Porphyrin-*o*-quinones as Model Systems for Electron Transfer and Catecholase Reactions

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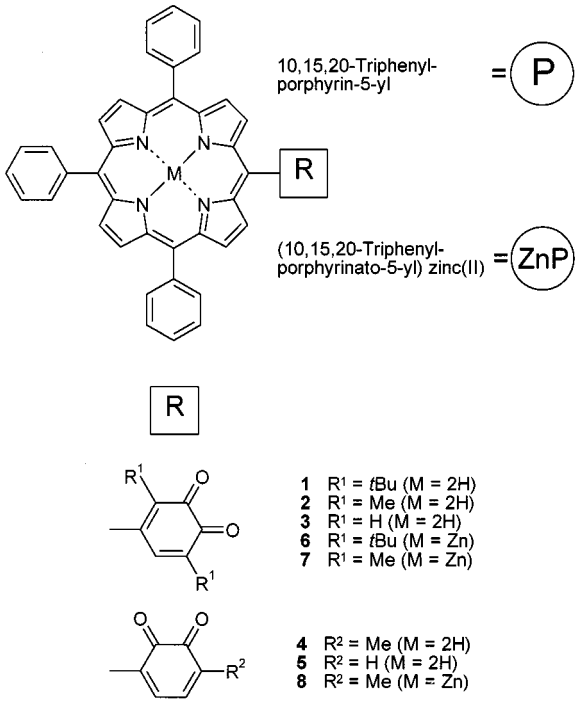
Various porphyrin-*o*-quinones **1**–**8** were prepared as model compounds for electron transfer reactions. The synthesis of these compounds could only be accomplished by using *o*-quinone components stabilized by sterically demanding substituents in the *o*,*o*′-positions and by using protected catechol aldehydes for the initial porphyrin condensation step. The stability of the target compounds strongly depends on the steric influence of substituents on the *o*-quinone, which are necessary to stabilize the *o*-quinones. To test this steric influence we synthesized the porphyrin-*o*-quinones both without and with methyl and *tert*-butyl groups and investigated the influence of the bridging position on the reactivity. The ^{1}H- and ^{13}C-NMR spectroscopic characteristics of all compounds are given. The electron transfer properties were determined using optical spectroscopy and cyclic voltammetry. The free base porphyrin-*o*-quinone **1** with two *tert*-butyl groups in the *o*,*o*′-positions of the quinone readily underwent degradation reactions to muconic acid derivatives similar to those observed in catecholase reactions. Nevertheless, this is the first report of such reactions that do not involve the addition of metal-containing catalysts. The respective zinc(II) complex **6** and the two separated components tetraphenylporphyrin **26** and 3,6-di-*tert*-butyl-*o*-quinone (**27**) did not undergo this reaction, and we surmise a photochemical mechanism that depends on the steric demand of the *o*-quinone.

Introduction

The preparation of model compounds for photosynthesis [(D)−(B)−(A)], consisting of a porphyrin donor (D) and a quinone acceptor (A), has been pursued for more than 20 years and has been described in several comprehensive reviews.[1] Many hundreds of compounds have been described that contain porphyrins and quinones linked by amide bridges, ester functions,[2] or C−C bonds.[3] Although numerous compounds are known in which porphyrin and quinone are linked by covalent linkages (B = bridge), only a limited number of directly linked porphyrin quinones (B = no bridge) have been synthesized.[4]

Many such systems have been prepared by cross condensation and often the 10,15,20-triphenylporphyrin-5-yl system has been used as porphyrin donor component (Scheme 1). Recently, we also described the use of porphyrins with various *meso*-alkyl groups for the preparation of porphyrin-quinones (P−Q) with Q = *p*-benzoquinone.[5] All these studies have exclusively utilized *p*-benzoquinones or their substituted analogs (anthraquinone, naphthoquinone, and triptycene quinone) as the quinone component.[6]

The potential use of *o*-quinones in electron transfer chains was first demonstrated by Giangiacomo and Dutton.[7] They modified native photosystems by exchanging the second quinone (Q_B) in the photosynthetic reaction center of the purple bacterium *Rhodobacter sphaeroides* with an *o*-quinone to utilize the significantly higher reduction potential of *o*-quinone. The synthesis of model systems containing *o*-quinones is of interest in connection with compounds that, according to the theory of electron transfer (ET), have a high $|\Delta G_{ET}|$. In addition, the reduction potential of the *o*-quinones may be further increased through formation of metal chelates with metals from the first and second main group.[8] Otherwise a similarly drastic increase of the reduction potential is possible only by introduction of strong electron-withdrawing substituents in *p*-quinones.



Scheme 1

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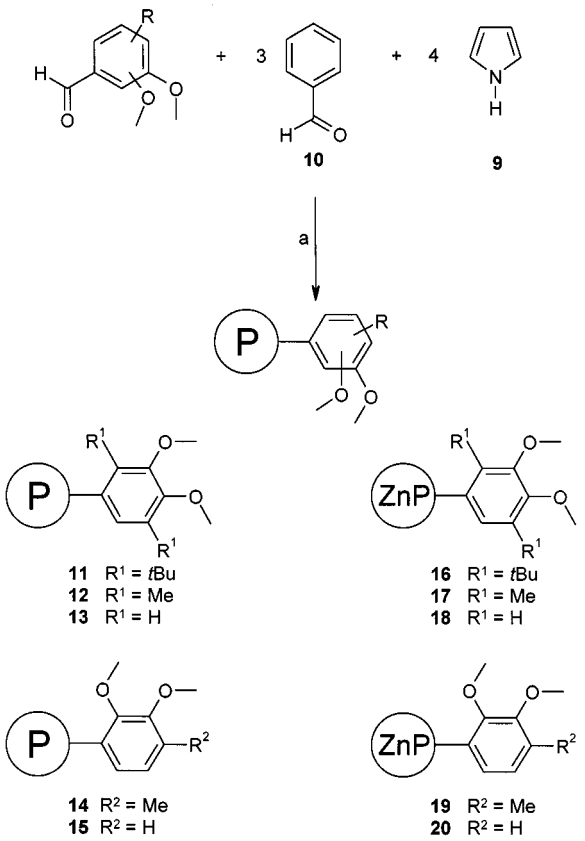
Since then we have successfully connected the more unstable *o*-quinones with porphyrins and have gained access to a new class of model compounds for ET studies.[9] Subsequent to our first report on porphyrin-*o*-quinones,[9b] D'Souza and co-workers published the synthesis of a porphyrin-*o*-quinone without additional substituents on the quinone.[10]

In the present work we describe the complete synthesis and spectroscopic characterization of porphyrin-*o*-quinones as model compounds for ET and various reactions and their dependence on the steric demand of substituents on the *o*-quinone. These reactions include the unexpected formation of muconic acid derivatives, which are of relevance for natural catecholase systems.

