Synthesis of Dendritic Metalloporphyrins with *Distal* H-Bond Donors as Model Systems for Hemoglobin

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We report the synthesis of the first- (G1) and second-generation (G2) dendritic Fe^{II} porphyrins **1**·**Fe**–**4**·**Fe** (G1) and **6**·**Fe** (G2) bearing *distal* H-bond donors ideally positioned for stabilization of $Fe^{II}-O_2$ adducts by H-bonding (*Fig. 1*). A first approach towards the construction of these novel biomimetic systems failed unexpectedly: the *Suzuki* cross-coupling between appropriately functionalized Zn^{II} porphyrins and *ortho*-ethynylated aryl derivatives, serving as anchors for the *distal* H-bond donor moieties, was unsuccessful (*Schemes 1*, *3*, and *5*), presumably due to steric hindrance resulting from unfavorable coordination of the ethynyl residue to the Pd species in the catalytic cycle (*Scheme 6*). The target molecules were finally prepared by a route in which the *ortho*-ethynylated *meso*-aryl ring is introduced during porphyrin construction in a mixed condensation involving the two dipyrrylmethanes **33** and **34**, and aldehyde **36** (*Schemes 7* and *8*). Following attachment of the dendrons (*Scheme 11*), the *distal* H-bond donors were introduced by *Sonogashira* cross-coupling (*Scheme 12*), and subsequent metallation afforded the dendritic Fe^{II} porphyrins **1**·**Fe**–**6**·**Fe**. ^{1}H-NMR Spectroscopy proved the location of the H-bond donor moiety atop the porphyrin surface, and X-ray crystal-structure analysis of model system **45** (*Fig. 2*) revealed that this moiety would not sterically interfere with gas binding. With 1,2-dimethyl-1*H*-imidazole (DiMeIm) as ligand, the dendritic Fe^{II} porphyrins formed five-coordinate *high-spin* complexes (*Figs. 3* and *4*) and addition of CO led reversibly to the corresponding stable six-coordinate gas complexes (*Fig. 6*). Oxygenation, however, did not result in defined $Fe^{II}-O_2$ complexes as rapid decomposition to Fe^{III} species took place immediately, even in the case of the G2 dendrimer **6**·**Fe**(DiMeIm) (*Fig. 7*). In contrast, stable gas adducts are formed between dendritic Co^{II} porphyrins and O_2 in the presence of DiMeIm as axial ligand, as revealed by electron paramagnetic resonance (EPR). The possible stabilization of these complexes through H-bonding involving the *distal* ligand is currently under investigation in multidimensional and multifrequency pulse EPR experiments.

1. Introduction. – Dendritically encapsulated metalloporphyrins mimic efficiently a number of functions expressed in biological systems. Examples are hemoglobin (Hb)- and myoglobin (Mb)-like gas-binding ability [1], heme monooxygenase activity [2,3], electron-acceptor capacity in light-harvesting antenna systems [4], and shell-modulated redox potentials as found in cytochromes [5]. The dendritic-generation dependence of properties of the metalloporphyrin core has been intensively investigated [2][6], and the branched shells have been shown to produce unique microenvironments [5][7]. H-Bonding to *distal* H-bond donors, such as histidine, as well as electrostatic and steric effects are assumed to represent the primary factors influencing the O_2 and CO binding affinities in Fe^{II} heme proteins [8].

We have recently studied a series of dendritic hemoglobin models and shown a strong influence of the nature of the dendritic shell on O_2 complexation [9]. An enhanced stability of the O_2 complex was observed for systems in which the five-coordinate Fe^{II} porphyrin is surrounded by secondary amide-linked dendrons. However, the question remains open whether H-bonding between metal-ion-bound

O_2 and amide H–N moieties provides a stabilizing effect in these complexes. To explore in more detail how H-bonding influences the affinity of the dendritic metalloporphyrins for O_2 and CO, it seemed, therefore, desirable to precisely position – in analogy to Hb and Mb [10] – *distal* H-bond donor groups above the gas-binding site. Here, we report the synthesis of a new family of dendritic porphyrins **1·Fe**–**6·Fe** (*Fig. 1*) functionalized with first- (G1) and second- (G2) generation dendrons. In these

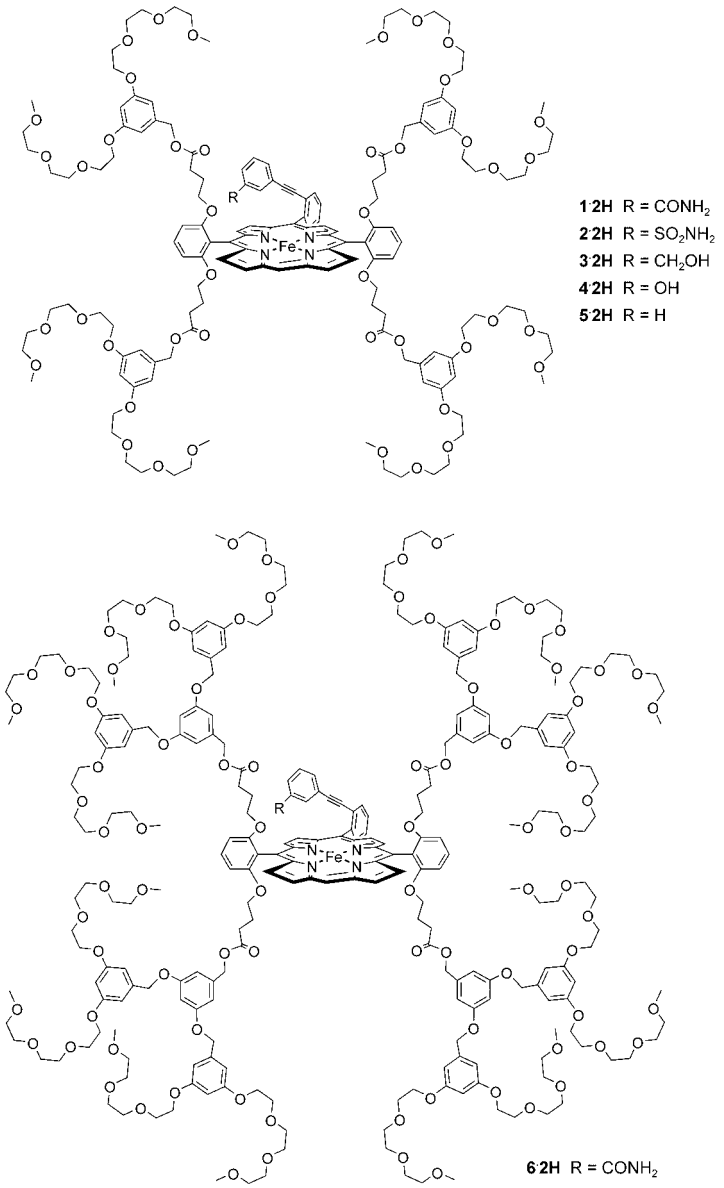
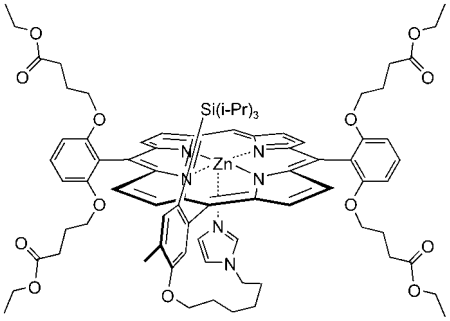


Fig. 1. *Novel dendritic Fe^{II} porphyrins with* distal *H-bond donors*

compounds, with the exception of **5·2H**, *distal* ligands are ideally positioned (according to molecular modeling) by ethynediyl linkers above the metalloporphyrin core for potential H-bonding with metal-ion-coordinated gases (for a preliminary communication of parts of this work, see [11]; for recent examples of dendritic porphyrins, see [12]). This paper also describes some quite unusual, unexpected results obtained in Pd^0-catalyzed cross-coupling reactions with Zn^{II} porphyrins. Furthermore, the preparation and stability of CO and O_2 complexes of the dendritic Fe^{II} and Co^{II} porphyrins are described.

2. Results and Discussion. – 2.1. *Synthesis of Porphyrin Cores with Appended* Distal *H-Bonding Sites.* 2.1.1. *Cross-Coupling Reactions with Monobrominated Zn^{II} Porphyrin as Electrophile.* On the way to a complete model for the active site of hemoglobin, we first targeted the synthesis of the Zn^{II} porphyrin intermediate **7·Zn** featuring *i*) four side chains for attachment of a globular dendritic shell, *ii*) a covalently attached *proximal* imidazole, and *iii*) a silyl-protected alkynyl residue, which, after deprotection, would allow the introduction of the *distal* H-donor moieties by *Sonogashira* cross-coupling [13][14]. We anticipated to introduce the alkynylated aryl ring with the tethered imidazole into the *meso*-position of the porphyrin ring *via Suzuki* cross-coupling [3][5d,e][15][16].

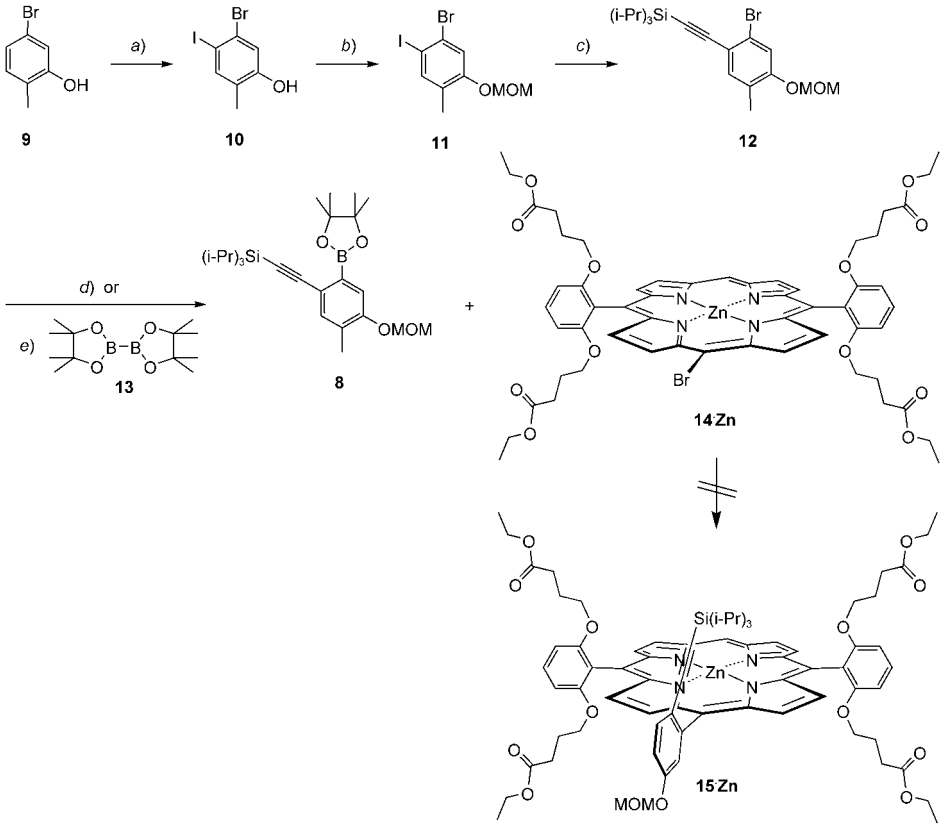


7·Zn

The synthesis of boronate **8** started from 5-bromo-2-methylphenol **9** [17], which was iodinated with NaOCl/NaI [18] to give **10** (*Scheme 1*). MOM (Methoxymethyl) Protection of the phenolic HO group (→**11**) and *Sonogashira* coupling afforded arylacetylene **12**. Boronate **8** was obtained either by lithiation with BuLi, followed by reaction with $B(OMe)_3$ and transesterification with pinacol (12%), or better, by Pd-catalyzed cross-coupling [19] with 2,2′-bis[1,3,2-dioxaborolane] **13** (23%). Whereas crude yields in the latter conversion were quite high (^{1}H-NMR), purification of **8** resulted in a substantial loss of material due to instability. Unexpectedly, all attempts (variation of solvent, base, and Pd catalyst) to achieve the *Suzuki* cross-coupling between mono-brominated Zn^{II} porphyrin **14·Zn** [5e][20] and boronate **8** to give **15·Zn**, an important intermediate on the way to **7·Zn**, failed. Complex product mixtures were obtained each time, with the reduced analog of **14·Zn** (Br → H) being the only identifiable product formed in low yield in some runs. This failure was quite surprising

in view of the successful *Suzuki* cross-couplings that had previously been executed with **14·Zn** in our laboratory [3][5e][20].

Scheme 1. *Attempted Synthesis of Zn^{II} Porphyrin* **15·Zn**

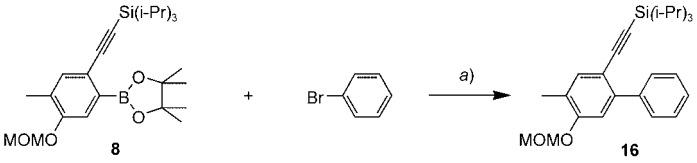


a) Aq. NaOCl, NaOH, NaI, MeOH, 20°, 6 h; 66%. *b*) MOMCl, K_2CO_3, MeCN, 0° → 20°, 2 h; 93%. *c*) H–C≡C–Si(i-Pr)$_3$, [$PdCl_2(PPh_3)_2$], CuI, $(i\text{-Pr})_2NH$, THF, 20°, 18 h; 66%. *d*) BuLi, THF, −70°, 60 min; then $B(OMe)_3$, −70° → 20°, 20 h; then pinacol (=2,3-dimethylbutane-2,3-diol), PhMe, Δ, 2 h; 12%. *e*) AcOK, [$PdCl_2$(dppf)], Me_2SO, 90°, 20 h; 23%. MOM = methoxymethyl, dppf = 1,1′-bis(diphenylphosphino)ferrocene.

In a test reaction, boronate **8** was coupled to PhBr under formation of biaryl **16** (45%; *Scheme 2*), which contrasts the incompatibility of the pair **14·Zn**/**8** to successfully complete the catalytic cycle of the *Suzuki* cross-coupling.

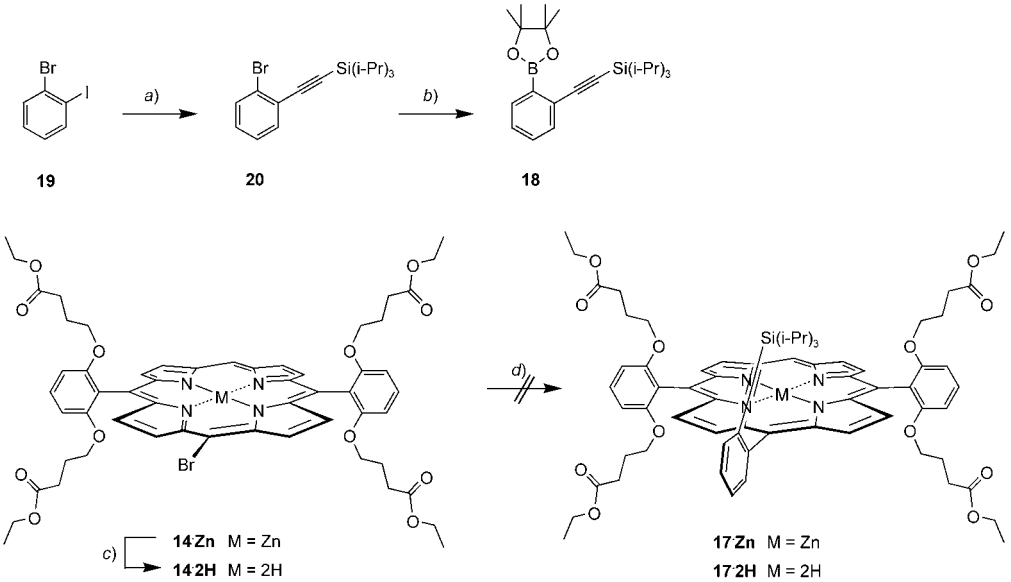
Similar disappointing results were obtained in efforts to prepare porphyrins **17·Zn** and **17·2H**, lacking the tethered *proximal* imidazole, by the same route (*Scheme 3*). While the synthesis of the required boronate **18** proceeded smoothly by *Sonogashira* cross-coupling of 1-bromo-2-iodobenzene (**19**) to give **20** [21], followed by Pd^0-catalyzed cross-coupling with **13**, the cross-coupling with Zn^{II} porphyrin **14·Zn** to give **17·Zn** was unsuccessful, leading only to a highly complex product mixture. We also tried the cross-coupling with the free-base porphyrin **14·2H**, obtained by demetalla-

Scheme 2. *Formation of Biaryl* **16**



a) [Pd(PPh$_3$)$_4$], Cs_2CO_3, THF/PhMe, Δ, 6 h; 45%.

Scheme 3. *Attempted Synthesis of Porphyrins* **17·Zn** *and* **17·2H**

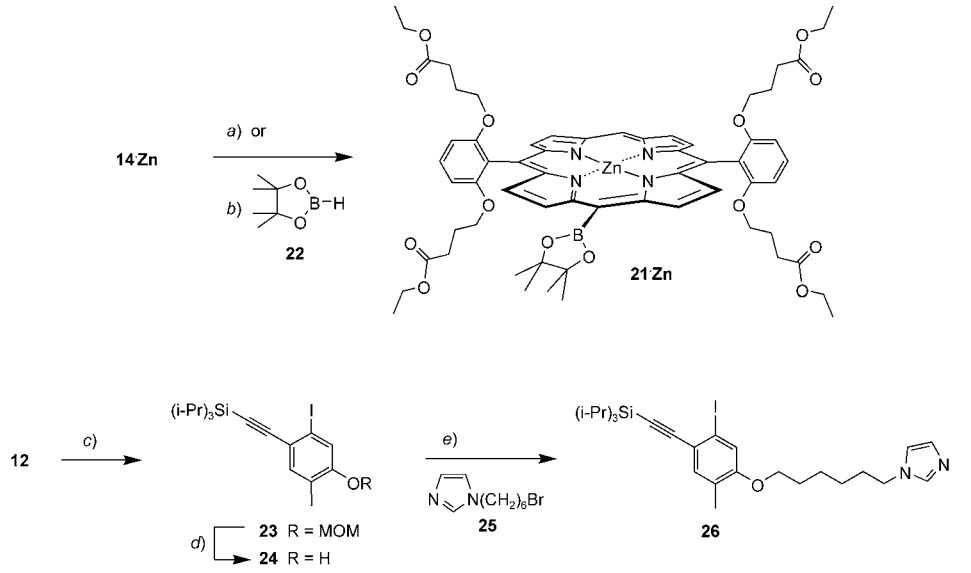


a) H−C≡C−Si(i-Pr)$_3$, [$PdCl_2(PPh_3)_2$], CuI, (i-Pr)$_2$NH, THF, 20°, 18 h; 86%. *b*) **13**, AcOK, [$PdCl_2$(dppf)], Me_2SO, 80°, 18 h; 99%. *c*) CF_3COOH, PhH, 0°, 10 min; quant. *d*) [Pd(PPh$_3$)$_4$], Cs_2CO_3, THF/PhMe, Δ, 6 h.

tion of **14·Zn** with CF_3COOH, but, again, the desired product **17·2H** was not formed (for cross-coupling reactions of metal-free porphyrins, see [22]).

2.1.2. *Cross-Coupling Reactions with Porphyryl Boronates as Transmetallating Agents.* In view of the poor results obtained in the *Suzuki* cross-couplings with *meso*-bromoporphyrins as electrophiles (see above), we decided to change to transformations using porphyryl boronates as transmetallating agents. For this purpose, **14·Zn** was converted into boronate ester **21·Zn** by Pd^0-mediated cross-coupling with either **13** [19] or 1,3,2-dioxaborolane **22** [23][24] (*Scheme 4*). As electrophile for the planned cross-coupling to **21·Zn**, we first prepared iodide **23** from **12** by Br/Li exchange, followed by conversion with I_2. In subsequent steps, **23** was deprotected with HCl in MeOH/THF to give the free phenol **24**, which was reacted with 1*H*-imidazole **25** [3][25] to provide aryl iodide **26**, the precursor to **7·Zn**.

Scheme 4. *Synthesis of Precursors for* Suzuki *Cross-Couplings Using Porphyrylboronates as Transmetallating Agents*

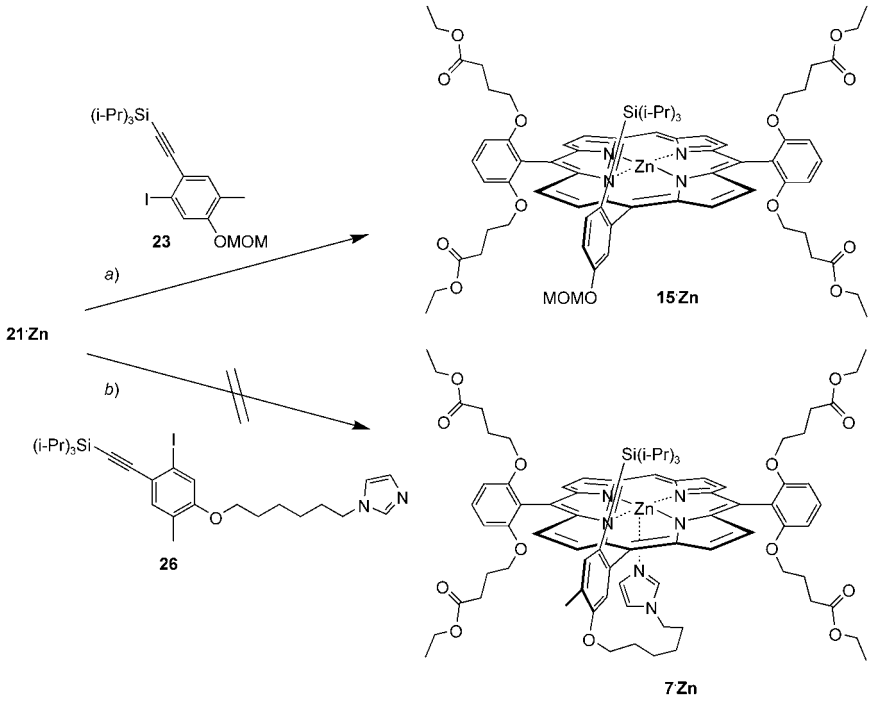


a) **13**, AcOK, [$PdCl_2$(dppf)], Me_2SO, 80°, 24 h; 33%. *b*) [$PdCl_2(PPh_3)_2$], Et_3N, ClH_2CCH_2Cl, 90°, 18 h; quant. *c*) BuLi, THF, −70°, 30 min, then I_2, −70° → 20°, 2 h; 82%. *d*) HCl, MeOH/THF, 20°, 60 h; 98%. *e*) Cs_2CO_3, DMF, 20°, 4 h; 56%.

The *Suzuki* cross-coupling of **21·Zn** with **23** in THF with [$Pd(PPh_3)_4$] as catalyst provided the desired porphyrin **15·Zn** (*ca.* 24% yield, NMR) together with a mixture of other porphyrin side-products (*Scheme 5*). However, isolation of the pure compound was not possible either by chromatography or crystallization. With [$PdCl_2$(dppf)] as the catalyst and Cs_2CO_3 as the base in a two-phase mixture (PhMe/EtOH/H_2O), the yield was even lower (< 5%), and a complex mixture of porphyrin side products was formed. In the cross-coupling of **21·Zn** with **26** under a variety of conditions, compound **7·Zn** was never formed in isolable amounts, and a complex product mixture was isolated in addition to unreacted **21·Zn**. Unproductive coordination of the imidazole moiety in **26** to the active Pd^0 catalyst could possibly explain the failure of this transformation.

