Dendritic Iron Porphyrins with a Tethered Axial Ligand as New Model Compounds for Heme Monooxygenases

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The novel iron(III) porphyrin dendrimers of generation zero ([**1**·Fe^{III}]Cl), one ([**2**·Fe^{III}]Cl), and two ([**3**·Fe^{III}]Cl) (*Fig. 1*) were prepared (*Schemes 1* and *3*) as models of heme monooxygenases. They feature controlled axial ligation at the Fe center by one imidazole tethered to the porphyrin core and possess a vacant coordination site available for ligand binding and catalysis. The high purity of the dendrimers and the absence of structural defects was demonstrated by matrix-assisted laser-desorption-ionization time-of-flight (MALDI-TOF) mass spectrometry (*Fig. 3*). The electronic properties of the Fe^{III} porphyrin dendrimers and comparison compounds [**4**·Fe^{III}]Cl and [**12**·Fe^{III}(1,2-Me_2Im)]Cl (1,2-Me_2Im = 1,2-dimethylimidazole) were investigated by UV/VIS and EPR (electronic paramagnetic resonance) spectroscopy, as well as by measurements of the magnetic moments by the *Evans-Scheffold* method. Epoxidation of olefins and oxidation of sulfides to sulfoxides, catalyzed by the new dendritic metalloporphyrins, were investigated in CH_2Cl_2 with iodosylbenzene as the oxidant (*Tables 1* and *2*). The total turnover numbers were found to increase with the size of the dendrimer, due to improved catalyst stability at higher dendritic generations (*Figs. 4* and *5*). The second-generation complex [**3**·Fe^{III}]Cl was, therefore, the most efficient catalyst in the series, despite the fact that its active site is considerably hindered by the encapsulation inside the sterically demanding, fluctuating dendritic wedges. Very high product selectivities were observed in all oxidation reactions, regardless of dendrimer generation.

1. Introduction. – Heme-containing monooxygenases such as cytochromes P450 [1], and peroxidases [2] catalyze a broad variety of important oxidation reactions in nature. They are the central enzymes in a large number of biosynthetic transformations, as well as in detoxification of organic toxins and growth regulation in higher organisms. The catalytic function of these enzymes is exerted by their prosthetic group, an iron porphyrin complex, which resides in the Fe^{III} form in the resting state. The protein shell around the heme core controls the access of substrates and oxidizing agent to the active site, and orients the substrate to favor the desired selective oxidation. In addition, it prevents the sensitive cofactor at the active site from degradation *via* undesirable side reactions. The activation of the oxidant under formation of highly reactive oxoferryl porphyrin species depends mostly on electronic effects mediated by a 'proximal' axial ligand, provided to the Fe center by the protein shell, and on the nature of 'distal' amino acid side chains on the opposite site of the porphyrin macrocycle where substrate binding and oxidation occurs.

Catalytic dendrimers have attracted considerable interest recently (for reviews on catalytically active dendrimers, see [3]), since their large molecular weights and multinanometer-sized dimensions allow application in membrane reactors without leaking, as well as versatile catalyst recycling. A variety of porphyrin dendrimers [4][5] have been prepared, and some of them have been successfully investigated for monooxygenase activity [4a,g] (for selected examples of other heme monooxygenase mimics, see [6]).

Here, we describe the preparation and characterization of the novel Fe^{III} porphyrin dendrimers [**1**·Fe^{III}]Cl, [**2**·Fe^{III}]Cl, and [**3**·Fe^{III}]Cl of generations zero, one, and two, featuring a covalently attached imidazole axial ligand to ensure formation of five-coordinate species with one free axial coordination site (*Fig. 1*) (for a preliminary communication on the synthesis and gas-binding properties of these dendrimers, see [7]). These compounds were expected to be functional mimics of heme-containing monooxygenases and to perform oxidation reactions along mechanisms similar to those of their natural counterparts. Axial N-ligands are well-known to enhance reactivity in metalloporphyrin-catalyzed oxidation reactions [8], and peroxidases also feature mono-imidazole ligation similar to the dendritic mimics described in this paper. The higher-generation derivatives include a dendritic shell of respectable size ([**3**·Fe^{III}]Cl: M_r 11588 D), which serves to model the protecting peptide shell of the heme proteins. We envisaged that the highly reactive iron-oxo species formed by O-atom transfer from an oxidizing agent to the Fe^{III} center through a peroxide shunt-type mechanism [9] could be considerably stabilized by encapsulation within a dendritic superstructure. This should prevent bimolecular degradation pathways, thereby extending the lifetime of the catalyst. The catalytic efficiency of the novel dendritic heme monooxygenase mimics in a number of different oxidation reactions is indeed found to be dependent on the size of the dendritic shell.

2. Results. – 2.1. *Synthesis and Characterization of the Porphyrin Core*. The three novel porphyrin dendrimers were synthesized by the convergent strategy developed in our previous work on dendritic cytochrome mimics [5]. The imidazole-appended Zn^{II} porphyrin core **4**·Zn was prepared (*Scheme 1*) by a high-yielding *Suzuki* cross-coupling (81%) [10] between the *meso*-brominated Zn^{II} porphyrin **5**·Zn [5b] and the imidazole-containing boronate **6**. The latter was obtained from 5-bromo-2-methylphenol (**7**) [11] by OH-group protection with MOM-Cl (MOM = methoxymethyl) in MeCN to give **8**, followed by lithiation (BuLi in THF), reaction with $B(OMe)_3$ in THF, and transesterification with pinacol in PhH to afford **9**. MOM Ether deprotection (HCl in THF/MeOH) provided phenol **10**, which was alkylated with 1-(6-bromohexyl)-1*H*-imidazole (**11**) [5b][12] to give **6**, in good overall yield with only one chromatographic purification step necessary in the entire sequence. ^{1}H-NMR spectroscopy of **4**·Zn in $CDCl_3$ clearly established the strong and complete internal complexation of the imidazole moiety to the central Zn-atom under formation of a defined five-coordinate complex. All signals were sharp and well-defined, and the resonances of the aromatic imidazole protons displayed impressive upfield shifts due to their positioning above the strongly shielding region of the porphyrin macrocycle, as a result of the internal coordination (*Fig. 2*). The signal of these protons appeared at 4.89, 2.15, and 1.97 ppm, with the extent of the upfield shift correlating with their degree of proximity to the porphyrin plane. When ^{1}H-NMR measurements were carried out in (D_5)pyridine, which, at the concentration present, efficiently displaces the internal imidazole from the Zn coordination site, the aromatic imidazole resonances were observed at their expected positions at 7.70, 7.25, and 7.11 ppm. Complete signal assignments in both solvents were achieved by means of 2D-NMR spectroscopy at 500 MHz. Acid-induced demetallation with CF_3COOH in benzene yielded the free-base porphyrin **4**·2 H, which showed a ^{1}H-NMR spectrum very similar to the one of **4**·Zn in (D_5)pyridine,

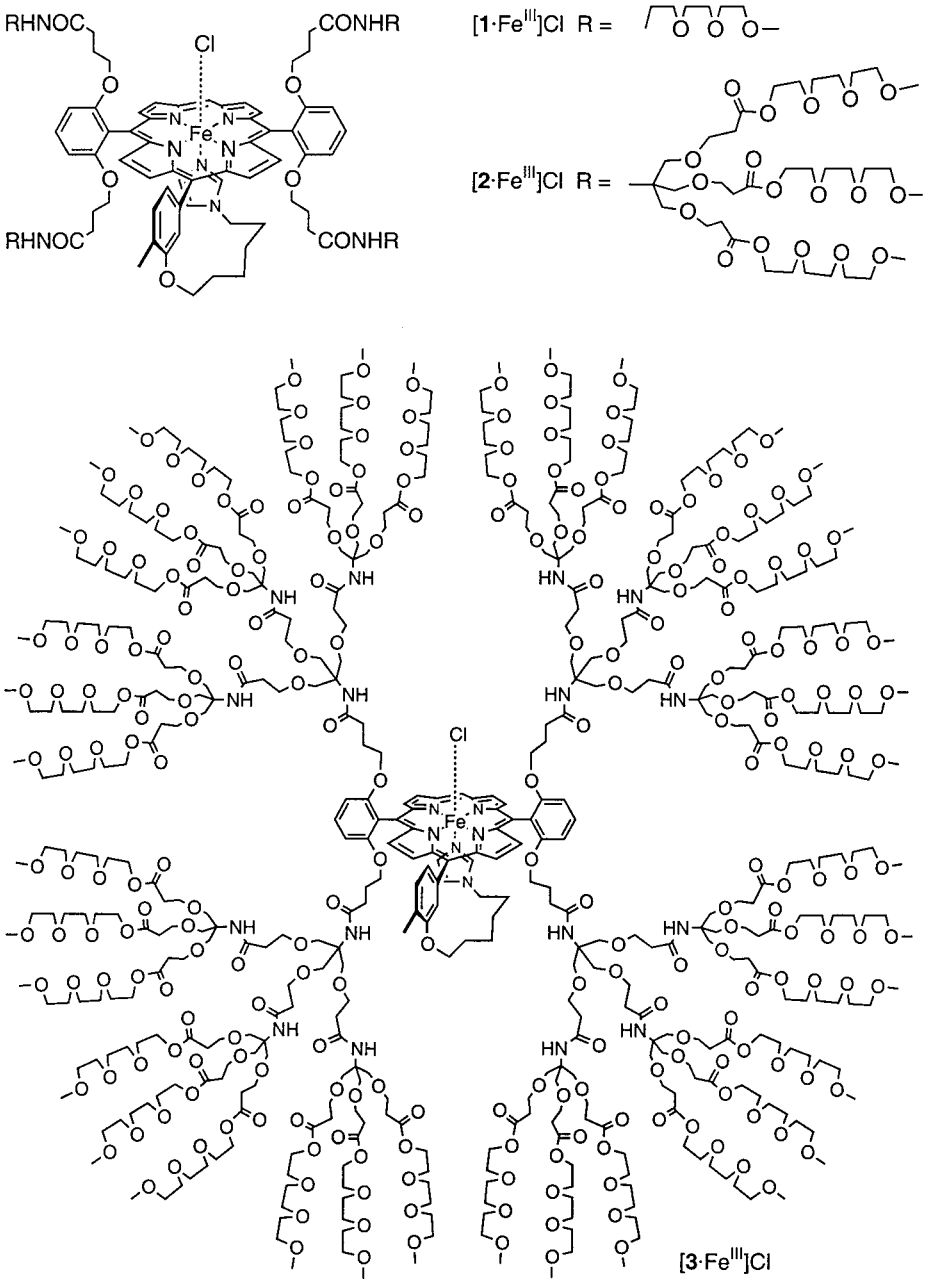
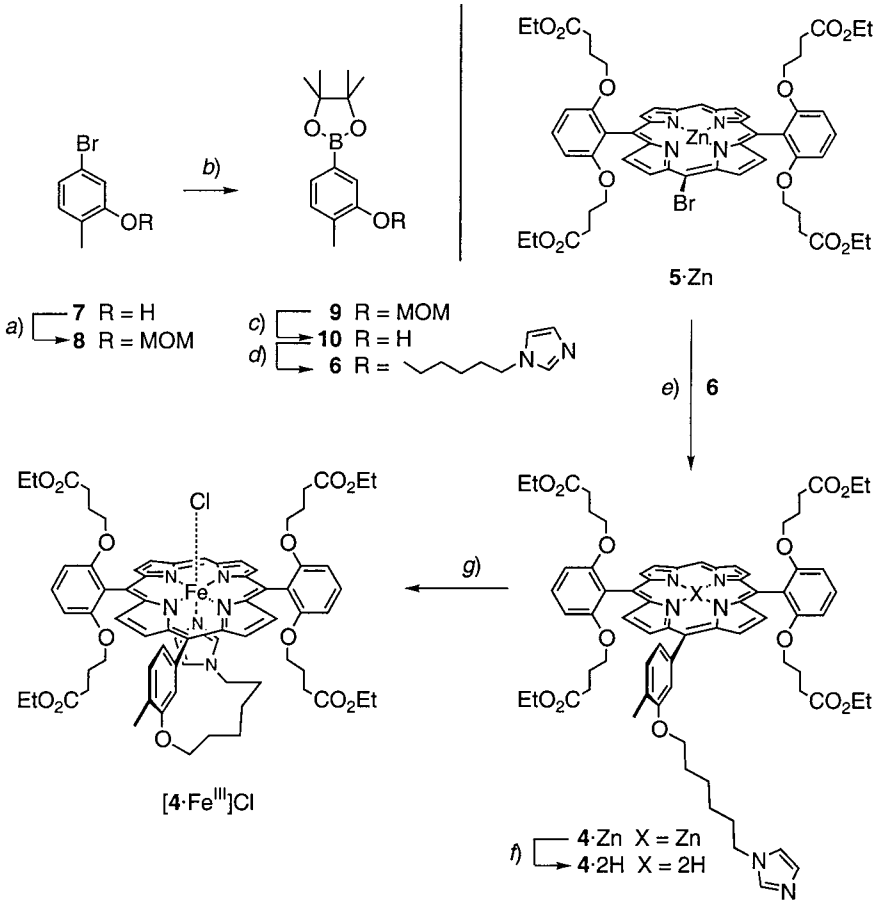