Results and Discussion

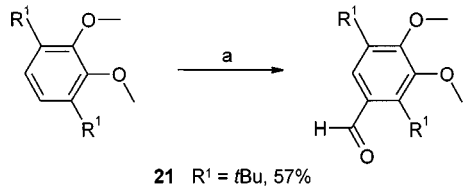
Tetra-*meso*-substituted porphyrins are normally prepared by mixed condensation of pyrrole and the respective substituted aldehydes. In order to control the high reactivity of *o*-quinones, we targeted porphyrins with *o*-quinone units that carry substituents with various degrees of steric demand in the *o*,*o*′-positions (Scheme 2). In contrast to the preparation of some porphyrin-*p*-quinones,[6b,11] the synthesis of porphyrin-*o*-quinones can only be accomplished by condensing an aldehyde bearing protected *o*-dihydroxy functions with pyrrole **9** and benzaldehyde **10** to give the desired porphyrins **11**−**15**.[12]



Scheme 2. a: BF_3Et_2O/CH_2Cl_2, room temp., DDQ

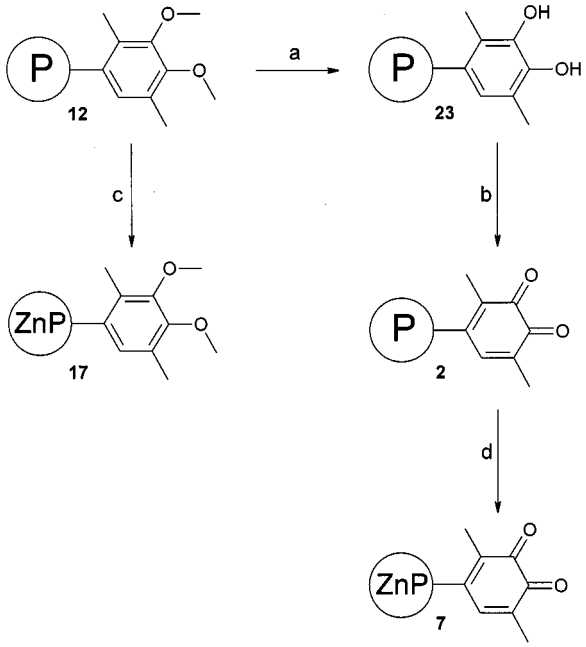
Initially we tested the use of dihydroxybenzaldehydes in mixed porphyrin condensation reactions. Only in the case of the dimethyl compound **23** was the target compound obtained, and even then only small amounts were formed. Attempts to synthesize porphyrins with dihydroxyaldehydes that contained more than one free aromatic position gave complex, fluorescing mixtures of porphyrins in all cases. Even after oxidation with silver(I) oxide the formation of porphyrin-*o*-quinones was not observed by NMR spectroscopy.

Thus, the 3,4-dimethoxybenzaldehydes **21** and **22** were utilized for the porphyrin condensation. Both aldehydes were prepared by Rieche formylation[13] from the respective 1,4-dialkyl-2,3-dimethoxybenzenes (Scheme 3). Despite the high steric demand in the veratrol, aldehyde **21** was obtained in 60% yield.



Scheme 3. a: $Cl_2CH-OMe$, $TiCl_4$, CH_2Cl_2, 0 °C

The protected porphyrin catechols were prepared using these aldehydes and this was followed by demethylation with boron tribromide. Subsequent oxidation of the porphyrin catechols with silver(I) oxide gave the target compounds as shown in Scheme 4.

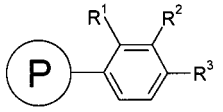


Scheme 4. General reaction scheme for the porphyrin synthesis using the dimethyl compound **12** as an example; a: BBr_3, CH_2Cl_2, −80 °C; b: Ag_2O; c, d: $Zn(ac)_2$, MeOH

Porphyrin-*o*-quinone **1**, which has the highest steric demand on the quinone, showed side reactions (vide supra) and thus we attempted to decrease the steric demand in the

porphyrin-*o*-quinones. Accordingly, the two stable porphyrin-*o*-quinones **2** and **4**, with methyl groups on the *o*-quinone fragment, were synthesized. Subsequently, the constitutional isomers of the unsubstituted porphyrin-*o*-quinones **3** and **5** were prepared to investigate whether the electronic and steric influence of the porphyrin alone is sufficient for the formation of stable porphyrin-*o*-quinones. In principle, *o*-quinones with only one additional substituent are quite unstable, with the relative position of the substituent also influencing the stability. With regard to the electron transfer in model systems, different dihedral angles between the porphyrin and quinone will be obtained as a result of the steric demand of the substituent.

Isolation and purification of the unsubstituted porphyrin-*o*-quinones **3** and **5** proved to be extremely difficult. Both the initial porphyrin catechols **24** and **25** (Scheme 5) and the expected porphyrin-*o*-quinones are sensitive to humidity and light. Even small impurities resulted in the immediate formation of numerous degradation products. Thus, these compounds were prepurified by column chromatography (silica gel, dichloromethane, column with cooling mantle, 5 °C). In order to prevent reduction reactions, activated lead dioxide and sodium sulfate (anhydrous) needed to be added to the column head. Only under these conditions was a crude purification possible at all. Subsequently, all porphyrins were purified by preparative HPLC. Assessment of the purity was performed by ^{1}H-NMR spectroscopy (500 MHz). Highly purified fractions of the unsubstituted porphyrin-*o*-quinones **3** and **5** can be stored for several weeks at −20 °C if light and air are excluded. The metalloporphyrins formed by reaction of the unsubstituted porphyrin-*o*-quinones **3** and **5** with ZnO and TFA could only be obtained with a purity of < 50% and were not characterized further. Use of the method described recently by D'Souza for related zinc(II) complexes did not lead to an improvement in the degree of purity.[10]



24 $R^1 = H, R^2 = R^3 = OH$
25 $R^1 = R^2 = OH, R^3 = H$
26 $R^1 = R^2 = R^3 = H$

Scheme 5

For spectroscopic studies in connection with the investigation of the theory of the electron transfer, all free bases were converted into the respective zinc(II) complexes (**6**−**8**, **16**−**20**) and characterized spectroscopically. While this is normally easily achieved using zinc(II) acetate,[14] we used a treatment of the free bases with zinc(II) oxide under the catalytic influence of TFA.[6a] This procedure prevents the occurrence of addition reactions at the *o*-quinone fragment.

^{1}H- and ^{13}C-NMR spectra were recorded for all compounds in order to obtain complete characterization of the porphyrin-*o*-quinones. ^{13}C-NMR spectroscopy is especially suited to the task of checking for the formation of the isomeric *p*-quinones or the reduced porphyrin catechols during the purification steps. Investigations by Hollenstein and von Philippsborn showed that the carbonyl resonances of *o*-quinones are the strongest high-field shifted carbonyl resonances of six-membered cyclic ketones.[15] The assignment of the individual resonances in the ^{1}H- and ^{13}C-NMR spectra was performed using 2D NMR methods. The strong high-field shift of the signal for one of the methyl groups in compound **2** is particularly noteworthy. This group lies over the porphyrin plane and is strongly influenced by the ring current of the porphyrin.[16]

The direct linkage of porphyrin and *o*-quinone results in strong electronic interactions, whose magnitude correlates with the dihedral angle due to the fact that orbital overlap between donor and acceptor is possible.[17] In the case of the unsubstituted porphyrin-*o*-quinone **3**, this results in an additional band in the UV/Vis spectrum that tails up to 900 nm (Figure 1). This is the first report on such strong electronic interactions in synthetic porphyrin donor-acceptor systems. The zinc(II) complex of **3** has been used by D'Souza and co-workers as a fluorescence sensor, although they did not mention any additional band in the visible spectrum.[10] Some of the NMR assignments do not agree with our values and this may be due to impurities.