To shed light on the difficulties encountered in the cross-coupling reactions, we decided to compare the transformation with halobenzenes ethynylated in *ortho*-, *meta*-, and *para*-positions. The results confirmed that the problems arise from the *ortho*-position of the ethynyl substituent in the electrophile. Whereas the reaction of the *meta*- and *para*-substituted derivatives **27** and **28** [26] with **21·Zn** provided the coupling products **29·Zn** and **30·Zn** in moderate yields, respectively, the *ortho*-derivative **20** [21] failed to yield the desired tris(*meso*-arylated) porphyrin **17·Zn** under any reaction conditions (*Scheme 6*); instead a complex product mixture was obtained. We then turned to a stepwise introduction of the *ortho*-ethynylated aryl ring by first coupling **21·Zn** with 1-bromo-2-iodobenzene to give **31·Zn** (63%). However, the subsequent

Scheme 5. Suzuki *Cross-Couplings with Porphyryl Boronates as Transmetallating Agents*

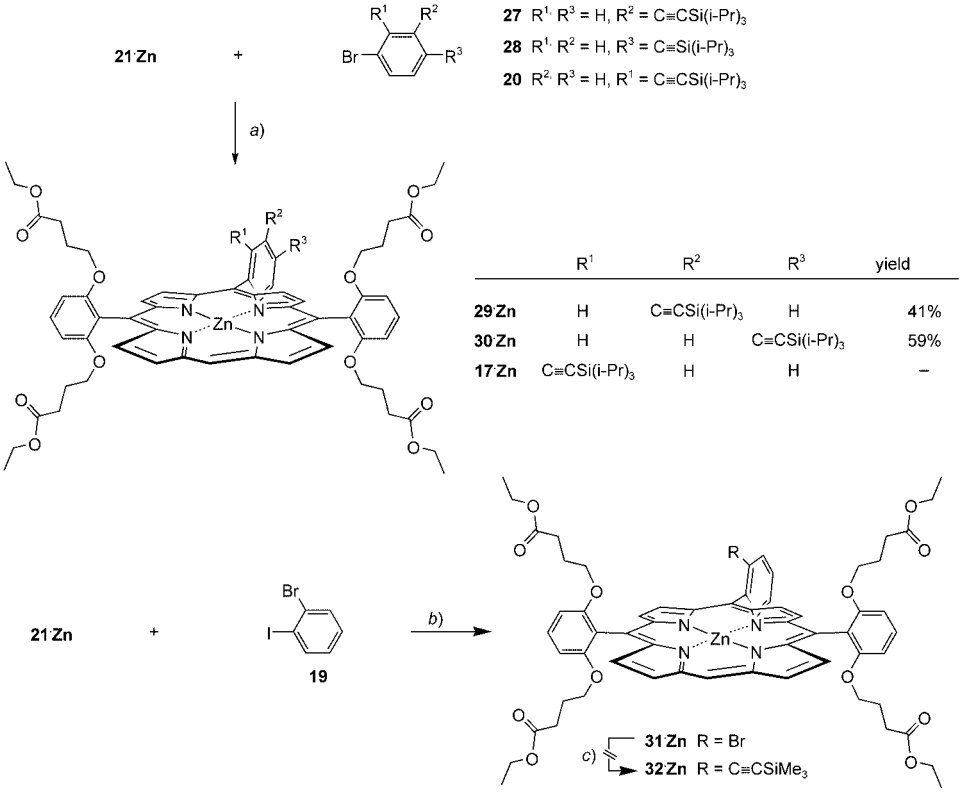


a) [Pd(PPh_3)$_4$], Cs_2CO_3, THF/PhMe, Δ, 5.5 h; 24% (impure crude product; yield determined by NMR). *b*) [Pd(PPh_3)$_4$], Cs_2CO_3, PhMe, Δ, 48 h.

Sonogashira cross-coupling with $Me_3Si-C\equiv CH$ to provide **32·Zn** was unsuccessful under all experimental conditions. These results combined suggested that the introduction of the *ortho*-ethynylated *meso*-aryl ring would not be successful by cross-coupling reactions, presumably due to steric hindrance resulting from unfavorable coordination of the ethynyl residue to the Pd species in the catalytic cycle, and, therefore, a new approach to the construction of the desired porphyrin core was taken.

2.1.3. *Introduction of the* ortho-*Ethynylated* meso-*Aryl Ring during Construction of the Porphyrin Macrocycle.* For the macrocyclization to the desired porphyrin **32·2H**, three starting materials were prepared. Dipyrrylmethane (**33**) was obtained from pyrrole and formaldehyde by the one-pot synthesis described by *Lindsey* and coworkers (*Scheme 7*) [27] (for other routes to dipyrrylmethanes, see [28]). The arylated dipyrrylmethane **34** was prepared by acid-catalyzed condensation [28c] of pyrrole with benzaldehyde **35** [29]. Compound **34** is quite unstable and decomposes in solution within hours. In contrast, crystals of **34** can be stored for weeks without decomposition at $-20°$ under Ar and exclusion of light. The third precursor for the macrocyclization, aldehyde **36**, was prepared in two steps from 2,6-dimethoxybenzaldehyde (**37**), according to published protocols [5c], by deprotection [30], followed by *Williamson* ether synthesis.

Scheme 6. *Experiments Demonstrating the Difficulty to Introduce an* ortho-*Ethynylated* meso-*Aryl Ring in Cross-Coupling Reactions with Porphyryl Boronate* **21·Zn**

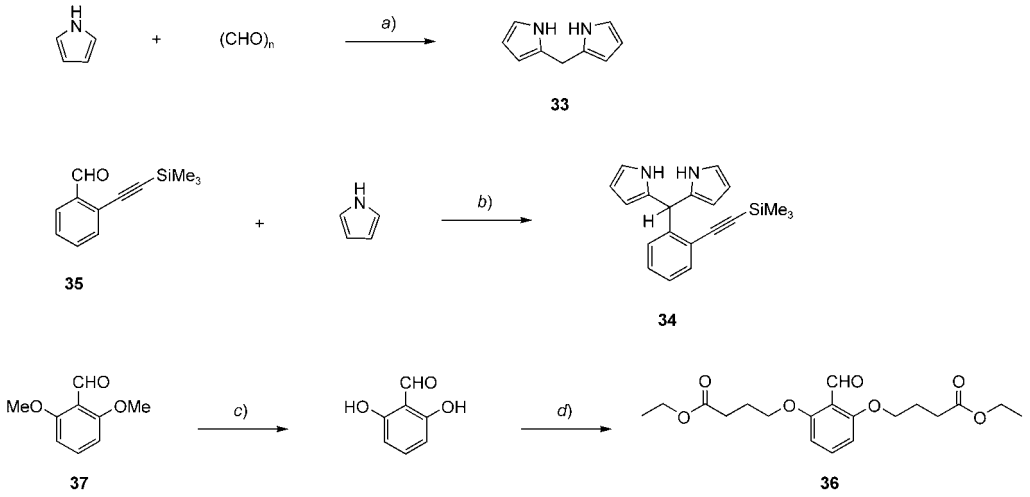


a) [$Pd(PPh_3)_4$], Cs_2CO_3, THF/PhMe, Δ, 20 h. *b*) [$Pd(PPh_3)_4$], Cs_2CO_3, PhMe, Δ, 6 h; 63%. *c*) H−C≡C−$SiMe_3$, [$PdCl_2(PPh_3)_2$], CuI, $(i\text{-Pr})_2NH$, THF, 20°, 72 h (or Et_3N, PhMe, 90°, 16 h).

The targeted porphyrin **32·2H** was finally prepared by a mixed condensation of the two dipyrrylmethanes **33** and **34** with aldehyde **36**, followed by oxidation with chloranil [31] (for the synthesis of *meso*-substituted porphyrins, see [32]). Repeated chromatography on SiO_2-*H* ($CHCl_3$/AcOEt 97:3) provided the four major products **32·2H** (17%), **38·2H** (4%), **39·2H** (4%), and **40·2H** (10%) [5c] (*Scheme 8*) that were fully characterized spectroscopically as well as by elemental analysis. According to the ^{1}H- and ^{13}C-NMR spectra, *anti*-diethynylated porphyrin **38·2H** possesses C_{2h} symmetry, whereas *syn*-diethynylated **39·2H** is C_{2v}-symmetric.

Before attachment of the dendrons, we were curious to find out whether *distal* H-bond donor sites could be attached to the (deprotected) ethynyl moiety in **32·2H** by *Sonogashira* cross-coupling. Alkyne-deprotection afforded **41·2H**, and the porphyrin was subsequently metallated to **41·Zn** in order to prevent insertion of undesirable metal ions (in particular Cu ions [33]) during the projected cross-coupling (*Scheme 9*). Alternatively, the Zn^{II} ion was inserted (→ **32·Zn**) before the deprotection to give **41·Zn** (**38·Zn** and **39·Zn** were also prepared from the corresponding free-base

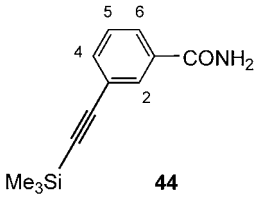
Scheme 7. *Preparation of Precursors for the Macrocyclization to Porphyrin* **32·2H**



a) CF_3COOH, 50°, 5 min; 44%. *b*) CF_3COOH, 20°, 5 min; 72%. *c*) $AlBr_3$, CS_2, then H_3O^+; 67%. *d*) $Br(CH_2)_3COOEt$, K_2CO_3, 60–80°, 5 h; 83%.

porphyrins). Both the Zn^{II} porphyrin **41·Zn** and the free-base porphyrin **41·2H** were cross-coupled to 3-iodobenzamide [34] or PhBr in good yields. With the Zn^{II} derivative, no transmetallation [35] was observed during formation of **42·Zn** and **43·Zn** under regular *Sonogashira* coupling conditions (Pd^0, CuI, base) [36]. The coupling of the free-base porphyrin **41·2H** to give **42·2H** was successfully accomplished according to the CuI-free [33] cross-coupling protocol.

A comparison with diphenylacetylene (tolane) shows that the ^{1}H-NMR chemical shifts of the terminal Ph ring attached to the acetylene moiety in **43·Zn** are strongly shifted upfield, indicating the positioning of this ring above the porphyrin plane. The same holds for the benzamide moiety in **42·Zn** and **42·2H**. Whereas the aromatic resonances of 3-[(trimethylsilyl)ethynyl]benzamide (**44**) appear between 7.91 and 7.38 ppm (360 MHz, $CDCl_3$), the corresponding signals in **42·Zn** are observed between 6.83 and 6.58 ppm (H–C(4,5,6); numbering as for **44**) and, notably, at 4.14 ppm (H–C(2)). The latter, remarkable upfield shift suggests that the benzamide moiety in **42·Zn** strongly prefers an orthogonal orientation with the carboxamide residue approaching the porphyrin plane.



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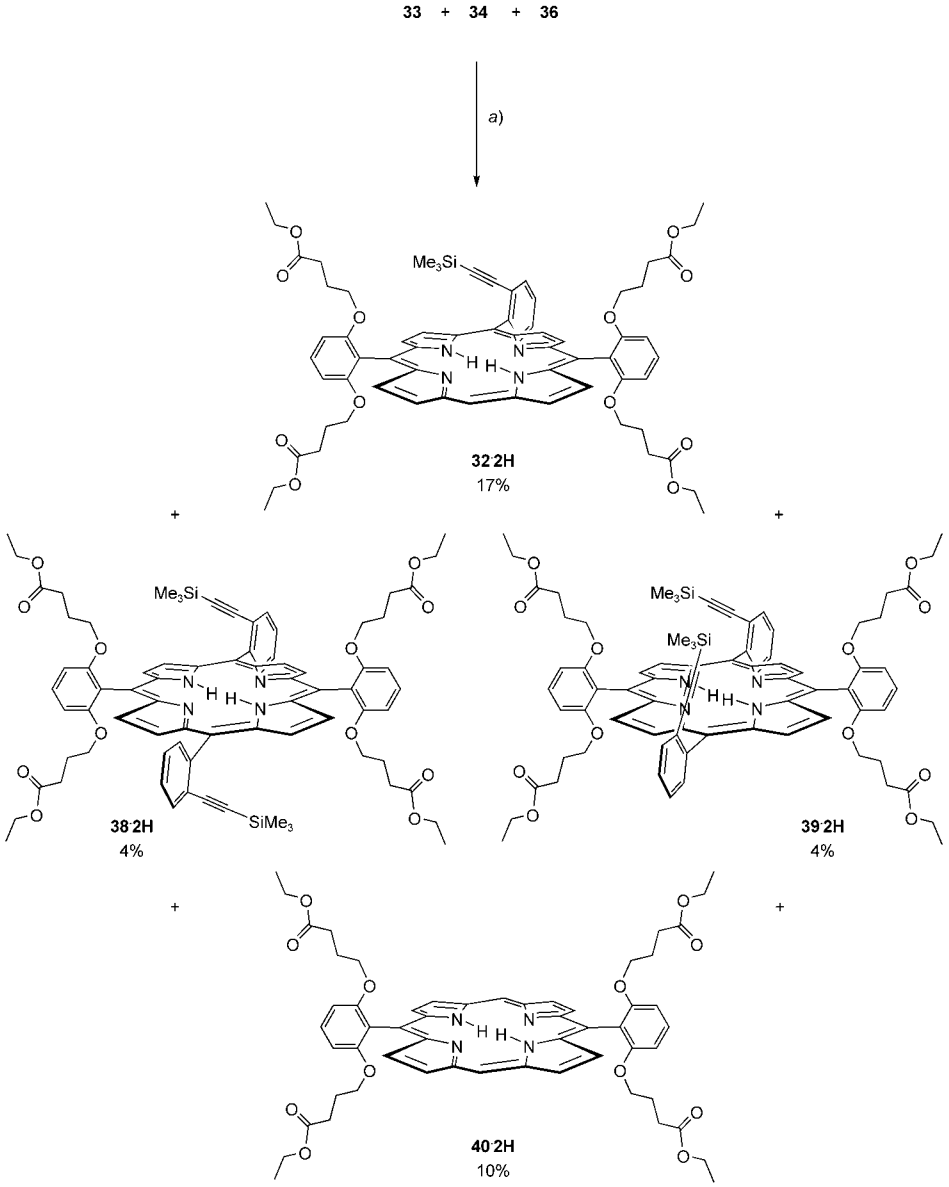
The orientation of the ethynyl moiety above the porphyrin plane was further confirmed by the X-ray crystal structure of a dimethanol solvate of **45·Zn** (*Cambridge*

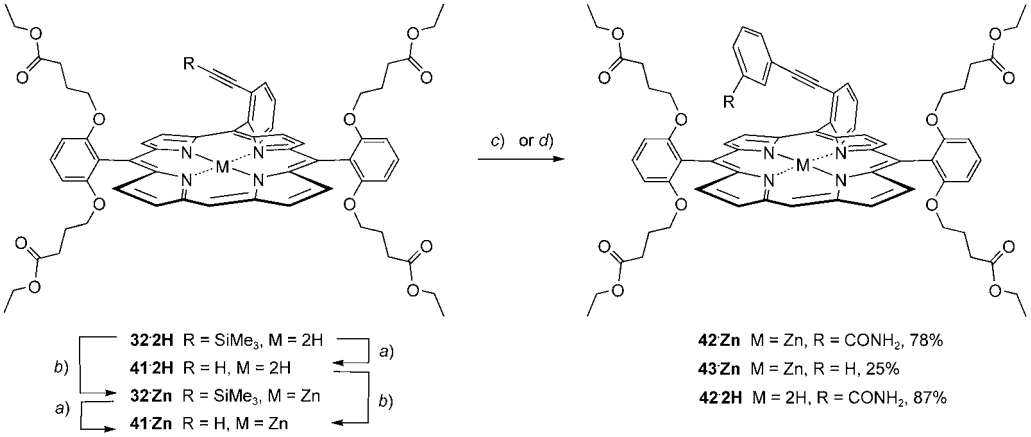
Scheme 8. *Synthesis of Porphyrin* **32·2H**



a) CF_3COOH, CH_2Cl_2, Δ, 16 h; then chloranil (=2,3,5-tetrachlorocyclohexa-2,5-dione-1,4-dione), CH_2Cl_2, Δ, 2 h.

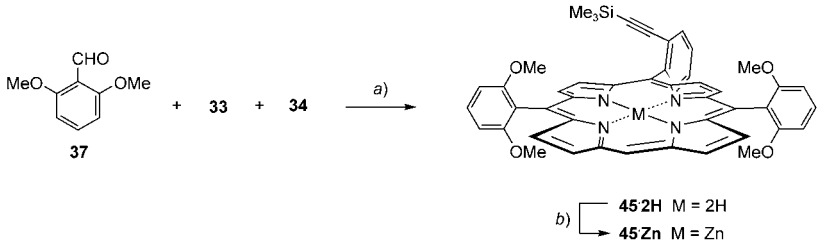
Crystallographic Data Centre reference No. 199402 [11]), prepared by mixed condensation of dipyrrylmethanes **33** and **34** with 2,6-dimethoxybenzaldehyde (**37**), to give **45·2H**, followed by metallation (*Scheme 10*). In the crystal lattice of **45·Zn**, one

Scheme 9. *Preparation of Porphyrins* **42·Zn**, **42·2H**, *and* **43·Zn** *by* Sonogashira *Cross-Coupling*



a) Bu_4NF, THF, 20°, 15 min; 74% (**41·2H**); quant. (**41·Zn**). *b*) $Zn(OAc)_2 \cdot 2\,H_2O$, $CHCl_3$/MeOH, 20°, 16–48 h; quant. *c*) Starting from **41·Zn**: 3-iodobenzamide or PhBr, $[PdCl_2(PPh_3)_2]$, CuI, Et_3N, PhMe, 90°, 22 h. *d*) Starting from **41·2H**: 3-iodobenzamide, $[PdCl_2(PPh_3)_2]$, Et_3N, PhMe, 90°, 22 h.

Scheme 10. *Synthesis of* Zn^{II} *Porphyrin* **45·Zn**



a) CF_3COOH, CH_2Cl_2, 20°, 16 h; then chloranil, CH_2Cl_2, Δ, 1 h; 5%. *b*) $Zn(OAc)_2 \cdot H_2O$, $CHCl_3$, MeOH, 20°, 14 h; quant.

MeOH molecule coordinates to the Zn^{II} ion and is H-bonded to the second MeOH molecule, which, in turn, interacts with the MeO residue on one of the *meso*-phenyl rings (*Fig. 2*). As a result of the fivefold coordination, the metal ion is pulled out of the mean porphyrin plane by *ca.* 0.3 Å. The Zn^{II}–MeOH binding mode resembles the bent geometry of heme Fe^{II}–O_2 complexes, and this comparison suggests that a *distal* H-bonding residue, anchored above the Fe^{II} porphyrin by the phenylethynyl spacer would not sterically interfere with O_2 binding, in agreement with computer-modeling predictions in the early phase of the project [37]. The Si-atom is located approximately above C(16) of the porphyrin unit, and the shortest distance between the Me_3Si group and the Zn^{II}-bound MeOH is 4.09 Å (C(53) ··· O(56)). The dihedral angle C(46)–C(45)–C(18)–C(19), which defines the relative orientation of porphyrin and phenethynyl fragments, amounts to *ca.* 66°.

2.1.4. *Synthesis of Dendritic Porphyrins with* Distal *H-Bond Donors.* The synthesis of the *Fréchet*-type [38] aryl-ether dendrons **46** (G1) and **47** (G2) with triethyleneglycol

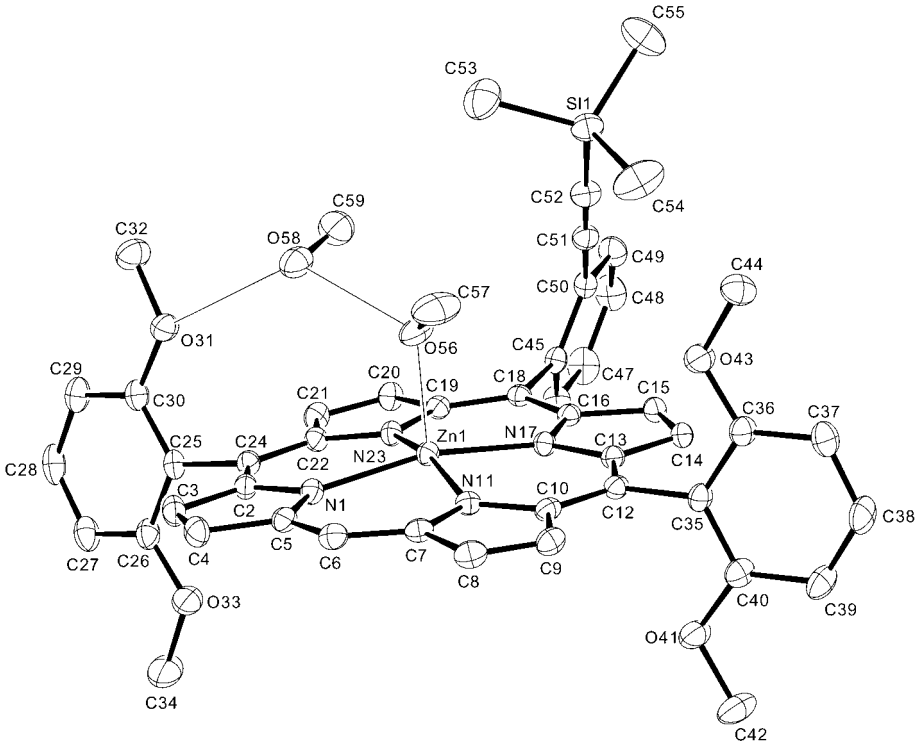
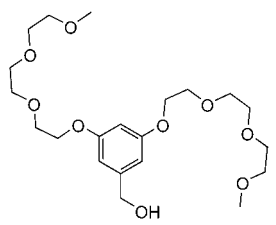


Fig. 2. *X-Ray crystal structure of the solvate* **45·Zn**·*2 MeOH*. Arbitrary numbering. Atomic displacement parameters obtained at 203 K are drawn at the 30% probability level. H-Atoms are omitted. Selected intermolecular distances: Zn(1)···O(56): 2.16 Å (angle (Zn(1)···O(56)–C(57)): 122°); O(56)···O(58): 2.74 Å; O(58)···O(31): 2.93 Å.

monomethyl ether end groups, needed for the preparation of **1·Fe**–**6·Fe**, had been reported by *Smith* [39]. The haloarenes bearing the H-bond donor groups for the *Sonogashira* cross-coupling were either commercially available or prepared according to literature protocols [34][40].