Fig. 1. *Dendritic Fe porphyrins [**1**·Fe^{III}]Cl, [**2**·Fe^{III}]Cl, and [**3**·Fe^{III}]Cl with mono-imidazole axial ligation as mimics of heme monooxygenases*

Scheme 1. *Synthesis of the Imidazole-Ligated Fe^{III} Porphyrin Core [**4**·Fe^{III}]Cl*



a) MOM-Cl, K_2CO_3, MeCN, 0°, 2 h; 95%. *b*) BuLi, TMEDA, THF, −78°, 60 min; then $B(OMe)_3$, r.t., 3 h; then pinacol, NH_4Cl, PhH, reflux, 4 h; 74%. *c*) Conc. aq. HCl soln., THF/MeOH, r.t., 1 d; 84%. *d*) 1-(6-Bromohexyl)-1*H*-imidazole (**11**), Cs_2CO_3, DMF, r.t., 4 h; 68%. *e*) [$Pd(PPh_3)_4$], Cs_2CO_3, PhMe, reflux, 6 h; 81%. *f*) CF_3COOH, PhH, 0°, 10 min; 92%. *g*) $FeCl_2$, 2,6-lutidine, THF, reflux, 2 h; then air; then 1% HCl in $CHCl_3$, r.t., 5 min; then 'proton sponge', THF, r.t., 15 min; 68%. MOM = Methoxymethyl; TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine; 'proton sponge' = 1,8-bis(dimethylamino)naphthalene.

with none of the signals displaying unusual chemical shifts (*Fig. 2*). Despite its instability towards light and air, which was particularly pronounced in dilute solution, **4**·2 H could be prepared in almost quantitative yield when workup and product isolation were carried out under an inert atmosphere.

The corresponding Fe^{III} complex [**4**·Fe^{III}]Cl was obtained from **4**·2 H by insertion of Fe^{II} ($FeCl_2$ in THF) and subsequent air oxidation (*Scheme 1*). An acidic workup step with HCl in $CHCl_3$ after the autoxidation led to complete displacement by chloride of any axial ligands present. Recomplexation of the internal imidazole was subsequently induced *via* treatment with 1,8-bis(dimethylamino)naphthalene ('proton

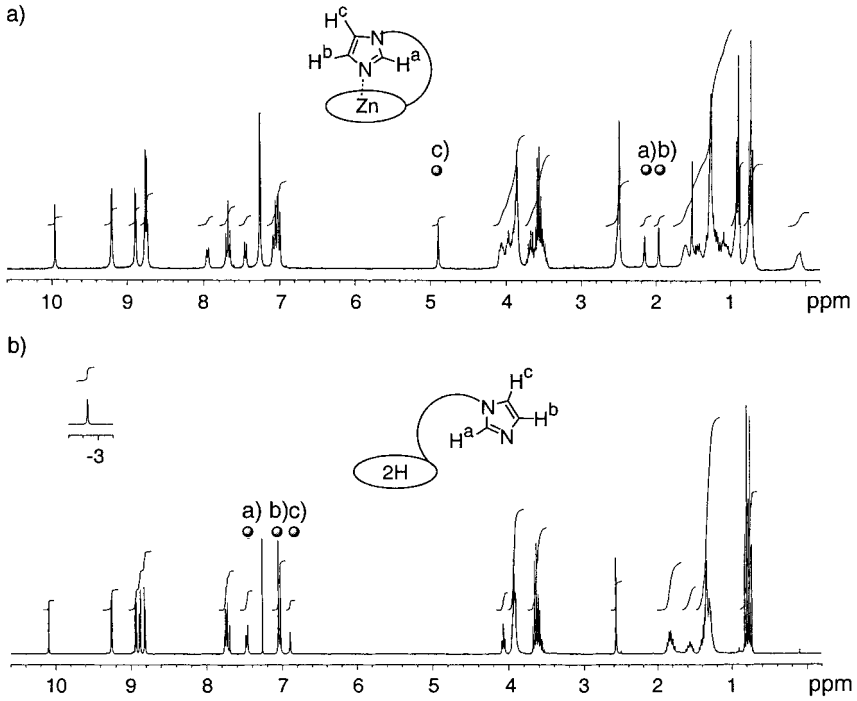
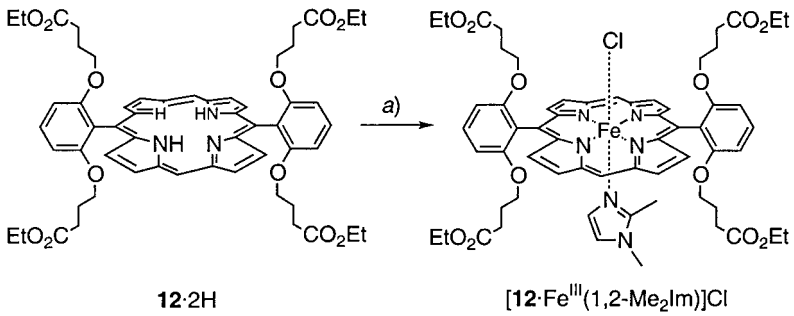


Fig. 2. *300-MHz ^{1}H-NMR Spectra of* **4**·*Zn* (a) *and* **4**·*2 H* (b) *in* $CDCl_3$. Assignments of the imidazole protons are shown in a schematic representation of the structures. Signal assignments were obtained by 2D-NMR spectroscopy at 500 MHz (H,H-COSY (DQFCOSY-45), C,H-COSY (HSQR and HMBC), and ROESY (mixing time 150 ms)).

sponge') in THF [5b][13]. The entire workup was performed under anhydrous conditions to prevent formation of hydroxy complexes. A model compound of very similar coordination environment, [**12**·Fe^{III}(1,2-Me_2Im)]Cl with 1,2-Me_2Im (1,2-Me_2Im = 1,2-dimethylimidazole) as axial ligand, was prepared by iron insertion into **12**·2 H [4b], followed by simple addition of a slight excess of 1,2-Me_2Im (*Scheme 2*).

Scheme 2. *Synthesis of Model Compound [***12**·*Fe^{III}(1,2-Me_2Im)]Cl*



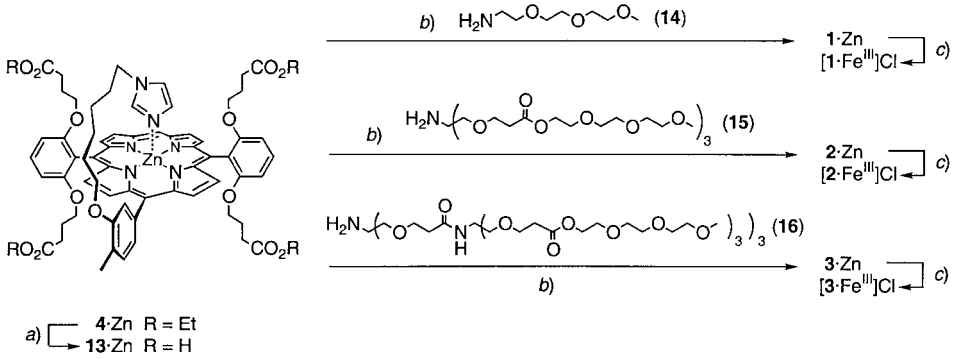
a) $FeCl_2$, 2,6-lutidine, THF, reflux, 2 h; then air; then 1M HCl; then 1,2-Me_2Im, CH_2Cl_2, r.t. 4 h; 69%.

Both Fe complexes were investigated by a number of physico-chemical techniques to elucidate the nature of their axial ligation sphere. The UV/VIS spectra of the two Fe^{III} derivatives were very similar to each other and were characteristic of high-spin complexes. They compared well with the spectra of similar compounds known from the literature [14]. The magnetic moments of $4.77 \pm 0.05\ \mu_B$ ([**4**·Fe^{III}]Cl and $5.78 \pm 0.05\ \mu_B$ ([**12**·Fe^{III}(1,2-Me_2Im)]Cl) are consistent with a high-spin configuration possessing five unpaired electrons [14c][15], although the value for [**4**·Fe^{III}]Cl is somewhat lower than expected. This is possibly due to the formation of head-to-tail dimers at the high solution concentration required for the measurement or, alternatively, due to weak complexation of chloride at the second axial coordination site. EPR Measurements on [**4**·Fe^{III}]Cl displayed the dominant axial signal typical for high-spin Fe^{III} porphyrins [14c][15b][16] and a minor rhombic contribution from a low-spin form. Surprisingly, the model compound [**12**·Fe^{III}(1,2-Me_2Im)]Cl was EPR-silent, preventing comparison of the EPR spectra. The experiments mentioned above clearly demonstrated that the internal imidazole in [**4**·Fe^{III}]Cl is coordinated to the Fe center to form a five-coordinate high-spin complex, and that the sixth coordination site is either completely vacant or partially occupied by a weakly bound chloride (which is easily replaced by an oxidant-donor atom during catalysis of oxidation reactions). Complete internal imidazole coordination was further confirmed by reduction of [**4**·Fe^{III}]Cl and [**12**·Fe^{III}(1,2-Me_2Im)]Cl to the five-coordinate Fe^{II} complexes [**4**·Fe^{II}] and [**12**·Fe^{II}(1,2-Me_2Im)], which exhibited UV/VIS spectra typical of five-coordinate high-spin Fe^{II} porphyrins [14][15a]. Their magnetic moments of $4.10 \pm 0.05\ \mu_B$ ([**4**·Fe^{II}]) and $4.78 \pm 0.05\ \mu_B$ ([**12**·Fe^{III}(1,2-Me_2Im)]) are consistent with the high-spin state, having four unpaired electrons, and agree very well with published values for similar complexes [15a][17]. *Collman et al.* had previously demonstrated that the sterically demanding ligand 1,2-Me_2Im forms exclusively five-coordinate high-spin Fe^{II} porphyrin adducts, even when present in large excess [18].

The two Fe^{II} species formed six-coordinate low-spin adducts with different ligands extremely easily and were, for this reason, very difficult to obtain in pure form. Only under rigorously O_2-free conditions did the five-coordinate species prevail, and traces of O_2 led immediately to the formation of O_2 complexes, which subsequently underwent autoxidation. Interestingly, [**4**·Fe^{II}] was considerably more stable than [**12**·Fe^{II}(1,2-Me_2Im)], as the former could be obtained by reduction with aqueous $Na_2S_2O_4$ solution in PhMe, whereas the presence of H_2O led to complete decomposition of the latter compound. Reduction in this case could only be achieved under anhydrous conditions. The presence of CO gas during the reduction led to the formation of stable, six-coordinate, low-spin CO complexes, which are diamagnetic and possess very characteristic UV/VIS spectroscopic properties [19]. These complexes show a narrow, extremely intense *Soret* band at 421 nm ([**4**·Fe^{II}]) and 414 nm ([**12**·Fe^{II}(1,2-Me_2Im)]), while the *Q* bands appear at 539 nm ([**4**·Fe^{II}]) and 526 nm ([**12**·Fe^{II}(1,2-Me_2Im)]). These results compared well with data reported previously for similar complexes [20] and, thus, proved again the presence of a coordinated imidazole axial ligand and one free coordination site in the reduced Fe^{II} state.