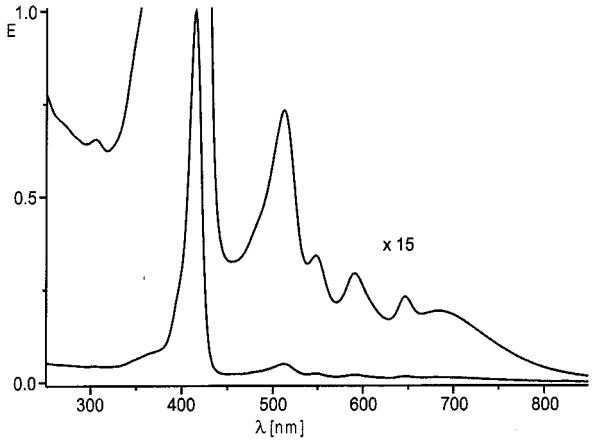


Figure 1. Electronic absorption spectrum of the porphyrin-*o*-quinone **3** in dichloromethane

We were able to measure the ^{1}H-NMR spectra of both unsubstituted porphyrin-*o*-quinones and completely assign all signals (Figure 2). The chemical shifts of the quinone protons are of special importance for the relative assignment of the two different constitutional isomers. For example, compound **3** gave two doublets with large couplings, with the signal at low field (30-H) showing an additional splitting. Due to the ^4J coupling with 30-H the signal for 26-H is split further. In contrast, for compound **5** a doublet of doublets with two large couplings is detected for 29-H. The two remaining quinone protons, 28-H and 30-H, each exhibit only one coupling with 29-H. As the signal for 30-H is obscured by the *m*- and *p*-phenyl protons, no further interpretation is possible for this signal. The exact chemical shift of this proton was determined from an HMQC spectrum.[16]

To test the utility of the porphyrin-*o*-quinones as model compounds for the photoinduced ET, the redox potentials of the various compounds were determined. In a first approximation the redox potentials of the model compounds are the sum of the two potentials − oxidation po-

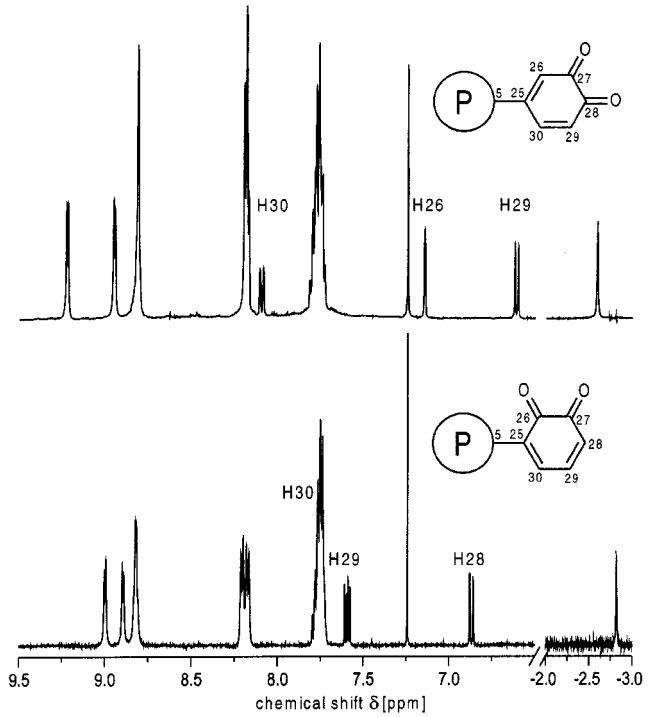


Figure 2. ^{1}H-NMR spectra of the two unsubstituted porphyrin-*o*-quinone isomers **3** and **5**

tential of the porphyrin and reduction potentials of the quinone. Hence, the oxidation potentials of the porphyrin-*o*-quinones do not differ significantly from the known values of 5,10,15,20-tetraarylporphyrins.

The experimental results in Table 1 indicate that the reduction potentials of the porphyrin-*o*-quinones are approximately 200 mV higher than the isomeric porphyrin-*p*-quinones.[18] Thus, according to the Rehm−Weller equation [Equation (1)], a greater $|\Delta G_{ET}|$ is found for the porphyrin-*o*-quinones compared to the respective *p*-quinone compounds.[19]

$$\Delta G_{ET} = e(E^0_{D^+/D} - E^0_{A/A^-}) - \Delta E\,(S_0 \Rightarrow S_1) + w^P - w^R \qquad (1)$$

The applicability of Equation (1) has been discussed with great controversy in the literature.[20] In the present case, this equation is solely used to indicate the magnitude of the differences in ΔG_{ET} for porphyrin-*o*-quinones and the isomeric porphyrin-*p*-quinones. An EPR and ENDOR investigation of the changes in spin density distribution upon

Table 1. Redox potentials of the model compounds in dichloromethane vs. SCE, working electrode Pt, conducting salt 0.1 M TBAP

Compound	E_2^{OX} [V]	E_1^{OX} [V]	$-E_1^{RED}$ [V]	$-E_2^{RED}$ [V]
1		1.16	0.52	1.27
4		1.13	0.23	
5	1.36	1.18	0.22	
2	1.31	1.13	0.27	1.25
3	1.35	1.17	0.36	
6		0.82	0.58	
8	1.18	0.88	0.42	

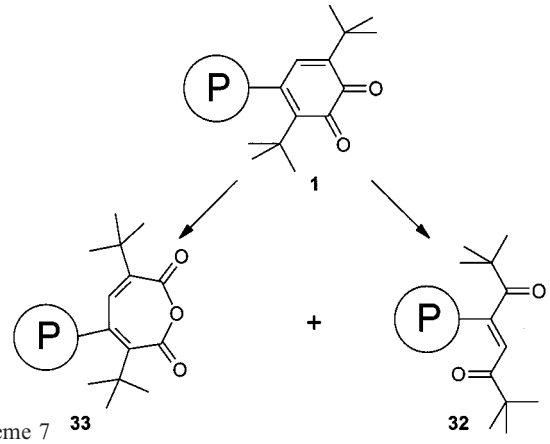
chelation of the porphyrin-*o*-semiquinone anion radicals with various counterions has been reported elsewhere.[9a,16]

We expected porphyrin-*o*-quinone **1** to be a stable compound as, in contrast to other *o*-quinones, the 3,6-di-*tert*-butyl-*o*-quinone **27** (Scheme 6) is a chemically and thermally stable product. Nevertheless, compound **1** immediately decomposed under the influence of light and air with initial formation of an olefinic diketone **32**. During the course of further purification attempts (column chromatography and preparative HPLC) the porphyrin quinone **1** also reacted to give the muconic acid derivative **33**, whose constitution was confirmed by a single crystal X-ray structure determination (Scheme 7).[9b] In order to elucidate the mechanism of these reactions, additional experiments were performed. Under standard conditions (room temperature, air) only partial decomposition of **1** is observed. When the sample is also irradiated with a 1000-W lamp,[21] decomposition is complete within 3 min. When a mixture of the two individual compounds 5,10,15,20-tetraphenylporphyrin (**26**) and 3,6-di-*tert*-butyl-*o*-quinone (**27**) (1:5) was irradiated under oxygenating conditions, the formation of the decomposition products was not observed. Similarly, neither **28** or **29** underwent photooxygenation in the presence of **26**. In addition, neither the metal complex **6** nor the homologous dimethyl compound **2** showed similar reactions. Thus, the observed side reactions are a consequence of both the steric demand of the two *tert*-butyl groups and the steric and electronic influence of the covalently linked porphyrin system.