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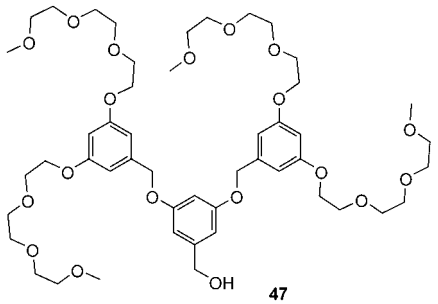

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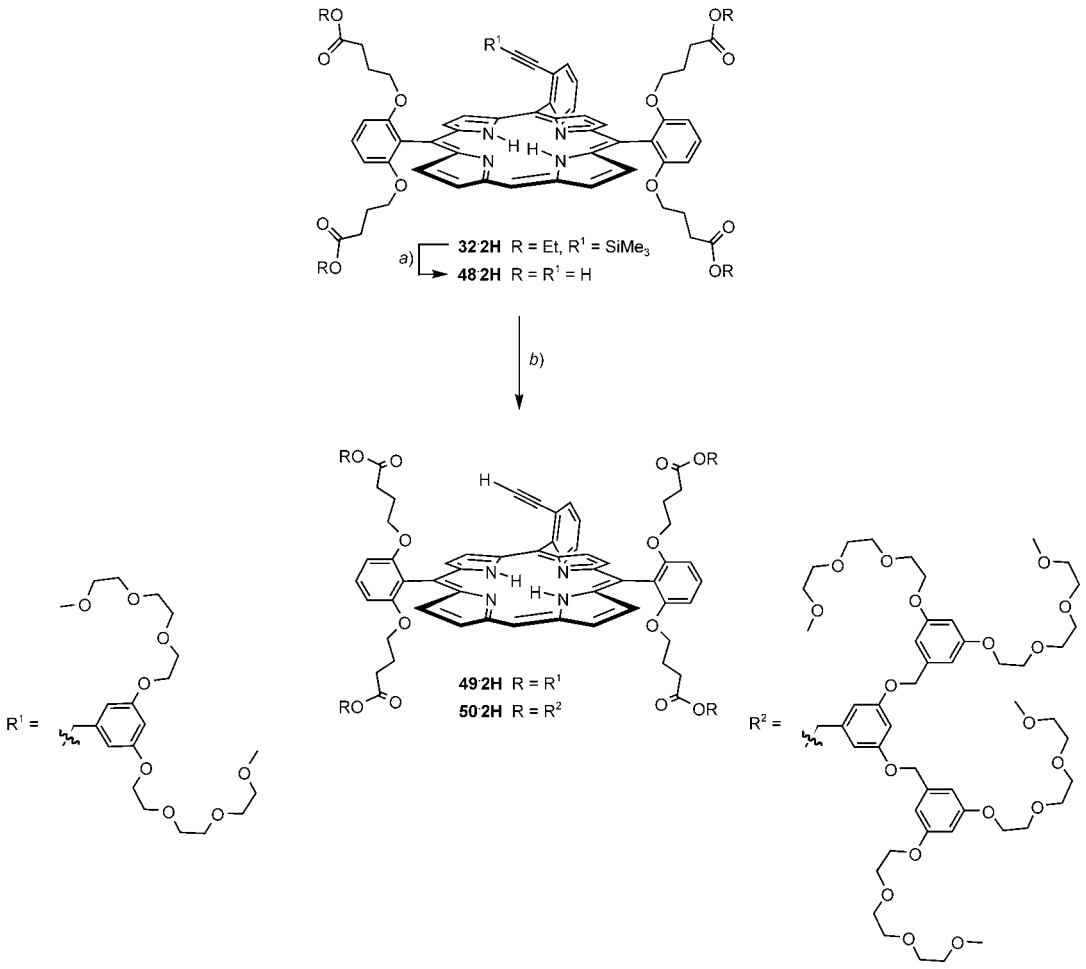
For the preparation of the dendritic porphyrins, ester **32·2H** was hydrolyzed, with simultaneous removal of the Me_3Si-protecting group, to tetraacid **48·2H**. Subsequent

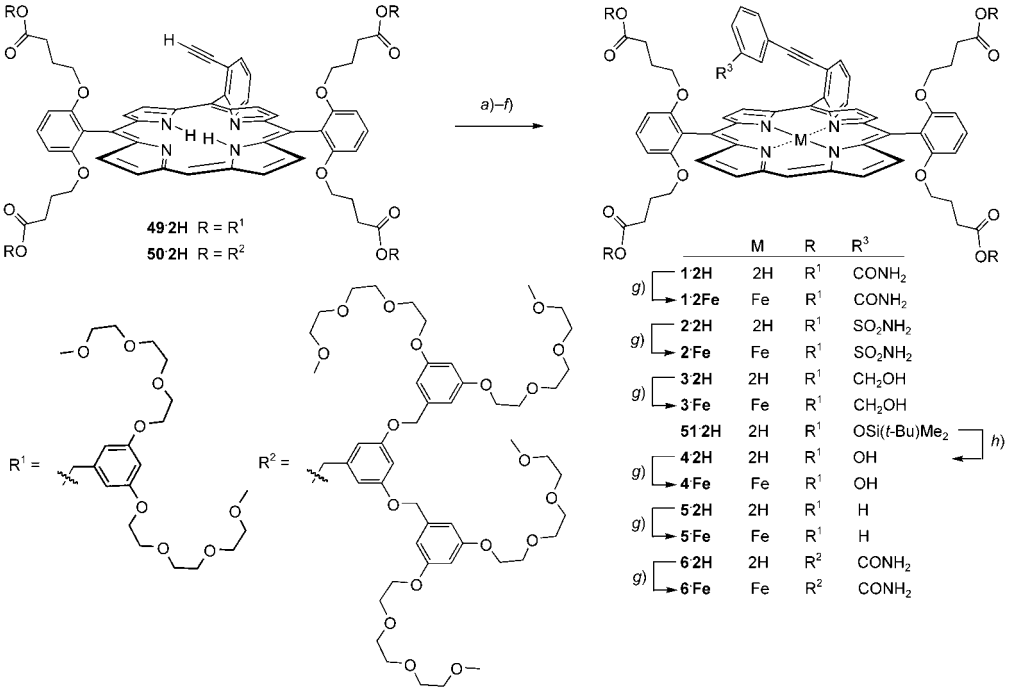
esterification, followed by gel-permeation chromatography (GPC, *BioBeads S-X1*), provided dendrimers **49·2H** (G1) and **50·2H** (G2) (*Scheme 11*). The targeted dendritic porphyrins **1·2H**–**6·2H** bearing *distal* H-bond donors were obtained by *Sonogashira* cross-coupling and fully characterized (*Scheme 12*). In the synthesis of **4·2H**, the coupling first furnished the silyl derivative **51·2H**, which was subsequently deprotected to give the free phenol. Finally, Fe^{II} insertion under formation of the target compounds **1·Fe**–**6·Fe** was carried out with $FeBr_2$ under N_2 in the presence of 2,6-lutidine [41].

Scheme 11. *Synthesis of Dendritic Porphyrins* **49·2H** *and* **50·2H**



a) NaOH, H_2O/dioxane, 20°, 3 d. *b*) DCC, DMAP, BtOH, THF, 20°, 3–7 d; 80% of **49·2H**; 66% of **50·2H**. DCC = Dicyclohexylcarbodiimide, DMAP = 4-(dimethylamino)pyridine, BtOH = 1-hydroxy-1*H*-benzotriazole.

Scheme 12. *Synthesis of the Dendritic Fe^{II} Porphyrins* **1 · Fe – 6 · Fe** *with* Distal *H-Bond Donors*



a) 3-Iodobenzamide, $[PdCl_2(PPh_3)_2]$, PhMe, Et_3N, 90°, 3 h; 57%. *b*) 3-Iodobenzenesulfonamide, $[PdCl_2(PPh_3)_2]$, DCB, Et_3N, 160°, 1 h; 54%. *c*) 3-Iodobenzyl alcohol, $[PdCl_2(PPh_3)_2]$, PhMe, Et_3N, 110°, 2 h; 45%. *d*) 1-Bromo-3-{[(*tert*-butyl)dimethylsilyl]oxy}benzene, $[PdCl_2(PPh_3)_2]$, PhMe, Et_3N, 110°, 12 h; 37%. *e*) PhBr, $[PdCl_2(PPh_3)_2]$, PhMe, Et_3N, 80°, 13 h; 63%. *f*) 3-Iodobenzamide, $[PdCl_2(PPh_3)_2]$, DCB, Et_3N, 110°, 15 h; 16%. *g*) $FeBr_2$, 2,6-lutidine, THF, 20°, 2–4 d; quant. *h*) Bu_4NF, THF, 20°, 2 h; 57%. DCB = 1,2-Dichlorobenzene.

2.1.5. *Metallation and Gas-Binding Studies. Collman* and *Reed* showed that addition of 1,2-dimethyl-1*H*-imidazole (DiMeIm) to Fe^{II} porphyrins yields five-coordinate Fe^{II} complexes capable of gas binding, thereby representing model systems for the *T*-state of hemoglobin [42]. Addition of DiMeIm (500 equiv.) to a *ca.* 10^{-6} M solution of the G1 derivatives **1 · Fe – 5 · Fe** in PhMe afforded quantitatively and nearly instantaneously the five-coordinate *high-spin* complexes. Their formation was clearly indicated by the appearance of a characteristic *Soret* band with a maximum at λ_{max} at 435 nm (*Fig. 3*) [16]. The second-generation derivative **6 · Fe** reacts much more slowly due to enhanced steric shielding by the larger dendritic shell: complete formation of the five-coordinate complex required a larger excess of DiMeIm (1000 equiv.) and several hours of reaction time (*Fig. 4*). Computer modeling suggests that DiMeIm coordinates as a *proximal* ligand preferentially at the sterically less-shielded porphyrin face.

On the other hand, the arylethynyl moiety with the *distal* H-bonding site does not prevent additional ligation to the Fe^{II} center, as shown in experiments with 1-methyl-1*H*-imidazole (MeIm) as base. Upon portionwise addition of MeIm (up to 200 equiv.) to a solution of **1 · Fe** in PhMe, the *Soret* band shifts, under sharpening, from $\lambda_{max} = 420$

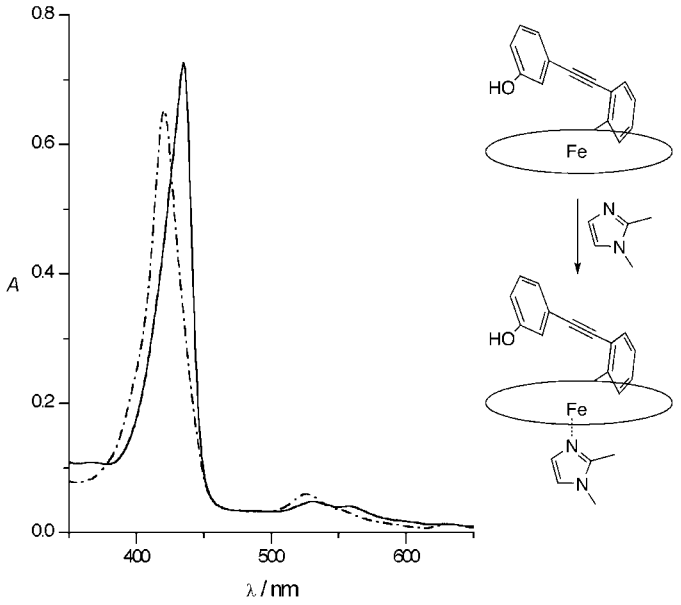


Fig. 3. *Upon addition of DiMeIm, the maximum of the* Soret *band* of **4**·**Fe** (420 nm, – · – · –) *shifts to 435 nm* (——), *indicative of formation of the five-coordinate complex* **4**·**Fe***(DiMeIm)*. DiMeIm = 1,2-Dimethyl-1*H*-imidazole.

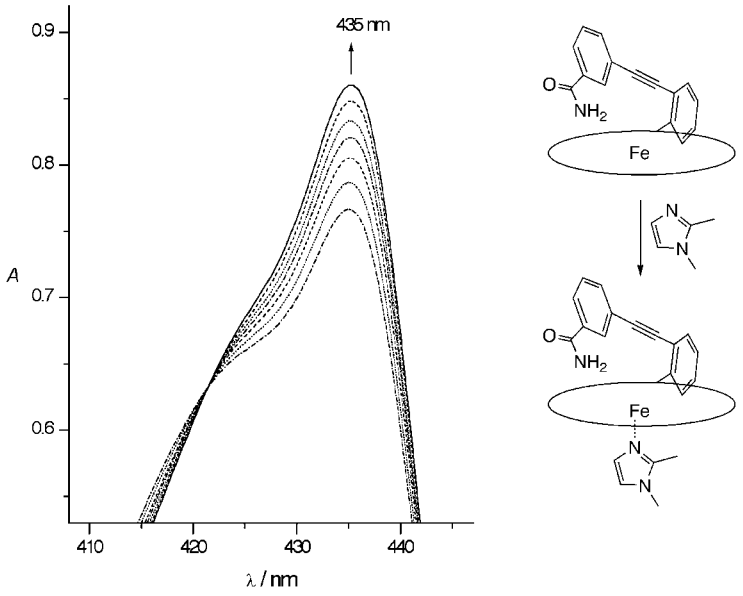


Fig. 4. *Formation of the five-coordinate complex* **6**·**Fe***(DiMeIm) upon addition of DiMeIm to* **6**·**Fe**, *as monitored by the increase in intensity of the* Soret *band at 435 nm.* Spectra were recorded in intervals of 15 min.

to 425 nm (*Fig. 5*). At the same time, the intensity of the *Q* band increases, and a second band appears as a distinct shoulder. These spectral features are in good agreement with those measured for dendritic Fe^{II} porphyrins with two covalently attached, axially coordinating 1*H*-imidazole ligands [5e][20]. They are indicative of the formation of a six-coordinate *low-spin* Fe^{II} complex. Even with the dendritic 1*H*-imidazole derivative **52**, prepared according to a procedure by *Aida* and co-workers [43], the spectral features of a six-coordinate *low-spin* complex were observed with **1·Fe**. Clearly, the introduction of the *distal* H-bond donor site does not prevent axial ligation to the Fe^{II} center on the same face of the porphyrin ring.

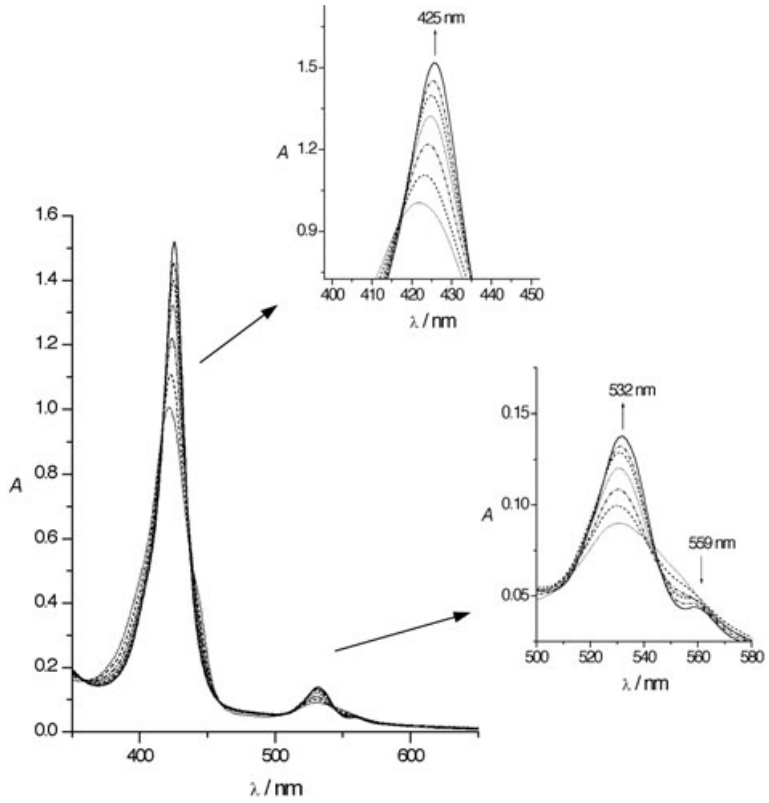


Fig. 5. *Addition of MeIm* to **1·Fe** *in PhMe shifts the maximum of the sharpened* Soret *band to 425 nm while at the same time a second* Q *band appears as a distinct shoulder*. An up to 200-fold excess of MeIm was used. MeIm = 1-Methyl-1*H*-imidazole.

Upon addition of CO to the five-coordinate complexes **1·Fe**(DiMeIm)–**6·Fe**-(DiMeIm), the *Soret* band shifts hypsochromically to λ_{max} 421 nm, indicative of quantitative formation of the corresponding six-coordinate gas complexes (*Fig. 6*) [16]. The complexes form spontaneously both with G1 and G2 dendrimers and are stable for days under exclusion of air. CO Gas binding is reversible, and the initial five-coordinate complexes can be quantitatively recovered after 4–7 freeze, pump, and thaw cycles.

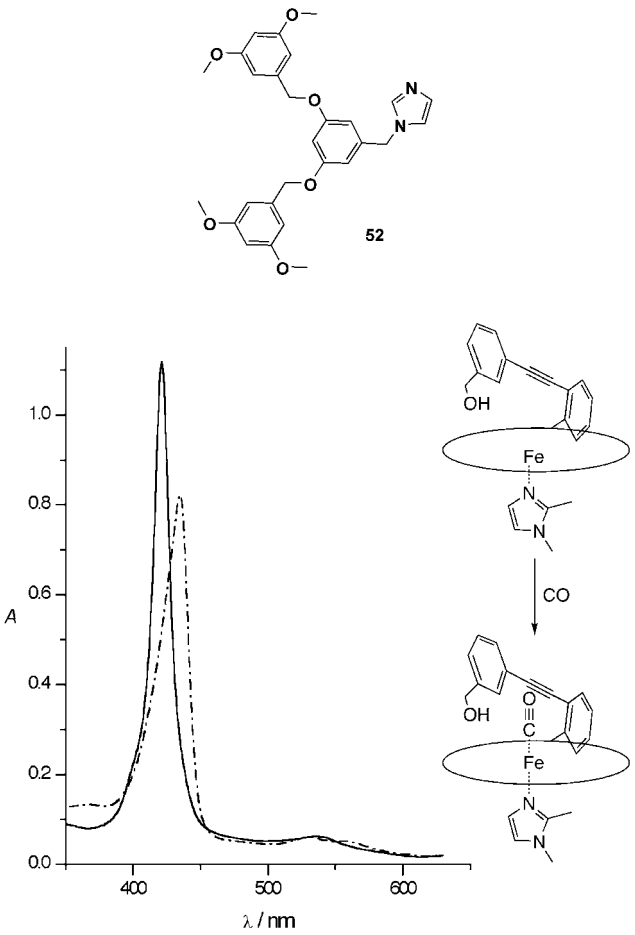


Fig. 6. *UV/VIS Spectra of five-coordinate* **3**·**Fe***(DiMeIm) with the* Soret *band at 435 nm* (– ·–·–) *and the CO adduct* **3**·**Fe***(DiMeIm)–CO with an intense absorption band at 421 nm* (—)

In contrast, the complexes of the dendritic Fe^{II} porphyrins with O_2 in PhMe are highly unstable and decompose rapidly under formation of Fe^{III} derivatives that were structurally not characterized. Thus the *Soret* band of **1**·**Fe**(DiMeIm) shifts upon addition of O_2 from 435 nm (five-coordinate Fe^{II} complex) to a maximum at 417 nm which we assign to irreversibly oxidized Fe^{III} species (*Fig. 7*). An intermediate shoulder at λ_{max} 421 nm could possibly be indicative of the intermediate formation of the desired dioxygen complex **1**·**Fe(II)**(DiMeIm)–O_2. Even the dendritic shell in the G2 derivative **6**·**Fe**(DiMeIm) is not sufficiently shielding to notably stabilize the Fe^{II}–O_2 complex, and oxidative decay occurs rapidly.

In another experiment, the six-coordinate *low-spin* Fe^{II} complex **1**·**Fe**(**52**)$_2$ was reversibly transformed in a CO atmosphere to the complex **1**·**Fe**(**52**)–CO, characterized by a *Soret* band at 426 and a *Q* band at 532 nm. Upon addition of O_2 to **1**·**Fe**(**52**)$_2$, the dioxygen complex **1**·**Fe**(**52**)–O_2 was formed with a *Q* band at 536 nm.

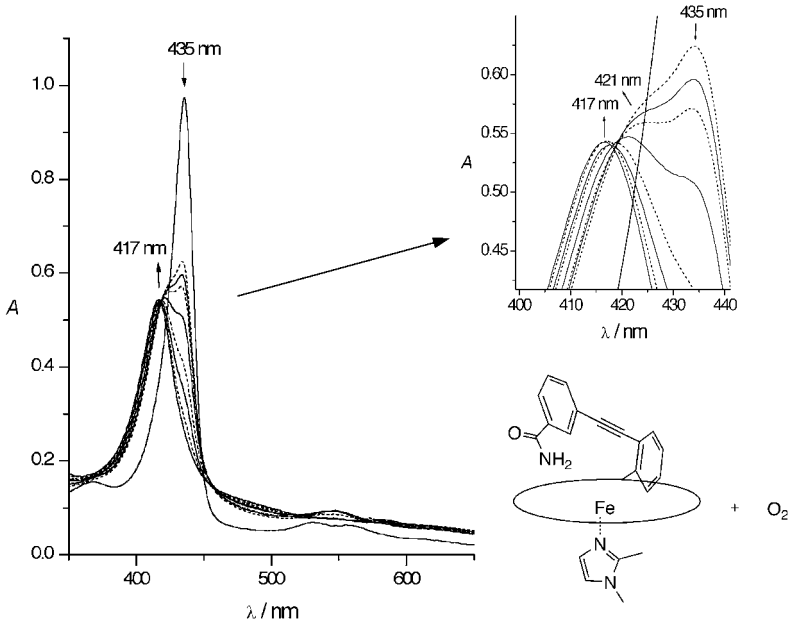


Fig. 7. *Upon addition of O_2 to* **1·Fe***(DiMeIm), the* Soret *band shifts from 435 to 417 nm.* In the course of the irreversible oxidation, a shoulder is observed at 421 nm, which could be indicative of the intermediate Fe(II)–O_2 complex.

However, it also decomposed rather rapidly under irreversible oxidation to a Fe^{III} species with a *Soret* band at 417 nm (*Fig. 8*).

Finally, the Co^{II} complexes **1·Co**–**3·Co** and **6·Co** were prepared by metallation of the corresponding free-base porphyrins with $CoCl_2$, since Co^{II} porphyrins are known to form much more stable gas complexes with O_2 than the Fe^{II} analogs [9c][44]. Upon addition of DiMeIm (300 equiv.) in PhMe, the corresponding five-coordinate complexes **1·Co**(DiMeIm)–**3·Co**(DiMeIm) and **6·Co**(DiMeIm) were formed, as evidenced by EPR spectroscopy [9c][45]. These complexes were subsequently exposed to air for 30–60 min, which led to the formation of the corresponding Co^{II}–O_2 complexes. The continuous-wave electron paramagnetic resonance (CW-EPR) spectra of these complexes in frozen solution (PhMe, 110 K) are typical of those for oxygenated Co^{II} complexes with magnetic parameters comparable to values reported in the literature [9c][11][45][46]. Multidimensional and multifrequency-pulse EPR experiments [47] are currently being conducted in collaboration with *A. Schweiger* and *C. Calle* (ETH-Zürich) to investigate possible H-bond interactions between Co^{II}-coordinate O_2 and the *distal* H-bond donors [46], and the results will be reported elsewhere.

3. Conclusions. – This paper describes the synthesis of new biomimetic systems designed to explore the role of H-bonding in the stabilization of gas complexes of hemoglobin, myoglobin, and dendritic analogs. The preparation of the first- (G1) and

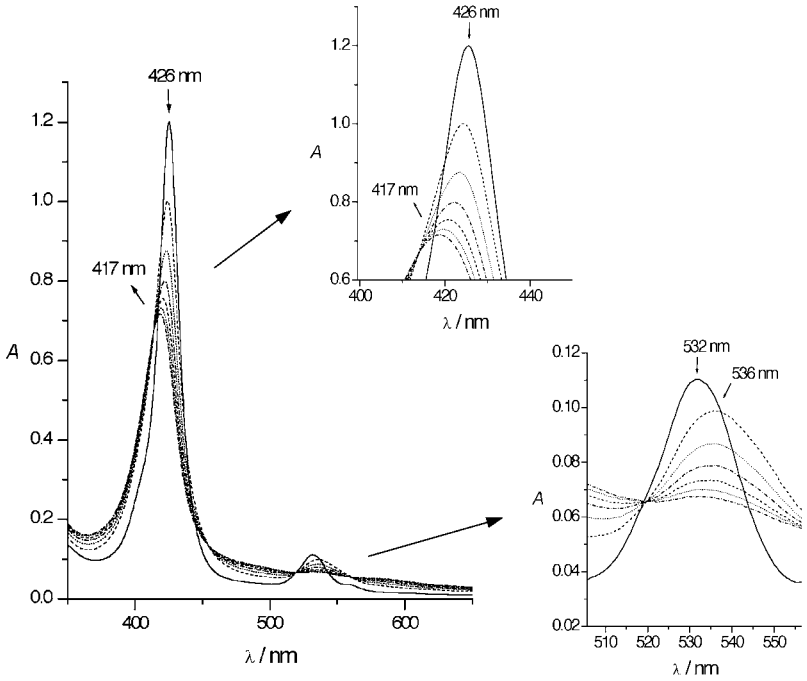


Fig. 8. *Addition of O_2 to* **1**·**Fe**(**52**)$_2$ *leads to the corresponding* $Fe^{II}-O_2$ *complex with a* Q *band at 536 nm.* This complex oxidizes rapidly to an undefined Fe^{III} derivative. UV/VIS Spectra are recorded at intervals of 11 min.

second-generation (G2) dendritic Fe^{II} porphyrins **1**·**Fe**–**4**·**Fe** and **6**·**Fe** (*Fig. 1*) was accomplished by a synthetic sequence involving construction of the *meso*-triarylated porphyrin macrocycle with the appended ethynyl moiety in a mixed condensation (*Scheme 8*), attachment of the dendrons to the macrocyclic core (*Scheme 11*), *Sonogashira* cross-coupling to attach the *distal* H-bond donors to the ethynyl residue, and metal-ion insertion under an inert atmosphere (*Scheme 12*). This modular strategy ensures great flexibility in the choice of *distal* H-bond donors, which are introduced only at the end of the synthesis. Another promising route, by which the *ortho*-ethynylated phenyl ring with the *distal* H-bond donor is introduced *via Suzuki* cross-coupling into the *meso*-position of a preformed Zn^{II} porphyrin, failed unexpectedly (*Schemes 1*, *3*, and *5*). A variety of control runs showed that this failure is probably due to steric hindrance resulting from unfavorable coordination of the ethynyl residue to the Pd species in the catalytic cycle (*Scheme 6*). ^{1}H-NMR-Spectroscopic analyses provide strong evidence that the *distal* H-bond donor in the dendrimers is located atop of the porphyrin plane. Additionally, X-ray-analysis on the MeOH solvate of model system **45**·**Zn** demonstrates that the *distal* H-bond donor leaves sufficient space for gas coordination on the same porphyrin face. The Fe^{II} porphyrins form five-coordinate complexes with DiMeIm as ligand (*Figs. 3* and *4*). Upon addition of CO, six-coordinate gas complexes are produced reversibly (*Fig. 6*), while the O_2 complexes of both first- (*e.g.*, **1**·**Fe**(DiMeIm)) and second-generation (**6**·**Fe**(DiMeIm)) dendrimers are highly

unstable and decay rapidly to non-characterized Fe^{III} species (*Fig. 7*). The G1 dendritic Fe^{II} porphyrin **1·Fe** reacts with both MeIm and the dendritic imidazole **52** to give the corresponding six-coordinate *low-spin* complexes (*Fig. 5*). Upon addition of CO, the six-coordinate gas complex is again obtained reversibly, whereas the corresponding O_2 adduct decomposes rather rapidly under generation of an undefined Fe^{III} species (*Fig. 8*). In contrast, stable gas adducts are formed between the dendritic Co^{II} porphyrins and O_2 in the presence of DiMeIm as axial ligand. Multidimensional and multifrequency-pulse EPR experiments are now being carried out to explore possible H-bonding interactions between Co^{II}-coordinate O_2 and the *distal* H-bond donors.

