8 Hz, 2H, *p*-Ph), 7.86 and 8.81 (AA′XX′, apparent J = 5.9 Hz, 4H, $-C_6H_4N$), 8.07 (d, J = 1.8 Hz, 4H, *o*-Ph), 8.91 and 9.66 (2 × d, J = 4.9 Hz, 4H, β-H on porphine), 8.94 and 9.67 (2 × d, J = 4.9 Hz, 4H, β-H on porphine). ES$^+$-MS (in THF/HCO_2H): 813.02 ([M + H]$^+$); calcd average mass for $C_{57}H_{57}N_5$ = 812.10. HRMS (ESI-MS): 812.46950; calcd for [M + H]$^+$ = 812.46867. Anal. Calcd C 84.30, H 7.07, N 8.62; found C 84.32, H 7.28, N 8.60.

4-Bromo-4′-[(trimethylsilyl)ethynyl]-1,1′-biphenyl (15). To a solution of 4,4′-dibromobiphenyl (1 g, 3.2 mmol) in THF (15 mL) containing diisopropylamine (4 mL) were added successively, under Ar, ethynyltrimethylsilane (526 μL, 3.8 mmol), $Pd(PPh_3)_2Cl_2$ (266.7 mg, 0.38 mmol), and CuI (72.4 mg, 0.38 mmol) before the reaction mixture was stirred at 50 °C for 24 h. After removal of the solvent under reduced pressure, the solid residue was dissolved in CH_2Cl_2 and

purified twice by FC using *n*-hexane as eluant to yield 135 mg (14%) of starting material, as the first eluted component, and 343 mg (33%) of **15**, which was eluted as the second moving band, followed closely by a small amount of 4,4′-bis[(trimethylsilyl)ethynyl]-1,1′-biphenyl, which was discarded. The analytical data of **15** are identical to those reported elsewhere.[47]

4-[(Triisopropylsilyl)ethynyl]-4′-[(trimethylsilyl)ethynyl]-1,1′-biphenyl (16a). Method A: Reaction of 4,4′-dibromobiphenyl (3.12 g, 10.0 mmol) with a mixture of ethynyltrimethylsilane (1.66 mL, 12 mmol) and ethynyltriisopropylsilane (2.19 mL, 12 mmol) under the same conditions as described for **15** afforded **16a** in 16% yield, as a viscous oil. **Method B:** A better yield (62%) was obtained reacting a solution of **15** (320 mg, 0.97 mmol) in 15 mL of THF with ethynyltriisopropylsilane (435.9 μL, 1.94 mmol) under the same conditions as described for **15**. Anal. Calcd C 78.07, H 8.89; found C 78.14, H 8.92. The analytical data are identical to those reported elsewhere.[48]

4-Ethynyl-4′-[(triisopropylsilyl)ethynyl]-1,1′-biphenyl (16b). To a solution of **16a** (260 mg, 0.6 mmol) in THF (7 mL) was added 3 mL of aq. NaOH (1 N), and the mixture was vigorously stirred for 2 h at 25 °C. After evaporation of the solvent under reduced pressure, the obtained oily residue was purified by FC using hexane/CH_2Cl_2 as eluant to yield 205.7 mg (95%) of **16b** as a light yellow oil which crystallized upon standing. Mp 42−43 °C (lit.[48] 41−42 °C). Anal. Calcd C 83.74, H 8.43; found C 83.55, H 8.32. The spectroscopic data are identical to those reported in ref 48.