27 R^1 = H, R^2 = *t*Bu
28 R^1 = *t*Bu, R^2 = H
29 R^1 = *t*Bu, R^2 = Ph

30 R^1 = H, R^2 = *t*Bu
31 R^1 = *t*Bu, R^2 = H

Scheme 6. *o*-Quinones with high steric demand and their corresponding pyrocatechols



Scheme 7

Formation of the oxidation products must occur independently from each other by two different routes, as first the diketone **32** is formed and the formation of the muconic

acid anhydride **33** from **32** is not possible for stoichiometric reasons. Nevertheless, both reactions appear to be mutually interconnected. The more slowly proceeding formation of the muconic acid derivatives depends on the reactivity of the *o*-quinones and is an example of the degradation of catechols under the influence of catecholases. Catecholases are nonheme iron oxygenases that catalyze the degradation of aromatic compounds through activation of molecular oxygen.[22]

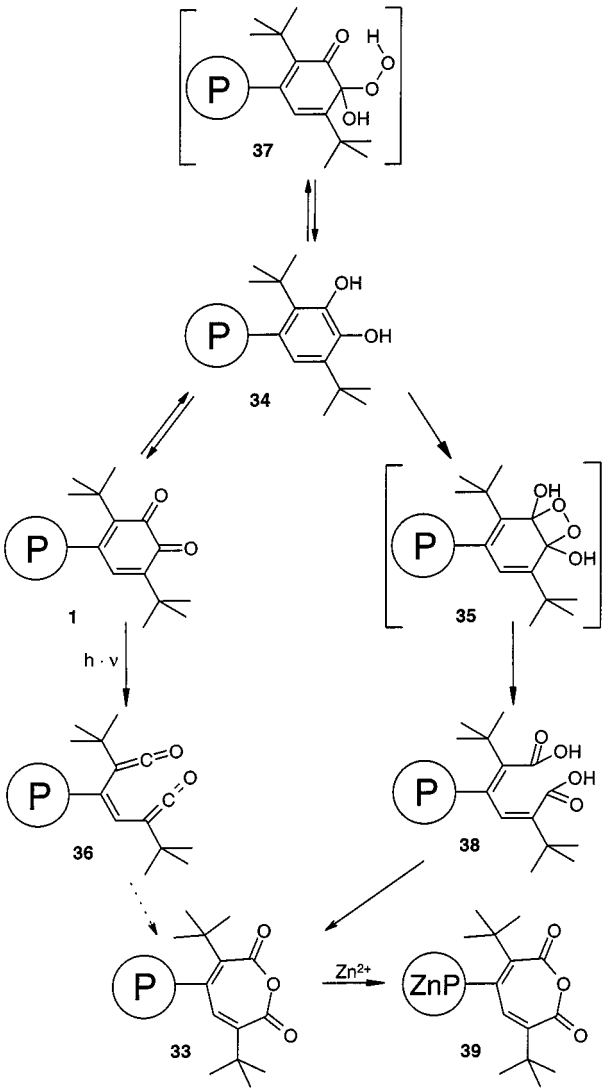
The known degradation reactions in microorganisms involve the formation of substituted catechols and protocatechuic acid derivatives from aromatic amino acids and carbohydrates. During the last four decades several groups have investigated the nonenzymatic reaction of oxygen with aromatic compounds to obtain information about the possible reaction products and their distribution.[23] To counteract the high reactivity of the initial reaction products, *tert*-butylated catechols were used in most model reactions. Despite their lower symmetry, which results in a larger number of possible reaction products, most catecholase model studies utilized 3,5-di-*tert*-butylcatechol (**31**) rather than the 3,6-isomer **30**, which is more difficult to prepare.

All known reactions required the addition of metal oxide containing catalysts for chelation of the 1,2-dioxo function, or the use of a peroxide-containing oxidant. Depending on the modification of the reaction conditions the product distribution varied considerably in the published reactions.[24] Of special environmental relevance is the degradation reaction of halogenated catechols recently described by Funabiki et al.[25] This involves oxidation with molecular oxygen by catalysis with a nonheme iron(III) complex.

As a result of the groundbreaking work of Que Jr. and co-workers the basic mechanism of the intradiol cleaving catechol dioxygenase is known.[26] Interestingly, one intermediate of this mechanism is a muconic acid anhydride that subsequently decomposes. This reaction is a result of the chelation of the catechol by an iron-containing catalyst, the latter being capable of activating molecular oxygen for initiation of an intradiol cleavage. In contrast to this, the oxidative cleavage of the catechol **34** described in this paper proceeds without additional catalyst.

In agreement with other known reactions of *o*-quinones we suggest the following mechanism (Scheme 8).[27–29] The peroxide **35** as well as bisketene **36** are possible intermediates in a complex mechanism for the formation of the muconic anhydride **33**. The discussion of a radical mechanism starting from catechol **34** presents an explanation for the different reactivity of the homologous dimethyl compound **2**, which will form a more stable benzyl radical. As the formation of muconic acid from the respective *o*-quinones can successfully be accomplished only with a Baeyer–Villiger oxidation, we favor a reaction mechanism that occurs via the catechol **34**.

The stability of the metalloporphyrin **6** can be explained in terms of the influence of the porphyrin chromophore; metal insertion results in a formally higher nucleophilicity of the porphyrin. In contrast, protonation should result in an increase in electrophilicity that, in turn, will lead to a



Scheme 8. Possible mechanism for the formation of the muconic acid derivative **33**

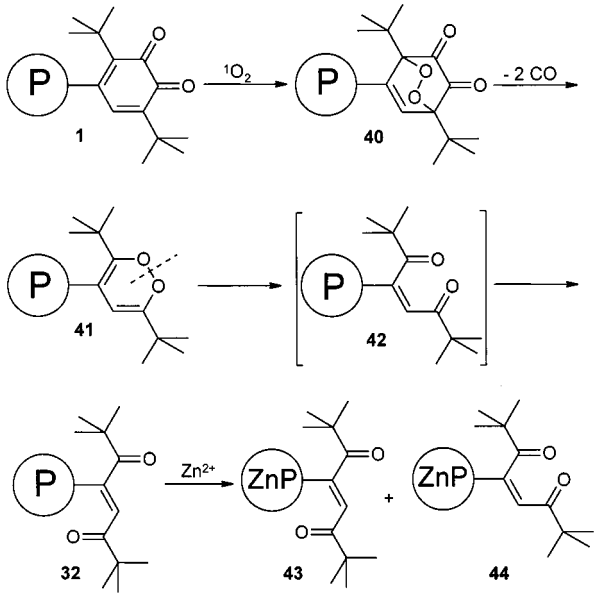
significantly higher reactivity. This assumption is confirmed by the observation that an acidic solution of **1** decomposes completely within a few minutes.