2.2. *Synthesis and Characterization of the Dendritic Porphyrins.* For the synthesis of the Zn^{II} porphyrin dendrimers of generation zero (**1**· Zn), one (**2**· Zn) and two (**3**· Zn; *Scheme 3*), tetraethyl ester **4**· Zn was hydrolyzed to give the core tetraacid

Scheme 3. *Synthesis of the Dendritic Heme Monooxygenase Mimics [**1**·Fe^{III}]Cl, [**2**·Fe^{III}]Cl, and [**3**·Fe^{III}]Cl*



a) NaOH, dioxane/H_2O, r.t., 3 d. *b*) **14**, **15**, or **16**, HATU, Et_3N, DMF, 0°, 1 d; 91% (**1**·Zn); 3 d, 70% (**2**·Zn); 7 d (reaction temperature: −15°); 65% (**3**·Zn); all yields starting from **4**·Zn. *c*) CF_3COOH, $CHCl_3$, 0°, 5 min; then $FeCl_2$, 2,6-lutidine, THF, reflux, 2–6 h; then air; then 1% HCl in $CHCl_3$, r.t., 5 min; then 'proton sponge', THF, r.t., 15 min; 49% ([**1**·Fe^{III}]Cl); 53% ([**2**·Fe^{III}]Cl); 59% ([**3**·Fe^{III}]Cl). HATU = *O*-(7-azabenzotriazol-1-yl)-*N*,*N*,*N*′,*N*′-tetramethyluronium hexafluorophosphate.

13·Zn, which was coupled with the triethyleneglycol-monomethyl-ether-functionalized dendritic wedges **14** [21], **15** [22], and **16** [5b], respectively, in DMF with the very reactive HATU (= *O*-(7-azabenzotriazol-1-yl)-*N*,*N*,*N*′,*N*′-tetramethyluronium hexafluorophosphate) as the coupling agent.

The dendritic Zn^{II} porphyrins were purified by repeated preparative gel-permeation chromatography (GPC, *Bio-Rad Bio-Beads S-X1*; CH_2Cl_2) and fully characterized by spectroscopic methods. The isolation of pure **3**·Zn required the combined use of preparative GPC (*Bio-Rad Bio-Beads S-X1*; CH_2Cl_2) and high-performance gel-permeation chromatography (HP-GPC, *NovoGROM 100*; THF), but nevertheless, the target compound was obtained in a remarkable yield of 65%. It was critical to maintain the reaction temperature below 0° at all times in this case to avoid formation of inseparable higher-mass by-products in the course of the coupling reaction. The lower-generation compounds were isolated in 70% (**2**·Zn) and 91% yield (**1**·Zn), thus demonstrating a pronounced increase in coupling efficiency with decreasing bulkiness of the dendritic wedges. UV/VIS and NMR spectroscopic analysis proved the complete coordination of the tethered imidazole to the Zn^{II} ion, and dendritic purity was confirmed by MALDI-TOF mass spectrometry. The spectrum of the second-generation dendrimer **3**·Zn (matrix: 2-(4-hydroxyphenylazo)benzoic acid (HABA)) featured the sodium complex of the molecular ion $[M+Na]^+$ (*m*/*z* 11586.1 (100%); calc. for $C_{524}H_{904}N_{22}O_{249}ZnNa$: 11584.8) and the molecular ion M^+ (30%) as the only prominent peaks. Lack of fragmentation and absence of structural defects were apparent from the absence of signals at lower masses.

Demetallation with CF_3COOH in $CHCl_3$ and Fe^{II} insertion with $FeCl_2$ and 2,6-lutidine in THF, followed by autoxidation, gave the air-stable dendritic Fe^{III} porphyrins [**1**·Fe^{III}]Cl, [**2**·Fe^{III}]Cl, and [**3**·Fe^{III}]Cl, respectively, which were purified by preparative TLC (SiO_2; CH_2Cl_2/MeOH 90:10), followed by preparative GPC (*Bio-Rad Bio-Beads S-X3*; CH_2Cl_2). The highly polar compounds were difficult to recover from SiO_2 after preparative TLC, which resulted in rather low isolated yields.

All three dendritic Fe^{III} complexes were shown to be highly monodisperse by MALDI-TOF mass spectrometry (*Fig. 3*). They exhibited UV/VIS absorption spectra characteristic of five-coordinate high-spin Fe^{III} porphyrins [14], and this spin configuration was also apparent from EPR measurements. The compounds displayed a predominant axial signal in the EPR spectrum, typical for high-spin Fe^{III} porphyrins [16] and a weak rhombic signal indicative of a low-spin Fe^{III} species [23]. These paramagnetic properties indicate a possible weak coordination of the chloride counterion at the vacant coordination site of the Fe^{III} porphyrin, as, in these cases, the formation of head-to-tail dimers is improbable, considering the steric bulkiness of the dendritic shells (for example, it has been shown previously that μ-oxo dimers do not form with higher-generation dendrimers [7][20]). Overall, the physico-chemical properties of the Fe^{III} porphyrin moiety in the dendrimers [**1**·Fe^{III}]Cl, [**2**·Fe^{III}]Cl, and [**3**·Fe^{III}]Cl were quite similar to those of the corresponding Fe^{III} porphyrin core [**4**·Fe^{III}]Cl.

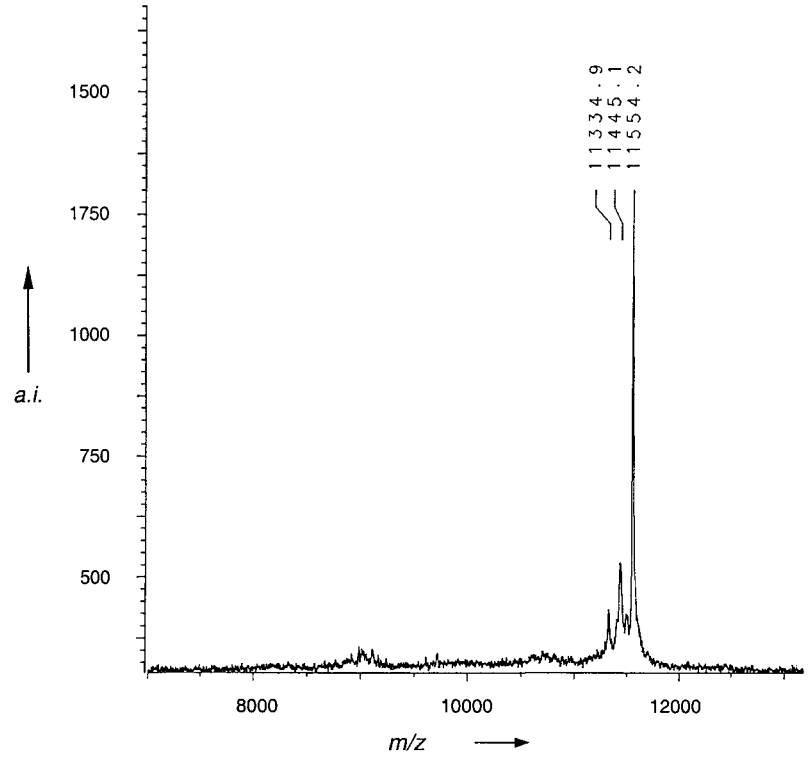


Fig. 3. *MALDI-TOF Mass spectrum of the dendritic Fe^{III} porphyrin [**3**·Fe^{III}]Cl.* Matrix: 0.01M 2-(4-hydroxyphenylazo)benzoic acid (HABA) in MeCN/H_2O 4:1, analyte in CH_2Cl_2; reflector mode.

2.3. *Catalytic Properties of the Dendritic Iron Porphyrins.* The catalytic performance of the new heme monooxygenase mimics was assessed in the epoxidation of olefins [6][24] and the oxidation of sulfides to sulfoxides [6a] in CH_2Cl_2 with iodosylbenzene as the oxidant. Epoxidation reactions were carried out on oct-1-ene (**17**) and cyclooctene

(**18**) as substrates with an excess of olefin compared to oxidant and *ca.* 1 mol-% of catalyst (*Table 1*). The oxidations of (methylsulfanyl)benzene (**19**) and diphenyl sulfide (**20**) were performed in a similar way (*Table 2*).

Table 1. *Epoxidation of Alkenes with Iodosylbenzene Catalyzed by the Dendritic Fe^{III} Porphyrins [**1**·Fe^{III}]Cl, [**2**·Fe^{III}]Cl, and [**3**·Fe^{III}]Cl in CH_2Cl_2,* T = *295 K*

Catalyst	Substrate	Yield[a]) [%]	Selectivity[b]) [%]	Turnovers[c])
[**1**·Fe^{III}]Cl	**17**	23	91	7
[**2**·Fe^{III}]Cl	**17**	24	94	14
[**3**·Fe^{III}]Cl	**17**	25	95	25
[**1**·Fe^{III}]Cl	**18**	46	97	28
[**2**·Fe^{III}]Cl	**18**	53	97	42
[**3**·Fe^{III}]Cl	**18**	56	98	57

[a]) Based on iodosylbenzene consumed, as determined by calibrated analytical GC. [b]) Determined by calibrated analytical GC. [c]) Moles of product formed per moles of catalyst used. Determined by calibrated analytical GC.

Table 2. *Oxidation of Sulfides with Iodosylbenzene Catalyzed by the Dendritic Fe^{III} Porphyrins [**1**·Fe^{III}]Cl, [**2**·Fe^{III}]Cl, and [**3**·Fe^{III}]Cl in CH_2Cl_2,* T = *295 K*

Catalyst	Substrate	Yield[a]) [%]	Selectivity[b]) [%]	Turnovers[c])
[**1**·Fe^{III}]Cl	**19**	66	> 99	38
[**2**·Fe^{III}]Cl	**19**	70	> 99	54
[**3**·Fe^{III}]Cl	**19**	59	> 99	77
[**1**·Fe^{III}]Cl	**20**	50	> 99	30
[**2**·Fe^{III}]Cl	**20**	80	> 99	63
[**3**·Fe^{III}]Cl	**20**	63	> 99	87

[a]) Based on iodosylbenzene consumed, as determined by calibrated analytical GC. [b]) Determined by calibrated analytical GC. [c]) Moles of product formed per moles of catalyst used. Determined by calibrated analytical GC.

Analysis of the crude product mixtures by calibrated quantitative analytical gas chromatography (GC) indicated that all three dendritic Fe^{III}-porphyrins catalyzed the formation of the desired oxidation product. The dendritic shell obviously does not hinder access of substrates or oxidant to the Fe^{III} porphyrin core. Catalyst deactivation by oxidative degradation processes was identified as the major reason for the rather low total turnover numbers measured (*Tables 1* and *2*). All three dendrimers, which are of intensely brown color, decomposed to nearly colorless degradation products in the course of the reactions, with the highest-generation derivative being clearly the most stable one. Contrasting the low total turnover numbers, product selectivities were excellent in all cases (*Tables 1* and *2*) and even in sulfide oxidations, where overoxidation to sulfones is a frequent problem [6a], no products other than the desired sulfoxide could be detected in significant amounts.

3. Discussion and Conclusions. – All oxidation reactions catalyzed by the dendritic Fe^{III} porphyrins occurred at similar rates, independent of the dendritic generation. Clearly, all substrates tested as well as the oxidant iodosylbenzene could easily reach

the active site at the core of the dendrimers. However, the three dendrimers are rather inferior compared with state-of-the-art metalloporphyrin catalysts [6a] and show only low total turnover numbers. These are caused by the inherent instability of the metalloporphyrin core against self-oxidation. The most probable point of attack is the single free *meso*-position at the porphyrin macrocycle, which can be readily oxidized leading to ring-opened oxidative degradation products [25]. This low stability made it impossible to draw conclusions concerning the beneficial effect of the axial imidazole ligand on catalysis or regarding the influence of the size of the dendritic shell on shape selectivity with different substrates.

Despite these limitations, a number of interesting findings were obtained. Thus, in both olefin epoxidation (*Fig. 4*) and sulfide oxidation (*Fig. 5*), the total turnover numbers increase with increasing size of the dendritic shell. With increasingly shielding dendritic shells, degradation slows down, and catalyst stability is improved. At the same time, side reactions are reduced, and the yield of the desired oxidation product based on consumed iodosylbenzene increases (*Figs. 4* and *5*). This makes the second-generation compound [**3** · Fe^{III}]Cl the best catalyst in the series, which is rather unusual in dendritic catalysis whereby a decrease in activity is commonly observed with increasing dendritic generation [3][22] (for dendrimers with a catalytically active core, see also [26]).