4-[(Triisopropylsilyl)ethynyl]-4′-[(pyrid-4-yl)ethynyl]-1,′1-biphenyl (17a). A solution of **16b** (759 mg, 2.12 mmol) and 4-iodopyridine[45] (612 mg, 2.98 mmol) in 102 mL of a mixture of toluene and triethylamine (5:1) was purged of air by passing Ar for 45 min before Pd_2dba_3 (291 mg, 317.8 μmol) and P(*o*-tol)$_3$ (773 mg, 2.54 mmol) were added, and the mixture was heated at 80 °C for 6 h. Then an aliquot of catalyst was added, and stirring was continued overnight. Thereafter, the solution was cooled to 25 °C, and the residue obtained after removal of the solvent under reduced pressure was purified by FC using CH_2Cl_2 and $CHCl_3$ as eluant to afford **17a** contaminated with traces of 4-iodopyridine, which was removed by sublimation in vacuo at 80 °C during 3 h to yield 604 mg of the product (66%); mp 95−98 °C. ^{1}H NMR (360.14 MHz): δ 1.15 (s, 21H, (*i*-Pr)$_3$Si), 7.40 and 8.62 (AA′XX′, apparent J = 5.9 Hz, 4H, C_6H_4N), 7.54−7.65 (m, 8H, phenylene). ^{13}C NMR (90.56 MHz): δ 11.5, 18.8, 87.7, 92.1, 93.9, 106.8, 121.4, 123.2, 125.7, 126.9, 127.2, 131.5, 132.5, 132.7, 139.9, 141.2, 149.9. FAB-MS (matrix, NBA): 436 (M^+); calcd average mass for $C_{30}H_{33}NSi$ = 435.68. HRMS (ESI-MS): 436.24424; calcd for $[M + H]^+$ = 436.244550.

4-Ethynyl-4′-[(pyrid-4-yl)ethynyl)]-1,1′-biphenyl (17b) was obtained reacting **17a** (604 mg, 1.39 mmol) with TBAF (1 M in THF, 1.6 mL) under the same conditions as described for **14b**. After evaporation of the solvent, the product separated by FC using successively $CHCl_3$/EtOAc (8:3) and $CHCl_3$/MeOH (9:1) as eluants was washed with MeOH to yield 229 mg (59%) of **17b** as a solid of mp 201.5 °C (dec), which is not soluble enough for recording a ^{13}C NMR spectrum. ^{1}H NMR (360.14 MHz): δ 3.16 (s, 1H, ethynyl), 7.40 and 8.62 (AA′XX′, apparent J = 5.9 Hz, 4H, C_6H_4N), 7.54−7.65 (m, 8H, phenylene). ES$^+$-MS (in THF/HCO_2H): 280.12 ($[M + H]^+$); calcd average mass for $C_{21}H_{13}N$ = 279.30. HRMS (ESI-MS): 280.11233; calcd for $[M + H]^+$ = 280.11208.

4,4′,4″-[1,3,5-Benzenetriyltris(2,1-ethynediyl)]tris[[(4′-triisopropylsilyl) ethynyl]-1,1′-biphenyl (18a). A solution of 1,3,5-triiodobenzene[70] (34 mg, 75 μmol), TBAI (55.2 mg, 149 μmol), CuI (12.8 mg, 67.2 μmol), and tris(2,4,6-trimethylphenyl)phosphine (17.4 mg, 45 μmol) in 10.5 mL of a mixture of DMF/*i*-Pr_2NEt (20:1) was purged of air by passing Ar for 30 min before Pd_2dba_3 (10.3 mg, 11.2 μmol) was added, and the mixture was stirred at 20 °C for 5 min. Thereon, the yellow mixture was cooled to −20 °C before **16b** (100 mg, 279 μmol) was added, and stirring was continued for 1 h. Thereafter, the reaction mixture was allowed to reach room temperature, and the resulting dark brown solution was stirred overnight at 25 °C. The solid residue obtained after removal of the solvent under reduced pressure was dissolved in CH_2Cl_2/hexane (1:5) and purified by FC using CH_2Cl_2/hexane (1:5) as eluant. The main fraction was separated and purified again by FC using CH_2Cl_2/hexane (1:9) as eluant to yield 73.10 mg (85%) of **18a**, as a solid of mp 125 °C, which is not soluble enough for recording a ^{13}C NMR spectrum. ^{1}H NMR (360.14 MHz): δ 1.15 (s, 63H, TIPS), 7.56 (br s, 12H, phenylene), 7.61 (br s, 12H, phenylene), 7.70 (s, 3H, benzenetriyl). FAB-MS (matrix, NBA): 1149.0 ($[M + H]^+$); calcd average mass for $C_{81}H_{90}Si_3$ = 1148.2. Anal. Calcd C 84.76, H 7.90; found C 84.08, H 8.00.