The +I effect of the *tert*-butyl groups as well as the +M effect of the porphyrin unit will determine the reactivity of the whole system. Accordingly no reaction is observed in the case when the separated porphyrin **26** and *o*-quinone **27** are irradiated. A photochemical oxidation may also provide a possible explanation and the different photochemical behavior of the free base and metalloporphyrins can have a determining influence on the reactivity of the various porphyrins.

In contrast to the known catecholase model reactions, we found the olefinic diketone **32** to be the first degradation product. Similar to related reactions in the literature we propose the formation of an *endo*-peroxide and subsequent decarbonylation as the key steps for the formation of **32**. A prerequisite for the formation of an *endo*-peroxide **40** is the generation of the required singlet oxygen by reaction of at-

mospheric oxygen with sensitizers such as, for example, tetraphenylporphyrin or chlorophyll.[30]

Investigations by Wasserman and Scheffer showed that the reactivity of the 1,3-diene in the middle ring of substituted anthracenes is dependent on the electron density at the 9- and 10-positions.[31] An increase of the electron density at both positions resulted in a higher reactivity with oxygen and gave a higher yield in the generation of singlet oxygen from the *endo*-peroxides formed.[32] These differences in reactivity might explain the fact that neither the metalloporphyrin **6** nor the homologous dimethyl compound **2** reacts according to the sequence given in Scheme 9. According to studies by Wilcox and Stevens, oxidation of cyclic ketones with singlet oxygen also yields subsequent decarbonylations, resulting in open-chain diketones.[33] Twofold cleavage of carbon monoxide from the *endo*-peroxide **40** will result in formation of the diketone as the thermodynamically more stable (*E*) compound **32**.



Scheme 9. Putative formation of the porphyrin diketones **32**, **43** and **44**

Treatment of the porphyrin mixture formed after demethylation with zinc(II) acetate results in an isomerization of the 1,4-diketone. The (*E*)-diketone **32** is converted into a 3:1 (*Z*)/(*E*) mixture of the respective metal complexes **43** and **44**. Analogous observations were also made during treatment of the pure (*E*) isomer **32**. A reinvestigation of the mixture of metal complexes after four weeks revealed only the pure *cis* isomer **44**. The metal complex of the (*E*) isomer **43** could not be obtained in its pure form. Nevertheless, the spectroscopic data were unambiguously assigned from the mixture with 2D NMR experiments and are in agreement with expected values.[34] Formation of the (*Z*)-diketone during the metallation is the result of a photoisomerization, similar to the observations made for (*E*)-2,2,7,7-tetramethyl-4-octene-3,6-dione by Rassat and coworkers.[35]

In order to obtain a pure sample of the porphyrin-*o*-quinone **1**, the stable metal complex **6** was carefully demetallated with dilute hydrochloric acid in the cold and under an inert gas and was immediately characterized spectroscopically.

Conclusion

According to the properties established here, the porphyrin-*o*-quinones present a new, interesting class of compounds for studying electron transfer processes. Although *o*-quinones are often highly unstable, this can be counteracted in porphyrin-*o*-quinones by using sterically demanding substituents. For example, compound **2** showed stability comparable to that of porphyrin-*p*-quinones and thus could be used for initial studies on their ET properties. All porphyrin-*o*-quinones showed the typical quenching of the porphyrin fluorescence by the *o*-quinone fragment. The two porphyrin-*o*-quinones **3** and **5**, without any additional substituents on the quinone fragment, exhibited a much lower stability but could be obtained in their pure form and characterized by NMR spectroscopy. As shown, the steric demand of additional substituents in the quinone fragment should not be too high. Thus, in contrast to our expectations, compound **1** was not a stable porphyrin-*o*-quinone. Instead, the formation of the various oxidation products is mainly a consequence of the photophysical properties of **1** combined with the covalent linkage of the donor and acceptor systems. As formation of a diketone during the oxidation of catechols has not been described under biological conditions, further studies are needed to address the question of whether diketones can also be formed under these conditions from other catechols, e.g. 3,5-di-*tert*-butylcatechol. As this is the first catecholase model reaction not involving additional metal catalysts, further studies are required. In addition, interesting synthetic possibilities reside in the 1,2-dicarbonyl function of the porphyrin-*o*-quinones that might allow the formation of higher porphyrin aggregates. Olefinic diketones like **32** have potential as synthetic building blocks, e.g. for the formation of bis(porphyrins).

Experimental Section

General Remarks: All chemicals used were of analytical grade and were purchased from Aldrich Co. unless stated otherwise. − Melting points were measured with a Büchi melting point apparatus and are uncorrected. − Silica gel 60 (Merck) was used for column chromatography. Analytical thin-layer chromatography (TLC) was carried out using Merck silica gel 60 plates (precoated sheets, 0.2 mm thick, fluorescence indicator F254). − ^{1}H-NMR spectra were recorded at frequencies of 500 MHz (Bruker, AMX 500), ^{13}C-NMR spectra at 126 MHz. All chemical shifts are given in ppm, referenced on the δ scale downfield from the TMS signal. $CDCl_3$ was used as internal standard. − Electronic absorption spectra were recorded with a Specord S10 (Carl Zeiss Jena) spectrophotometer using dichloromethane as solvent. − Mass spectra were recorded with a Varian MAT 711 mass spectrometer using EI technique with a direct insertion probe and, if not otherwise noted, with an excitation energy of 80 eV. − Elemental analyses were performed with a Perkin−Elmer 240 Analyzer. − HPLC Columns:

Nucleosil 50 SiO_2 (5μ), 300 mm × 5 mm i.d. and 107 mm × 32 mm i.d.; HPLC instrumentation: Knauer HPLC pump 64 high pressure, Knauer MPLC pump and variable-wavelength monitor UV/Vis detector from Knauer; all chromatograms were taken at ambient temperature with the detector wavelength fixed at λ = 420 nm.