We thank the *Roche Research Foundation* (doctoral fellowship to *B. F.*) and the *NCCR Basel* 'Nanoscale Science' for support of this work, Dr. *C. Thilgen* (ETH-Zürich) for help with the nomenclature, and *H. Dube* (ETH-Zürich) for assistance in the preparation of the manuscript.

Experimental Part

General. All reactions were carried out under N_2. Solvents and reagents were reagent-grade and used without further purification unless otherwise stated. Abs. THF and abs. PhMe were freshly distilled from sodium benzophenone ketyl or sodium, resp. 1-Bromo-2-iodobenzene (**19**) [48], 3-iodobenzamide [34], 3-iodosulfonamide [40], 1-bromo-3-{[(*tert*-butyl)dimethylsilyl]oxy}benzene [49], 5-bromo-2-methylphenol (**9**) [17], *meso*-bromoporphyrin **14·Zn** [5e], alkyne **20** [21], 1*H*-imidazole **25** [3][25], alkyne **28** [26], dipyrrylmethane **33** [28a–c], aldehydes **35** [29], **36** [5c], and **37** [50], dendrons **46** and **47** [39], and dendritic 1*H*-imidazole **52** [43] were prepared according to literature protocols. Evaporation *in vacuo* was conducted at H_2O aspirator pressure or with a membrane pump (*Vacuubrand CVC 2,* 10 mbar) on a *Büchi Rotavapor-R* connected to a *Büchi Vacuum Controller B-720*. Flash chromatography (FC): SiO_2 *60* (230–400 mesh, 0.040–0.063 mm) or SiO_2-*H* (0.005–0.040 mm) from *Fluka* at 0.3 bar pressure, visualization by UV light. Prep. gel-permeation chromatography (GPC): *BioBeads® SX-1* (200–400 mesh) from *Bio-Rad*, eluent CH_2Cl_2 or THF, visualization by UV light. Column chromatography (CC) of the Co^{II} and Fe^{II} porphyrins conducted unter N_2: neutral Al_2O_3, dried by heating for 24 h at 250° *in vacuo* (10^{-5}–10^{-6} mbar), then stored unter N_2 for minimum 3 d. Molecular sieves (*UOP 3 Å, 1/16″)* from *Fluka* were activated by heating at 300° *in vacuo* (10^{-5}–10^{-6} mbar) for 24 h. Metal insertion into the dendritic free-base porphyrins was conducted unter N_2 with a residual O_2 concentration < 1 ppm (with a *Mecaplex* dry-box *Mecabox 80-1*, equipped with an oxygen sensor *MAP Check 9000-1* from *PBI Dansensor*, and a humidity indicator *Xentaur Dewpoint-Transmitter XDT-PM*). M.p.: *Büchi Melting Point B-540* apparatus; uncorrected. UV/VIS Spectra [nm]: *Varian Cary 5 UV/Vis/NIR* or *Varian Cary 500 UV/Vis/NIR* spectrophotometer; recorded at a resolution of 0.5 nm, molar extinction coefficient ε in $dm^3\ mol^{-1}\ cm^{-1}$. IR Spectra [cm^{-1}]: *Perkin-Elmer 1600-FT-IR*. NMR Spectra: *Bruker AMX-500* and *Varian Gemini 300* or *200* at 296 or 300 K, with solvent peak as reference; non-resolved coupling patterns of higher order are described as followed: m_d (*doublet* without resolved *meta*-coupling), $m_{sext.}$ (*multiplet* of *sextet*-like pattern), quotation marks indicate not completely resolved signal multiplicities due to overlap with other couplings. MS (*m/z* (%)): EI: *VG TRIBRID* spectrometer at 70 eV; MALDI-MS: *Ion Spec Ultima FT-ICR* (2,5-dihydroxybenzoic acid (DHB) or 2-{(2*E*)-3-[4-(*tert*-butyl)phenyl]-2-methylprop-2-enylidene}malononitrile (DCTB) as matrix); positive-ion mode. Elemental analyses were performed by the Mikrolabor at the Laboratorium für Organische Chemie, ETH Zürich.

General Procedure for Fe^{II} Insertion into the Free-Base Porphyrins (→**1·Fe**–**6·Fe**). To a soln. of dendritic porphyrin (10 mg, 3–4 μmol) in abs. THF (1 ml) under N_2 in a dry-box, $FeBr_2$ (7.5 equiv.) and 2,6-lutidine (10 μl) were added, and the mixture was stirred for 2–7 d at 20°. The solvent was evaporated *in vacuo*, and the residue was purified by CC (neutral Al_2O_3; abs. THF/abs. MeOH 9:1 → 5:3). A dark-red, highly viscous oil was obtained, which was dissolved in abs. PhMe (1 ml). This soln. was stored at 20° under N_2 and served as stock soln. for the UV/VIS studies.

General Procedure for Co^{II} Insertion into the Free-Base Porphyrins (→**1·Co**–**3·Co** and **6·Co**). To a soln. of dendritic porphyrin (10 mg, 3–4 μmol) in abs. THF (1 ml) under N_2 in a dry-box, $CoCl_2$ (1.0 equiv.) and 2,6-lutidine (10 μl) were added, and the mixture was stirred for 1–4 d at 20°. The solvent was evaporated *in vacuo*, and the residue was purified by CC (neutral Al_2O_3; abs. THF/abs. MeOH 9:1 → 5:3). A dark-red, highly

viscous oil was obtained, which was then dissolved in abs. PhMe (1 ml). This soln. was stored at 20° under N_2 and served as stock soln. for EPR studies.

5-Bromo-4-iodo-2-methylphenol (**10**). To **9** (744 mg, 4.0 mmol) in MeOH (10 ml), NaOH (159 mg, 4.0 mmol) was added. The resulting soln. was treated with NaI (596 mg, 4.0 mmol), then aq. NaOCl soln. (4.3%, 5.4 ml, 4.0 mmol) was added dropwise. After stirring for 3 h at 20°, another portion of aq. NaOCl soln. (4.3%, 5.4 ml, 4.0 mmol) was added, and the mixture was stirred for 3 h at 20°. The reaction was stopped by addition of sat. aq. sodium dithionite soln. (10 ml), then neutralized with 1M HCl, and extracted with CH_2Cl_2 (3×50 ml). The combined org. layers were dried ($MgSO_4$), and the solvent was evaporated *in vacuo*. Crystallization (hot hexane) yielded **10** (822 mg, 66%). Colorless needles. M.p. 108°. TLC (SiO_2; hexane/AcOEt 9:1): R_f 0.36. IR ($CHCl_3$): 3689*m*, 3278*w* (br.), 2356*s*, 2322*s*, 1600*s*, 1472*m*, 1383*w*, 1283*w*, 1244*m*, 1167*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.57 (*s*, 1 H); 7.07 (*s*, 1 H); 4.83 (br. *s*, 1 H); 2.15 (*s*, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 154.70; 141.55; 126.68; 125.73; 119.27; 89.49; 14.86. EI-MS: 312/314 (100/95, M^+). Anal. calc. for C_7H_6BrIO (312.93): C 26.87, H 1.93, I 40.55; found: C 27.03, H 1.91, I 40.31.

1-Bromo-2-iodo-5-(methoxymethoxy)-4-methylbenzene (**11**). To **10** (1.12 g, 3.6 mmol) in MeCN (36 ml) at 0°, K_2CO_3 (1.98 g, 28.6 mmol) was added, and, after stirring for 45 min, chloromethyl methyl ether (MOMCl) (0.55 ml, 7.2 mmol) was slowly added keeping the reaction temp. below 5°. The mixture was stirred for 60 min at 0°, warmed to 20°, and stirred for another 60 min. MeOH (20 ml) was added, and, after standing for 12 h at 20°, the solvent was removed *in vacuo*. The solid residue was dissolved in H_2O (100 ml) and extracted with AcOEt (3×100 ml). The combined org. layers were dried ($MgSO_4$), and the solvent was evaporated *in vacuo*. The orange oil was purified by bulb-to-bulb distillation (125°/0.13 Torr) to yield **11** (1.19 g, 93%) as a colorless, highly viscous oil, which crystallized slowly at 20°. Colorless solid. M.p. 50–51°. TLC (SiO_2; hexane/AcOEt 3:1): R_f 0.66. IR ($CHCl_3$): 3007*w*, 2961*w*, 2935*w*, 2902*w*, 1476*s*, 1442*w*, 1339*m*, 1278*m*, 1165*s*, 1153*s*, 1081*s*, 999*s*, 878*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.60–7.58 (*m*, 1 H); 7.33–7.31 (br. *s*, 1 H); 5.16 (*s*, 2 H); 3.47 (*s*, 3 H); 2.14 (*s*, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 156.18; 141.20; 128.87; 126.70; 118.24; 94.51; 90.80; 56.11; 15.39. EI-MS: 356/358 (55/54, M^+), 326/328 (12/8, $[M - MeO]^+$), 45 (100, $[CH_2OMe]^+$). Anal. calc. for $C_9H_{10}BrIO_2$ (312.93): C 30.28, H 2.82, Br 22.38, I 35.55, O 8.96; found: C 30.38, H 2.68, Br 22.30, I 35.27, O 9.11.

1-Bromo-5-(methoxymethoxy)-4-methyl-2-[(triisopropylsilyl)ethynyl]benzene (**12**). To a degassed soln. of **11** (986 mg, 3.15 mmol) and (triisopropylsilyl)acetylene (778 µl, 632 mg, 3.47 mmol) in abs. THF (34 ml) and (i-Pr)$_2$NH (6 ml), $[PdCl_2(PPh_3)_2]$ (111 mg, 0.15 mmol, 5 mol-%) and CuI (30 mg, 0.15 mmol, 5 mol-%) were added, and the mixture was stirred for 18 h at 20°. After adsorptive filtration through a plug of SiO_2 (hexane), the filtrate was evaporated, and the brown residue was purified by FC (SiO_2; hexane/AcOEt 6:1 + 0.5 vol-% Et_3N) to give **12** (0.858 g, 66%) as an oil, which slowly solidified. Light-yellow, waxy solid. M.p. 38–39°. TLC (SiO_2; hexane/AcOEt 9:1 + 0.5 vol-% Et_3N): R_f 0.54. IR ($CHCl_3$): 2943*m*, 2865*m*, 2154*w*, 1596*w*, 1482*m*, 1454*m*, 1223*s*, 1212*s*, 1206*s*, 1153*m*, 1082*m*, 997*s*, 974*m*, 883*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.30–7.29 (*m*, 1 H); 7.27–7.25 (*m*, 1 H); 5.18 (*s*, 2 H); 3.47 (*s*, 3 H); 2.16 (*s*, 3 H); 1.14 (*m*, 21 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 155.80; 135.38; 126.64; 123.39; 118.63; 117.60; 105.01; 94.44; 93.84; 56.08; 18.56; 15.57; 11.21. EI-MS: 410/412 (12/13, M^+), 367/369 (97/100, $[M - i\text{-}Pr]^+$), 325/327 (31/27), 297/299 (51/48). Anal. calc. for $C_{20}H_{31}BrO_2Si$ (411.46): C 58.38, H 7.59, Br 19.42; found: C 58.39, H 7.70, Br 19.23.

2-{5-(Methoxymethoxy)-4-methyl-2-[(triisopropylsilyl)ethynyl]phenyl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**8**). *Procedure A:* To a soln. of **12** (560 mg, 1.36 mmol) in abs. THF (8.5 ml) at −70°, BuLi (1.6M soln. in hexane, 0.9 ml, 1.5 mmol) was added dropwise, and the mixture was stirred for 60 min. $(MeO)_3B$ (0.29 g, 0.30 ml, 2.8 mmol) was added, the cooling bath was removed, and the mixture was stirred for 20 h at 20°. After removal of the solvent *in vacuo*, the residue was dissolved in benzene (8.5 ml), and pinacol (193 mg, 1.63 mmol) was added. The resulting mixture was heated in a water separator for 2 h to reflux, then cooled to 20°, and diluted with PhMe (20 ml). The mixture was washed with sat. aq. $NaHCO_3$ soln. (30 ml), and sat. aq. NaCl soln. (30 ml), and dried ($MgSO_4$). After evaporation of the solvent *in vacuo* and bulb-to-bulb destillation (230°/0.05 Torr), a colorless oil (386 mg, 62%) was obtained, which solidified upon standing at 20°. Further purification by recrystallization (MeOH) yielded **8** (75 mg, 12%).

Procedure B: A mixture of **12** (500 mg, 1.22 mmol), AcOK (358 mg, 3.65 mmol), **13** (339 mg, 1.34 mmol), and $[PdCl_2(dppf)]$ (30 mg, 37 µmol, 3 mol-%) in abs. Me_2SO (7.5 mg) was heated for 20 h to 90°. After cooling to 20°, Et_2O (100 ml) was added, and the org. layer was washed with sat. aq. NaH_2PO_4 soln. (50 ml) and sat. aq. NaCl soln. (50 ml) and filtered through a plug of SiO_2 (Et_2O). Evaporation *in vacuo* and recrystallization (MeOH) yielded **8** (128 mg, 23%). Colorless, microcrystalline powder. M.p. 65–67°. Decomposition on SiO_2. IR ($CHCl_3$): 3678*w*, 3011*w*, 2944*m*, 2867*m*, 2144*w*, 1600*m*, 1500*w*, 1467*w*, 1417*w*, 1389*s*, 1377*m*, 1339*m*, 1194*m*, 1148*s*, 1028*w*, 994*m*, 661*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.32 (br. *s*, 2 H); 5.23 (*s*, 2 H); 3.47 (*s*, 3 H); 2.22 (*s*, 3 H); 1.31 (*s*, 12 H); 1.14 (*m*, 21 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 154.79; 136.78; 130.33; 121.85; 119.76; 107.86;

94.35; 90.53; 83.73; 56.16; 24.71; 18.71; 16.00; 11.34; signal for the C-atom next to the B-atom not resolved. HR-MALDI-MS (DHB): 481.292 ($[M+Na]^+$, $C_{26}H_{43}BO_4SiNa^+$; calc. 481.292).

Syntheses of **20** [21], **27**, *and* **28** [26]. To a degassed soln. of **19**, 1-bromo-3-iodobenzene or 1-bromo-4-iodobenzene resp. (1.0 g, 3.5 mmol), and (triisopropylsilyl)acetylene (0.87 ml, 3.9 mmol) in abs. THF (37.5 ml) and $(i\text{-Pr})_2NH$ (6.5 ml), $[PdCl_2(PPh_3)_2]$ (124 mg, 0.18 mmol, 5 mol-%), and CuI (34 mg, 0.18 mmol, 5 mol-%) were added, and the mixture was stirred for 24 h at 20°. After adsorptive filtration through a plug of SiO_2 (hexane), the filtrate was evaporated *in vacuo*, and the brown residue was purified by FC (SiO_2; pentane) to give **20** (86%), **27** (87%), and **28** (81%), resp., as oils.

1-Bromo-3-[(triisopropylsilyl)ethynyl]benzene (**27**). Colorless oil. TLC (SiO_2; pentane): R_f 0.75. IR ($CHCl_3$): 2945*s*, 2892*m*, 2866*s*, 2158*w*, 1590*m*, 1559*w*, 1472*m*, 1404*w*, 1264*w*, 1072*w*, 996*m*, 883*m*, 862*s*, 637*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.61 (*t*, *J* = 1.6, 1 H); 7.46–7.42 (*m*, 1 H); 7.41–7.37 (*m*, 1 H); 7.17 (*t*, *J* = 8.0, 1 H); 1.12 (*s*, 21 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 134.7; 131.5; 130.6; 129.7; 125.5; 122.0; 105.3; 92.4; 18.6; 11.3. EI-MS: 336/338 (6, M^+), 293/295 (100, $[M-i\text{-Pr}]^+$), 267/265 (27, $[M-i\text{-Pr}-C_2H_4]^+$), 253/251 (29, $[M+H-2\ (i\text{-Pr})]^+$), 239/237 (46, $[M-i\text{-Pr}-2\ C_2H_4]^+$), 225/223 (57, $[M+H-2\ (i\text{-Pr})-C_2H_4]^+$), 209/207 (18, $[M-3\ (i\text{-Pr})]^+$). Anal. calc. for $C_{17}H_{25}BrSi$ (337.37): C 60.52, H 7.47, Br 23.68; found: C 60.58, H 7.39, Br 23.64.

4,4,5,5-Tetramethyl-2-{2-[(triisopropylsilyl)ethynyl]phenyl}-1,3,2-dioxaborolane (**18**). A degassed soln. of **20** (100 mg, 0.30 mmol) [21], AcOK (87 mg, 0.89 mmol), **13** (83 mg, 0.33 mmol), and $[PdCl_2(dppf)]$ (7 mg, 10 μmol, 3 mol-%) in abs. Me_2SO (2 ml) was stirred for 18 h at 90°. After cooling to 20°, the mixture was diluted with Et_2O (100 ml), and washed with sat. aq. NaH_2PO_4 soln. (50 ml) and sat. aq. NaCl soln. (50 ml). Adsorptive filtration of the org. layer through a plug of SiO_2 (hexane/AcOEt 95:5) and evaporation *in vacuo* provided **18** (114 mg, quant.). Light-yellow oil. Decomposition on SiO_2. IR (CCl_4): 2943*m*, 2865*m*, 2155*w*, 1592*w*, 1561*w*, 1484*w*, 1463*w*, 1437*m*, 1384*m*, 1371*m*, 1354*s*, 1318*m*, 1268*w*, 1212*w*, 1146*m*, 1116*w*, 1069*m*, 1036*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.81–7.76 (m_{dd}, 1 H); 7.58–7.53 (m_{dd}, 1 H); 7.42–7.26 (*m*, 2 H); 1.36 (*s*, 12 H); 1.18 (*s*, 21 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 135.48; 134.08; 130.36; 128.43; 127.38; 107.70; 92.59; 83.79; 24.72; 18.65; 11.32; signal for the C-atom next to B-atom not resolved. EI-MS: 384 (2, M^+), 341 (65, $[M-i\text{-Pr}]^+$), 241 (100, $[M-BO_2C_6H_{12}-Me]^+$), 171 (25, $[M-2\ (i\text{-Pr})]^+$).

(Tetraethyl 4,4′,4″,4‴-{[10-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)porphyrin-5,15-diyl-κN^{21},κN^{22},κN^{23},κN^{24}]bis[benzene-2,1,3-triylbis(oxy)]}tetrabutanoato(2−))zinc (**21·Zn**). *Procedure A:* A degassed soln. of **14·Zn** (30 mg, 27 μmol) [5e], AcOK (8 mg, 80 μmol), **13** (7 mg, 27 μmol), and $[PdCl_2(PPh_3)_2]$ (1 mg, 1.4 μmol, 5 mol-%) in abs. Me_2SO (0.2 ml) was stirred for 24 h at 80°. The mixture was cooled to 20° and diluted with Et_2O (15 ml). The org. layer was separated and washed with sat. aq. NaH_2PO_4 soln. (10 ml) and sat. aq. NaCl soln. (10 ml). After adsorptive filtration through a plug of SiO_2 (Et_2O), the solvent was removed *in vacuo*, and the residue was purified by FC (SiO_2-*H*; $CHCl_3$/AcOEt 97:3). Recrystallization (CH_2Cl_2/hexane) yielded **21·Zn** (10 mg, 33%).

Procedure B: A degassed soln. of **14·Zn** (150 g, 133 μmol), **22** (145 mg, 164 μl, 1.13 mmol), Et_3N (175 mg, 241 μl, 1.73 mmol), and $[PdCl_2(PPh_3)_2]$ (3 mg, 4 μmol, 3 mol-%) in abs. 1,2-dichloroethane (13.5 ml) was heated to reflux for 18 h. After cooling to 20°, Et_2O (20 ml) and sat. aq. NaH_2PO_4 soln. (15 ml) were added, and the org. layer was separated and washed with H_2O (15 ml) and sat. aq. NaCl soln. (15 ml). The solvent was evaporated *in vacuo*, and the residue was dissolved in Et_2O (7 ml) and filtered through a plug of SiO_2 (Et_2O). Evaporation *in vacuo* and recrystallization (CH_2Cl_2/hexane) afforded **21·Zn** (156 mg, quant.). Purple crystals. M.p. 117–118°. TLC (SiO_2; $CHCl_3$/AcOEt 97:3): R_f 0.18. UV/VIS (PhMe): 583 (sh, 2600), 554 (18800), 517 (2900), 423 (574300), 403 (sh, 42800), 317 (23299). IR (CCl_4): 2980*w*, 2876*w*, 1733*s*, 1585*m*, 1524*m*, 1456*s*, 1379*m*, 1306*m*, 1248*m*, 1179*s*, 1145*m*, 1103*s*, 1059*m*, 996*m*, 857*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 10.15 (*s*, 1 H); 9.83 (*d*, *J* = 4.6, 2 H); 9.30 (*d*, *J* = 4.4, 2 H); 9.00 (*d*, *J* = 4.6, 2 H); 8.95 (*d*, *J* = 4.4, 2 H); 7.71 (*t*, *J* = 8.5, 2 H); 7.05 (*d*, *J* = 8.5, 4 H); 3.88–3.83 (*m*, 8 H); 3.31–3.26 (*m*, 8 H); 1.83 (*s*, 12 H); 1.21–1.14 (*m*, 8 H); 0.99–0.95 (*m*, 8 H); 0.60 (*t*, *J* = 7.1, 12 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 172.77; 160.00; 153.87; 150.72; 150.25; 148.73; 132.79; 131.80; 131.62; 131.04; 129.91; 122.63; 112.14; 106.61; 106.33; 84.86; 67.88; 59.43; 29.21; 25.23; 23.69; 13.40; signal for the C-atom next to B-atom not resolved. HR-MALDI-MS (DCTB): 1169.437 (M^+, $C_{62}H_{71}BN_4O_{14}Zn^+$; calc. 1169.438). Anal. calc. for $C_{62}H_{71}BN_4O_{14}Zn$ (1172.45): C 63.51, H 6.10, N 4.78; found: C 63.41, H 6.20, N 4.98.

1-Iodo-5-(methoxymethoxy)-4-methyl-2-[(triisopropylsilyl)ethynyl]benzene (**23**). BuLi (1.6M soln. in hexane, 3.8 ml, 6.08 mmol) was added, dropwise to **12** (2.00 g, 4.86 mmol) in abs. THF (30 ml) at −70°, and the mixture was stirred for 30 min at that temp. I_2 (2.5 g, 8.7 mmol) was added, and the mixture was stirred without cooling for 2 h, then quenched by the addition of sat. aq. $Na_2S_2O_3$ soln. (20 ml). Extraction with CH_2Cl_2 (3 × 30 ml), drying of the combined org. layers ($MgSO_4$), and evaporation *in vacuo* yielded the crude product. FC (SiO_2; hexane/AcOEt 95:5) and recrystallization (MeCN) provided **23** (1.80 g, 82%). Colorless microcrystalline powder. M.p. 37°. TLC (SiO_2; hexane/AcOEt 95:5): R_f 0.52. IR ($CHCl_3$): 2958*s*, 2942*s*, 2924*s*, 2865*s*,

2150*w*, 1591*m*, 1478*s*, 1153*s*, 1082*m*, 996*s*, 967*m*, 883*m*, 654*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.46 (*s*, 1 H); 7.28–7.26 (m_d, 1 H); 5.17 (*s*, 2 H); 3.46 (*s*, 3 H); 2.15 (*s*, 3 H); 1.16 (*s*, 21 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 155.44; 134.73; 127.43; 123.47; 123.24; 108.08; 97.47; 94.33; 92.99; 56.15; 18.72; 15.83; 11.35. EI-MS: 458 (7, M^+), 415 (36, $[M - \text{i-Pr}]^+$), 345 (11), 45 (24, $[\text{i-Pr}]^+$), 32 (25), 28 (100, $C_2H_4^+$). Anal. calc. for $C_{20}H_{31}IO_2Si$ (458.45): C 52.40, H 6.82, I 27.68; found: C 52.48, H 6.68, I 27.68.