4,4′,4″-[1,3,5-Benzenetriyltris(2,1-ethynediyl)]tris[(4′-ethynyl)-1,1′-biphenyl] (18b). The ethynyl groups of **18a** (64 mg, 55.8 μmol) were deprotected by treatment with TBAF (1 M in THF, 200 μL) as described previously for **14b**, yielding, after FC using CH_2Cl_2/hexane (9:1) as eluant, 36.7 mg (97%) of **18b**. Mp 182 °C (dec), which is not soluble enough for recording a ^{13}C NMR spectrum. ^{1}H NMR (360.14 MHz): δ 3.16 (s, 3H, ethynyl), 7.59 (br s, 12H, phenylene), 7.62 (br s, 12H, phenylene), 7.70 (s, 3H, benzenetriyl). FAB-MS (matrix, NBA): 678.00 (M^+); calcd average mass for $C_{54}H_{30}$ = 678.80. HRMS (MALDI-MS, dithranol): 678.23222; calcd for M^+ = 678.23420.

[(2,3,7,8,12,13,17,18-$^2H_8$)-5,15-Bis(4-iodophenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrinato(2-)]zinc(2+) (19-d_8). A solution of mesitylaldehyde[71] (1.47 mL, 10 mmol) in pyrrole-d_5[72] (27.8 mL, 400 mmol) was purged from air by passing Ar for 30 min before BF_3 etherate (0.369 mL, 3.0 mmol) was added. The reaction mixture was stirred for 30 min at 25 °C and thereon neutralized adding 20 g of anhydrous K_2CO_4. After evaporation of the solvent under reduced pressure, unreacted pyrrole was removed by vacuum distillation, and the obtained residue was purified twice by FC, using EtOAc/*n*-hexane (1:9) as eluant, to yield 1.4 g (55%) of (3,3′,4,4′5,5′-$^2H_6$)-*meso*-(2,4,6-trimethylphenyl)-2,2′-dipyrrylmethane containing 82−89% ^{2}H on the C-atoms. The isotope content was subsequently increased by dissolving a sample (470 mg, 0.173 mmol) in 10 mL of dry CH_2Cl_2 and shaking the solution for 12 h at 25 °C with a mixture of ^2H_2O (10 mL) and acetic acid-d_1 (5 mL) in the dark. Thereafter, 100 mL of CH_2Cl_2 was added, and the aqueous suspension was neutralized by adding 12 g of anhydrous K_2CO_3; the organic layer was separated, dried on $MgSO_4$, filtered, and the solvent was removed under reduced pressure. The thus obtained dipyrrylmethane-d_6, which contained >95 mol % deuterium, was dissolved together with 401 mg (0.173 mmol) of 4-iodobenzaldehyde[30] in 175 mL of amylene-stabilized $CHCl_3$ containing 1.75 mL of ethanol-*d*. The solution was purged from air passing Ar for 10 min, and then 235 μL from a 2.5 M stock solution of BF_3 etherate in $CHCl_3$ was added. The mixture was stirred for 1 h at 25 °C, and thereafter, DDQ (298 mg, 1.31 mmol) was added and stirring was continued for 30 min before the solvent was removed. Purification of the residue by FC using CH_2Cl_2 as eluant afforded, as the first moving band, 271 mg (33%) of 5,15-bis(4-iodophenyl)-10,20-bis(2,4,6-trimethylphenyl)porphine-d_8 containing 90% deuterium on the β-C-atoms of the pyrrole rings. Finally, the porphyrin was transformed into **19**-d_8 by reaction with zinc acetate following the procedure given in ref 28.