3,4-Dimethoxy-2,5-dimethylbenzaldehyde (22): To a magnetically stirred solution of the corresponding veratrol, prepared at 0 °C from 3.32 g (20 mmol) of 3,6-dimethylpyrocatechol dimethyl ether[36] in 100 mL of dichloromethane, was added 4.74 g (25 mmol) of titanium(IV) chloride and, dropwise, 3.45 g (30 mmol) of freshly distilled dichloromethyl methyl ether. The reaction mixture was allowed to warm up to room temperature and stirred for 1 h before it was poured into ice/water. Extraction was effected with dichloromethane. The combined organic layers were washed with 5% aqueous $NaHCO_3$ and dried with sodium sulfate. Evaporation of the solvent and vacuum distillation gave 3.5 g (87%) of **22** as a colorless liquid, $b.p._{003}$ 114 °C. − ^1H NMR ($CDCl_3$): δ = 10.11 (1 H, s, −CHO), 7.38 (1 H, s, arom.), 3.89 (3 H, s, −OMe), 3.77 (3 H, s, −OMe), 2.51 (3 H, s, −Me), 2.25 (3 H, s, −Me). − ^{13}C NMR ($CDCl_3$): δ = 191.45, 156.12, 151.19, 132.86, 129.94, 129.69, 129.47, 59.87, 59.72, 15.38, 10.54. − MS (70 eV); *m/z* (%): 195 $[M + 1]^{\bullet+}$ (12), 194 $[M]^{\bullet+}$ (100), 179 $[M - CH_3]^{\bullet+}$ (47), 91 $[C_7H_7]^+$ (17). − HRMS: calcd. for $C_{11}H_{14}O_3$ 194.09430; found 194.09428.

2,5-Di-*tert*-butyl-3,4-dimethoxybenzaldehyde (21): According to the above procedure the aldehyde **21** was obtained as a colorless solid, 2.8 g (52%), m.p. 67−68 °C. For further purification the product was sublimated. − ^1H NMR ($CDCl_3$): δ = 10.65 (1 H, s, −CHO), 7.35 (1 H, s, arom.), 3.87 (3 H, s, −OMe), 3.77 (3 H, s, −OMe), 1.55 (9 H, s, *t*Bu), 1.36 (9 H, s, *t*Bu). − ^{13}C NMR ($CDCl_3$): δ = 193.95, 157.33, 153.53, 142.62, 141.67, 133.01, 122.94, 59.92, 59.53, 37.10, 34.83, 33.58, 30.19. − MS; *m/z* (%): 279 $[M + 1]^{\bullet+}$ (7), 278 $[M]^{\bullet+}$ (37), 263 $[M - CH_3]^{\bullet+}$ (100), 91 $[C_7H_7]^+$ (4), 57 $[C_4H_9]^+$ (14). − HRMS: calcd. for $C_{17}H_{26}O_3$ 278.18820; found 278.18811.

Synthesis of the Porphyrins

General Procedure According to Lindsey Conditions:[12] Pyrrole (0.8 mL, 7.5 mmol), benzaldehyde and 2.5 mmol of a second aldehyde were dissolved in 1 L of CH_2Cl_2 (+ 7.5 mL of anhydrous ethanol) under Ar. Condensation was initiated by addition of 4 mmol of a 25% BF_3−diethyl ether solution in the dark. After stirring for 1 h, the porphyrinogen formed was oxidized with *p*-chloranil followed by stirring for about 12 h. The reaction mixture was neutralized with triethylamine[37] and the product extracted. Purification was achieved by repeated column chromatography on silica gel followed by preparative HPLC.

5-(2,5-Di-*tert*-butyl-3,4-dimethoxyphenyl)-10,15,20-triphenylporphyrin (11): 2,5-Di-*tert*-butyl-3,4-dimethoxybenzaldehyde (**21**) (1.04 g, 3.75 mmol) was treated according to the general procedure. For purification the crude reaction mixture was concentrated after separation of the polypyrrole condensates. Due to the excellent solubility of **11** in *n*-hexane the product was separated almost completely from TPP by extraction in a Soxhlet extractor. Despite a starting material ratio of pyrrole/benzaldehyde/aldehyde **21** = 8:7:1, HPLC/UV coupling detected high molecular mass porphyrins, which were identified as di- and trimeric products by preliminary NMR investigations. The low polarity of the porphyrins made purification of the crude product with preparative HPLC quite difficult. Porphyrin **11** was obtained as purple crystals (4%), m.p. > 330 °C. − HPLC: *n*-hexane/diisopropyl ether = 99:1. − ^1H NMR ($CDCl_3$): δ = 8.82 (4 H, s, β-pyrrole), 8.80 (2 H, d, ^3J = 4.6 Hz, β-pyrrole), 8.75 (2 H, d, ^3J = 4.6 Hz, β-pyrrole), 8.32−8.27 (2 H, m, *o*-phenyl), 8.27−8.22 (1 H, m, *o*-phenyl), 8.19−8.13 (3 H, m, *o*-phenyl), 7.80−7.68 (9 H, m, *m*- and *p*-phenyl), 7.47 (1 H, s, arom.), 4.15 (3 H, s, −OMe), 4.13 (3 H, s, −OMe), 1.35 (9 H, s, *t*Bu), 0.81 (9 H, s, *t*Bu), −2.67 (2 H, s, −NH). − ^{13}C NMR ($CDCl_3$): δ = 153.55, 153.30, 142.86, 142.25, 142.12, 137.07, 134.57, 134.45, 134.37, 134.11, ca. 131, 130.15, 127.62, 126.64, 123.77, 119.92, 119.71, 59.80, 59.52, 37.77, 34.63, 32.59, 30.59. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 420 (5.6), 517 (4.3), 552 (3.8), 592 (3.7), 649 nm (3.6). − MS; *m/z* (%): 787 $[M + 1]^{\bullet+}$ (15), 786 $[M]^{\bullet+}$ (100), 729 $[M - C_4H_9]^{\bullet+}$ (12), 699 $[M - C_5H_{12}]^{\bullet+}$ (4), 671 $[M - C_6H_{13}]^{\bullet+}$ (6), 57 $[C_4H_9]^+$ (11). − HRMS: calcd. for $C_{54}H_{50}O_2N_4$ 786.39338; found 786.39300.

5-(2,5-Dimethyl-3,4-dimethoxyphenyl)-10,15,20-triphenylporphyrin (12): According to the general procedure 0.78 g (4 mmol) of 2,5-dimethyl-3,4-dimethoxybenzaldehyde (**22**) was allowed to react and gave 351 mg (12.4%) of purple crystals, m.p. 204−208 °C. − HPLC: *n*-hexane/ethyl acetate = 94:6. − ^1H NMR ($CDCl_3$): δ = 8.85 (4 H, s, β-pyrrole), 8.84 (2 H, d, ^3J = 4.6 Hz, β-pyrrole), 8.78 (2 H, d, ^3J = 4.6 Hz, β-pyrrole), 8.27−8.22 (3 H, m, *o*-phenyl), 8.22−8.18 (3 H, m, *o*-phenyl), 7.80−7.72 (9 H, m, *m*- and *p*-phenyl), 7.63 (1 H, q, ^4J = 1.9 Hz, arom.), 4.17 (3 H, s, −OMe), 4.08 (3 H, s, −OMe), 2.48 (3 H, s, −Me), 1.92 (3 H, s, −Me), −2.75 (2 H, s, −NH). − ^{13}C NMR ($CDCl_3$): δ = 151.39, 150.51, 142.19, 142.06, 137.50, 134.54, 134.51, 134.46, 132.02, 131.72, ca. 131, 127.68, 127.23, 126.67, 120.11, 119.95, 118.71, 60.52, 60.50, 15.94, 14.55 . − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 418 (5.61), 514 (4.24), 548 (3.84), 589 (3.74), 645 nm (3.57). − MS: *m/z* (%): 703 $[M + 1]^{\bullet+}$ (54), 702 $[M]^{\bullet+}$ (100), 687 $[M - CH_3]^{\bullet+}$ (8), 672 $[M - 2CH_3]^{\bullet+}$ (8), 657 $[M - 3\,CH_3]^{\bullet+}$ (8), 644 $[M - 4\,CH_3]^{\bullet+}$ (3). − HRMS: calcd. for $C_{48}H_{38}O_2N_4$ 702.29948; found 702.29870.