Sulfide oxidation was more efficiently catalyzed than olefin epoxidation, which correlates with the observation that sulfides are generally much easier to oxidize than alkenes. Cyclooctene (**18**) gave clearly better results than oct-1-ene (**17**), which is

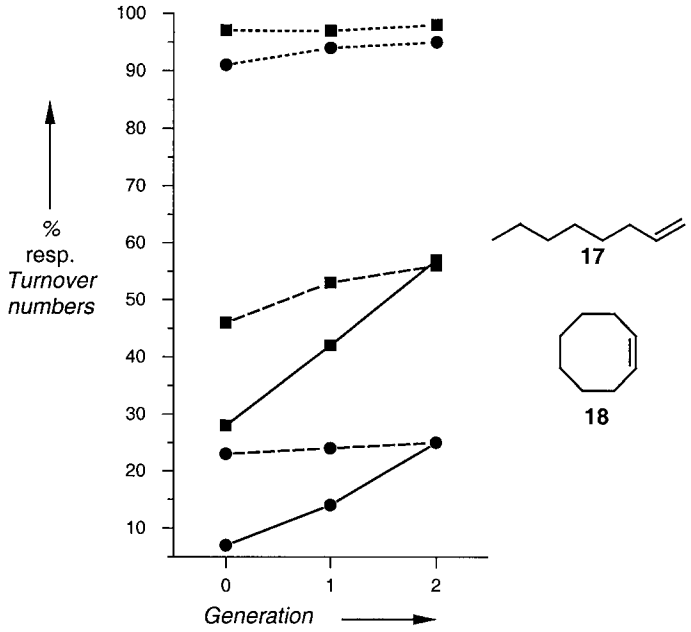


Fig. 4. *Epoxidation of oct-1-ene* (**17**; ●) *and cyclooctene* (**18**; ■) *with iodosylbenzene in* CH_2Cl_2, *catalyzed by the dendritic* Fe^{III} *porphyrins [***1** · Fe^{III}*]Cl, [***2** · Fe^{III}*]Cl, and [***3** · Fe^{III}*]Cl.* Plot of the total turnover numbers (—), yields (– – – –; in %), and selectivities (· · · · · ; in %) *vs.* dendrimer generation. $T = 295$ K.

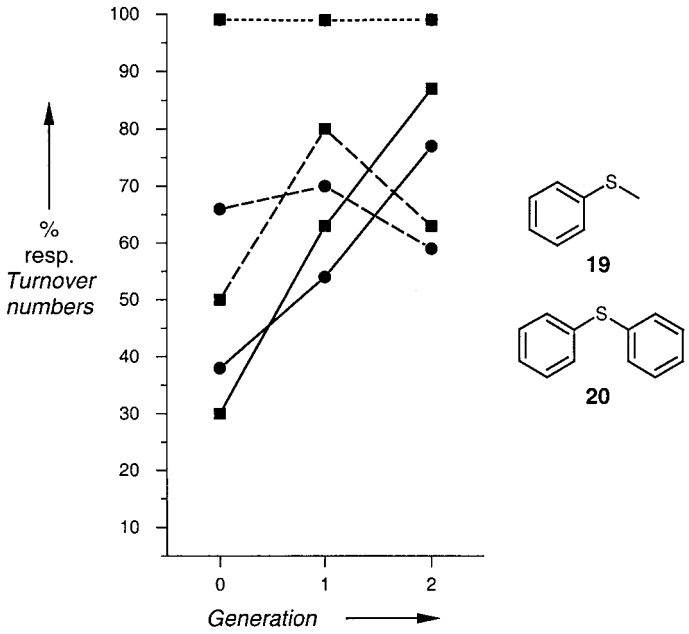


Fig. 5. *Oxidation of (methylsulfanyl)benzene* (**19**; ●) *and diphenyl sulfide* (**20**; ■) *with iodosylbenzene in* CH_2Cl_2, *catalyzed by the dendritic* Fe^{III} *porphyrins [***1**$\cdot Fe^{III}$*]Cl, [***2**$\cdot Fe^{III}$*]Cl, and [***3**$\cdot Fe^{III}$*]Cl.* Plot of the total turnover numbers (—), yields (– – – –; in %), and selectivities (·····; in %) *vs.* dendrimer generation. $T = 295$ K.

known to be a difficult compound for epoxidation, whereas the former is referred to as an excellent epoxidation substrate [6a]. On the other hand, the two sulfides **19** and **20** employed in this study are very similar in structure and, expectedly, are oxidized with similar efficiency.

A positive aspect of our new catalytic dendrimers are the very high product selectivities observed, particularly in sulfide oxidations, for which by-products resulting from overoxidation are frequently observed with a variety of other catalysts including metalloporphyrins [6a].

In summary, we have prepared a series of structurally elaborate mimics for heme monooxygenases and shown their ability to catalyze olefin epoxidation and sulfide oxidation reactions. Dendritic encapsulation mimics the function of the protein shell in the natural heme proteins and significantly enhances the stability of the catalyst. In future work, catalyst stability (and efficiency) will be further improved by attachment of electron-withdrawing substituents to the porphyrin macrocycle and by blocking its fourth *meso*-position (for examples of improved catalyst stability due to the introduction of electron-withdrawing substituents, see [27]). This would then allow full exploitation of the advantages of the dendritic structure, such as excellent solubility, facile catalyst separation and recycling, and utilization in economically efficient membrane reactors.

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Experimental Part

General. See [5b]. Compounds **5** · Zn [5b], **7** [11], **11** · AcOH [5b][12], **12** · 2 H [4b], **14** [21], **15** [22], and **16** [5b] were prepared according to published procedures or by slight modifications of such. Prep. TLC: *Merck PSC* glass plates, 2 mm SiO_2 with F_{254}, 20 × 20 cm, visualization by UV light at 254 and 366 nm, as well as by visible light. Anal. GC: *Perkin-Elmer PE Auto System* with FID detector and H_2 as carrier gas, separation in a temp. gradient on an *OPTIMA-1701* 0.25-mm *Macherey-Nagel* capillary column (0.25 mm × 25 m) at a carrier-gas pressure of 2.6 bar. Magnetic moments $\mu_{eff}^{25°}$ (μ_B) were determined by the *Evans-Scheffold* method in deuterated solvents with 2% Me_4Si or *t*-BuOH as reference compounds [28].

General Procedure 1 (*GP 1*): *Hydrolysis of Porphyrin Tetraethyl Ester to Porphyrin Tetraacid*. The porphyrin tetraethyl ester (0.020 mmol) was dissolved in dioxane (2 ml), and 2M NaOH (2 ml) was added. The two-phase system was vigorously stirred in the dark at r.t. for 3 d. The mixture was extracted with $CHCl_3$ (10 ml), and the deep purple aq. phase carefully acidified with 0.5M HCl, until a stable, voluminous purple precipitate formed. The resulting suspension was saturated with NaCl by addition of solid NaCl, upon which the precipitate aggregated to form black crystals, which were filtered off. The crude porphyrin tetraacid was washed with H_2O (10 ml), acetone (5 ml), and Et_2O (25 ml), and dried under h.v. in the dark for 2 h.

General Procedure 2 (*GP 2*): *Zn^{II}-to-Fe^{III} Metal Exchange in the Dendritic Porphyrins.* A deep-purple soln. of the dendritic Zn^{II} porphyrin (0.010 mmol) in abs. $CHCl_3$ (10 ml) was carefully degassed by three 'freeze-pump-thaw' cycles and then cooled to 0° in an ice bath. Subsequently, CF_3COOH (23.0 µl, 0.300 mmol) was added, and the dark-green soln. was stirred at r.t. for 5 min. The resulting mixture was titrated with 2,6-lutidine, until its color changed to brown-purple and then washed with degassed H_2O (3 × 10 ml). The aq. phase was removed between washings and, at the end, with a syringe equipped with a long, thin needle. All solvent was then distilled off under h.v. at r.t., and the residue of free-base porphyrin was dried under h.v. for 2 h. The crude, amorphous product was dissolved in abs. THF (15 ml), 2,6-lutidine (8.7 µl, 0.075 mmol) was added, and the soln. was heated to reflux for 15 min. The brown-purple soln. was treated with anh. $FeCl_2$ (19.0 mg, 0.150 mmol) and heated to reflux for 2–6 h. After cooling the now red-brown soln. to r.t., the mixture was exposed to air with stirring for 30 min to ensure complete oxidation to the Fe^{III} complex. Subsequently, the mixture was filtered through a 1-cm layer of *Celite*, then concentrated *in vacuo* and dried under h.v. The residue was dissolved in $CHCl_3$ (5 ml), 1% HCl in $CHCl_3$ (20 ml) was added, and the mixture was stirred at r.t. for 5 min. The solvent was evaporated *in vacuo* and the dark-brown residue taken up in abs. THF (10 ml). The resulting soln. was treated with 1,8-bis(dimethylamino)naphthalene (34.3 mg, 0.160 mmol), upon which its color changed from dark brown to red-brown. The mixture was stirred at r.t. for an additional 15 min and concentrated *in vacuo*. The crude, oily product was subjected to prep. TLC (SiO_2; CH_2Cl_2/MeOH 90:10), the red-brown porphyrin zone was separated from the plate, and the product was recovered by soaking the SiO_2 in hot MeOH (100 ml) in an ultrasonic bath for 30 min. After filtration over a 1-cm layer of *Celite* and concentration of the red-brown filtrate *in vacuo*, the product was purified by prep. GPC (*Bio-Beads S-X3*; CH_2Cl_2) and dried under h.v. for at least 3 d.

4-Bromo-2-(methoxymethoxy)-1-methylbenzene (**8**). A soln. of *5-bromo-2-methylphenol* (**7**; 2.806 g, 15.0 mmol) in MeCN (60 ml) was cooled to 0° in an ice bath, and anh. K_2CO_3 (8.800 g, 60.0 mmol) was added. After 30 min, the green-yellow suspension was treated dropwise with MOM-Cl (2.44 ml, 30.0 mmol) and subsequently stirred at r.t. for 2 h. MeOH (20 ml) was added, and the mixture was stirred at r.t. overnight. After evaporation *in vacuo*, H_2O (75 ml) was added to the residue, and the resulting mixture was extracted with Et_2O (3 × 50 ml). The combined org. phases were washed with 1M NaOH (30 ml) and 25 ml of H_2O (25 ml), dried ($MgSO_4$), and concentrated *in vacuo*. The resulting orange oil was purified by distillation under h.v. to yield **8** (3.277 g, 95%). Colorless oil. B.p. 110° (0.50 Torr). TLC (SiO_2; hexane/AcOEt 90:10): R_f 0.59. IR (film): 2955*m*, 2910*m*, 2880*m*, 2840*w*, 2825*w*, 1590*s*, 1485*s*, 1440*m*, 1410*w*, 1385*s*, 1305*w*, 1285*s*, 1205*w*, 1185*s*, 1155*s*, 1125*s*, 1080*s*, 1000*s*, 925*m*, 870*w*, 850*s*, 800*m*, 760*w*, 650*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.22 (*d*, *J* = 1.6, 1 H); 6.98–7.07 (*m*, 2 H); 5.19 (*s*, 2 H); 3.49 (*s*, 3 H); 2.20 (*s*, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 156.1; 131.0; 126.4; 124.5; 119.5; 117.2; 94.5; 56.0; 15.8. EI-MS: 232 (25, M^+, $C_9H_{11}{}^{81}BrO_2$), 230 (22, M^+, $C_9H_{11}{}^{79}BrO_2$), 171 (17, $[M - OCH_2OMe]^+$, $C_7H_6{}^{81}Br$), 169 (18, $[M - OCH_2OMe]^+$, $C_7H_6{}^{79}Br$), 45 (100, CH_2OMe^+). Anal. calc. for $C_9H_{11}BrO_2$ (231.09): C 46.78, H 4.80, Br 34.58; found: C 46.78, H 4.88, Br 34.47.

2-[3-(Methoxymethoxy)-4-methylphenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**9**). A soln. of TMEDA (0.24 ml, 16.0 mmol) in abs. THF (20 ml) was cooled to −78° and treated with 1.6M BuLi in hexane (10.00 ml, 16.0 mmol), and the mixture was stirred at this temp. for 30 min. Subsequently, **8** (2.311 g, 10.0 mmol) in abs. THF (20 ml) was added dropwise, and the soln. was stirred for 60 min at −78°. $B(OMe)_3$ (0.57 ml, 50.0 mmol) was added in one batch, and, after 60 min, the cooling bath was removed, and the white suspension was stirred at r.t. for 3 h. After addition of sat. aq. NH_4Cl soln. (50 ml), the mixture was extracted with CH_2Cl_2 (3 × 50 ml).