[5,15-Bis(4-{[3-(3,3-diethyl-1-triazenyl)-5-(1,1-dimethylethyl)-phenyl]ethynyl}phenyl)-10,20-bis(2,4,6-trimethylphenyl)porphinato-(2−)]zinc(2+) (20a). A solution of **19**[50] (1.5 g, 1.48 mmol) and 1-[3-(1,1-dimethylethyl)-5-ethynylphenyl]-3,3-diethyl-1-triazene[19] (0.952 g, 3.7 mmol) in 260 mL of DMF/Et_3N (5:1) was purged of air by passing Ar for 30 min. Then, $Pd(PPh_3)_2Cl_2$ (207.8 mg, 0.296 mmol) and CuI (114.3 mg, 0.6 mmol) were added, and deaeration was continued for 10 min, before 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, using $CHCl_3$/*n*-hexane/Et_3N (gradient from 50:50:0.2

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(72) (a) Bean, G. P. *Chem. Commun*. **1971**, 421. (b) Fajer, J. *Ann. NY Acad. Sci*. **1973**, 349−364.

to 80:20:0.2) as eluant to yield 1.38 g (73%) of **20a**. UV−vis (CH_2Cl_2): 294 (4.92), 423 (5.74), 550 (4.43), 591 (3.83). ^{1}H NMR (360.14 MHz): δ 1.32 (t, J = 7.3 Hz, 12H, Et), 1.42 (s, 18H, *t*-Bu), 1.84 (s, 12H, *o*-Me), 2.64 (s, 6H, *p*-Me), 3.82 (q, J = 7.0 Hz, 8H, Et), 7.49 (d, J = 1.7 Hz, 4H), 7.59 (t, J = 1.7 Hz, 2H), 7.93 and 8.23 (AA′XX′, apparent J = 8.5 Hz, 8H, Ph), 8.80 and 8.90 (2 × d, J = 4.9 Hz, 8H, β-H on porphine). ES$^+$-MS (in THF/HCO_2H): 1274.05 ([M + H]$^+$), 637.46 ([M + 2H]$^{2+}$); calcd average mass for $C_{82}H_{82}N_{10}Zn$ = 1273.0. HRMS (ESI-MS): 1271.60803, 636.30800; calcd for [M + H]$^+$ and [M + 2H]$^{2+}$ = 1271.60882 and 636.30805, respectively (monoisotopic peaks corresponding to ^{64}Zn).

By the same procedure, **20a**-d_8 was prepared from **19**-d_8.

[5,15-Bis[4-[[3-(1,1-dimethylethyl)-5-iodophenyl]ethynyl]phenyl]-10,20-bis(2,4,6-trimethylphenyl)porphinato(2−)]zinc(2+) (20b). A solution of **20a** (100 mg, 78.6 μmol) in iodomethane (20 mL) contained in a thick-walled screw cap tube was flushed with argon before the tube was sealed and the mixture heated to 135 °C for 2 h. The mixture was then cooled to 25 °C, and the crude product obtained after evaporation of the solvent under reduced pressure was purified by FC using $CHCl_3$/hexane/Et_3N (50:50:0.1) as eluant to yield 102 mg (98%) of **20b**. UV−vis (CH_2Cl_2): 288 (4.76), 422 (5.72), 549 (4.39), 591 (3.82). ^{1}H NMR (360.14 MHz): δ 1.38 (s, 18H, *t*-Bu), 1.83 (s, 12H, *o*-Me), 2.64 (s, 6H, *p*-Me), 7.29 (s, 4H, *m*-H), 7.66 (t, J = 1.4 Hz), 7.75 (t, J = 1.4.Hz, 2H), 7.86 (t, J = 1.4 Hz, 2H), 7.92 and 8.24 (AA′XX′, apparent J = 8.1 Hz, 8H), 8.80 and 8.89 (2 × d, J = 4.8 Hz, 8H, β-H on porphine). ES$^+$-MS (in THF/HCO_2H): 1326.23 ([M + H]$^+$), 1264.33 ([M − Zn + 2H]$^+$), 632.16 ([M − Zn + 2H]$^{2+}$); calcd average mass for $C_{74}H_{62}I_2N_4Zn$ = 1326.52. HRMS (ESI-MS): 1324.23931, 1263.32980; calcd for M$^+$ and [M − Zn + 3H]$^+$ = 1324.23498 and 1263.32931, respectively (monoisotopic peaks corresponding to ^{64}Zn).