5-(3,4-Dimethoxyphenyl)-10,15,20-triphenylporphyrin (13): As described above, 0.42 g (2.5 mmol) of 3,4-dimethoxybenzaldehyde (Fluka) was condensed with pyrrole and benzaldehyde to give the porphyrin. − Yield: 189 mg (11%) of purple crystals, m.p. > 330 °C. − ^1H NMR ($CDCl_3$): δ = 8.97 (2 H, d, ^3J = 4.5 Hz, β-pyrrole), 8.94−8.87 (6 H, AB, β-pyrrole), 8.30−8.27 (3 H, m, *o*-phenyl), 8.27−8.25 (3 H, m, *o*-phenyl), 7.85 (1 H, d, ^4J = 2.0 Hz, arom.), 7.84−7.76 (9 H, m, *m*- and *p*-phenyl), 7.76 (1 H, dd, arom.), 7.25 (1 H, d, ^3J = 8.5 Hz, arom.), 4.18 (3 H, s, −OMe), 4.03 (3 H, s, −OMe), −2.70 (2 H, s, −NH). − ^{13}C NMR ($CDCl_3$): δ = 148.89, 147.08, 142.17, 134.80, 134.53, ca. 131, 127.69, 127.44, 126.67, 120.13, 120.09, 119.93, 118.34, 109.45, 56.12. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 417 (5.59), 514 (4.26), 548 (3.84), 589 (3.73), 646 nm (3.60). − MS; *m/z* (%): 675 $[M + 1]^{\bullet+}$ (50), 674 $[M]^{\bullet+}$ (100), 659 $[M - CH_3]^{\bullet+}$ (7), 614 $[M - C_2H_6O_2]^{\bullet+}$ (12), 337 $[M]^{\bullet++}$ (4). − HRMS: calcd. for $C_{46}H_{34}O_2N_4$ 674.26818; found 674.26835.

5-(2,3-Dimethoxy-4-methylphenyl)-10,15,20-triphenylporphyrin (14): 0.45 g (2.5 mmol) of 2,3-Dimethoxy-4-methylbenzaldehyde[38] was allowed to react to give porphyrin **14**. − Yield: 190 mg (11%) of purple crystals, m.p. 308−310 °C. − HPLC: *n*-hexane/ethyl acetate = 92:8. − ^1H NMR ($CDCl_3$): δ = 9.08 (2 H, AB, β-pyrrole), 9.06 (6 H, s, β-pyrrole), 8.48−8.40 (3 H, m, *o*-phenyl), 8.40−8.32 (3 H, m, *o*-phenyl), 7.94−7.81 (9 H, m, *m*- and *p*-phenyl), 7.80 (1 H, d, ^3J = 7.8 Hz, arom.), 7.35 (1 H, d, ^3J = 7.8 Hz, arom.), 4.24 (3 H, s, −OMe), 3.41 (3 H, s, −OMe), 2.74 (3 H, s, −Me), −2.49 (2 H, s, −NH). − ^{13}C NMR ($CDCl_3$): δ = 153.36, 150.97, 142.20, 142.13, 134.56, 134.52, 134.48, 134.29, 132.93, ca. 131.1, 130.48, 127.68, 126.66, 124.03, 120.33, 120.00, 115.66, 60.81, 60.57, 16.36. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 417 (5.52), 514 (4.18), 549 (3.80), 589 (3.69), 645 nm (3.49). − MS: *m/z* (%): 689 $[M + 1]^{\bullet+}$ (53), 688 $[M]^{\bullet+}$ (100), 673 $[M - CH_3]^{\bullet+}$ (6), 658 $[M - 2\,CH_3]^{\bullet+}$ (5), 344

$[M]^{\bullet+\,+}$ (10). − HRMS: calcd. for $C_{47}H_{36}O_2N_4$ 688.28383; found 688.28403.

5-(2,3-Dimethoxyphenyl)-10,15,20-triphenylporphyrin (15): 0.42 g (2.5 mmol) of 2,3-Dimethoxybenzaldehyde was treated with pyrrole and benzaldehyde following the general procedure. − Yield: 136 mg (8%) of purple crystals, m.p. > 330 °C. − HPLC: dichloromethane. − ^{1}H NMR ($CDCl_3$): δ = 8.98 (2 H, d, β-pyrrole), 8.97 (6 H, s, β-pyrrole), 8.39−8.35 (2 H, m, *o*-phenyl), 8.34 (1 H, m, *o*-phenyl), 8.32 (1 H, m, *o*-phenyl), 8.32−8.27 (2 H, m, *o*-phenyl), 7.88−7.78 (9 H, m, *m*- and *p*-phenyl), 7.77 (1 H, dd, ^3J = 7.5 Hz, ^4J = 1.5 Hz, arom.), 7.43 (1 H, dd, ^3J = 8.3 Hz, ^3J = 7.5 Hz, arom.), 7.37 (1 H, dd, ^3J = 8.3 Hz, ^4J = 1.5 Hz, arom.), 4.14 (3 H, s, −OMe), 3.31 (3 H, s, −OMe), −2.59 (2 H, s, −NH). − ^{13}C NMR ($CDCl_3$): δ = 152.46, 149.66, 142.27, 142.19, 136.35, 134.56, ca. 131, 128.02, 127.68, 126.67, 122.05, 120.34, 120.03, 115.49, 112.67, 60.83, 56.04. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 417 (5.64), 513 (4.30), 547 (3.85), 589 (3.76), 645 nm (3.57). − MS; *m*/*z* (%): 675 $[M + 1]^{\bullet+}$ (50), 674 $[M]^{\bullet+}$ (100), 659 $[M - CH_3]^{\bullet+}$ (6), 337 $[M]^{\bullet+\,+}$ (6). − HRMS: calcd. for $C_{46}H_{34}O_2N_4$ 674.26818; found 674.26834.

Demethylation of the Dimethoxyporphyrins

General Procedure: For demethylation 0.1 mmol of the porphyrin was dissolved in 50 mL of dichloromethane and treated dropwise (1 h) under Ar at −80 °C under vigorous stirring with 15 mL of BBr_3. The reaction mixture was warmed to room temperature, poured onto ice and adjusted to pH = 7.0 with $NaHCO_3$. The combined dichloromethane extracts were dried with Na_2SO_4 and purified as described below.