The combined org. layers were dried (Na_2SO_4) and evaporated *in vacuo*. The resulting yellow, oily residue was taken up in benzene (150 ml), and pinacol (11.800 g, 100.0 mmol) and NH_4Cl (1.070 g, 20.0 mmol) were added. After heating to reflux for 4 h with continuous azeotropic removal of H_2O by means of a *Dean-Stark* trap, the mixture was extracted with H_2O (5×50 ml), dried (Na_2SO_4), and evaporated *in vacuo*. Distillation of the residue under h.v. (150°/0.50 Torr) provided **9** (2.056 g, 74%) as a viscous oil, which slowly crystallized at r.t. Colorless solid. M.p. 44–47°. TLC (SiO_2; hexane/AcOEt 90:10): R_f 0.25. IR ($CHCl_3$): 2990*m*, 2980*m*, 2930*w*, 1610*w*, 1570*w*, 1510*w*, 1460*w*, 1440*w*, 1420*m*, 1390*s*, 1355*s*, 1310*w*, 1295*w*, 1270*w*, 1235*m*, 1185*m*, 1145*s*, 1090*m*, 1010*s*, 965*w*, 920*w*, 895*w*, 855*w*, 825*w*, 685*w*, 665*s*, 620*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.40 (*s*, 1 H); 7.38 (*d*, J_{AB} = 7.5, 1 H); 7.17 (*d*, J_{AB} = 7.5, 1 H); 5.25 (*s*, 2 H); 3.50 (*s*, 3 H); 2.28 (*s*, 3 H); 1.33 (*s*, 12 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 155.0; 131.2; 130.5; 128.4; 119.3; 94.4; 83.6; 56.1; 24.7; 16.4; one signal not observed. EI-MS: 278 (100, M^+), 263 (10, $[M - Me]^+$), 248 (67, $[M - 2\,Me]^+$), 233 (21, $[M - CH_2OMe]^+$), 45 (52, CH_2OMe^+). Anal. calc. for $C_{15}H_{23}BO_4$ (278.16): C 64.77, H 8.33; found: C 64.92, H 8.12.

2-(3-Hydroxy-4-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxoborolane (**10**). To **9** (1.391 g, 5.00 mmol) in 160 ml THF (160 ml) and MeOH (90 ml), conc. aq. HCl soln. (0.25 ml) was added, and the soln. was stirred at r.t. for 24 h. Ice/H_2O (100 ml) was added and the mixture was extracted with CH_2Cl_2 (3×100 ml). The combined org. phases were washed with H_2O (100 ml), dried ($MgSO_4$), and concentrated *in vacuo*. The crude, oily product was purified by bulb-to-bulb distillation under h.v. (125°/0.50 Torr) and the resulting solid recrystallized (hexane) to give **10** (0.986 g, 84%). Colorless cubes. M.p. 111–112°. TLC (SiO_2; hexane/AcOEt 75:25): R_f 0.36. IR (KBr): 3375*s*, 2980*s*, 2925*m*, 1620*m*, 1580*m*, 1530*m*, 1460*m*, 1435*m*, 1410*s*, 1365*s*, 1310*s*, 1280*s*, 1250*s*, 1220*m*, 1190*m*, 1170*m*, 1140*s*, 1110*m*, 1085*s*, 990*m*, 965*m*, 920*m*, 890*w*, 850*m*, 815*m*, 785*w*, 725*m*, 705*w*, 685*s*, 580*w*, 525*w*, 430*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.30 (*d*, J_{AB} = 7.2, 1 H); 7.19 (*s*, 1 H); 7.14 (*d*, J_{AB} = 7.2, 1 H); 5.25 (*s*, 1 H); 2.27 (*s*, 3 H); 1.34 (*s*, 12 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 153.5; 130.8; 127.8; 127.3; 120.7; 111.4; 83.8; 24.7; 15.9. EI-MS: 234 (62, M^+), 219 (30, $[M - Me]^+$), 134 (100). Anal. calc. for $C_{13}H_{19}BO_3$ (234.10): C 66.70, H 8.18; found: C 66.91, H 8.18.

*2-{[6-(1*H*-Imidazol-1-yl)hexyl]oxy}-1-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxoborolan-1-yl)benzene* (**6**). A soln. of **11** · AcOH (730 mg, 2.50 mmol) in CH_2Cl_2 (40 ml) was rapidly extracted with 1M KOH (20 ml) at 0°. The org. layer was thoroughly dried (Na_2SO_4), abs. DMF (5 ml) was added, and, after concentration *in vacuo* at r.t., **10** (234 mg, 1.00 mmol) was added. The soln. was treated with anh. Cs_2CO_3 (652 mg, 2.00 mmol) and stirred at r.t. for 4 h. The resulting suspension was diluted with CH_2Cl_2 (20 ml), filtered through a 1-cm layer of *Celite*, and the CH_2Cl_2 was evaporated at r.t. *in vacuo*. The remaining DMF was distilled off under h.v. at 40°. FC (SiO_2 (15 g); AcOEt) and drying under h.v. afforded **6** (522 mg, 68%) as a highly viscous oil, which very slowly solidified at −20°. Colorless, crystalline powder. M.p. 63–64°. TLC (SiO_2; AcOEt/MeOH 99:1): R_f 0.15. IR (KBr): 3115*w*, 2970*m*, 2935*m*, 2850*w*, 1570*w*, 1540*w*, 1510*w*, 1475*w*, 1445*w*, 1385*m*, 1355*m*, 1250*s*, 1210*w*, 1155*s*, 1145*m*, 1115*m*, 1045*s*, 1030*m*, 1010*m*, 995*w*, 975*w*, 905*w*, 845*w*, 820*w*, 760*m*, 735*w*, 710*w*, 670*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.47 (*s*, 1 H); 7.32 (*d*, J_{AB} = 7.3, 1 H); 7.20 (*s*, 1 H); 7.15 (*d*, J_{AB} = 7.3, 1 H); 7.06 (*s*, 1 H); 6.91 (*s*, 1 H); 4.00 (*t*, *J* = 6.1, 2 H); 3.94 (*t*, *J* = 7.0, 2 H); 2.23 (*s*, 3 H); 1.74–1.87 (*m*, 4 H); 1.43–1.56 (*m*, 2 H); 1.34–1.42 (*m*, 2 H); 1.34 (*s*, 12 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 156.7; 137.1; 130.5; 130.2; 129.5; 127.1; 118.8; 116.3; 110.0; 83.7; 67.5; 47.0; 31.1; 29.2; 26.3; 25.7; 24.9; 16.5. FAB-MS: 385.2 (100, MH^+). Anal. calc. for $C_{22}H_{33}BN_2O_3$ (384.33): C 68.75, H 8.65, N 7.29; found: C 68.79, H 8.46, N 7.28.

*(*SP*-5-13)-({Tetraethyl 4,4′,4″,4‴-[10-(3-{[6-(1*H*-Imidazol-1-yl)hexyl]oxy}-4-methylphenyl)-21*H*,23*H*-porphine-5,15-diylbis(benzene-2,1,3-triyldioxy)]tetrakis(butanoato)}(2−)-*N^{21},N^{22},N^{23},N^{24},N^{3}*)zinc(II)* (**4** · Zn). A suspension of **5** · Zn (112.5 mg, 0.100 mmol), **6** (137.6 mg, 0.250 mmol), anh. Cs_2CO_3 (154.0 mg, 0.800 mmol), and $[Pd(PPh_3)_4]$ (96.1 mg, 0.050 mmol) in abs. PhMe (30 ml) was carefully degassed with five 'freeze-pump-thaw' cycles. The mixture was placed in a preheated oil bath and heated to reflux for 6 h in the dark. After cooling to r.t., the suspension was filtered through a 1-cm layer of *Celite*, and the residue was washed with PhMe (100 ml). After evaporation of the combined filtrate and washing soln. *in vacuo*, the remaining dark-purple solid was purified by FC (SiO_2 – *H* (25 g); CH_2Cl_2/MeOH/AcOH 97:2:1 → CH_2Cl_2/MeOH/Et_3N 97:2:1). The product-containing fraction (*ca.* 200 ml) was washed with 1M NaOH (200 ml), dried (Na_2SO_4), and evaporated to dryness *in vacuo*. The resulting purple solid was recrystallized ($CHCl_3$/heptane) at −20° to yield **4** · Zn (105.2 mg, 81%). Fine, purple needles. M.p. 95–97°. TLC (SiO_2; CH_2Cl_2/MeOH 95:5): R_f 0.87. UV/VIS ($CHCl_3$): 596 (3700), 560 (14400), 521 (2400), 426 (427200), 404 (33100), 313 (17300). IR (KBr): 2930*m*, 2856*w*, 1728*s*, 1583*m*, 1520*w*, 1455*s*, 1378*m*, 1289*w*, 1246*s*, 1179*s*, 1094*s*, 1056*m*, 1028*m*, 990*m*, 933*w*, 833*w*, 791*w*, 780*w*, 717*m*, 650*w*, 628*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 9.95 (*s*, 1 H); 9.20 (*d*, *J* = 4.3, 2 H); 8.89 (*d*, *J* = 4.3, 2 H); 8.76 (*d*, *J* = 4.5, 2 H); 8.73 (*d*, *J* = 4.5, 2 H); 7.93 (*d*, *J* = 7.1, 1 H); 7.68 (*t*, *J* = 8.5, 2 H); 7.44 (*d*, *J* = 7.1, 1 H); 7.08 (*s*, 1 H); 7.04 (*d*, *J* = 8.5, 2 H); 7.00 (*d*, *J* = 8.5, 2 H); 4.89 (*s*, 1 H); 4.05 (*t*, *J* = 6.8, 2 H); 3.80–4.01 (*m*, 8 H); 3.47–3.72 (*m*, 8 H); 2.51 (*t*, *J* = 6.7, 2 H); 2.49 (*s*, 3 H); 2.15 (*s*, 1 H); 1.97 (*s*, 1 H); 1.59 (br. *s*, 2 H); 1.39–1.48

(*m*, 4 H); 1.29–1.34 (*m*, 8 H); 1.00–1.19 (*m*, 4 H); 0.94 (br. *s*, 2 H); 0.89 (*t*, *J* = 7.1, 6 H); 0.73 (br. *s*, 2 H); 0.73 (*t*, *J* = 7.1, 6 H); 0.09 (br. *s*, 2 H). ^{1}H-NMR (500 MHz, (D_5)pyridine): 10.14 (*s*, 1 H); 9.40 (*d*, *J* = 4.4, 2 H); 9.28 (*d*, *J* = 4.9, 2 H); 9.27 (*d*, *J* = 4.9, 2 H); 9.20 (*d*, *J* = 4.4, 2 H); 7.89 (*d*, *J* = 7.5, 1 H); 7.88 (*t*, *J* = 8.5, 2 H); 7.87 (*s*, 1 H); 7.70 (*s*, 1 H); 7.49 (*s*, 1 H); 7.27 (*d*, *J* = 8.5, 2 H); 7.26 (*d*, *J* = 8.5, 2 H); 7.25 (*s*, 1 H); 7.11 (*s*, 1 H); 4.00–4.15 (*m*, 8 H); 3.96 (*t*, *J* = 6.3, 2 H); 3.78 (*t*, *J* = 7.2, 2 H); 3.58–3.76 (*m*, 8 H); 2.60 (*s*, 3 H); 1.68–1.79 (*m*, 2 H); 1.47–1.67 (*m*, 10 H); 1.30–1.47 (*m*, 10 H); 1.12–1.20 (*m*, 2 H); 0.78 (*t*, *J* = 7.2, 6 H); 0.72 (*t*, *J* = 7.2, 6 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 173.1; 172.7; 160.1; 159.8; 153.0; 150.2; 150.0; 149.4; 148.9; 142.9; 131.8; 131.4; 131.0; 130.7; 130.0; 129.4; 128.4; 125.3; 124.9; 123.4; 122.6; 119.3; 118.9; 115.0; 111.0; 106.1; 105.3; 104.3; 67.6; 67.4; 66.0; 59.8;59.6; 46.1; 29.6; 29.4; 29.4; 26.5; 24.8; 24.0; 24.0; 23.9; 16.3; 13.9; 13.7. ^{13}C-NMR (125 MHz, (D_5)pyridine): 172.6; 172.5; 160.4; 160.3; 155.5; 151.1; 151.1; 143.3; 137.7; 132.1; 131.9; 131.9; 131.1; 129.7; 129.4; 128.6; 127.9; 125.3; 122.3; 120.7; 119.5; 119.1; 112.5; 106.1; 106.0; 105.2; 68.0; 67.9; 67.8; 59.9 (2×); 46.7; 31.3; 29.8; 29.8; 29.5; 26.5; 25.9; 24.5; 24.4; 16.5; 14.0; 13.9. FAB-MS: 1300.5 (100, M^+). Anal. calc. for $C_{72}H_{80}N_6O_{13}Zn$ (1302.85): C 66.38, H 6.19, N 6.45; found: C 66.24, H 6.27, N 6.46.