5-Iodo-2-methyl-4-[(triisopropylsilyl)ethynyl]phenol (**24**). A soln. of **23** (200 mg, 0.44 mmol) and conc. HCl (37%, 360 µl, 4.4 mmol) in MeOH (8 ml) and THF (15 ml) was stirred for 65 h at 20°. The mixture was poured on ice/H_2O (50 ml), and the aq. layer was extracted with CH_2Cl_2 (2 × 80 ml). The combined org. layers were dried ($MgSO_4$), and the solvent was evaporated *in vacuo*. The residual oil was purified by FC (SiO_2; hexane/AcOEt 4:1) to yield **24** (178 mg, 98%). Light-yellow oil. TLC (SiO_2; hexane/AcOEt 9:1 + 0.5 vol-% Et_3N): R_f 0.27. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.25 (*s*, 1 H); 7.22 (*s*, 1 H); 5.04 (br. *s*, 1 H); 2.16 (*s*, 3 H); 1.15 (*s*, 21 H).

*1-(6-{5-Iodo-2-methyl-4-[(triisopropylsilyl)ethynyl]phenoxy}hexyl)-1*H*-imidazole* (**26**). A soln. of **25**·AcOH (260 mg, 0.893 mmol) [3][25] in CH_2Cl_2 (20 ml) was washed with 1M NaOH (15 ml), and the org. layer was dried ($MgSO_4$). Subsequently, **24** (150 mg, 0.362 mmol) in abs. DMF (2 ml) was added, and the co-solvent CH_2Cl_2 was evaporated *in vacuo*. Cs_2CO_3 (236 mg, 0.724 mmol) was added, and the mixture was stirred for 4 h at 20°, then diluted with CH_2Cl_2 (30 ml), and filtered through *Celite* (CH_2Cl_2). The filtrate was washed with H_2O (30 ml), and the org. layer was evaporated *in vacuo*. Purification by FC (SiO_2; CH_2Cl_2/MeOH 95:5) and GPC (*BioBeads SX-1*; CH_2Cl_2) gave **26** (114 mg, 56%). Yellow oil. TLC (SiO_2; CH_2Cl_2/MeOH 95:5): R_f 0.20. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.46 (*s*, 1 H); 7.24 (*d*, *J* = 0.6, 1 H); 7.16 (*s*, 1 H); 7.06 (*s*, 1 H); 6.90 (*s*, 1 H); 3.94 (*t*, *J* = 7.2, 2 H); 3.90 (*t*, *J* = 6.2, 2 H); 2.10 (*s*, 3 H); 1.85–1.72 (*m*, 4 H); 1.55–1.30 (*m*, 4 H); 1.14 (*s*, 21 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 157.23; 137.02; 134.52; 129.47; 126.90; 121.88; 120.70; 118.71; 108.23; 97.64; 92.58; 67.92; 46.88; 31.02; 28.88; 26.26; 25.58; 18.71; 15.73; 11.35. EI-MS: 564 (13, M^+), 521 (100, $[M - \text{i-Pr}]^+$), 437 (8, $[M - \text{I}]^+$). HR-MALDI-MS (DHB): 565.211 (MH^+, $C_{27}H_{42}IN_2OSi^+$; calc. 565.211).

*(Tetraethyl 4,4′,4″,4‴-{(10-{3-[(Triisopropylsilyl)ethynyl]phenyl}porphyrin-5,15-diyl-*κ*N^{21},*κ*N^{22},*κ*N^{23},*κ*N^{24})bis[benzene-2,1,3-triylbis(oxy)]}tetrabutanoato(2−))zinc* (**29·Zn**). A degassed soln. of **21·Zn** (20 mg, 17 µmol), **27** (7.0 mg, 21 µmol), Cs_2CO_3 (56 mg, 17 µmol), and $[Pd(PPh_3)_4]$ (2.0 mg, 1.7 µmol, 10 mol-%) in abs. THF (3 ml) and abs. PhMe (3 ml) was stirred for 20 h at 110°. After cooling to 20°, Et_2O (50 ml) was added, and the org. layer was washed with sat. aq. NaH_2PO_4 soln. (50 ml), H_2O (50 ml), and sat. aq. NaCl soln. (50 ml). Adsorptive filtration through a plug of SiO_2 (Et_2O) and evaporation *in vacuo*, followed by FC (SiO_2-*H*; $CHCl_3$/AcOEt 97:3, then hexane/AcOEt 7:3), afforded **29·Zn** (9.0 mg, 41%). Purple, highly viscous oil. TLC (SiO_2; hexane/AcOEt 7:3): R_f 0.32. UV/VIS (PhMe): 594 (4100), 557 (19000), 519 (3200), 426 (487800), 405 (40200), 317 (23200). IR (CCl_4): 2980*w*, 2943*m*, 2866*w*, 2154*w*, 1735*s*, 1593*m*, 1586*m*, 1456*s*, 1381*m*, 1249*s*, 1179*s*, 1103*s*, 1060*m*, 997*s*, 933*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 10.11 (*s*, 1 H); 9.30 (*d*, *J* = 4.6, 2 H); 8.99 (*d*, *J* = 4.6, 2 H); 8.89 (*d*, *J* = 4.7, 2 H); 8.86 (*d*, *J* = 4.7, 2 H); 8.38 ('*t*', '*J*' = 1.5, 1 H); 8.17 ('*dt*', '*J*' = 8.0, 1.5, 1 H); 7.87 ('*dt*', '*J*' = 7.8, 1.4, 1 H); 7.71 (*t*, *J* = 8.3, 2 H); 7.64 ('*t*', '*J*' = 7.8, 1 H); 7.05 (*d*, *J* = 8.3, 4 H); 3.92–3.84 (*m*, 8 H); 3.39–3.28 ($m_{sext.}$, 8 H); 1.14 (*s*, 21 H); 1.35–0.96 (*m*, 16 H); 0.66–0.60 (*m*, 12 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 172.68; 172.63; 159.76; 159.67; 150.39 (2×); 149.53; 149.16; 143.67; 137.46; 134.61; 131.52; 131.45; 130.97; 130.84; 129.87; 126.10; 122.14; 121.54; 118.90; 112.27; 107.45; 106.30; 106.19; 104.88; 90.35; 67.71; 67.67; 59.56 (2×); 29.35; 29.26; 23.80 (2×); 18.66; 13.58 (2×); 11.33; one signal was not resolved. HR-MALDI-MS (DCTB): 1300.513 (M^+, $C_{73}H_{84}N_4O_{12}SiZn^+$; calc. 1300.514).

*(Tetraethyl 4,4′,4″,4‴-{(10-{4-[(Triisopropylsilyl)ethynyl]phenyl}porphyrin-5,15-diyl-*κ*N^{21},*κ*N^{22},*κ*N^{23},*κ*N^{24})bis[benzene-2,1,3-triylbis(oxy)]}tetrabutanoato(2−))zinc* (**30·Zn**). A degassed soln. of **21·Zn** (100 mg, 85.3 µmol), **28** (34.5 mg, 102 µmol), Cs_2CO_3 (228 mg, 853 µmol), and $[Pd(PPh_3)_4]$ (9.9 mg, 8.5 µmol, 10 mol-%) in abs. THF (15 ml) and abs. PhMe (15 ml) was stirred for 20 h at 110°. After cooling to 20°, Et_2O (50 ml) and sat. aq. NaH_2PO_4 soln. (50 ml) were added, the org. layer was separated and washed with H_2O (50 ml) and sat. aq. NaCl soln. (50 ml). FC (SiO_2-*H*; $CHCl_3$/AcOEt 97:3, then hexane/AcOEt 7:3) and recrystallization (CH_2Cl_2/hexane) afforded **30·Zn** (65 mg, 59%). Purple crystals. M.p. 149–150°. TLC (SiO_2; hexane/AcOEt 3:2): R_f 0.46. UV/VIS (PhMe): 596 (4700), 557 (20900), 519 (3100), 427 (530000), 407 (sh, 44300), 317 (25600). IR (CCl_4): 2981*w*, 2945*w*, 2866*w*, 2155*w*, 1735*s*, 1593*m*, 1586*m*, 1456*s*, 1381*m*, 1249*s*, 1179*m*, 1103*s*, 1061*m*, 997*s*, 885*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 10.09 (*s*, 1 H); 9.28 (*d*, *J* = 4.4, 2 H); 8.98 (*d*, *J* = 4.4, 2 H); 8.87 (*d*, *J* = 4.6, 2 H); 8.85 (*d*, *J* = 4.6, 2 H); 8.19 (*d*, *J* = 8.2, 2 H); 7.84 (*d*, *J* = 8.2, 2 H); 7.70 (*t*, *J* = 8.2, 2 H); 7.04 (*d*, *J* = 8.2, 4 H); 3.91–3.84 (*m*, 8 H); 3.33 (*q*, *J* = 7.1, 8 H); 1.25 (*s*, 21 H); 1.23–1.16 (*m*, 8 H); 1.04–0.98 (*m*, 8 H); 0.62 (*t*, *J* = 7.1, 12 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 172.63; 159.69; 150.40; 150.34; 149.53; 149.01; 143.84; 134.63; 131.55; 131.46; 131.39; 130.89; 130.00; 129.89; 122.19; 122.06; 119.28; 112.30; 107.42; 106.22; 104.93; 91.27; 67.68; 59.54;

29.32; 23.80; 18.78; 13.56; 11.44. HR-MALDI-MS (DCTB): 1300.513 (M^+, $C_{73}H_{84}N_4O_{12}SiZn^+$; calc. 1300.514). Anal. calc. for $C_{73}H_{84}N_4O_{12}SiZn$ (1302.96): C 67.29 H 6.50, N 4.30; found: C 67.45, H 6.25, N 4.27.

(Tetraethyl 4,4′,4″,4‴-{[10-(2-Bromophenyl)porphyrin-5,15-diyl-κN^{21}*,κN*^{22}*,κN*^{23}*,κN*^{24}*]bis[benzene-2,1,3-triylbis(oxy)]}tetrabutanoato(2−))zinc* (**31**·**Zn**). A degassed soln. of **21**·**Zn** (200 mg, 171 μmol), **19** (483 mg, 1.71 mmol) [48], Cs_2CO_3 (556 mg, 1.71 mmol), and $[Pd(PPh_3)_4]$ (5 mg, 4 mmol, 10 mol-%) in abs. PhMe (30 ml) was stirred for 6 h at 110°. After cooling to 20°, Et_2O (50 ml) and sat. aq. NaH_2PO_4 soln. (50 ml) were added, and the layers were separated. The org. layer was washed with H_2O (50 ml) and sat. aq. NaCl soln. (50 ml), and the solvent was evaporated *in vacuo*. FC (SiO_2-*H*; $CHCl_3$/AcOEt 97:3) gave **31**·**Zn** (125 mg, 63%). Purple solid. M.p. 69–71°. TLC (SiO_2; hexane/AcOEt 3:2): R_f 0.27. UV/VIS (PhMe): 594 (3300), 557 (17000), 518 (2500), 425 (444500), 405 (36000), 317 (19400). IR (CCl_4): 2980*w*, 2936*m*, 2873*w*, 1734*s*, 1593*m*, 1586*m*, 1456*s*, 1381*m*, 1374*m*, 1248*s*, 1179*s*, 1103*s*, 1060*m*, 997*s*, 852*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 10.11 (*s*, 1 H); 9.29 (*d*, *J* = 4.4, 2 H); 8.98 (*d*, *J* = 4.4, 2 H); 8.88 (*d*, *J* = 4.5, 2 H); 8.71 (*d*, *J* = 4.5, 2 H); 8.21 ('*dd*', '*J*' = 7.3, 1.8, 1 H); 7.98 ('*dd*', '*J*' = 8.1, 1.4, 1 H); 7.69 (*t*, *J* = 8.5, 2 H); 7.66–7.60 (*m*, 2 H); 7.031 (*d*, *J* = 8.5, 2 H); 7.027 (*d*, *J* = 8.5, 2 H); 3.92–3.81 (*m*, 8 H); 3.40–3.29 (*m*, 8 H); 1.23–1.17 (*m*, 8 H); 1.09–0.95 (*m*, 8 H); 0.65 (*t*, *J* = 7.1, 6 H); 0.63 (*t*, *J* = 7.1, 6 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 172.76; 172.67; 159.76; 159.69; 150.54; 150.43; 149.42; 148.95; 144.09; 135.25; 131.61; 131.48 (2×); 131.28; 130.85; 129.90; 129.32; 127.91; 125.40; 122.01; 118.07; 112.32; 106.22; 106.21; 105.29; 67.74; 67.70; 59.60; 59.55; 29.50; 29.37; 23.95; 23.85; 13.65; 13.61. HR-MALDI-MS (DCTB): 1198.292 (M^+, $C_{62}H_{63}BrN_4O_{12}Zn^+$; calc. 1198.291).

3-[(Trimethylsilyl)ethynyl]benzamide (**44**). To a degassed soln. of 3-iodobenzamide (50 mg, 0.20 mmol) [34] and (trimethylsilyl)acetylene (24 mg, 34 μl, 0.24 mmol) in abs. THF (2 ml) and (i-Pr)$_2$NH (0.4 ml), $[PdCl_2(PPh_3)_2]$ (14 mg, 20 μmol, 10 mol-%) and CuI (4 mg, 20 μmol, 10 mol-%) were added, and the mixture was stirred for 20 h at 20°. The mixture was diluted with Et_2O (10 ml), and washed with sat. aq. NaH_2PO_4 soln. (7 ml), H_2O (7 ml), and sat. aq. NaCl soln. (7 ml). The org. layer was dried ($MgSO_4$), and the solvent was evaporated *in vacuo*. Purification by FC (SiO_2; Et_2O) yielded **44** (33 mg, 75%). Colorless crystals. M.p. 150–151°. TLC (SiO_2; Et_2O): R_f 0.54. IR ($CHCl_3$): 3529*w*, 3412*m*, 3005*w*, 2959*w*, 2164*w*, 1680*s*, 1601*w*, 1587*s*, 1369*m*, 908*m*, 846*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.91–7.87 (*m*, 1 H); 7.79–7.74 (*m*, 1 H); 7.60 (*td*, *J* = 7.8, 1.4, 1 H); 7.38 (*t*, *J* = 7.8, 1 H); 6.22 (br., 2 H); 0.24 (*s*, 9 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 168.92; 135.20; 133.63; 130.85; 128.74; 127.50; 123.81; 103.86; 95.67; −0.32. EI-MS: 217 (7, M^+), 202 (46, $[M-Me]^+$), 184 (14), 32 (24), 28 (100, $C_2H_4^+$). Anal. calc. for $C_{12}H_{15}NOSi$ (217.34): C 66.32, H 7.06, N 6.44; found: C 66.48, H 7.06, N 6.39.

*2-({2-[(Trimethylsilyl)ethynyl]phenyl}(1*H*-pyrrol-2-yl)methyl)-1*H*-pyrrole* (**34**). To a degassed soln. of **35** (11.0 g, 54.4 mmol) in freshly distilled 1*H*-pyrrole (145 g, 150 ml, 2.16 mol), CF_3COOH (TFA) (620 mg, 416 μl, 5.44 mmol) was added dropwise. After 5 min, 1M NaOH (50 ml) was added, and the soln. was extracted with AcOEt (3 × 100 ml). The combined org. layers were dried (Na_2SO_4), and the solvent was evaporated *in vacuo*. FC (SiO_2; hexane/AcOEt 9:1 + 0.5 vol-% Et_3N) and recrystallization (EtOH, −20°) yielded **34** (12.54 g, 72%). Light-green powder. M.p. 50–60° (dec.). TLC (SiO_2; hexane/AcOEt 9:1 + 0.5 vol-% Et_3N): R_f 0.33. IR ($CHCl_3$): 3465*m*, 3004*m*, 2962*w*, 2898*w*, 2154*m*, 1601*w*, 1561*w*, 1480*w*, 1444*w*, 1403*w*, 1251*s*, 1087*m*, 1028*m*, 870*s*, 845*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 8.06 (br. *s*, 2 H); 7.49–7.47 (*m*, 1 H); 7.28–7.24 (*m*, 1 H); 7.20–7.16 (*m*, 2 H); 6.70–6.69 (*m*, 2 H); 6.16–6.15 (m_q, 2 H); 6.00 (br. *s*, 1 H); 5.95–5.93 (*m*, 2 H); 0.22 (*s*, 9 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 144.71; 132.89; 132.03; 128.99; 128.08; 126.65; 122.47; 116.92; 108.40; 107.14; 103.36; 99.39; 41.97; −0.09. EI-MS: 318 (86, M^+), 245 (100, $[M-Me_3Si]^+$), 73 (51, Me_3Si^+).

Mixed Condensation of Aldehyde **36** *with* **33** *and* **34**. To a degassed soln. of **33** (731 mg, 5.07 mmol) [28a–c], **34** (3.23 g, 10.1 mmol), and **36** (5.58 g, 15.2 mmol) [5c] in CH_2Cl_2 (3 l), TFA (1.74 g, 1.21 ml, 15.2 mmol) was added dropwise, and the soln. was stirred for 16 h at 20°. Chloranil (15.0 g, 15.2 mmol) was added, and the mixture was heated to reflux for 2 h. Evaporation *in vacuo* and adsorptive filtration through a plug of SiO_2 (CH_2Cl_2/AcOEt 9:1) gave a mixture of porphyrins, which was separated by FC (SiO_2-*H*; $CHCl_3$/AcOEt 97:3 → 13:2) to give **32**·**2H** (986 mg, 17%), **38**·**2H** (284 mg, 4%), **39**·**2H** (296 mg, 4%), and **40**·**2H** (509 mg, 10%).

Tetraethyl 4,4′,4″,4‴-{(10-{2-[(Trimethylsilyl)ethynyl]phenyl}porphyrin-5,15-diyl)bis[benzene-2,1,3-triylbis-(oxy)]}tetrabutanoate (**32**·**2H**). Dark-purple, highly viscous oil. TLC (SiO_2; hexane/AcOEt 3:2): R_f 0.30. UV/VIS (PhMe): 641 (1100), 585 (5600), 540 (4200), 508 (18800), 415 (370800), 398 (sh, 79900), 370 (22500). IR (CCl_4): 3315*w*, 2980*w*, 2959*w*, 2940*w*, 2876*w*, 2161*w*, 1734*s*, 1587*m*, 1457*s*, 1373*m*, 1263*m*, 1249*m*, 1180*m*, 1104*s*, 965*w*, 957*w*, 860*w*, 846*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 10.08 (*s*, 1 H); 9.23 (*d*, *J* = 4.5, 2 H); 8.90 (*d*, *J* = 4.5, 2 H); 8.78 (*d*, *J* = 4.7, 2 H); 8.69 (*d*, *J* = 4.7, 2 H); 8.08 ('*dd*', '*J*' = 8.1, 1.0, 1 H); 7.88 ('*dd*', '*J*' = 7.9, 1.1, 1 H); 7.70 ('*dt*', '*J*' = 7.7, 1.4, 1 H); 7.70 (*t*, *J* = 8.5, 2 H); 7.64 ('*dt*', '*J*' = 7.5, 1.4, 1 H); 7.03 (*dd*, *J* = 8.5, 0.6, 2 H); 7.00 (*dd*, *J* = 8.5, 0.6, 2 H); 3.96–3.85 (*m*, 4 H); 3.87 ('*t*', '*J*' = 5.8, 4 H); 3.72–3.67 (2 × m_{dq}, '*J*' = 7.1, 2.0, 8 H); 1.52–1.23 (*m*, 16 H); 0.84 (*t*, *J* = 7.1, 6 H); 0.79 (*t*, *J* = 7.1, 6 H); −1.17 (*s*, 9 H); −2.84 (br. *s*, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 172.86 (2×); 159.77; 159.63; 145.66; 144.70–147.80 (br., 4×); 134.86; 131.00–129.80 (br., 4×); 131.10;

130.12; 127.67; 126.86; 126.46; 120.25; 117.27; 111.51; 105.43; 105.33 (br., 2 ×); 103.99; 99.18; 67.29 (2 ×); 59.79; 59.69; 29.61 (2 ×); 23.82; 23.74; 13.84; 13.81; −1.42. HR-MALDI-MS (DCTB): 1193.485 ([*M* + K]$^+$), 1177.508 ([*M* + Na]$^+$), 1155.515 (*M*H$^+$, $C_{67}H_{75}N_4O_{12}Si^+$; calc. 1155.515). Anal. calc. for $C_{67}H_{74}N_4O_{12}Si$ (1155.43): C 69.65, H 6.46, N 4.85; found: C 69.57, H 6.27, N 4.88.

*Tetraethyl 4,4′,4″,4‴-{(*anti-*10,20-Bis{2-[(trimethylsilyl)ethynyl]phenyl}porphyrin-5,15-diyl)bis[benzene-2,1,3-triylbis(oxy)]}tetrabutanoate* (**38·2H**). Dark-purple powder. M.p. 122–123°. TLC (SiO_2; hexane/AcOEt 3:2): R_f 0.38. UV/VIS (PhMe): 648 (1700), 591 (6200), 546 (5200), 514 (21500), 421 (441200), 404 (sh, 82300), 372 (23600). IR (CCl_4): 3319*w*, 2980*w*, 2960*w*, 2938*w*, 2904*w*, 2160*w*, 1734*s*, 1591*m*, 1457*s*, 1373*m*, 1348*m*, 1249*s*, 1182*s*, 1103*s*, 966*m*, 886*m*, 861*m*, 845*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 8.74 (*d*, *J* = 4.6, 4 H); 8.68 (*d*, *J* = 4.6, 4 H); 8.14 (‘*dd*’, ‘*J*’ = 7.4, 0.7, 2 H); 7.89 (‘*dd*’, ‘*J*’ = 7.8, 1.4, 2 H); 7.72–7.65 (*m*, 4 H); 7.69 (*t*, *J* = 8.5, 2 H); 7.00 (*d*, *J* = 8.5, 4 H); 3.91–3.83 (*m*, 8 H); 3.69 (*q*, *J* = 7.1, 8 H); 1.56–1.52 (*m*, 4 H); 1.40–1.34 (*m*, 8 H); 1.28–1.23 (*m*, 4 H); 0.82 (*t*, *J* = 7.1, 12 H); −1.06 (*s*, 18 H); −2.58 (br. *s*, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 172.87; 159.67; 145.30; 140.00–145.00 (br., 2 ×); 135.04; 131.53–128.82 (br., 2 ×); 131.34; 129.96; 127.61; 126.84; 126.49; 120.78; 117.06; 111.86; 105.29 (2 ×); 99.03; 67.24; 59.77; 29.65; 23.79; 13.84; −1.32. HR-MALDI-MS (DCTB): 1349.575 ([*M* + Na]$^+$), 1326.576 (*M*$^+$, $C_{78}H_{86}N_4O_{12}Si_2^+$; calc. 1326.578), 1297.532 ([*M*H − 2 Me]$^+$), 1253.527 ([*M* − Me_3Si]$^+$), 1195.514 ([*M* − O(CH_2)$_3$COOEt]$^+$). Anal. calc. for $C_{78}H_{86}N_4O_{12}Si_2$ (1327.71): C 70.56, H 6.53, N 4.22; found: C 70.53, H 6.71, N 4.23.