By the same procedure, **20b**-d_8 was prepared from **20a**-d_8.

[5,15-Bis(2,4,6-trimethylphenyl)-10,20-bis[4-[(trimethylsilyl)ethynyl] phenyl] porphinato(2−)]zinc(2+) (21a). Air was removed from a solution of **19**[50] (64 mg, 63.1 μmol) in 12 mL of DMF/Et_3N (5:1) by blowing Ar for 30 min. Then, $Pd(PPh_3)_2Cl_2$ (4.4 mg, 6.3 μmol) and CuI (2.4 mg, 12.6 μmol) were added, and the mixture was flushed with argon for an additional 10 min before ethynyltrimethylsilane (52 μL, 379μmol) was added and the mixture was heated at 35 °C for 15 h. The solid residue obtained after evaporation of the solvent under reduced pressure was purified by FC eluting with $CHCl_3$/*n*-hexane (1:1) to yield 41 mg (68%) of **21a**. UV−vis (CH_2Cl_2): 305 (4.14), 421 (5.49), 549 (4.12), 588 (3.40). ^{1}H NMR (360.14 MHz): δ 0.37 (s, 18H, Me_3Si), 1.82 (s, 12H, *o*-Me), 2.63 (s, 6H, *p*-Me), 7.28 (s, 4H, *m*-H), 7.86 and 8.18 (AA′XX′, apparent J = 8.1 Hz, 8H), 8.78 and 8.84 (2 × d, J = 4.8 Hz, 8H, β-H on porphine). ES$^+$-MS (in THF/HCO_2H): 955.34 ([M + H]$^+$), 892.43 ([M − Zn + 3H]$^+$); calcd average mass for $C_{60}H_{56}N_4Si_2Zn$ = 954.34. HRMS (ESI-MS): 952.33155, 891.42663; calcd for M$^+$ and [M − Zn + 3H]$^+$ = 952.33295 and 891.42728, respectively (monoisotopic peaks corresponding to ^{64}Zn).

By the same procedure, **21a**-d_8 was prepared from **19**-d_8.

5,15-Bis(4-ethynylphenyl)-10,20-bis(2,4,6-trimethylphenyl)-21*H*,23*H*-porphine (21b, M = 2H). To a solution of **21a** (729 mg, 0.76 mmol) in $CHCl_3$ (230 mL) was added TFA (23 mL), and the mixture was stirred at 25 °C for 2 h. The solution was then neutralized with saturated aq. $NaHCO_3$, and the aqueous residue obtained after evaporation of the organic solvent under reduced pressure was diluted with 102 mL of THF. NaOH (2.28 g) was added, and the mixture was vigorously stirred for 3 h at 25 °C. Then, the mixture was diluted with CH_2Cl_2 (300 mL), the organic layer was separated, washed with water, and dried ($MgSO_4$) before the solvent was evaporated. The obtained solid residue was purified by FC using successively a 55:45 and a 70:30 mixture of $CHCl_3$/hexane as eluant to afford **21b** in quantitative yield (569 mg). UV−vis (CH_2Cl_2): 303 (4.26), 419 (5.68), 515 (4.30), 550 (3.93), 591 (3.76), 646 (3.64). ^{1}H NMR (360.14 MHz): δ −2.66 (br, 2H, NH), 1.83 (s, 12H, *o*-Me), 2.63 (s, 6H, *p*-Me), 3.31 (s, 2H, ethynyl), 7.28 (s, 4H, *m*-H), 7.88 and 8.19 (AA′XX′, apparent J = 8.1 Hz, 8H), 8.70 and 8.77 (2 × d, J = 4.5 Hz, 8H, β-H on porphine). ES$^+$-MS (in $CHCl_3$/MeOH): 747.35 ([M + H]$^+$), 374.18 ([M + 2H]$^{2+}$); calcd average mass for $C_{54}H_{42}N_4$ = 746.95. HRMS (ESI-MS): 747.34781; calcd for ([M + H]$^+$) = 747.34822. Anal. Calcd C 86.83, H 5.67, N 7.50; found C 86.49, H 5.58, N 7.49.