*Tetraethyl 4,4′,4″,4‴-[10-(3-{[6-(1*H*-Imidazol-1-yl)hexyl]oxy}-4-methylphenyl)-21*H*,23*H*-porphine-5,15-diylbis(benzene-2,1,3-triyldioxy)]tetrakis(butanoate)* (**4**·2 H). A purple soln. of **4**·Zn (26.1 mg, 0.02 mmol) in abs. benzene (5 ml) was degassed by three 'freeze-pump-thaw' cycles and then treated dropwise at 0° with CF_3COOH (0.10 ml, 1.30 mmol). The resulting dark-green soln. was stirred at r.t. for 10 min, degassed sat. aq. Na_2CO_3 soln. (10 ml) was added, the resulting two-phase system shaken vigorously, and the colorless aq. phase was separated from the now brown-purple org. layer by means of a syringe with a long, thin needle. The org. layer was washed 3× in a similar fashion with degassed H_2O (5 ml) and then directly subjected to FC under N_2 (SiO_2 (10 g); $CH_2Cl_2 \rightarrow CH_2Cl_2$/MeOH 95:5). The product-containing fractions were pooled and evaporated to dryness *in vacuo* in the dark. The resulting residue was recrystallized under N_2 from $CHCl_3$/heptane at −20° to give **4**·2 H (23.0 mg, 92%), which, in the solid state, was stable towards light and air for a few h. Brown-purple powder. M.p. 70–72°. TLC (SiO_2; CH_2Cl_2/MeOH 95:5): R_f 0.19. UV/VIS ($CHCl_3$): 639 (1400), 584 (5600), 542 (4800), 509 (18300), 415 (398500), 400 (sh, 84600), 302 (15800). IR (KBr): 3688*w*, 2977*m*, 2933*m*, 1725*s*, 1589*m*, 1506*w*, 1457*s*, 1411*w*, 1372*w*, 1344*w*, 1320*w*, 1251*m*, 1178*s*, 1104*s*, 1044*w*, 967*w*, 955*w*, 910*m*, 850*w*, 817*w*, 617*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 10.09 (*s*, 1 H); 9.25 (*d*, *J* = 4.6, 2 H); 8.93 (*d*, *J* = 4.6, 2 H); 8.88 (*d*, *J* = 4.8, 2 H); 8.81 (*d*, *J* = 4.8, 2 H); 7.76 (*d*, *J* = 7.5, 1 H); 7.76 (*s*, 1 H); 7.72 (*t*, *J* = 8.5, 2 H); 7.47 (*s*, 1 H); 7.46 (*s*, 1 H); 7.05 (*s*, 1 H); 7.03 (*d*, *J* = 8.5, 4 H); 6.90 (*s*, 1 H); 4.07 (*t*, *J* = 6.2, 2 H); 3.82–3.99 (*m*, 10 H); 3.46–3.70 (*m*, 8 H); 2.57 (*s*, 3 H); 1.74–1.92 (*m*, 4 H); 1.50–1.63 (*m*, 2 H); 1.20–1.46 (*m*, 18 H); 0.81 (*t*, *J* = 7.1, 6 H); 0.76 (*t*, *J* = 7.1, 6 H); −2.86 (*s*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 172.9; 172.8; 159.7 (2×); 155.2; 145.0–148.6 (4× br.); 141.5; 137.1; 129.6–131.7 (4× br.); 130.2; 129.6; 128.5; 127.4; 125.8; 120.3; 119.6; 118.8; 118.3; 111.6; 105.5 (2×); 103.7; 67.8; 67.4; 67.4; 59.7 (2×); 46.9; 31.0; 29.6 (2×); 29.3; 26.4; 25.8; 23.9; 23.8; 16.4; 13.8; 13.7. FAB-MS: 1239.2 (100, MH$^+$). HR-FAB$^+$-MS: 1239.6018 (M^+, $C_{72}H_{82}N_6O_{13}$; calc. 1239.6018).

*(*SP*-5-13)-([Tetraethyl 4,4′,4″,4‴-[10-(3-{[6-(1*H*-Imidazol-1-yl)hexyl]oxy}-4-methylphenyl)-21*H*-23*H*-porphine-5,15-diylbis(benzene-2,1,3-triyldioxy)]tetrakis(butanoato)](2−)-*N^{21},N^{22},N^{23},N^{24},N^{3}*)iron(III) Chloride* ([**4**·Fe^{III}]Cl). To **4**·2 H (24.8 mg, 0.020 mmol) in abs. THF (5 ml) degassed by three 'freeze-pump-thaw' cycles, 2,6-lutidine (11.6 µl, 0.200 mmol) was added, and the purple soln. was heated to reflux for 15 min. Anh. $FeCl_2$ (25.3 mg, 0.200 mmol) was added, and the mixture was heated to reflux for 2 h. The now red-brown soln. was left to cool to r.t. and then exposed to air for 30 min. Direct CC of the entire mixture (Al_2O_3 (10 g); THF → THF/MeOH 80:20) provided a red-brown oil, which was dried under h.v. The resulting crude product was dissolved in $CHCl_3$ (5 ml), treated with 1% HCl in $CHCl_3$ (20 ml), and stirred at r.t. for 5 min. After evaporation *in vacuo*, the residue was taken up in abs. THF (10 ml), and 1,8-bis-(dimethylamino)naphthalene (34.3 mg, 0.160 mmol) was added, leading to an immediate color change from dark brown to red-brown. The mixture was stirred at r.t. for 15 min and then evaporated to dryness *in vacuo*. The crude, oily product was purified by prep. GPC (*Sephadex LH-20*; MeOH), dried under h.v., and recrystallized ($CHCl_3$/heptane) to provide, after drying under h.v., [**4**·Fe^{III}]Cl (18.1 mg, 68%). Red-brown crystalline solid. M.p. 78–79°. TLC (Al_2O_3; THF/MeOH 60:40): R_f 0.86. UV/VIS ($CHCl_3$): 680 (sh, 1900), 649 (2300), 570 (sh, 3700), 507 (9400), 415 (78200), 385 (sh, 27100). IR (KBr): 2933*m*, 2867*w*, 1729*s*, 1633*w*, 1585*m*, 1458*s*, 1372*w*, 1250*s*, 1179*m*, 1125*w*, 1099*s*, 1022*w*, 995*w*, 795*w*, 770*w*, 718*w*, 655*w*, 630*w*. EPR ($CHCl_3$): $g_\perp = 5.79$; $g_\parallel \approx 1.98$; in addition, a weak rhombic signal was observed. $\mu_{eff}^{25°}$ ($CDCl_3$): $4.77 \pm 0.05\ \mu_B$. FAB-MS: 1293.0 (100, $[M-Cl]^+$). Anal. calc. for $C_{72}H_{80}ClFeN_6O_{13} \cdot 2H_2O$ (1364.79): C 63.63, H 6.40, N 6.16; found: C 63.42, H 6.07, N 5.96.

To synthesize the reduced Fe^{II} complex [**4**·Fe^{II}], a soln. of [**4**·Fe^{III}]Cl in PhMe of appropriate concentration was degassed by three 'freeze-pump-thaw' cycles and then mixed with half its volume of a freshly prepared 0.1M soln. of $Na_2S_2O_4$ in degassed H_2O, upon which the color changed from red-brown to deep red. The two-phase system was vigorously stirred for 90 min and then left standing for 30 min to allow for complete phase

separation. The org. layer containing the desired [**4**·Fe^{II}] was then transferred into the vessels for the individual measurements, or evaporated and the product dried under h.v. Red, amorphous solid. UV/VIS (PhMe): 552 (sh, 11300), 533 (13600), 432 (163400). $\mu_{eff}^{25°}$ ($CDCl_3$): 4.10 ± 0.05 μ_B.

*(SP-5-12)-({Tetraethyl 4,4′,4″,4‴-[21*H*,23*H*-Porphine-5,15-diylbis(benzene-2,1,3-triyldioxy)]tetrakis-(butanoato)}(2−)-*N^{21}*,*N^{22}*,*N^{23}*,*N^{24}*)(1,2-dimethylimidazolato](0)-*N^3*)iron(III) Chloride* ([**12**·(1,2-Me_2Im)-Fe^{III}]Cl). To **12**·2 H (49.0 mg, 0.050 mmol) in abs. THF (10 ml) degassed by three 'freeze-pump-thaw' cycles, 2,6-lutidine (25.0 µl, 0.200 mmol) was added, and the purple soln. was heated to reflux for 15 min. Anh. $FeCl_2$ (63.0 mg, 0.500 mmol) was added, and the mixture was heated to reflux for 2 h. The brown soln. was left to cool to r.t. and was then exposed to air for 30 min. Direct CC of the entire mixture (Al_2O_3 (15 g); THF) provided a dark brown oil, which was dried under h.v. The resulting black oil was dissolved in Et_2O (20 ml), washed with 1M HCl (10 ml) and sat. aq. NaCl soln. (10 ml), dried ($MgSO_4$), and concentrated *in vacuo*. The remaining black solid was recrystallized (Et_2O/pentane) and dried under h.v. to yield a black crystalline solid of [**12**·Fe^{III} Cl], which was taken up in CH_2Cl_2 (5 ml). The dark-brown soln. was treated with 1,2-Me_2Im (5.3 mg, 0.060 mmol) and stirred at r.t. for 4 h, which led to a color change from dark brown to red-brown. Evaporation *in vacuo*, crystallization of the crude oily product from MeOH/Et_2O, and drying under h.v. gave [**12**·(1,2-Me_2Im)Fe^{III}]Cl (40.3 mg, 69%). Red-brown, crystalline solid. M.p. 132°. TLC (Al_2O_3; THF/MeOH 60:40): R_f 0.92. UV/VIS (0.01M 1,2-Me_2Im in $CHCl_3$): 629 (sh, 2700), 568 (5900), 498 (9900), 408 (85700), 380 (36500). IR (KBr): 2923*m*, 2867*w*, 1726*s*, 1591*m*, 1522*w*, 1458*s*, 1378*w*, 1311*w*, 1289*w*, 1250*s*, 1178*s*, 1103*s*, 1055*w*, 1022*w*, 994*s*, 855*w*, 833*w*, 795*w*, 765*w*, 715*w*, 695*w*, 640*w*, 630*w*. $\mu_{eff}^{25°}$ (0.01M 1,2-Me_2Im in $CDCl_3$): 5.78 ± 0.05 μ_B. FAB-MS: 1036.2 (100, [*M* − 1,2-Me_2Im − Cl]$^+$). Anal. calc. for $C_{61}H_{68}ClFeN_6O_{12}$ (1168.52): C 62.70, H 5.87, N 7.19; found: C 62.64, H 6.10, N 6.99.

To prepare the reduced, five-coordinate Fe^{II} complex [**12**·(1,2-Me_2Im)Fe^{II}], a soln. of appropriate concentration of [**12**·(1,2-Me_2Im)Fe^{III}]Cl in 0.01M 1,2-Me_2Im in PhMe was degassed by three 'freeze-pump-thaw' cycles and then mixed with an excess of a sat. soln. of $Na_2S_2O_4$/18-crown-6 in degassed abs. Me_2SO, upon which the color slowly changed from red-brown to deep red. The soln. was stirred for 120 min and then transferred into the vessels required for the individual measurements, or evaporated and dried under h.v. Red, amorphous solid. UV/VIS (0.01M 1,2-Me_2Im in PhMe): 548 (sh, 7500), 522 (15800) 419 (176900). $\mu_{eff}^{25°}$ (0.01M 1,2-Me_2Im in $CDCl_3$): 4.78 ± 0.05 μ_B.