*Tetraethyl 4,4′,4″,4‴-{(*syn-*10,20-Bis{2-[(trimethylsilyl)ethynyl]phenyl}porphyrin-5,15-diyl)bis[benzene-2,1,3-bis(oxy)]}tetrabutanoate* (**39·2H**). Dark-purple microcrystalline powder. M.p. 161–162°. TLC (SiO_2; hexane/AcOEt 3:2): R_f 0.33. UV/VIS (PhMe): 647 (1700), 591 (6300), 546 (5000), 514 (21600), 420 (435000), 403 (sh, 78300), 372 (23000). IR (CCl_4): 3320*w*, 2981*w*, 2960*w*, 2937*w*, 2904*w*, 2161*w*, 1734*s*, 1592*m*, 1563*w*, 1457*s*, 1373*m*, 1348*m*, 1249*s*, 1182*s*, 1103*s*, 966*m*, 860*m*, 845*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 8.72 (*d*, *J* = 4.6, 4 H); 8.64 (*d*, *J* = 4.6, 4 H); 8.09 (‘*dd*’, ‘*J*’ = 7.4, 1.0, 2 H); 7.86 (‘*dd*’, ‘*J*’ = 7.8, 1.3, 2 H); 7.69 (‘*dt*’, ‘*J*’ = 6.4, 1.3, 2 H); 7.67 (*t*, *J* = 8.5, 2 H); 7.63–7.67 (*m*, 2 H); 7.03 (*d*, *J* = 8.5, 2 H); 6.96 (*d*, *J* = 8.5, 2 H); 3.92–3.88 (*m*, 8 H); 3.82 (‘*t*’, ‘*J*’ = 5.8, 4 H); 3.51 (*q*, *J* = 7.1, 4 H); 1.67 (‘*t*’, ‘*J*’ = 7.0, 4 H); 1.38 (‘*quint.*’, ‘*J*’ = 6.7, 4 H); 1.31–1.22 (*m*, 8 H); 1.05 (*t*, *J* = 7.1, 6 H); 0.77 (*t*, *J* = 7.1, 6 H); −1.28 (*s*, 18 H); −2.57 (br. *s*, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 172.91; 172.86; 159.90; 159.49; 145.81; 144.35–141.30 (br., 2 ×); 134.37; 131.40–129.50 (br., 2 ×); 130.65; 129.96; 127.68; 126.89; 126.55; 120.78; 117.05; 111.87; 105.56; 105.47; 105.23; 99.17; 67.34; 67.26; 60.56; 60.03; 29.72; 29.57; 23.91; 23.70; 14.08; 13.81; −1.51. HR-MALDI-MS (DCTB): 1365.594 ([*M* + K]$^+$), 1349.615 ([*M* + Na]$^+$), 1326.613 (*M*$^+$, $C_{78}H_{86}N_4O_{12}Si_2^+$; calc. 1326.578) 1297.571 ([*M*H − 2 Me]$^+$), 1253.579 ([*M* − Me_3Si]$^+$), 1195.564 ([*M* − O(CH_2)$_3$COOEt]$^+$). Anal. calc. for $C_{78}H_{86}N_4O_{12}Si_2$ (1327.71): C 70.56, H 6.53, N 4.22; found: C 70.80, H 6.75, N 4.23.

Tetraethyl 4,4′,4″,4‴-{(Porphyrin-5,15-diyl)bis[benzene-2,1,3-triylbis(oxy)]}tetrabutanoate (**40·2H**) [5a]. Dark-purple oil. ^{1}H-NMR (500 MHz, $CDCl_3$): 10.18 (*s*, 2 H); 9.30 (*d*, *J* = 4.5, 4 H); 8.97 (*d*, *J* = 4.5, 4 H); 7.73 (*t*, *J* = 8.5, 2 H); 7.04 (*d*, *J* = 8.5, 4 H); 3.92 (*t*, *J* = 5.8, 8 H); 3.62 (*q*, *J* = 7.1, 8 H); 1.35–1.24 (*m*, 16 H); 0.81 (*t*, *J* = 7.1, 12 H); −2.97 (br. *s*, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 172.80; 159.71; 147.49; 144.99; 131.13; 131.03; 130.26; 119.75; 111.13; 105.47; 104.17; 67.35; 59.69; 29.61; 23.80; 13.77.

General Procedure for the Zn^{II}-Ion Insertion into the Free-Base Porphyrins **32·2H**, **38·2H**, *and* **39·2H**. $Zn(OAc)_2 \cdot 2\ H_2O$ (1.16 g, 5.27 mmol) was added to a soln. of the free-base porphyrin (0.527 mmol) in $CHCl_3$ (20 ml) and MeOH (20 ml), and the mixture was stirred for 16 h at 20°. After evaporation *in vacuo*, CH_2Cl_2 (20 ml) was added to the residue, and the org. phase was washed with H_2O (2 × 15 ml). Drying ($MgSO_4$) and evaporation *in vacuo* gave the desired product in approx. quant. yield.

(Tetraethyl 4,4′,4″,4‴-{(10-{2-[(Trimethylsilyl)ethynyl]phenyl}porphyrin-5,15-diyl-κN^{21},κN^{22},κN^{23},κN^{24})bis-[benzene-2,1,3-triylbis(oxy)]}tetrabutanoato(2−))zinc (**32·Zn**). Purple, highly viscous oil. TLC (SiO_2; hexane/AcOEt 3:2): R_f 0.39. UV/VIS (PhMe): 593 (3900), 557 (22700), 519 (3400), 426 (592700), 406 (48000), 316 (25900). IR (CCl_4): 2979*w*, 2960*w*, 2937*w*, 2872*w*, 2159*w*, 1735*s*, 1592*m*, 1587*m*, 1524*w*, 1456*s*, 1381*m*, 1249*s*, 1179*m*, 1104*s*, 1060*m*, 997*s*, 861*m*, 846*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 10.12 (*s*, 1 H); 9.30 (*d*, *J* = 4.4, 2 H); 8.98 (*d*, *J* = 4.4, 2 H); 8.87 (*d*, *J* = 4.5, 2 H); 8.79 (*d*, *J* = 4.5, 2 H); 8.11 (‘*dd*’, ‘*J*’ = 7.5, 1.0, 1 H); 7.87 (‘*dd*’, ‘*J*’ = 7.8, 1.2, 1 H); 7.70 (*t*, *J* = 8.5, 2 H); 7.69 (‘*dt*’, ‘*J*’ = 7.7, 1.4, 1 H); 7.64 (‘*dt*’, ‘*J*’ = 7.6, 1.5, 1 H); 7.06 (*dd*, *J* = 8.5, 0.7, 2 H); 7.02 (*dd*, *J* = 8.5, 0.7, 2 H); 3.94–3.85 (*m*, 4 H); 3.83 (*t*, *J* = 6.0, 4 H); 3.55–3.48 (m_{dq}, 4 H); 3.34–3.28 (m_{dq}, 4 H); 1.37–1.13 (*m*, 12 H); 1.02–0.90 (*m*, 4 H); 0.77 (*t*, *J* = 7.1, 6 H); 0.60 (*t*, *J* = 7.1, 6 H); −1.18 (*s*, 9 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 172.73; 172.62; 159.89; 159.64; 150.39; 149.65 (2 ×); 149.23; 146.26; 134.76; 131.38; 131.06 (2 ×); 130.86; 130.81; 129.81; 127.40; 126.84; 126.32; 122.16; 118.14; 112.19; 106.23; 106.16; 105.65; 105.07; 98.61; 67.73; 67.63; 59.70; 59.50; 29.48; 29.30; 23.87; 23.80; 13.74; 13.57; −1.35. HR-MALDI-MS (DCTB): 1255.372 ([*M* + K]$^+$), 1239.402 ([*M* + Na]$^+$), 1216.420 (*M*$^+$, $C_{67}H_{72}N_4O_{12}SiZn^+$; calc. 1216.421), 1143.385 ([*M* −

$SiMe_3]^+$), 1101.337 ($[M-(CH_2)_3COOEt]^+$). Anal. calc. for $C_{67}H_{72}N_4O_{12}SiZn$ (1218.78): C 66.20, H 6.13, N 4.54; found: C 66.07, H 6.29, N 4.56.

*(Tetraethyl 4,4′,4″,4‴-{(*anti-*10,20-Bis[2-[(trimethylsilyl)ethynyl]phenyl}porphyrin-5,15-diyl-*κN^{21},κN^{22},κN^{23},κN^{24}*)bis[benzene-2,1,3-triylbis(oxy)]]tetrabutanoato(2−))zinc* (**38·Zn**). Purple solid. Mp: 57–58°. TLC (SiO_2; hexane/AcOEt 3:2): R_f 0.52. UV/VIS (PhMe): 601 (4000), 563 (16900), 525 (2700), 432 (545800), 412 (sh, 44100), 319 (19300). IR (CCl_4): 2980*w*, 2901*w*, 2876*w*, 2159*w*, 1735*s*, 1592*m*, 1528*w*, 1476*w*, 1456*s*, 1373*w*, 1336*w*, 1249*s*, 1202*m*, 1179*m*, 1103*s*, 999*s*, 861*m*, 845*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 8.82 (*d*, *J* = 4.6, 4 H); 8.76 (*d*, *J* = 4.6, 4 H); 8.14 ('*dd*', '*J*' = 7.4, 1.3, 2 H); 7.87 ('*dd*', '*J*' = 7.7, 1.5, 2 H); 7.69 ('*dt*', '*J*' = 7.3, 1.4, 2 H); 7.68 (*t*, *J* = 8.5, 2 H); 7.64 ('*dt*', '*J*' = 7.4, 1.5, 2 H); 7.01 (*d*, *J* = 8.5, 4 H); 3.89–3.82 (*m*, 8 H); 3.51 (*q*, *J* = 7.1, 8 H); 1.36–1.08 (*m*, 16 H); 0.72 (*t*, *J* = 7.1, 12 H); −1.14 (*s*, 18 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 172.78; 159.69; 150.41; 149.69; 146.21; 134.80; 131.51; 131.17; 130.85; 129.73; 127.39; 126.84; 126.38; 122.07; 118.05; 112.60; 105.88; 105.64; 98.58; 67.51; 59.70; 29.48; 23.84; 13.76; −1.30. HR-MALDI-MS (DCTB): 1427.450 ($[M+K]^+$), 1411.481 ($[M+Na]^+$), 1388.490 (M^+, $C_{78}H_{84}N_4O_{12}Si_2Zn^+$; calc. 1388.492). Anal. calc. for $C_{78}H_{84}N_4O_{12}Si_2Zn$ (1391.10): C 67.35, H 6.09, N 4.03; found: C 67.31, H 6.18, N 4.12.

*(Tetraethyl 4,4′,4″,4‴-{(*syn-*5,15-10,20-Bis[2-[(trimethylsilyl)ethynyl]phenyl]porphyrin-5,15-diyl-*κN^{21},κN^{22},κN^{23},κN^{24}*)bis[benzene-2,1,3-triylbis(oxy)]]tetrabutanoato(2−))zinc* (**39·Zn**). Purple needles. M.p. 162–163°. TLC (SiO_2; hexane/AcOEt 3:2): R_f 0.44. UV/VIS (PhMe): 602 (5000), 563 (21500), 525 (3400), 432 (551600), 412 (sh, 45400), 318 (24200). IR (CCl_4): 2980*w*, 2961*w*, 2901*w*, 2874*w*, 2160*w*, 1735*s*, 1592*m*, 1527*w*, 1456*s*, 1374*m*, 1336*m*, 1249*s*, 1179*m*, 1104*s*, 999*s*, 893*m*, 861*m*, 845*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 8.83 (*d*, *J* = 4.6, 4 H); 8.75 (*d*, *J* = 4.6, 4 H); 8.14–8.12 (m_{dd}, 2 H); 7.87–7.85 (m_{dd}, 2 H); 7.69 ('*dt*', '*J*' = 7.7, 1.5, 2 H); 7.68 (*t*, *J* = 8.5, 2 H); 7.67 ('*dt*', '*J*' = 7.5, 1.5, 2 H); 7.06 (*dd*, *J* = 8.5, 0.7, 2 H); 6.97 (*dd*, *J* = 8.5, 0.7, 2 H); 3.91 (*t*, *J* = 6.5, 4 H); 3.84 (*q*, *J* = 7.1, 4 H); 3.77 (*t*, *J* = 6.0, 4 H); 3.29 (*q*, *J* = 7.1, 4 H); 1.60 (*t*, *J* = 7.0, 4 H); 1.43–1.34 ($m_{quint.}$, 4 H); 1.16–1.10 ($m_{quint.}$, 4 H); 1.02 (*t*, *J* = 7.1, 6 H); 0.90 (*t*, *J* = 7.5, 4 H); 0.56 (*t*, *J* = 7.1, 6 H); −1.29 (*s*, 18 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 172.85; 172.57; 160.03; 160.36; 150.46; 150.69; 146.43; 134.38; 131.40; 130.89; 130.69; 129.75; 127.47; 126.86; 126.43; 122.05; 118.14; 112.74; 106.04; 105.95; 105.77; 98.67; 67.34; 67.26; 60.56; 60.03; 29.72; 29.57; 23.91; 23.70; 14.08; 13.81; −1.51. HR-MALDI-MS (DCTB): 1427.449 ($[M+K]^+$), 1411.481 ($[M+Na]^+$), 1388.490 (M^+, $C_{78}H_{84}N_4O_{12}Si_2Zn^+$; calc. 1388.492). Anal. calc. for $C_{78}H_{84}N_4O_{12}Si_2Zn$ (1391.10): C 67.35, H 6.09, N 4.03; found: C 67.44, H 6.18, N 4.05.

Tetraethyl 4,4′,4″,4‴-{[10-(2-Ethynylphenyl)porphyrin-5,15-diyl]bis[benzene-2,1,3-triylbis(oxy)]}tetrabutanoate (**41·2H**). To a soln. of **32·2H** (25 mg, 22 μmol) in abs. THF (1.5 ml), Bu_4NF (1M soln. in THF, 22 μl, 22 μmol) was added, and the mixture was stirred for 15 min at 20°. After addition of H_2O (2 ml) and extraction with CH_2Cl_2 (3 × 5 ml), the combined org. layers were dried ($MgSO_4$) and evaporated *in vacuo* to give **41·2H** (16 mg, 74%). Dark-purple oil. TLC (SiO_2; hexane/AcOEt 3:2): R_f 0.26. UV/VIS (PhMe): 641 (900), 585 (5100), 541 (3900), 508 (17000), 415 (332000), 398 (sh, 69000), 369 (20700). IR (CCl_4): 3312*w*, 2980*w*, 2960*w*, 2930*w*, 2874*w*, 2856*w*, 1735*s*, 1587*m*, 1456*s*, 1373*m*, 1250*m*, 1180*m*, 1104*s*, 1047*m*, 1032*m*, 965*m*, 958*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 10.10 (*s*, 1 H); 9.25 (*d*, *J* = 4.6, 2 H); 8.93 (*d*, *J* = 4.6, 2 H); 8.80 (*d*, *J* = 4.8, 2 H); 8.69 (*d*, *J* = 4.8, 2 H); 8.15 ('*dd*', '*J*' = 7.1, 1.6, 1 H); 7.92 ('*dd*', '*J*' = 7.7, 1.6, 1 H); 7.74 ('*dt*', '*J*' = 7.4, 1.4, 1 H); 7.70 (*t*, *J* = 8.4, 2 H); 7.68 ('*dt*', '*J*' = 7.4, 1.4, 1 H); 7.02 (*dd*, *J* = 8.4, 2 H); 7.01 (*dd*, *J* = 8.4, 2 H); 3.94–3.86 (*m*, 8 H); 3.71–3.58 ($m_{dquint.}$, 8 H); 2.27 (*s*, 1 H); 1.46–1.24 (*m*, 16 H); 0.84 (*t*, *J* = 7.1, 6 H); 0.80 (*t*, *J* = 7.1, 6 H); −2.86 (br. *s*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 172.91; 172.84; 159.72; 159.64; 145.58; 147.65–145.00 (br., 4 ×); 134.63; 131.67; 131.00–130.00 (br., 4 ×); 130.20; 127.82; 126.67; 126.09; 120.02; 116.93; 111.62; 105.31 (2 ×); 104.05; 83.05; 81.61; 67.34; 67.29; 59.79; 59.71; 29.79; 29.60; 23.85; 23.77; 13.82; 13.79. HR-MALDI-MS: 1121.423 ($[M+K]^+$), 1105.448 ($[M+Na]^+$), 1082.468 (M^+, $C_{64}H_{66}N_4O_{12}^+$; calc. 1082.468), 1037.465 ($[M-EtO]^+$). Anal. calc. for $C_{64}H_{66}N_4O_{12}$ (1083.25): C 70.96, H 6.14, N 5.17; found: C 70.87, H 6.40, N 4.97.

(Tetraethyl 4,4′,4″,4‴-{[10-(2-Ethynylphenyl)porphyrin-5,15-diyl-κN^{21},κN^{22},κN^{23},κN^{24}*]bis[benzene-2,1,3-triylbis(oxy)]]tetrabutanoato(2−))zinc* (**41·Zn**). *Procedure A:* To a soln. of **32·Zn** (150 mg, 123 μmol) in abs. THF (15 ml), Bu_4NF (1M soln. in THF, 123 μl, 123 μmol) was added, and the mixture was stirred for 15 min at 20°. After addition of H_2O (10 ml) and extraction with CH_2Cl_2 (3 × 20 ml), the combined org. layers were dried ($MgSO_4$) and evaporated *in vacuo* to give **41·2H** (146 mg, quant).

Procedure B: To **41·2H** (50 mg, 46 μmol) in $CHCl_3$ (1.5 ml) and MeOH (1.5 ml), $Zn(OAc)_2 \cdot H_2O$ (100 mg, 0.46 mmol) was added, and the soln. was stirred for 48 h at 20°. The solvent was evaporated *in vacuo*, and the residue was dissolved in CH_2Cl_2 (10 ml). The org. layer was washed with H_2O (10 ml), dried ($MgSO_4$), and evaporated *in vacuo* to give **41·Zn** (52 mg, quant.). Purple oil. TLC (SiO_2; hexane/AcOEt 3:2): R_f 0.34. UV/VIS (PhMe): 593 (2500), 557 (13900), 518 (2200), 426 (362300), 405 (29000), 317 (16300). IR (CCl_4): 2980*w*, 2959*w*, 2935*w*, 2872*w*, 1735*s*, 1592*m*, 1586*m*, 1523*w*, 1456*s*, 1381*m*, 1248*m*, 1179*m*, 1103*s*, 1060*m*, 997*s*. ^{1}H-NMR

(500 MHz, $CDCl_3$): 10.13 (*s*, 1 H); 9.30 (*d*, *J* = 4.4, 2 H); 8.99 (*d*, *J* = 4.4, 2 H); 8.87 (*d*, *J* = 4.6, 2 H); 8.76 (*d*, *J* = 4.6, 2 H); 8.20 ('*dd*', '*J*' = 7.4, 1.3, 1 H); 7.90 ('*dd*', '*J*' = 7.7, 1.4, 1 H); 7.74 – 7.71 ('*dt*', '*J*' = 7.7, 1.5, 1 H); 7.70 (*t*, *J* = 8.5, 2 H); 7.70 – 7.67 ('*dt*', '*J*' = 7.5, 1.5, 1 H); 7.05 (*dd*, *J* = 8.5, 0.7, 2 H); 7.04 (*dd*, *J* = 8.5, 0.7, 2 H); 3.90 – 3.82 (*m*, 8 H); 3.40 – 3.26 (m_{dq}, m_t, 8 H); 2.16 (*s*, 1 H); 1.24 – 1.17 ($m_{quint.}$, 8 H); 1.08 – 0.96 (*m*, 8 H); 0.63 (*t*, *J* = 7.2, 12 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 172.67 (2 ×); 159.72 (2 ×); 150.42; 150.36; 149.35; 149.32; 146.15; 134.39; 131.62; 131.43; 131.23 (2 ×); 131.07; 129.87; 127.56; 126.56; 126.02; 122.06; 117.74; 112.22; 106.30; 106.22; 105.12; 83.37; 80.87; 67.81; 67.67; 59.53 (2 ×); 29.45; 29.31; 23.85; 23.79; 13.60 (2 ×). HR-MALDI-MS (DCTB): 1144.380 (M^+, $C_{64}H_{64}N_4O_{12}Zn^+$; calc. 1144.381); 1029.314 ([M – $(CH_2)_3COOEt$]$^+$). Anal. calc. for $C_{64}H_{64}N_4O_{12}Zn$ (1146.62): C 67.04, H 5.63, N 4.84; found: C 66.89, H 5.72, N 4.75.

*(Tetraethyl 4,4',4'',4'''-{[10-(2-{[3-(Aminocarbonyl)phenyl]ethynyl}phenyl)porphyrin-5,15-diyl-*κ*N^{21},*κ*N^{22},*κ*N^{23},*κ*N^{24}]bis[benzene-2,1,3-triylbis(oxy)]]tetrabutanoato(2 –))zinc* (**42 · Zn**). To a degassed soln. of **41 · Zn** (423 mg, 358 μmol) in PhMe (10 ml) and Et_3N (10 ml), 3-iodobenzamide (106 mg, 429 μmol) [34], [$PdCl_2(PPh_3)_2$] (25.1 mg, 36 μmol, 10 mol-%), and CuI (6.8 mg, 36 μmol, 10 mol-%) were added, and the mixture was stirred under N_2 for 22 h at 90°. After cooling to 20°, sat. NaH_2PO_4 soln. (80 ml) was added, and the aq. layer was extracted with CH_2Cl_2 (2 × 80 ml). The combined org. layers were dried ($MgSO_4$), and the solvent was removed *in vacuo*. FC (SiO_2-*H*; CH_2Cl_2/MeOH 97 :3) afforded **42 · Zn** (355 mg, 78%). Purple, highly viscous oil. ^{1}H-NMR (500 MHz, $CDCl_3$): 10.10 (*s*, 1 H); 9.29 (*d*, *J* = 4.4, 2 H); 8.97 (*d*, *J* = 4.4, 2 H); 8.86 (*d*, *J* = 4.6, 2 H); 8.84 (*d*, *J* = 4.6, 2 H); 8.36 – 8.34 (*m*, 1 H); 7.89 – 7.87 (*m*, 1 H); 7.79 – 7.73 (*m*, 2 H); 7.68 (*t*, *J* = 8.5, 2 H); 7.04 (*dd*, *J* = 8.5, 0.7, 2 H); 7.00 (*dd*, *J* = 8.5, 0.7, 2 H); 6.83 – 6.86 (m_t, 1 H); 6.62 – 6.58 (*m*, 2 H); 4.14 (*m*, 1 H); 3.85 – 3.76 (*m*, 6 H); 3.68 – 3.63 (*m*, 2 H); 3.40 – 3.26 (*m*, 8 H); 2.84 – 3.06 (2 br. *s*, 2 H); 1.27 – 1.07 (*m*, 10 H); 0.99 – 0.92 (*m*, 6 H); 0.86 (*t*, *J* = 7.1, 6 H); 0.63 (*t*, *J* = 7.1, 6 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 172.66; 172.65; 166.64; 159.85; 159.23; 150.38; 150.37; 149.71; 149.22; 146.43; 134.16; 132.55; 132.26; 131.60 – 131.18 (br., 4 ×); 130.23; 129.92; 129.08; 127.69; 127.57; 127.35; 126.82; 126.69; 122.37; 122.04; 118.07; 112.02; 106.40; 106.25; 105.29; 92.74; 91.32; 67.72; 67.63; 59.82; 59.57; 29.40; 29.31; 23.81; 23.51; 13.83; 13.59. HR-MALDI-MS (DCTB): 1302.372 ([M + K]$^+$), 1286.401 ([M + Na]$^+$), 1263.418 (M^+, $C_{71}H_{69}N_5O_{13}Zn^+$; calc. 1263.418); 1148.359 ([M – $(CH_2)_3COOEt$]$^+$).

*[Tetraethyl 4,4',4'',4'''-({10-[2-(Phenylethynyl)phenyl]porphyrin-5,15-diyl-*κ*N^{21},*κ*N^{22},*κ*N^{23},*κ*N^{24}}bis[benzene-2,1,3-triylbis(oxy)]}tetrabutanoato(2 –)]zinc* (**43 · Zn**). To a degassed soln. of **41 · Zn** (24.3 mg, 41 μmol) in PhMe (1 ml) and Et_3N (1 ml), PhBr (5.2 μl, 49 μmol), [$PdCl_2(PPh_3)_2$] (3 mg, 4 μmol, 10 mol-%), and CuI (0.8 mg, 4 μmol, 10 mol-%) were added, and the mixture was stirred under N_2 for 11 h at 90°. After cooling to 20°, sat. aq. NaH_2PO_4 soln. (10 ml) was added, and the aq. layer was extracted with CH_2Cl_2 (3 × 10 ml). Evaporation *in vacuo* and FC (SiO_2-*H*; CH_2Cl_2/MeOH 99 :1) gave **43 · Zn** (6.2 mg, 25%). Highly viscous, purple oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 10.10 (*s*, 1 H); 9.29 (*d*, *J* = 4.4, 2 H); 8.97 (*d*, *J* = 4.4, 2 H); 8.87 (*d*, *J* = 4.7, 2 H); 8.84 (*d*, *J* = 4.7, 2 H); 8.14 ('*dd*', *J* = 7.4, 1.0, 1 H); 7.96 ('*dd*', '*J*' = 7.7, 1.3, 1 H); 7.75 ('*dt*', '*J*' = 7.6, 1.4, 1 H); 7.68 (*t*, *J* = 8.4, 2 H); 7.65 ('*dt*', '*J*' = 7.6, 1.6, 1 H); 7.03 (*d*, *J* = 8.4, 2 H); 7.02 (*d*, *J* = 8.4, 2 H); 6.83 – 6.86 ('*dt*', '*J*' = 7.6, 1.3, 1 H); 6.41 – 6.36 (m_{dt}, 2 H); 5.97 – 5.93 (m_{dt}, 2 H); 3.89 – 3.79 (*m*, 8 H); 3.40 – 3.23 (*m*, 8 H); 1.26 – 0.93 (*m*, 16 H); 0.68 (*t*, *J* = 7.1, 6 H); 0.63 (*t*, *J* = 7.1, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 172.71; 172.65; 159.76; 159.66; 150.37 (2 ×); 149.58; 149.22; 145.68; 134.94; 131.49; 131.33; 131.30; 131.02 (2 ×); 130.62; 129.79; 127.53; 127.20; 127.11; 126.93; 126.14; 122.58; 122.27; 118.13; 112.08; 106.49; 106.22; 104.99; 93.15; 90.06; 67.83; 67.65; 59.59; 59.54; 29.32; 29.22; 23.79; 23.71; 13.63; 13.58. HR-MALDI-MS (DCTB): 1259.367 ([M + K]$^+$), 1243.395 ([M + Na]$^+$), 1220.412 (M^+, $C_{70}H_{68}N_4O_{12}Zn^+$; calc. 1220.413); 1105.334 ([M – $(CH_2)_3COOEt$]$^+$).