By the same procedure, **21b**-d_8 (M = 2H) was prepared from **21a**-d_8.

[5,15-Bis(4-ethynylphenyl)-10,20-bis(2,4,6-trimethylphenyl)porphinato(2-)] nickel (21b, M = Ni). To a solution of **21b** (M = 2H) (100 mg, 134 μmol) in 10 mL of $CHCl_3$/AcOH (9:1) was added nickel acetate tetrahydrate (600 mg, 2.4 mmol), and the mixture was refluxed for 48 h. Thereafter, the solvent was removed under reduced pressure, and the obtained solid residue was purified twice by FC on silica gel eluting with a 40:60 and a 30:70 mixture of $CHCl_3$/*n*-hexane, respectively. The yield of **21b (M = Ni)** amounts to 70 mg (65%). UV−vis (CH_2Cl_2): 294 (4.22), 414 (5.36), 527 (4.23). ^{1}H NMR (360.14 MHz): δ 1.80 (s, 12H, *o*-Me), 2.57 (s, 6H, *p*-Me), 3.28 (s, 2H, ethynyl), 7.27 (s, 4H, *m*-H), 7.81 and 8.00 (AA′XX′, apparent J = 8.2 Hz, 8H), 8.60 and 8.67 (2 × d, J = 5.0 Hz, 8H, β-H on porphine). ES$^+$-MS (in THF/HCO_2H): 803.72 (M$^+$); calcd average mass for $C_{54}H_{40}N_4Ni$ = 803.64. HRMS (ESI-MS): 803.26788, 802.26014; calcd for [M + H]$^+$) and M$^+$ = 803.26792 and 802.26010, respectively (monoisotopic peaks corresponding to ^{58}Ni).

5-[4-[3-[[4-[10,20-Bis(2,4,6-trimethylphenyl)-15-(4-ethynylphenyl)-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−)-κN^{21},κN^{22},κN^{23},κN^{24}]zinc(2+) (22b, M = 2H). To a solution of **22a** (M = 2H)[19] (48 mg, 24 μmol) in 4.0 mL of THF was added 2.9 mL of aq. NaOH (1 N), and the mixture was stirred vigorously for 3 h at 25 °C. Thereafter, the mixture was diluted with 15 mL of CH_2Cl_2 before 15 mL of water was added, and the organic layer was separated, washed with water, and dried ($MgSO_4$). The residue obtained after evaporation of the solvent under reduced pressure was purified by FC using $CHCl_3$/*n*-hexane (60:40) as eluant to yield 39 mg (84%) of **22b** (M = 2H) as a violet solid. UV−vis (CH_2Cl_2): 288 (4.86), 422 (5.89), 516 (4.37), 550 (4.50), 590 (4.06), 646 (3.81). ^{1}H NMR (360.14 MHz): δ −2.63 (br, 2H, NH), 1.38 (s, 9H, *t*-Bu), 1.49 (s, 9H, *t*-Bu), 1.84 (s, 24H, *o*-Me), 2.64 (s, 12H, *p*-Me), 3.32 (s, 1H, ethynyl), 7.29 (s, 8H, *m*-H), 7.66 (t, J = 1.5 Hz, 1H), 7.75 (t, J = 1.5 Hz, 2H), 7.76 (t, J = 1.5 Hz, 1H), 7.84 (t, J = 1.5 Hz, 1H), 7.86 (t, J = 1.5 Hz, 1H), 7.88 and 8.20 (AA′XX′, apparent J = 8.4 Hz, 4H), 7.92 and 8.25 (AA′XX, apparent J = 8.4 Hz, 8H), 7.98 and 8.24 (AA′XX, apparent J = 8.4 Hz, 4H), 7.98 and 8.27 (AA′XX, apparent J = 8.4 Hz, 4H), 8.71 and 8.77 (2 × d, J = 4.8 Hz, 4H, β-H on porphine), 8.73 and 8.84 (2 × d, J = 4.8 Hz, 4H, β-H on porphine), 8.80 and 8.89 (2 × d, J = 4.8 Hz, 4H, β-H on porphine), 8.81 and 8.92 (2 × d, J = 4.8 Hz, 4H, β-H on porphine). ES$^+$-MS (in THF): 1946.54 ([M + H]$^+$), MALDI-MS (matrix, dithranol) 1945.6 (M$^+$); calcd average mass for $C_{128}H_{103}IN_8Zn$ = 1945.55. HRMS (MALDI): 1942.66652; calcd for M$^+$ = 1942.66418 (monoisotopic peak corresponding to ^{64}Zn).