*(SP-5-13)-({Tetrakis{2-[2-(2-methoxyethoxy)ethoxy]ethyl} 4,4′,4″,4‴-[10-(3-{[6-(1*H*-Imidazol-1-yl)hexyl]-oxy}-4-methylphenyl)-21*H*,23*H*-porphine-1,15-diylbis(benzene-2,1,3-triyldioxy)]tetrakis[butanamido]}(2−)-*N^{21}*,*N^{22}*,*N^{23}*,*N^{24}*,*N^3*)zinc(II)* (**1**·Zn). Compound **13**·Zn was prepared from **4**·Zn (29.4 mg, 0.020 mmol) according to *GP 1*. The black-purple powder was immediately dissolved in abs. DMF (5 ml), and **14** (130.6 mg, 0.800 mmol) was added. The soln. was cooled to 0° in an ice bath, and HATU (45.2 mg, 0.120 mmol) and Et_3N (112.0 µl, 0.800 mmol) were added. After 2 h at 0°, the ice bath was removed, and stirring was continued for 1 d at r.t. in the dark. The solvent was distilled off under h.v. at 40°, and the residue was taken up in CH_2Cl_2/MeOH 95:5 (10 ml) and purified by FC (SiO_2 (5 g); CH_2Cl_2/MeOH 95:5). The porphyrin fraction was concentrated *in vacuo* and dried under h.v. overnight. Prep. GPC (*Bio-Beads S-X1*; CH_2Cl_2) and drying under h.v. provided **1**·Zn (32.1 mg, 91%). Purple, amorphous solid. TLC (SiO_2; CH_2Cl_2/MeOH 90:10): R_f 0.34. UV/VIS ($CHCl_3$): 596 (4400), 560 (16500), 512 (2400), 427 (389100), 405 (39300), 313 (19400). IR ($CHCl_3$): 3405*w*, 2933*m*, 2878*m*, 1662*s*, 1583*w*, 1521*m*, 1456*s*, 1378*w*, 1350*w*, 1330*w*, 1290*w*, 1248*m*, 1101*s*, 1050*w*, 1022*w*, 992*m*, 909*s*, 850*m*, 650*w*, 625*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 10.03 (*s*, 1 H); 9.28 (*d*, *J* = 4.4, 2 H); 8.98 (*d*, *J* = 4.4, 2 H); 8.85 (*d*, *J* = 4.5, 2 H); 8.80 (*d*, *J* = 4.5, 2 H); 7.85 (*d*, *J* = 7.1, 1 H); 7.70 (*t*, *J* = 8.5, 2 H); 7.47 (*d*, *J* = 7.1, 1 H); 7.04 (*d*, *J* = 8.5, 2 H); 7.00 (*s*, 1 H); 6.99 (*d*, *J* = 8.5, 2 H); 4.99 (*s*, 1 H); 4.96 (*s*, 2 H); 4.01 (*t*, *J* = 6.8, 2 H); 3.78–3.99 (*m*, 8 H); 3.64 (*s*, 8 H); 3.54 (*s*, 8 H); 3.34 (*s*, 6 H); 3.18 (*s*, 4 H); 3.04 (*s*, 8 H); 3.02 (*s*, 6 H); 2.78–2.99 (*m*, 8 H); 2.50–2.70 (*m*, 8 H); 2.49 (*s*, 3 H); 2.18 (*s*, 1 H); 1.99 (*s*, 8 H); 1.72 (*s*, 1 H); 1.55 (br. *s*, 2 H); 1.12–1.38 (*m*, 8 H); 0.81–1.05 (*m*, 8 H); 0.73 (br. *s*, 2 H); 0.56 (br. *s*, 2 H); 0.00 (br. *s*, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 172.3; 171.4; 159.9; 159.5; 153.3; 150.5; 150.4; 149.2; 149.0; 142.0; 131.6; 131.6; 131.5; 131.1; 130.8; 130.0; 128.8; 125.6; 124.7; 123.1; 121.4; 119.9; 118.5; 115.8; 112.3; 105.7; 104.9; 104.0; 71.9; 71.2; 70.5; 70.5; 70.1; 69.6; 69.6; 69.5; 69.0; 68.9; 67.4; 66.9; 66.0; 59.0; 58.6; 46.3; 38.6; 37.7; 31.2; 31.1; 29.4; 26.5; 24.9; 24.5 (2×); 23.8; 16.3. FAB-MS: 1770.4 (100, M^+, $C_{92}H_{124}N_{10}O_{21}Zn$; calc. 1770.8). MALDI-TOF-MS (10^{-5} M in CH_2Cl_2; matrix: 0.02M HABA in MeCN/H_2O 4:1): 1793.9 (37, [*M* + Na]$^+$, $C_{92}H_{124}N_{10}NaO_{21}Zn$; calc. 1793.8), 1771.5 (100, M^+, $C_{92}H_{124}N_{10}O_{21}Zn$; calc. 1770.8).

*(SP-5-13)-({Tetrakis{2-[2-(2-methoxyethoxy)ethoxy]ethyl} 17,17′,17″,17‴-[10-(3-{[6-(1*H*-Imidazol-1-yl)-hexyl]oxy}-4-methylphenyl)-21*H*,23*H*-porphine-1,15-diylbis{benzene-2,1,3-triylbis[oxy(1-oxobutane-4,1-diyl)-imino]}]tetrakis[12-oxo-17-(5-oxo-2,6,9,12,15-pentaoxahexadec-1-yl)-2,5,8,11,15,19-hexaoxadocosan-22-ato]}(2−)-*N^{21}*,*N^{22}*,*N^{23}*,*N^{24}*,*N^3*)zinc(II)* (**2**·Zn). Compound **13**·Zn was prepared from **4**·Zn (29.4 mg, 0.020 mmol)

according to *GP 1*. The black-purple powder was immediately dissolved in abs. DMF (2 ml), **15** (124.0 mg, 0.160 mmol) was added, and the mixture was cooled to 0° in an ice bath. After addition of HATU (45.2 mg, 0.120 mmol) and Et_3N (31.8 µl, 0.240 mmol) at 0°, the soln. was slowly warmed to r.t. during 24 h and stirred at r.t. for 2 d in the dark. The solvent was distilled off under h.v. at 40°, and the residue was taken up in CH_2Cl_2/MeOH 95:5 (10 ml) and purified by FC (SiO_2 (5 g); CH_2Cl_2/MeOH 95:5). The porphyrin fraction was concentrated *in vacuo* and dried under h.v. overnight. Prep. GPC (*Bio-Beads S-X1*; CH_2Cl_2) and drying under h.v. afforded **2**·Zn (59.0 mg, 70%). Purple, viscous oil. TLC (SiO_2; CH_2Cl_2/MeOH 90:10): R_f 0.42. UV/VIS ($CHCl_3$): 596 (4400), 560 (17000), 522 (3100), 427 (464000), 405 (sh, 39200), 312 (22600). IR ($CHCl_3$): 3411*w*, 2930*m*, 2880*m*, 1734*s*, 1669*m*, 1583*w*, 1511*w*, 1456*m*, 1378*w*, 1350*w*, 1316*w*, 1278*w*, 1250*m*, 1183*m*, 1103*s*, 1028*w*, 993*w*, 950*w*, 850*w*, 620*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 9.93 (*s*, 1 H); 9.20 (*d*, *J* = 4.4, 2 H); 8.90 (*d*, *J* = 4.4, 2 H); 8.75 (*d*, *J* = 4.5, 2 H); 8.71 (*d*, *J* = 4.5, 2 H); 7.88 (*d*, *J* = 7.6, 1 H); 7.67 (*t*, *J* = 8.5, 2 H); 7.45 (*d*, *J* = 7.6, 1 H); 7.05 (*d*, *J* = 8.5, 2 H); 7.04 (*s*, 1 H); 6.98 (*d*, *J* = 8.5, 2 H); 5.74 (*s*, 2 H); 5.61 (*s*, 2 H); 5.04 (*s*, 1 H); 4.17–4.19 (*m*, 12 H); 4.02 (*t*, *J* = 6.8, 2 H); 3.98–4.00 (*m*, 12 H); 3.82–3.88 (*m*, 8 H); 3.39–3.65 (*m*, 168 H); 3.33 (*s*, 18 H); 3.29 (*s*, 18 H); 2.78 (br. *s*, 2 H); 2.52 (*t*, *J* = 6.4, 12 H); 2.47 (*s*, 3 H); 2.43 (*t*, *J* = 6.4, 12 H); 2.10 (*s*, 1 H); 1.88 (*s*, 1 H); 1.58 (br. *s*, 2 H); 1.22–1.45 (*m*, 8 H); 0.97–1.21 (*m*, 8 H); 0.93 (br. *s*, 2 H); 0.76 (br. *s*, 2 H); 0.06 (br. *s*, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 172.6; 171.9; 171.3; 171.3; 160.1; 159.5; 153.1; 150.3; 150.0; 149.2; 148.8; 142.7; 131.8; 131.1; 131.0; 130.9; 130.3; 129.5; 128.5; 124.9; 124.9; 123.6; 121.8; 119.2; 118.7; 115.5; 111.5; 105.6; 105.0; 104.1; 71.8; 71.7; 70.5; 70.5 (2×); 70.3 (2×); 70.3; 69.1; 69.0 (2×); 68.8; 67.4; 67.2; 66.6; 66.5; 66.0; 63.5; 63.3; 59.7; 59.6; 58.9; 58.9; 46.1; 34.7; 34.6; 32.3; 32.0; 29.6; 26.6; 24.8; 24.6; 24.4; 23.9; 16.2. MALDI-TOF-MS (10^{-5} M in CH_2Cl_2; matrix: 0.5M 2,5-DHB in MeOH): 4245.8 (49, $[M + Na]^+$, $C_{200}H_{316}N_{10}NaO_{81}Zn$; calc. 4245.0), 4222.7 (100, M^+, $C_{200}H_{316}N_{10}O_{81}Zn$; calc. 4222.0).