5,15-Bis(2,6-dimethoxyphenyl)-10-{2-[(trimethylsilyl)ethynyl]phenyl}porphyrin (**45 · 2 H**). To a degassed soln. of **33** (731 mg, 5.07 mmol) [28a – c], **34** (3.23 g, 10.1 mmol), and **37** (2.53 g, 15.2 mmol) [50] in CH_2Cl_2 (3 l), TFA (1.21 ml, 1.74 g, 15.2 mmol) was added dropwise, and the mixture was stirred for 16 h at 20°. Chloranil (15.0 g, 15.2 mmol) was added, and the mixture was heated to reflux for 1 h. After cooling to 20°, the solvent was evaporated *in vacuo*, the residue was dissolved in CH_2Cl_2 (50 ml) and prepurified by adsorptive filtration through a plug of SiO_2 (CH_2Cl_2 → CH_2Cl_2/AcOEt 9 :1). The porphyrin-containing fraction was collected, the solvent was removed *in vacuo*, and the crude product was purified by FC (SiO_2-*H*; CH_2Cl_2). Recrystallization from CH_2Cl_2/MeOH gave **45 · 2 H** (176 mg, 5%). The other porphyrin derivatives formed as by-products in this reaction were not isolated. Dark-purple crystals. M.p. 325 – 327°. TLC (SiO_2; CH_2Cl_2): R_f 0.48. UV/VIS (PhMe): 640 (800), 584 (4800), 539 (3200), 508 (16600), 415 (317100), 399 (sh, 68300), 369 (20500). IR (CCl_4): 3442*w* (br.), 2953*w*, 2936*w*, 2835*w*, 2161*w*, 1690*m*, 1679*m*, 1583*m*, 1470*s*, 1430*m*, 1248*s*, 1108*s*, 964*m*, 957*m*, 856*m*, 796*m*, 755*w*, 615*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 10.08 (*s*, 1 H); 9.24 (*d*, *J* = 4.6, 2 H); 8.89 (*d*, *J* = 4.6, 2 H); 8.77 (*d*, *J* = 4.6, 2 H); 8.72 (*d*, *J* = 4.6, 2 H); 8.09 (*d*, *J* = 7.3, 1.4, 1 H); 7.88 (*dd*, *J* = 7.8, 1.5, 1 H); 7.74 (*t*, *J* = 7.9, 2 H); 7.70 – 7.61 (*m*, 2 H); 7.04 (*d*, *J* = 7.9, 2 H); 7.01 (*d*, *J* = 7.9, 2 H); 3.54 (*s*, 6 H); 3.48 (*s*, 6 H); – 1.07 (*s*, 9 H); – 2.84 (br. *s*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 160.60; 160.42; 149.80 – 143.80 (br., 4 ×); 145.36; 134.82; 131.41 –

129.55 (br., 4 ×); 131.17; 130.01; 127.56; 126.88; 126.41; 119.69; 117.16; 111.35; 105.18; 104.31; 104.17; 103.95; 99.25; 56.10; 56.04; −1.24. HR-MALDI-MS (DHB): 755.303 (MH$^+$, $C_{47}H_{43}N_4O_4Si^+$; calc. 755.305).

(Tetraethyl 4,4′,4″,4‴-{(10-{2-[(Trimethylsilyl)ethynyl]phenyl}porphyrin-5,15-diyl-κN^{21},κN^{22},κN^{23},κN^{24})bis-[benzene-2,1,3-triylbis(oxy)]}tetrabutanoato(2−))zinc (**45·Zn**). A soln. of **45·2H** (100 mg, 0.132 mmol) and $Zn(OAc)_2 \cdot 2\,H_2O$ (0.269 g, 1.22 mmol) in $CHCl_3$ (7 ml) and MeOH (7 ml) was stirred for 14 h at 20°. and the solvent was subsequently evaporated *in vacuo*. The residue was dissolved in CH_2Cl_2 (10 ml), and the org. layer was washed with H_2O (3 × 10 ml) and dried ($MgSO_4$). Evaporation *in vacuo* provided **45·Zn** (107 mg, quant.). Purple crystals. M.p. 237–239°. TLC (SiO_2; CH_2Cl_2): R_f 0.35. UV/VIS (PhMe): 591 (2600), 556 (17400), 425 (41600), 405 (37000), 317 (20400). IR (CCl_4): 3441*w* (br.), 2955*w*, 2932*w*, 2833*w*, 2159*w*, 1689*m*, 1587*m*, 1521*m*, 1469*s*, 1430*m*, 1247*s*, 1109*s*, 1060*m*, 995*s*, 858*m*, 845m, 790*m*, 761*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 10.14 (*s*, 1 H); 9.33 (*d*, *J* = 4.4, 2 H); 8.98 (*d*, *J* = 4.4, 2 H); 8.86 (*d*, *J* = 4.6, 2 H); 8.82 (*d*, *J* = 4.6, 2 H); 8.11 (*dd*, *J* = 7.5, 1.4, 1 H); 7.87 (*dd*, *J* = 7.8, 1.5, 1 H); 7.73 (*t*, *J* = 8.5, 2 H); 7.68 (*dt*, *J* = 7.8, 1.4, 1 H); 7.64 (*dt*, *J* = 7.5, 1.5, 1 H); 7.03 (*d*, *J* = 8.5, 2 H); 7.02 (*d*, *J* = 8.5, 2 H); 3.51 (*s*, 6 H); 3.50 (*s*, 6 H); −1.09 (*s*, 9 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 160.65; 160.56; 150.41; 150.33; 149.74; 149.30; 145.96; 134.83; 131.83; 131.50; 131.25; 131.21; 130.87; 129.85; 127.43; 126.88; 126.42; 120.55; 118.20; 112.08; 105.49; 105.23; 104.30; 104.19; 98.78; 56.13; 56.02; −1.33. HR-MALDI-MS (DCTB): 839.202 ([M + Na]$^+$), 816.210 (M^+, $C_{47}H_{40}N_4O_4SiZn^+$; calc. 816.211). Crystal structure: *Fig. 2*.

Tetrakis(3,5-bis{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}benzyl) 4,4′,4″,4‴-{[10-(2-Ethynylphenyl)porphyrin-5,15-diyl]bis[benzene-2,1,3-triylbis(oxy)]}butanoate (**49·2H**). A soln. of **32·2H** (773 mg, 0.669 mmol) in dioxane (25 ml) and 3M NaOH (25 ml) was stirred for 3 d at 20°, then neutralized by the addition of 1M HCl. The precipitate formed was dissolved by addition of AcOEt (100 ml), the org. layer was separated, and the aq. layer was extracted with AcOEt (100 ml). The combined org. layers were evaporated *in vacuo*, and the residue was dried for 4 h at 10^{-2} Torr. The obtained crude **48·2H** was dissolved in abs. THF (25 ml), and **46** (1.45 g, 3.34 mmol) [49], DCC (690 mg, 3.34 mmol), DMAP (65 mg, 0.54 mmol), and BtOH (4.6 mg, 0.034 mmol) were added. The mixture was stirred for 3 d at 20°, and the solvent was evaporated. The resulting oil was filtered through a plug of SiO_2 (CH_2Cl_2/MeOH 9:1), and purification by GPC (*BioBeads S-X1*; THF or CH_2Cl_2) yielded **49·2H** (1.41 g, 80%). Highly viscous, dark-purple oil. TLC (SiO_2; CH_2Cl_2/MeOH 95:5): R_f 0.39. UV/VIS (PhMe): 641 (1300), 585 (5700), 541 (4600), 509 (18900), 416 (358800), 399 (sh, 80200), 369 (22900), 351 (19400). IR (CCl_4): 3315*w*, 2926*m*, 2877*m*, 2822*w*, 1736*m*, 1597*s*, 1456*s*, 1352*w*, 1296*w*, 1251*m*, 1201*m*, 1173*s*, 1145*s*, 1128*s*, 1107*s*, 1075*m*, 965*m*, 957*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 10.02 (*s*, 1 H); 9.19 (*d*, *J* = 4.5, 2 H); 8.89 (*d*, *J* = 4.5, 2 H); 8.78 (*d*, *J* = 4.7, 2 H); 8.65 (*d*, *J* = 4.7, 2 H); 8.07 ('*d*', '*J*' = 7.4, 1 H); 7.86 ('*d*', '*J*' = 7.0, 1 H); 7.69 ('*dt*', '*J*' = 7.9, 1.2, 1 H); 7.68 (*t*, *J* = 8.5, 2 H); 7.57 ('*dt*', '*J*' = 7.5, 1.3, 1 H); 6.995 (*d*, *J* = 8.5, 2 H); 6.989 (*d*, *J* = 8.5, 2 H); 6.40 ('*t*', '*J*' = 2.3, 4 H); 6.39 ('*t*', '*J*' = 2.3, 4 H); 6.31–6.29 (m_c, 4 H); 4.68–4.58 (*m*, 8 H); 4.01 ('*t*', '*J*' = 4.8, 16 H); 3.97–3.85 (*m*, 8 H); 3.78 ('*t*', '*J*' = 4.8, 16 H); 3.70–3.60 (*m*, 48 H); 3.52–3.49 (*m*, 16 H); 3.339 (*s*, 12 H); 3.336 (*s*, 12 H); 2.21 (*s*, 1 H); 1.57–1.48 (*m*, 8 H); 1.39–1.23 (*m*, 8 H); −2.89 (br. *s*, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 172.53; 172.49; 159.90; 159.88; 159.64; 159.59; 147.00–145.00 (br., 4 ×); 145.46; 138.14; 138.10; 134.48; 131.59; 131.50–129.92 (br., 4 ×); 130.25; 127.80; 126.74; 125.97; 119.97; 116.94; 111.52; 106.61; 106.58; 105.35 (br., 3 ×); 101.16; 101.12; 83.05; 81.68; 71.89 (2 ×); 70.76 (2 ×); 70.60 (2 ×); 70.52 (2 ×); 69.60 (2 ×); 67.42 (2 ×); 67.28; 67.23; 65.57; 65.50; 58.99 (2 ×); 29.75; 29.57; 23.81; 23.73. HR-MALDI-MS (DHB): 2650.228 ([M + Na]$^+$), 2628.250 (MH$^+$, $C_{140}H_{187}N_4O_{44}^+$; calc. 2628.251). Anal. calc. for $C_{140}H_{186}N_4O_{44}$ (2629.01): C 63.96, H 7.13, N 2.13; found: C 64.15, H 7.17, N 2.22.

Tetrakis{3,5-bis[(3,5-bis{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}benzyl)oxy]benzyl} 4,4′,4″,4‴-{[10-(2-Ethynylphenyl)porphyrin-5,15-diyl]bis[benzene-2,1,3-triylbis(oxy)]}tetrabutanoate (**50·2H**). A soln. of **32·2H** (102 mg, 88.5 μmol) in dioxane (2.5 ml) and 3M NaOH (2.5 ml) was stirred for 3 d at 20°, then neutralized by addition of 1M HCl. The precipitate was dissolved in AcOEt (15 ml), the layers were separated, and the aq. layer was extracted with AcOEt (15 ml). The combined org. layers were evaporated *in vacuo*, and the residue was dried for 4 h at 10^{-2} Torr. The highly viscous oil of crude **48·2H** was dissolved in abs. THF (10 ml), and **47** (429 mg, 442 μmol) [39], DCC (91.3 mg, 442 μmol), DMAP (8.6 mg, 70.8 μmol), and BtOH (0.6 mg, 4 μmol, 5 mol-%) were added. The mixture was stirred for 7 d at 20°, and the solvent was removed *in vacuo*. Adsorptive filtration through a plug of SiO_2 (CH_2Cl_2/MeOH 9:1) and purification by GPC (*BioBeads S-X1*; CH_2Cl_2) afforded **50·2H** (279 mg, 66%). Highly viscous, dark-purple oil. TLC (SiO_2; CH_2Cl_2/MeOH 95:5): R_f 0.25. UV/VIS (PhMe): 640 (1300), 585 (5900), 542 (4700), 509 (19500), 416 (364600), 398 (sh, 73800), 370 (23100), 351 (sh, 20000). IR (CCl_4): 3330*w*, 2925*m*, 2876*s*, 2822*m*, 1735*m*, 1596*s*, 1456*s*, 1371*m*, 1350*m*, 1322*m*, 1296*m*, 1250*m*, 1200*m*, 1172*s*, 1146*s*, 1109*s*, 1071*m*, 852*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 10.00 (*s*, 1 H); 9.17 (*d*, *J* = 4.5, 2 H); 8.89 (*d*, *J* = 4.5, 2 H); 8.78 (*d*, *J* = 4.8, 2 H); 8.65 (*d*, *J* = 4.8, 2 H); 8.07 ('*d*', '*J*' = 7.4, 1 H)); 7.83 ('*d*', '*J*' = 7.4, 1 H); 7.65 (*t*, *J* = 8.6, 2 H); 7.66–7.63 (*m*, 1 H); 7.55 ('*t*', '*J*' = 7.4, 1 H); 6.98 (*d*, *J* = 8.6, 2 H); 6.97 (*d*, *J* = 8.6, 2 H); 6.53–6.52

(t, J = 2.2, 16 H); 6.48–6.46 ($m_{quint.}$, 4 H); 6.42–6.40 (m, 8 H); 6.37 (t, J = 2.2, 8 H); 4.85 (br. s, 16 H); 4.72–4.63 (m, 8 H); 4.05–4.02 (m, 32 H); 3.90–3.84 (m, 8 H)); 3.78–3.75 (m, 32 H); 3.67–3.59 (m, 96 H); 3.51–3.49 (m, 32 H); 3.34 (s, 48 H); 2.24 (s, 1 H); 1.60–1.56 (m_t, 4 H); 1.52–1.48 (m, 4 H); 1.31–1.24 (m, 8 H); −2.88 (br. s, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 172.52; 172.47; 160.04 (2×); 159.88; 159.86; 159.60; 159.55; 147.00–145–00 (br., 4×); 145.40; 138.96 (2×); 138.31; 138.28; 134.55; 131.59; 131.50–129.90 (br., 4×); 130.28; 127.87; 126.83; 125.96; 119.87; 116.98; 111.59; 106.82; 106.77; 106.05 (4×); 105.34; 101.55 (2×); 101.09 (2×); 83.08; 81.80; 71.88 (2×); 70.72 (2×); 70.58 (2×); 70.50 (2×); 69.90 (2×); 69.59 (2×); 67.42 (2×); 67.26; 67.21; 65.56; 65.48; 58.98 (2×); 29.72; 29.53; 23.78; 23.70. HR-MALDI-MS (DCTB): 4812.236 ($[M+K]^+$), 4795.289 ($[M+Na]^+$), 4772.296 (M^+, $C_{252}H_{346}N_4O_{84}^+$; calc. 4772.292), 4357.291 ($[M-CH_2Ph[(OCH_2CH_2)_3OMe]_2]^+$), 3821.233 ($[M-CH_2Ph\{OCH_2Ph[(OCH_2CH_2)_3OMe]_2\}_2]^+$).

Tetrakis(3,5-bis{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}benzyl) 4,4′,4″,4‴-{[10-(2-{[3-(Aminocarbonyl)-phenyl]ethynyl}phenyl)porphyrin-5,15-diyl]bis[benzene-2,1,3-triylbis(oxy)]}tetrabutanoate (**1·2H**). To a degassed soln. of **49·2H** (400 mg, 152 μmol) and 3-iodobenzamide (75.2 mg, 304 μmol) [34] in PhMe (16 ml) and Et_3N (8 ml), $[PdCl_2(PPh_3)_2]$ (10mg, 15 μmol, 10 mol-%) was added, and the mixture was stirred under N_2 for 3 h at 90°. After cooling to 20°, sat. aq. NaH_2PO_4 soln. (100 ml) was added, and the soln. was extracted with CH_2Cl_2 (3 × 100 ml). The combined org. layers were dried ($MgSO_4$), and the solvent evaporated *in vacuo*. FC (SiO_2-*H*; $CHCl_3$/MeOH 97.5:2.5), then GPC (*BioBeads S-X1*; CH_2Cl_2), and adsorptive filtration through a plug of SiO_2-*H* ($CHCl_3$/MeOH 97.5:2.5) afforded **1·2H** (240 mg, 57%). Highly viscous, dark-purple oil. TLC (SiO_2; CH_2Cl_2/MeOH 95:5): R_f 0.19. UV/VIS (PhMe): 640 (1100), 585 (5400), 542 (4200), 509 (18000), 416 (347400), 400 (sh, 72600), 367 (21000), 348 (19800). IR (CCl_4): 3309*w*, 2920*m*, 2877*m*, 2821*w*, 1736*m*, 1681*m*, 1597*s*, 1456*s*, 1351*m*, 1317*w*, 1295*m*, 1250*m*, 1197*m*, 1172*s*, 1125*s*, 1107*s*, 965*m*, 851*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 10.04 (s, 1 H); 9.21 (d, J = 4.6, 2 H); 8.90 (d, J = 4.6, 2 H); 8.79 (d, J = 4.7, 2 H); 8.73 (d, J = 4.7, 2 H); 8.20 ('*dd*', 'J' = 7.5, 1.0, 1 H); 7.85 ('*dd*', 'J' = 7.9, 1.0, 1 H); 7.74 ('*dt*', 'J' = 7.8, 1.2, 1 H); 7.66 (t, J = 8.6, 2 H); 7.64 ('*dt*', 'J' = 7.6, 1.4, 1 H); 6.98 (d, J = 8.6, 2 H); 6.96 (d, J = 8.6, 2 H); 6.92 ('*dt*', 'J' = 8.2, 1.5, 1 H); 6.47 (t, J = 7.8, 1 H); 6.41 (t, J = 2.2, 2 H); 6.40 (t, J = 2.2, 2 H); 6.32 (d, J = 2.2, 4 H); 6.31–6.30 (m, 1 H); 6.30 (d, J = 2.2, 4 H); 4.68, 4.65 (*AB*, J = 12.5, 4 H); 4.64, 4.61 (*AB*, J = 12.5, 4 H); 4.31 (br. s, 1 H); 4.06–4.00 (m, 16 H); 3.92–3.84 (m, 8 H); 3.81–3.78 (m, 16 H); 3.71–3.68 (m, 16 H); 3.66–3.60 (m, 32 H); 3.51–3.49 (m, 16 H); 3.34 (s, 12 H); 3.33 (s, 12 H); 2.81 (br. s, 1 H); 2.58 (br. s, 1 H); 1.50–1.47 ('*t*', 'J' = 7.2, 4 H); 1.38–1.23 (m, 8 H); 1.09–1.02 (m, 4 H); −2.82 (br. s, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 172.45; 172.44; 166.14; 159.90; 159.88; 159.49; 159.41; 147.83–144.35 (br., 4×); 144.94; 138.19; 138.14; 133.88; 132.62; 132.05; 131.74–129.57 (br., 4×); 130.83; 130.34; 130.13; 128.43; 128.11; 127.61; 127.02; 126.82; 122.18; 119.70; 117.39; 111.68; 106.59 (2×); 105.38; 105.27; 104.38; 101.09 (2×); 93.30; 91.10; 71.87; 71.86; 70.75 (2×); 70.59 (2×); 70.50; 70.49; 69.61; 69.59; 67.41 (2×); 67.19; 67.04; 65.54; 65.50; 58.96; 58.95; 29.66; 29.18; 23.71; 23.44. HR-MALDI-MS (DHB): 2785.238 ($[M+K]^+$), 2769.270 ($[M+Na]^+$), 2747.289 (MH^+, $C_{147}H_{192}N_5O_{45}^+$; calc. 2747.288).

Tetrakis(3,5-bis[2-[2-(2-methoxyethoxy)ethoxy]ethoxy}benzyl) 4,4′,4″,4‴-{[10-(2-{[3-(Aminosulfonyl)phenyl]ethynyl}phenyl)porphyrin-5,15-diyl]bis[benzene-2,1,3-triylbis(oxy)]}tetrabutanoate (**2·2H**). To a degassed soln. of **49·2H** (200 mg, 76.1 μmol) and 3-iodobenzenesulfonamide (43.1 mg, 152 μmol) [40] in 1,2-dichlorobenzene (DCB) (4 ml) and Et_3N (4 ml), $[PdCl_2(PPh_3)_2]$ (5 mg, 8 μmol, 10 mol-%) was added, and the mixture was heated under N_2 for 1 h to 160°. After cooling to 20°, sat. aq. NaH_2PO_4 soln. (20 ml) was added, and the soln. was extracted with CH_2Cl_2 (3 × 20 ml). Drying of the combined org. layers ($MgSO_4$) and evaporation *in vacuo*, followed by FC (SiO_2-*H*; CH_2Cl_2/MeOH 92.5:7.5), GPC (*BioBeads S-X1*; CH_2Cl_2), and FC (SiO_2-*H*; $CHCl_3$/MeOH 97:3), provided anal. pure **2·2H** (114 mg, 54%). Highly viscous, dark-purple oil. TLC (SiO_2; CH_2Cl_2/MeOH 95:5): R_f 0.25. UV/VIS (PhMe): 640 (1300), 585 (5500), 541 (4400), 509 (18000), 416 (337900), 399 (sh, 71700), 368 (21600), 351 (sh, 19500). IR (CCl_4): 3313*w*, 2937*m*, 2877*m*, 2821*w*, 1736*m*, 1597*s*, 1456*s*, 1350*m*, 1296*m*, 1249*m*, 1172*s*, 1148*s*, 1127*s*, 1107*s*, 1073*m*, 965*m*, 851*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 10.06 (s, 1 H); 9.21 (d, J = 4.6, 2 H); 8.90 (d, J = 4.6, 2 H); 8.78 (d, J = 4.7, 2 H); 8.71 (d, J = 4.7, 2 H); 8.09 ('*dd*', 'J' = 6.9, 1.0, 1 H); 7.89 ('*dd*', 'J' = 7.9, 1.0, 1 H); 7.67 (t, J = 8.5, 2 H); 7.75 ('*dt*', 'J' = 7.7, 1.2, 1 H); 7.60 ('*dt*', 'J' = 7.6, 1.3, 1 H); 6.99 (d, J = 8.5, 2 H); 6.98 (d, J = 8.5, 2 H); 6.95–6.93 (m_{dt}, 1 H); 6.41 (t, J = 2.2, 2 H); 6.34 (t, J = 2.2, 2 H); 6.31 ('*t*', 'J' = 7.8, 1 H); 6.29 (d, J = 2.2, 4 H); 6.20 (d, J = 2.2, 4 H); 6.01 (br. s, 1 H); 5.87–5.86 (m_{dt}, 1 H); 4.63, 4.60 (*AB*, J = 12.5, 4 H); 4.45, 4.49 (*AB*, J = 12.5, 4 H); 4.02–4.00 (m_t, 8 H); 3.97–3.96 (m_t, 8 H); 3.89–3.80 (m, 8 H); 3.80–3.76 (m_t, 8 H); 3.76–3.72 (m_q, 8 H); 3.71–3.55 (m, 48 H); 3.52–3.48 (m, 8 H); 3.47–3.44 (m, 8 H); 3.37 (br. s, 1 H); 3.34 (br. s, 1 H); 3.33 (s, 12 H); 3.29 (s, 12 H); 1.48–1.43 (m, 4 H); 1.36–1.33 (m, 4 H); 1.30–1.26 (m, 4 H); 1.24–1.14 (m, 4 H); −2.87 (br. s, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 172.40; 172.37; 159.86; 159.70; 159.53; 159.38; 148.18–144.53 (br., 4×); 145.21; 142.28; 138.07; 138.06; 134.60; 133.55; 131.67–129.93 (br., 4×); 130.80; 130.29; 128.00; 127.72; 127.65; 126.88; 126.27; 124.37; 123.07; 119.87; 117.10; 111.57; 106.54; 106.46; 105.57; 105.33; 104.44; 101.05; 101.01; 92.10; 91.40; 71.81; 71.75; 70.71; 70.64; 70.54; 70.46; 70.45;

70.37; 69.55; 69.53; 67.37; 67.29 (2×); 67.14; 65.45; 65.36; 58.91; 58.85; 29.49; 29.30; 23.65; 23.48. HR-MALDI-MS (DHB): 2805.237 ([M + Na]$^+$), 2783.256 (MH$^+$, $C_{146}H_{192}N_5O_{46}S^+$; calc. 2783.255).