{μ-{5-{4-[3-[[4-[10,20-Bis(2,4,6-trimethylphenyl)-15-(4-ethynylphenyl)-21*H*,23*H*-porphin-5-yl-κN^{21},κN^{22},κN^{23},κN^{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-)-κN^{21},κN^{22},κN^{23},κN^{24}}}(nickel(2+))-zinc(2+) (22b, M = Ni) was obtained from **22a** (M = Ni)[19] (83 mg, 40 μmol) as described for **22b** (M = 2H). After purification by FC using $CHCl_3$/hexane (50:50) as eluant, **22b** (M = Ni) was obtained as a violet solid in 97% yield (78 mg). UV−vis (CH_2Cl_2): 289 (4.87), 422 (5.76), 536 (4.32), 549 (4.41), 590 (3.75). ^{1}H NMR (360.14 M Hz): δ 1.38 (s, 9H, *t*-Bu), 1.47 (s, 9H, *t*-Bu), 1.81 (s, 12H, *o*-Me), 1.84 (s, 12H, *o*-Me), 2.57 (s, 6H, *p*-Me), 2.63 (s, 6H, *p*-Me), 3.26 (s, 1H, ethynyl), 7.21 (s, 4H, *m*-H), 7.28 (s, 4H, *m*-H), 7.66 (t, J = 1.5 Hz, 1H), 7.72 (t, J = 1.5 Hz, 1H), 7.75 (t, J = 1.5 Hz, 2H), 7.80 and

8.01 (AA′XX′, apparent $J = 8.2$ Hz, 4H), 7.82 (t, $J = 1.5$ Hz, 1H), 7.86 (t, $J = 1.5$ Hz, 1H), 7.89 and 8.07 (AA′XX′, apparent $J = 8.2$ Hz, 4H), 7.91 and 8.24 (AA′XX′, apparent $J = 8.2$ Hz, 4H), 7.96 and 8.26 (AA′XX′, apparent $J = 8.2$ Hz, 4H), 8.60 and 8.68 ($2 \times$ d, $J = 4.8$ Hz, 4H, β-H on porphine), 8.62 and 8.74 ($2 \times$ d, $J = 4.8$ Hz, 4H, β-H on porphine), 8.80 and 8.89 ($2 \times$ d, $J = 4.8$ Hz, 4H, β-H on porphine), 8.81 and 8.92 ($2 \times$ d, $J = 4.8$ Hz, 4H, β-H on porphine). MALDI-MS (matrix, dithranol): 2001.97 (M^+); calcd average mass for $C_{128}H_{101}IN_8NiZn = 2002.23$. HRMS (MALDI): 1998.58544; calcd for $M^+ = 1998.58386$ (monoisotopic peak corresponding to $^{58}Ni^{64}Zn$).

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Supporting Information Available: Copies of ^{1}H NMR and mass spectra (MS, MALDI-MS, MALDI-TOF) for all new compounds as well as copies of the UV−vis spectra of all new porphyrinic compounds and of the ^{13}C NMR spectra of compounds **17a,b** and **18a,b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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