*(*SP*-5-13)-({Octakis[2-[2-(2-methoxyethoxy)ethoxy]ethyl} 13,13′,13″,13‴-[10-(3-{[6-(1*H*-Imidazol-1-yl)-hexyl]oxy}-4-methylphenyl)-21*H*,23*H*-porphine-1,15-diylbis[benzene-2,1,3-triylbis[oxy(1-oxobutane-4,1-diyl)-imino]]]tetrakis[13-[5,12-dioxo-7,7-bis(5-oxo-2,6,9,12,15-pentaoxahexadec-1-yl)-2,9,13,16,19,22-hexaoxa-6-aza-tricos-1-yl]-8,18-dioxo-6,6,20,20-tetrakis(5-oxo-2,6,9,12,15-pentaoxahexadec-1-yl)-4,11,15,22-tetraoxa-7,19-di-azapentacosanedioato]}(2−)-N^{21},N^{22},N^{23},N^{24},N^{3})zinc(II)* (**3**·Zn). Compound **13**·Zn was prepared from **4**·Zn (29.4 mg, 0.020 mmol) according to *GP 1*. The black-purple powder was immediately mixed with a soln. of **16** (627.0 mg, 0.240 mmol) in abs. PhMe (10 ml), and the mixture was evaporated to dryness *in vacuo* and further dried azeotropically by co-evaporation with abs. PhMe (3 × 5 ml). The residue was dissolved in abs. DMF (2 ml) and cooled in an ice/NaCl bath to −15°. HATU (45.6 mg, 0.120 mmol) and Et_3N (31.8 µl, 0.240 mmol) were added, and the soln. was left to warm very slowly to 0° in the dark during 5 d and then stirred for an additional 2 d at 0° in an ice bath in the dark. The entire mixture was directly subjected to prep. GPC (*Bio-Beads S-X1*; CH_2Cl_2). The resulting crude product was filtered through a poly(tetrafluoroethylene) (PTFE) membrane (∅ = 13 mm, pore size 0.45 µm) and then subjected to prep. HP-GPC (*NovoGROM 100*; THF, 20 mg of mixture per run). Finally, the product was again purified by prep. GPC (*Bio-Beads S-X1*; CH_2Cl_2) and dried under h.v. to yield **3**·Zn (153.1 mg, 65%). Purple, highly viscous oil. TLC (SiO_2; CH_2Cl_2/MeOH 90:10): R_f 0.58. UV/VIS ($CHCl_3$): 595 (4300), 558 (17000), 522 (3500), 426 (442600), 405 (sh, 45900), 312 (21900). IR ($CHCl_3$): 3426*w*, 2920*m*, 2880*m*, 1734*s*, 1670*m*, 1585v*w*, 1517*m*, 1457*m*, 1380*w*, 1350*w*, 1323*w*, 1282*m*, 1245*m*, 1186*s*, 1105*s*, 1031*w*, 990*w*, 949*w*, 854*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 9.85 (*s*, 1 H); 9.12 (*d*, *J* = 4.2, 2 H); 8.83 (*d*, *J* = 4.2, 2 H); 8.68 (*d*, *J* = 4.3, 2 H); 8.62 (*d*, *J* = 4.3, 2 H); 7.81 (*d*, *J* = 7.4, 1 H); 7.63 (*t*, *J* = 8.5, 2 H); 7.39 (*d*, *J* = 7.4, 1 H); 7.07 (*d*, *J* = 8.5, 2 H); 6.97 (*s*, 1 H); 6.96 (*d*, *J* = 8.5, 2 H); 6.09 (*s*, 6 H); 6.08 (*s*, 6 H); 6.01 (*s*, 2 H); 5.98 (*s*, 2 H); 4.99 (*s*, 1 H); 4.17 (*t*, *J* = 6.8, 2 H); 4.14 (*t*, *J* = 4.9, 36 H); 4.11 (*t*, *J* = 4.9, 36 H); 3.71–3.82 (*m*, 8 H); 3.38–3.65 (*m*, 552 H); 3.30 (*s*, 54 H); 3.27 (*s*, 54 H); 2.53 (br. *s*, 2 H); 2.49 (*t*, *J* = 6.3, 36 H); 2.48 (*t*, *J* = 6.3, 36 H); 2.42 (*s*, 3 H); 2.33 (br. *t*, *J* = 6.1, 12 H); 2.32 (br. *t*, *J* = 6.1, 12 H); 1.99 (*s*, 1 H); 1.00–1.81 (*m*, 19 H); 0.89 (br. *s*, 2 H); 0.72 (br. *s*, 2 H); 0.01 (br. *s*, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 172.1; 171.7; 171.3 (2×); 170.8; 170.7; 160.1; 159.3; 153.0; 150.2; 150.0; 149.1; 148.7; 142.7; 131.9; 131.0; 131.0; 130.8; 130.3; 129.5; 128.4; 124.8; 124.7; 123.6; 121.8; 119.1; 118.7; 115.3; 111.4; 105.8; 105.1; 103.9; 71.8; 71.7; 70.4; 70.4 (2×); 70.3; 70.3 (2×); 69.1 (3×); 68.9 (2×) 68.8; 67.9; 67.7; 67.4 (2×); 66.6; 66.6; 59.9; 63.5; 63.4; 60.3 (2×); 59.7; 59.7; 58.9; 58.8; 46.0; 37.0; 36.9; 34.6; 34.6; 31.9; 31.9; 29.5; 26.6; 24.7; 24.1; 23.9; 23.7; 16.2. MALDI-TOF-MS (10^{-5} M in CH_2Cl_2; matrix: 0.02M HABA in MeCN/H_2O 4:1): 11586.1 (100, $[M + Na]^+$, $C_{524}H_{904}N_{22}NaO_{249}Zn$; calc. 11584.8), 11562.6 (30, M^+, $C_{524}H_{904}N_{22}O_{249}Zn$; calc. 11561.8).

*(*SP*-5-13)-({Tetrakis[2-[2-(2-methoxyethoxy)ethoxy]ethyl} 4,4′,4″,4‴-[10-(3-{[6-(1*H*-Imidazol-1-yl)hexyl]-oxy}-4-methylphenyl)-21*H*,23*H*-porphine-1,15-diylbis(benzene-2,1,3-triyldioxy)]tetrakis[butanamido]](2−)-N^{21},N^{22},N^{23},N^{24},N^{3})iron(III) Chloride* ([**1**·Fe^{III}]Cl). Compound [**1**·Fe^{III}]Cl (13.2 mg, 49%) was prepared from **1**·Zn (26.6 mg, 0.015 mmol) according to *GP 2*. The reaction time in the metal insertion step was 2 h. Red-brown, amorphous solid. TLC (SiO_2; CH_2Cl_2/MeOH 90:10): R_f 0.12. UV/VIS ($CHCl_3$): 646 (2100), 577 (sh,

4500), 507 (10400), 415 (90000), 385 (sh, 50300), 350 (sh, 25200). IR ($CHCl_3$): 3428*w*, 2930*w*, 2867*m*, 1662*s*, 1588*m*, 1517*m*, 1458*s*, 1378*w*, 1349*w*, 1290*w*, 1253*m*, 1102*s*, 1017*w*, 998*m*, 855*w*, 840*w*, 640*w*. EPR ($CHCl_3$): $g_\perp = 5.82$; $g_\parallel \approx 1.99$; in addition, a weak rhombic signal was observed. FAB-MS: 1761.6 (100, $[M-Cl]^+$; calc. for $C_{92}H_{124}FeN_{10}O_{21}$: 1761.8). MALDI-TOF-MS (10^{-5} M in CH_2Cl_2; matrix: 0.02M HABA in MeCN/H_2O 4:1): 1786.0 (17, $[M-Cl+Na]^+$, $C_{92}H_{124}FeN_{10}NaO_{21}$; calc. 1784.8), 1762.4 (100, $[M-Cl]^+$, $C_{92}H_{124}FeN_{10}O_{1}$; calc. 1761.8).

*(*SP*-5-13)-({Tetrakis{2-[2-(2-methoxyethoxy)ethoxy]ethyl} 17,17′,17″,17‴-[10-(3-{[6-(1*H*-Imidazol-1-yl)-hexyl]oxy}-4-methylphenyl)-21*H*,23*H*-porphine-1,15-diylbis{benzene-2,1,3-triylbis[oxy(1-oxobutane-4,1-diyl)-imino]}]tetrakis[12-oxo-17-(5-oxo-2,6,9,12,15-pentaoxahexadec-1-yl)-2,5,8,11,15,19-hexaoxadocosan-22-ato]}(2−)-*N^{21},N^{22},N^{23},N^{24},N^{3}*)iron(III) Chloride* ([**2**·Fe^{III}]Cl). Compound [**2**·Fe^{III}]Cl (22.5 mg, 53%) was prepared from **2**·Zn (42.5 mg, 0.010 mmol) according to *GP 2*. The reaction time in the metal-insertion step was 4 h. Red-brown, viscous oil. TLC (SiO_2; CH_2Cl_2/MeOH 90:10): R_f 0.24. UV/VIS ($CHCl_3$): 645 (3400), 575 (sh, 5700), 507 (12000), 415 (96000), 385 (sh, 46600), 350 (sh, 27000). IR ($CHCl_3$): 3425*w*, 2925*m*, 2880*s*, 1734*s*, 1670*m*, 1591*w*, 1514*m*, 1458*m*, 1378*m*, 1351*m*, 1316*m*, 1252*s*, 1185*s*, 1103*s*, 1028*m*, 992*m*, 951*w*, 853*w*. EPR ($CHCl_3$): $g_\perp = 5.86$; $g_\parallel \approx 2.01$; in addition, a weak rhombic signal was observed. MALDI-TOF-MS (10^{-5} M in CH_2Cl_2; matrix: 0.02M HABA in MeCN/H_2O 4:1): 4436.6 (6, $[M-Cl+Na]^+$; calc. for $C_{200}H_{316}FeN_{10}NaO_{81}$: 4235.0), 4214.6 (100, $[M-Cl]^+$; $C_{200}H_{316}FeN_{10}O_{81}$; calc. 4212.0).

*(*SP*-5-13)-({Octakis{2-[2-(2-methoxyethoxy)ethoxy]ethyl} 13,13′,13″,13‴-[10-(3-{[6-(1*H*-Imidazol-1-yl)-hexyl]oxy}-4-methylphenyl)-21*H*,23*H*-porphine-1,15-diylbis{benzene-2,1,3-triylbis[oxy(1-oxobutane-4,1-diyl)-imino]}]tetrakis{13-[5,12-dioxo-7,7-bis(5-oxo-2,6,9,12,15-pentaoxahexadec-1-yl)-2,9,13,16,19,22-hexaoxa-6-aza-tricos-1-yl]-8,18-dioxo-6,6,20,20-tetrakis(5-oxo-2,6,9,12,15-pentaoxahexadec-1-yl)-4,11,15,22-tetraoxa-7,19-diazapentacosanedioato}}(2−)-*N^{21},N^{22},N^{23},N^{24},N^{3}*)iron(III) Chloride* ([**3**·Fe^{III}]Cl). Compound [**3**·Fe^{III}]Cl (44.6 mg, 59%) was prepared from **3**·Zn (86.7 mg, 0.0075 mmol) according to *GP 2*. The reaction time in the metal insertion step was 6 h. Red-brown, highly viscous oil. TLC (SiO_2; CH_2Cl_2/MeOH 90:10): R_f 0.35. UV/VIS ($CHCl_3$): 645 (sh, 2200), 585 (sh, 5700), 507 (12200), 415 (99900), 395 (sh, 74000), 350 (sh, 27400). IR ($CHCl_3$): 3427*w*, 2879*s*, 2822*m*, 1733*s*, 1669*m*, 1590*w*, 1540*w*, 1506*w*, 1485*w*, 1457*m*, 1400*w*, 1372*w*, 1352*w*, 1320*w*, 1284*m*, 1175*m*, 1104*s*, 1022*w*, 997*w*, 950*w*, 862*w*, 640*w*. EPR ($CHCl_3$): $g_\perp = 5.85$; $g_\parallel \approx 2.03$; in addition a weak rhombic signal was observed. MALDI-TOF-MS (10^{-5} M in CH_2Cl_2; matrix: 0.02M HABA in MeCN/H_2O 4:1): 11552.0 (100, $[M-Cl]^+$, $C_{524}H_{904}FeN_{22}O_{249}$; calc. 11551.8).

Catalysis Studies. All experiments were carried out with the Fe^{III} forms of the dendritic porphyrins.

Epoxidations. A soln. of alkene (0.250 mmol), dendritic porphyrin (0.001–0.002 mmol), and dodecane (0.1319 mmol) as an internal standard in abs. CH_2Cl_2 (2.00 ml) was degassed by three 'freeze-pump-thaw' cycles and then treated with iodosylbenzene (0.200 mmol) in the dark at 295 ± 2 K. The mixture was stirred for 4 h, subsequently it was filtered over SiO_2 (1.0 g), and the SiO_2 was washed with CH_2Cl_2 (3 ml). The filtrate and washing soln. were combined, and 0.5 µl of this soln. was directly subjected to anal. GC. A temp. program from 50° to 200° with a gradient of 10° min^{-1} was applied.

Sulfide Oxidations. A soln. of sulfide (0.250 mmol), dendritic porphyrin (0.001–0.002 mmol), and dodecane (0.1319 mmol) as an internal standard in abs. CH_2Cl_2 (2.00 ml) was degassed by three 'freeze-pump-thaw' cycles and then treated with iodosylbenzene (0.200 mmol) in the dark. The mixture was stirred at 295 ± 2 K for 4 h, subsequently it was filtered over SiO_2 (1.0 g) and the SiO_2 washed with CH_2Cl_2 (1.0 ml), followed by Et_2O (3.0 ml). The filtrate and washing solns. were combined, and 1.0 µl of this soln. was directly subjected to anal. GC. A temp. program from 150° to 300° with a gradient of 10° min^{-1} was applied. Yields based on consumed iodosylbenzene and total turnover numbers were calculated by quantification of the anal. GC traces with help of the internal standard according to established methods [29]. All catalysis reactions were performed at least in duplicate and showed good reproducibility between experiments. The background reaction in absence of catalyst was negligibly slow.

Calibration for Anal. GC Quantification. Response factors for reactants and products were determined from linear regression analysis of anal. GC traces from serial dilutions of these compounds in CH_2Cl_2 with dodecane as an internal standard [29]. All calibrations were run in duplicate.

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