Tetrakis(3,5-bis{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}benzyl) 4,4′,4″,4‴-{[10-(2-{[3-(Hydroxymethyl)-phenyl]ethynyl}phenyl)porphyrin-5,15-diyl]bis[benzene-2,1,3-triylbis(oxy)]}tetrabutanoate (**3·2H**). To a degassed soln. of **49·2H** (200 mg, 76.1 μmol) and 3-iodobenzyl alcohol (19 μl, 0.15 mmol) in PhMe (8 ml) and Et_3N (4 ml), [$PdCl_2(PPh_3)_2$] (5 mg, 8 μmol, 10 mol-%) was added, and the mixture was stirred under N_2 for 2 h at 110°. After cooling to 20°, sat. aq. NaH_2PO_4 soln. (10 ml) was added, and the soln. was extracted with CH_2Cl_2 (2 × 30 ml). The combined org. layers were dried ($MgSO_4$) and evaporated *in vacuo*. FC (SiO_2-*H*; CH_2Cl_2/MeOH 92.5:7.5), GPC (*BioBeads S-X1*; CH_2Cl_2), and FC (SiO_2-*H*; $CHCl_3$/MeOH 97:3) gave **3·2H** (93 mg, 45%). Highly viscous, dark-purple oil. TLC (SiO_2; CH_2Cl_2/MeOH 95:5): R_f 0.20. UV/VIS (PhMe): 640 (2300), 585 (6600), 541 (5500), 509 (19300), 416 (345100), 399 (sh, 73000), 368 (23100), 351 (21500). IR (CCl_4): 3516*w*, 3310*w*, 2925*m*, 2877*m*, 2825*w*, 1735*m*, 1597*s*, 1456*s*, 1350*m*, 1321*w*, 1295*m*, 1250*m*, 1172*s*, 1127*s*, 1107*s*, 965*m*, 958*m*, 851*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 10.05 (*s*, 1 H); 9.21 (*d*, *J* = 4.6, 2 H); 8.90 (*d*, *J* = 4.6, 2 H); 8.77 (*d*, *J* = 4.7, 2 H); 8.72 (*d*, *J* = 4.7, 2 H); 8.15 ('*dd*', '*J*' = 7.6, 0.8, 1 H); 7.85 ('*dd*', '*J*' = 7.9, 1.0, 1 H); 7.72 ('*dt*', '*J*' = 7.8, 1.3, 1 H); 7.66 (*t*, *J* = 8.5, 2 H); 7.59 ('*dt*', '*J*' = 7.6, 1.4, 1 H); 6.98 (*d*, *J* = 8.5, 2 H); 6.96 (*d*, *J* = 8.5, 2 H); 6.42–6.40 (*m*, 5 H); 6.30 (*d*, *J* = 1.7, 8 H); 6.27 (*t*, *J* = 7.8, 1 H); 5.83 ('*d*', '*J*' = 7.8, 1 H); 4.78 (br. *s*, 1 H); 4.64, 4.61 (*AB*, *J* = 12.5, 4 H); 4.63 (*s*, 4 H); 4.04–4.00 (*m*, 16 H); 3.91–3.82 (*m*, 4 H); 3.81–3.78 (*m*, 16 H); 3.76–3.71 (*m*, 4 H); 3.71–3.60 (*m*, 48 H); 3.54–3.50 (*m*, 16 H); 3.37 (br. *s*, 1 H); 3.33 (*s*, 24 H); 2.84 (*d*, *J* = 5.9, 2 H); 1.49 (*t*, *J* = 7.1, 4 H); 1.35–1.25 (*m*, 8 H); 1.11–1.02 (*m*, 4 H); −2.79 (br. *s*, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 172.67; 172.49; 159.90; 159.87; 159.56; 159.50; 148.75–144.58 (br., 4 ×); 145.24; 140.38; 138.13 (2×); 134.19; 132.50–129.58 (br., 4 ×); 130.50; 130.24; 129.12; 128.91; 127.94; 127.22; 127.16; 126.43; 125.82; 122.04; 120.06; 117.50; 111.48; 106.62; 106.58; 105.63; 105.38; 104.25; 101.11 (2×); 93.95; 89.97; 71.87 (2×); 70.75 (2×); 70.59 (2×); 70.50 (2×); 69.61; 69.60; 67.41 (2×); 67.27; 67.21; 65.55; 65.50; 62.93; 58.97 (2×); 29.56; 29.32; 23.72; 23.52. HR-MALDI-MS (DHB): 2756.268 ([M + Na]$^+$), 2734.294 (MH$^+$, $C_{147}H_{193}N_4O_{45}^+$; calc. 2734.293).

*Tetrakis(3,5-bis{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}benzyl) 4,4′,4″,4‴-({10-[2-({3-[(*tert*-Butyl)dimethylsilyloxy]phenyl}ethynyl)phenyl]porphyrin-5,15-diyl}bis[benzene-2,1,3-triylbis(oxy)])tetrabutanoate* (**51·2H**). To a degassed soln. of **49·2H** (127 mg, 48.3 μmol) and 1-bromo-3-[(*tert*-butyldimethylsilyl)oxy]benzene (28 mg, 99.6 μmol) [49] in PhMe (9 ml) and Et_3N (3 ml), [$PdCl_2(PPh_3)_2$] (3 mg, 4 mmol, 10 mol-%) was added, and the mixture was stirred under N_2 for 12 h at 110°. After cooling to 20°, sat. aq. NaH_2PO_4 soln. (20 ml) was added. The soln. was extracted with CH_2Cl_2 (3 × 20 ml), and the combined org. layers were dried ($MgSO_4$). After evaporation *in vacuo*, purification by FC (SiO_2-*H*; $CHCl_3$/MeOH 97:3), GPC (*BioBeads S-X1*; CH_2Cl_2), and adsorptive filtration through a plug of SiO_2 ($CHCl_3$/MeOH 97:3) delivered **51·2H** (51 mg, 37%). Highly viscous, dark-purple oil. TLC (SiO_2; CH_2Cl_2/MeOH 95:5): R_f 0.33. UV/VIS (PhMe): 641 (1300), 585 (5300), 541 (4500), 509 (17800), 416 (329900), 399 (sh, 68800), 370 (21400), 348 (19900). IR (CCl_4): 3315*w*, 2928*m*, 2876*m*, 2820*w*, 1735*m*, 1597*s*, 1456*s*, 1350*m*, 1322*w*, 1295*m*, 1251*m*, 1171*s*, 1146*s*, 1128*s*, 1107*s*, 972*m*, 853*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 10.01 (*s*, 1 H); 9.18 (*d*, *J* = 4.5, 2 H); 8.88 (*d*, *J* = 4.5, 2 H); 8.76 (*d*, *J* = 4.7, 2 H); 8.70 (*d*, *J* = 4.7, 2 H); 8.03 ('*dd*', '*J*' = 7.7, 1.0, 1 H); 7.92 ('*dd*', '*J*' = 8.1, 1.1, 1 H); 7.71 ('*dt*', '*J*' = 7.8, 1.2, 1 H); 7.66 (*t*, *J* = 8.5, 2 H); 7.54 ('*dt*', '*J*' = 7.6, 1.4, 1 H); 6.97 (*d*, *J* = 8.5, 4 H); 6.43 (*t*, *J* = 2.2, 2 H); 6.40 (*t*, *J* = 2.2, 2 H); 6.39 (*d*, *J* = 2.2, 4 H); 6.29 (*d*, *J* = 2.2, 4 H); 6.12 (*t*, *J* = 8.1, 1 H); 6.07–6.05 (*ddd*, *J* = 8.1, 2.5, 1.1, 1 H); 5.42–5.41 ('*t*', '*J*' = 1.9, 1 H); 5.33–5.31 ('*dt*', '*J*' = 7.7, 1.0, 1 H); 4.79, 4.76 (*AB*, *J* = 12.5, 4 H); 4.64, 4.61 (*AB*, *J* = 12.5, 4 H); 4.06 (*t*, *J* = 4.9, 8 H); 4.00 (*t*, *J* = 4.9, 8 H); 3.91–3.77 (*m*, 8 H); 3.83 (*t*, *J* = 4.9, 8 H); 3.78 (*t*, *J* = 4.9, 8 H); 3.73–3.61 (*m*, 48 H); 3.53–3.50 (*m*, 16 H); 3.35 (*s*, 12 H); 3.34 (*s*, 12 H); 1.54–1.42 (*m*, 6 H); 1.31–1.13 (*m*, 8 H); 0.91–0.83 (*m*, 2 H); 0.33 (*s*, 9 H); −1.00 (*s*, 6 H); −2.83 (br. *s*, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 172.66; 172.54; 159.97; 159.93; 159.66; 159.56; 154.35; 146.52–143.48 (br., 4 ×); 145.04; 138.28; 138.18; 134.85; 131.30–129.30 (br., 4 ×); 130.97; 130.21; 128.33; 127.86; 126.86; 126.38; 123.97; 123.37; 121.77; 120.12; 119.64; 117.32; 111.55; 106.77; 106.60; 105.49; 105.33; 104.16; 101.16 (2×); 93.45; 89.60; 71.93; 71.92; 70.82; 70.79; 70.65; 70.63; 70.57; 70.55; 69.68; 69.63; 67.48; 67.44; 67.26; 67.16; 65.66; 65.52; 59.02 (2×); 29.61; 29.42; 25.03; 23.76; 23.64; 17.42; 1.03; −5.66. HR-MALDI-MS (DCTB): 2872.300 ([M + K]$^+$), 2856.343 ([M + Na]$^+$), 2833.356 (M^+, $C_{152}H_{204}N_4O_{45}Si^+$; calc. 2833.357).

Tetrakis(3,5-bis{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}benzyl) 4,4′,4″,4‴-{(10-{2-[(3-Hydroxyphenyl)ethynyl]phenyl}porphyrin-5,15-diyl)bis[benzene-2,1,3-triylbis(oxy)]}tetrabutanoate (**4·2H**). A soln. of **51·2H** (22.3 mg, 7.9 μmol) in THF (1 ml) was treated with Bu_4NF (1 M soln. in THF, 12 μl, 12 μmol), and the mixture was stirred for 2 h at 20°. After addition of H_2O (10 ml), the mixture was extracted with CH_2Cl_2 (3 × 15 ml) and the combined org. layers were dried ($MgSO_4$). The solvent was removed *in vacuo*, and purification by FC (SiO_2-*H*; $CHCl_3$/MeOH 95:5) gave **4·2H** (12.1 mg, 57%). Highly viscous, dark-purple oil. TLC (SiO_2; CH_2Cl_2/MeOH 9:1): R_f 0.22. UV/VIS (PhMe): 640 (1300), 585 (5600), 542 (4600), 510 (18500), 417 (341400), 400 (sh,

70300), 369 (21900), 348 (20500). IR (CCl_4): 3314*w*, 2926*m*, 2876*m*, 2823*w*, 1734*m*, 1597*s*, 1456*s*, 1350*m*, 1319*w*, 1296*m*, 1250*m*, 1172*s*, 1127*s*, 1107*s*, 965*m*, 957*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 10.05 (*s*, 1 H); 9.21 (*d*, *J* = 4.6, 2 H); 8.90 (*d*, *J* = 4.6, 2 H); 8.77 (*d*, *J* = 4.7, 2 H); 8.72 (*d*, *J* = 4.7, 2 H); 8.06 ('*d*', '*J*' = 6.7, 1 H); 7.87 ('*dd*', '*J*' = 8.0, 1.1, 1 H); 7.72 ('*dt*', '*J*' = 7.8, 1.3, 1 H); 7.67 (*t*, *J* = 8.5, 2 H); 7.56 ('*dt*', '*J*' = 7.6, 1.4, 1 H); 6.98 (*d*, *J* = 8.5, 2 H); 6.97 (*d*, *J* = 8.5, 2 H); 6.41 (*t*, *J* = 2.3, 2 H); 6.37 (*t*, *J* = 2.3, 2 H); 6.30 (*d*, *J* = 2.3, 4 H); 6.26 (*t*, *J* = 8.1, 1 H); 6.25 (*d*, *J* = 2.3, 4 H); 5.98 (*ddd*, *J* = 8.1, 2.6, 1.0, 1 H); 5.70 ('*dt*', '*J*' = 7.8, 1.2, 1 H); 5.57 (*m*, 1 H); 4.65, 4.61 (*AB*, *J* = 12.5, 4 H); 4.58, 4.51 (*AB*, *J* = 12.5, 4 H); 4.46 (*m*, 1 H); 4.01 (*t*, *J* = 5.0, 8 H); 3.99 (*t*, *J* = 5.0, 8 H); 3.91 – 3.86 (*m*, 8 H); 3.81 – 3.74 (*m*, 16 H); 3.69 – 3.55 (*m*, 48 H); 3.47 – 3.44 (*m*, 16 H); 3.30 (*s*, 12 H); 3.29 (*s*, 12 H); 1.50 ('*t*', '*J*' = 7.3, 4 H); 1.36 – 1.24 (*m*, 8 H); 1.17 – 1.09 (*m*, 4 H); – 2.85 (br. *s*, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 172.71; 172.54; 159.94; 159.84; 159.58; 159.56; 155.15; 140.00 – 137.18 (br., 4 ×); 144.96; 138.19; 138.16; 134.54; 131.24 – 130.00 (br., 4 ×); 130.82; 130.32; 128.41; 127.94; 127.06; 126.37; 122.94; 122.01; 120.06; 117.63; 117.09; 115.10; 111.59; 106.64; 106.55; 105.72; 105.41; 104.30; 101.14; 101.09; 93.91; 89.46; 71.87; 71.84; 70.77; 70.73; 70.60; 70.58; 70.50; 70.48; 69.63 (2 ×); 67.45; 67.38 (2 ×); 67.22; 65.55; 65.48; 58.96; 58.94; 29.61; 29.31; 23.77; 23.56. HR-MALDI-MS (DCTB): 2758.241 ([*M* + K]$^+$), 2742.263 ([*M* + Na]$^+$), 2719.267 (*M*$^+$, $C_{146}H_{190}N_4O_{45}^+$; calc. 2719.270).

Tetrakis(3,5-bis{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}benzyl) 4,4′,4″,4‴-({10-[2-(Phenylethynyl)phenyl]-porphyrin-5,15-diyl}bis[benzene-2,1,3-triylbis(oxy)])tetrabutanoate (**5·2H**). To a degassed soln. of **49·2H** (200 mg, 76.1 μmol) and PhBr (24 mg, 16 μl, 0.15 mmol) in PhMe (8 ml) and Et_3N (4 ml), [$PdCl_2(PPh_3)_2$] (5g, 8 μmol, 10 mol-%) was added, and the mixture was stirred unter N_2 for 13 h at 80°. After cooling to 20°, sat. aq. NaH_2PO_4 soln. (30 ml) was added, and the mixture was extracted with CH_2Cl_2 (3 × 40 ml). The combined org. layers were dried ($MgSO_4$), and the solvent was removed *in vacuo*. Purification by FC (SiO_2-*H*; CH_2Cl_2/MeOH 95 : 5), GPC (*BioBeads S-X1*; CH_2Cl_2), and adsorptive filtration through a plug of SiO_2-*H* (CH_2Cl_2/MeOH 95 : 5) afforded **5·2H** (122 mg, 63%). Highly viscous, dark-purple oil. TLC (SiO_2; CH_2Cl_2/MeOH 95 : 5): R_f 0.23. UV/VIS (PhMe): 641 (900), 585 (5000), 542 (3400), 509 (16900), 416 (333900), 401 (sh, 74600), 370 (17900), 348 (17500). IR (CCl_4): 3312*w*, 2926*m*, 2876*m*, 2824*w*, 1735*m*, 1597*s*, 1456*s*, 1351*m*, 1322*w*, 1296*w*, 1249*m*, 1172*s*, 1129*s*, 1107*s*, 965*m*, 957*m*, 851*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 10.03 (*s*, 1 H); 9.20 (*d*, *J* = 4.6, 2 H); 8.89 (*d*, *J* = 4.6, 2 H); 8.77 (*d*, *J* = 4.7, 2 H); 8.73 (*d*, *J* = 4.7, 2 H); 8.02 ('*dd*', '*J*' = 7.5, 0.8, 1 H); 7.93 ('*dd*', '*J*' = 7.9, 1.1, 1 H); 7.71 ('*dt*', '*J*' = 7.8, 1.3, 1 H); 7.67 (*t*, *J* = 8.5, 2 H); 7.54 ('*dt*', '*J*' = 7.6, 1.3, 1 H); 6.982 (*d*, *J* = 8.5, 2 H); 6.980 (*d*, *J* = 8.5, 2 H); 6.57 ('*dt*', '*J*' = 7.5, 1.2, 1 H); 6.42 (*t*, *J* = 2.2, 2 H); 6.40 (*t*, *J* = 2.2, 2 H); 6.34 (*d*, *J* = 2.2, 4 H); 6.34 ('*t*', '*J*' = 7.9, 2 H); 6.29 (*d*, *J* = 2.2, 4 H); 5.90 ('*dd*', '*J*' = 8.3, 1.2, 2 H); 4.69 (*s*, 4 H); 4.64, 4.60 (*AB*, *J* = 12.5, 4 H); 4.05 – 4.03 (*m*, 8 H); 4.02 – 4.00 (*m*, 8 H); 3.91 – 3.83 (*m*, 4 H); 3.82 – 3.77 (*m*, 20 H); 3.73 – 3.50 (*m*, 64 H); 3.344 (*s*, 12 H); 3.340 (*s*, 12 H); 1.51 – 1.43 (*m*, 8 H); 1.31 – 1.10 (*m*, 8 H); – 2.82 (br. *s*, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 172.56; 172.51; 159.91; 159.89; 159.62; 159.55; 148.64 – 144.44 (br., 4 ×); 144.84; 138.19; 138.14; 134.99; 132.73 – 130.00 (br., 4 ×); 130.89; 130.67; 130.20; 127.84; 127.21 (2 ×); 126.81; 126.35; 122.36; 120.11; 117.35; 111.52; 106.68; 106.57; 105.54; 105.32; 104.14; 101.13 (2 ×); 93.57; 89.78; 71.88 (2 ×); 70.77; 70.75; 70.61; 70.59; 70.52; 70.51; 69.62; 69.60; 67.43; 67.41; 67.22 (2 ×); 65.56; 65.49; 58.98 (2 ×); 29.58; 29.40; 23.73; 23.62. HR-MALDI-MS (DHB): 2742.237 ([*M* + K]$^+$), 2726.263 ([*M* + Na]$^+$), 2704.280 (*M*H$^+$, $C_{146}H_{191}N_4O_{44}^+$; calc. 2704.283).

Tetrakis{3,5-bis[(3,5-bis{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}benzyl)oxy]benzyl} 4,4′,4″,4‴-{[10-(2-{[3-(Aminocarbonyl)phenyl]ethynyl}phenyl)porphyrin-5,15-diyl]bis[benzene-2,1,3-triylbis(oxy)]}tetrabutanoate (**6·2H**). To a soln. of **50·2H** (250 mg, 52.4 μmol) and 3-iodobenzamide (25.8 mg, 52.4 μmol) in DCB (5 ml) and Et_3N (5 ml), [$PdCl_2(PPh_3)_2$] (3.7 mg, 5.2 μmol, 10 mol-%) was added, and the mixture was stirred under N_2 for 15 h at 110°. After cooling to 20°, the mixture was diluted with CH_2Cl_2 (10 ml) and washed with sat. aq. NaH_2PO_4 soln. (10 ml). After evaporation *in vacuo*, the residue was purified by FC (SiO_2-*H*; CH_2Cl_2/MeOH 9 : 1), GPC (*BioBeads S-X1*; CH_2Cl_2), and repeated FC (SiO_2-*H*; $CHCl_3$/MeOH 95 : 5) to afford anal. pure **6·2H** (40 mg, 16%). Highly viscous, dark-purple oil. TLC (SiO_2; CH_2Cl_2/MeOH 95 : 5): R_f 0.14. UV/VIS (PhMe): 640 (1300), 585 (5200), 542 (4200), 510 (16900), 417 (313200), 398 (sh, 60500), 368 (20300), 347 (19700). IR (CCl_4): 2926*m*, 2877*s*, 2820*w*, 1735*m*, 1678*w*, 1596*s*, 1456*s*, 1373*m*, 1350*m*, 1322*m*, 1296*m*, 1249*m*, 1172*s*, 1146*s*, 1109*s*, 1071*m*, 991*w*, 965*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 10.02 (*s*, 1 H); 9.19 (*d*, *J* = 4.6, 2 H); 8.90 (*d*, *J* = 4.6, 2 H); 8.80 (*d*, *J* = 4.7, 2 H); 8.75 (*d*, *J* = 4.7, 2 H); 8.16 ('*d*', '*J*' = 7.8, 1 H); 7.84 ('*d*', '*J*' = 7.8, 1 H); 7.63 (*t*, *J* = 8.5, 2 H); 7.69 ('*t*', '*J*' = 7.8, 1 H); 7.58 ('*t*', '*J*' = 7.8, 1 H); 7.02 – 7.00 (m_d, 1 H); 6.95 (*d*, *J* = 8.5, 4 H); 6.55 (*d*, *J* = 2.1, 8 H); 6.52 (*d*, *J* = 2.1, 8 H); 6.52 – 6.36 (*m*, 6 H); 6.43 (*d*, *J* = 2.1, 4 H); 6.41 (*t*, *J* = 2.1, 4 H); 6.40 (*t*, *J* = 2.1, 4 H); 6.38 (*d*, *J* = 2.1, 4 H); 4.89 (*s*, 8 H); 4.85 (*s*, 8 H); 4.77, 4.74 (*AB*, *J* = 10.9, 4 H); 4.66 (*s*, 4 H); 4.51 (br. *s*, 1 H); 4.05 – 4.00 (*m*, 32 H); 3.89 – 3.83 (*m*, 8 H); 3.79 – 3.74 (*m*, 32 H); 3.67 – 3.59 (*m*, 96 H); 3.51 – 3.48 (*m*, 32 H); 3.334 (*s*, 24 H); 3.328 (*s*, 24 H); 3.11 (br. *s*, 2 H); 1.52 – 1.06 (*m*, 16 H); – 2.88 (br. *s*, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 172.49; 172.45; 166.35; 160.03 (2 ×); 159.89 (2 ×); 159.51; 159.32; 148.60 – 144.70 (br., 4 ×); 145.28; 138.98; 138.94; 138.33; 138.27; 134.23; 132.88; 132.26; 131.40 – 130.30 (br., 4 ×); 131.23; 130.42; 130.41; 128.40;

128.11; 127.69; 127.04; 126.86; 122.18; 119.54; 117.42; 111.78; 106.86; 106.81; 106.06; 106.04; 105.32; 105.23; 104.36; 101.57; 101.50; 101.07 (2×); 93.22; 91.01; 71.85 (2×); 70.70; 70.69; 70.54 (2×); 70.47 (2×); 69.90 (2×); 69.57 (2×); 67.41 (2×); 67.14; 67.04; 65.65; 65.52; 58.96 (2×); 29.49; 29.27; 23.67; 23.44. HR-MALDI-MS (DHB): 4515.318 ($[M+Na]^+$), 4892.336 (MH^+, $C_{259}H_{352}N_5O_{85}^+$; calc. 4892.337), 4479.080 ($[M+3\,H-CH_2Ph[(OCH_2CH_2)_3OMe]_2]^+$), 3821.233 ($[M-CH_2Ph\{OCH_2Ph[(OCH_2CH_2)_3\text{-}OMe]_2\}_2]^+$).

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