3,6-Di-*tert*-butyl-4-(10,15,20-triphenylporphyrin-5-yl)-1,2-benzoquinone (1): For synthesis of the porphyrin-*o*-quinone **1** 79 mg of the protected porphyrin pyrocatechol **11** was demethylated as described above. After warming the reaction mixture to room temperature, stirring was continued under Ar for 12 h. The initially formed catechol was oxidized by atmospheric oxygen during the column chromatographic workup (silica; *n*-hexane/CH_2Cl_2 = 1:4, v/v). During workup two additional porphyrins were formed, a substituted muconic anhydride **33** and an olefinic 1,4-diketone **32**. In contrast to **1**, both porphyrins **32** and **33** are stable to light and air. Due to this phenomenon, only the decomposition products **32** and **33** could be separated in pure form by preparative HPLC. Depending on the conditions (air, light) the *o*-quinone **1** formed and slowly decomposed. The relative composition of the reaction mixture was determined by ^{1}H-NMR spectroscopy directly after column chromatography and found to be: muconic acid anhydride **33**/*o*-quinone **1**/1,4-diketone **32** = 1:13:3.7. For purification of **1** the reaction components were first converted into the respective zinc(II) complexes and the stable zinc(II) complex **6** of the *o*-quinone **1** was separated. Then 50 mg of **6** was dissolved in 10 mL of degassed deuteriochloroform[39] and stirred for 1 h with 1 mL of HCl (20%) under Ar and with exclusion of light. The reaction mixture was neutralized under Ar with a saturated solution of sodium hydrogen carbonate. The organic phase was separated and dried with Na_2SO_4. Subsequently, the solution was used for NMR studies. Both NMR and HPLC/UV coupling showed only one product. The complete workup must be performed in the dark. − HPLC: *n*-hexane/diisopropyl ether = 97:3.

3,6-Di-*tert*-butyl-4-(10,15,20-triphenylporphyrin-5-yl)-1,2-benzoquinone (1): Reddish brown crystals, m.p. 78−81 °C (dec.) − ^{1}H NMR ($CDCl_3$): δ = 9.22 (2 H, d, ^3J = 4.5 Hz, β-pyrrole), 8.97 (2 H, d, ^3J = 4.5 Hz, β-pyrrole), 8.84 (4 H, s, β-pyrrole), 8.33−8.28 (2 H, m, *o*-phenyl), 8.26−8.22 (1 H, m, *o*-phenyl), 8.17−8.11 (3 H, m, *o*-phenyl), 7.83−7.71 (9 H, m, *m*- and *p*-phenyl), 7.47 (1 H, s, quinoid), 1.19 (9 H, s, *t*Bu), 0.78 (9 H, s, *t*Bu), −2.68 (2 H, s, −NH). − ^{13}C NMR ($CDCl_3$): δ = 185.24, 181.71, 148.98, 147.90, 143.42, 142.66, 141.83, 141.58, 134.52, 134.44, 134.35, 127.95, 127.89, 126.83, 126.80, 126.74, 121.09, 120.64, 117.73, 37.88, 34.72, 31.17, 29.11. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 416 (5.41), 516 (4.15), 550 (3.87), 595 (3.84), 652 nm (3.67). − MS; *m*/*z* (%): 759 $[M + 2H + 1]^{\bullet+}$ (17), 758 $[M + 2H]^{\bullet+}$ (29), 728 $[M - 2CH_3]^{\bullet+}$ (7), 716 $[M - C_3H_6]^{\bullet+}$ (9), 700 $[M + 2H - C_4H_8]^{\bullet+\,+}$ (41), 644 $[M + 2H - 2C_4H_8]^{\bullet+\,+}$ (68), 157 (100). − HRMS: calcd. for $C_{52}H_{46}O_2N_4$ 758.36208; found 758.36227 as pyrocatechol.

(*E*)-2,2,7,7-Tetramethyl-4-(10,15,20-triphenylporphyrin-5-yl)-oct-4-ene-3,6-dione (32): Purple crystals, m.p. 248−250 °C − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.59 (2 H, d, ^3J = 4.8 Hz, β-pyrrole), 8.92 (2 H, d, ^3J = 4.8 Hz, β-pyrrole), 8.83 (4 H, AB, ^3J = 4.6 Hz, β-pyrrole), 8.40−8.34 (2 H, m, *o*-phenyl), 8.34−8.28 (1 H, m, *o*-phenyl), 8.09−8.01 (3 H, m, *o*-phenyl), 7.84−7.68 (9 H, m, *m*- and *p*-phenyl), 7.50 (1 H, s, olef.), 1.44 (9 H, s, *t*Bu), 0.85 (9 H, s, *t*Bu), −2.79 (2 H, s, −NH). − ^{13}C NMR ($CDCl_3$): δ = 213.42, 205.39, 156.85, 141.91, 141.62, 135.72, 134.46, 127.90, 126.78, 126.73, 126.70, 121.51, 120.83, 113.05, 45.67, 43.71, 27.08, 26.33. − UV/Vis (CH_2Cl_2): λ_{max} (rel. int.) = 423 (1.000), 520 (0.050), 557 (0.032), 595 (0.018), 650 nm (0.017). − MS; *m*/*z* (%): 733 $[M + 1]^{\bullet+}$ (15), 732 $[M]^{\bullet+}$ (27), 716 $[M - O]^{\bullet+}$ (100), 676 $[M - C_4H_8]^{\bullet+}$ (75), 647 $[M - C_4H_9 - CO]^{\bullet+}$ (32), 563 (81). − HRMS: calcd. for $C_{50}H_{44}O_2N_4$ 732.34643; found 732.34621.

3,6-Di-*tert*-butyl-4-(10,15,20-triphenylporphyrin-5-yl)-2,7-dihydrooxepin-2,7-dione (33): Purple crystals, m.p. 260−262 °C − ^{1}H NMR ($CDCl_3$): δ = 9.12 (2 H, br. s, β-pyrrole), 8.95 (2 H, d, ^3J = 4.4 Hz, β-pyrrole), 8.84 (4 H, s, β-pyrrole), 8.35−8.29 (2 H, m, *o*-phenyl), 8.29−8.25 (1 H, m, *o*-phenyl), 8.14−8.08 (3 H, m, *o*-phenyl), 7.83−7.70 (9 H, m, *m*- and *p*-phenyl), 7.17 (1 H, s, arom.), 1.21 (9 H, s, *t*Bu), 0.79 (9 H, s, *t*Bu), −2.79 (2 H, s, −NH). − ^{13}C NMR ($CDCl_3$): δ = 163.84, 162.28, 147.24, 141.84, 141.59, 141.46, 136.78, 134.55, 134.47, 134.33, 127.92, 127.87, 126.80, 126.72, 121.24, 120.57, 112.69, 37.58, 36.15, 30.45, 28.99. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 419 (5.52), 515 (4.14), 550 (3.72), 590 (3.62), 646 nm (3.39). − MS; *m*/*z* (%): 773 $[M + 1]^{\bullet+}$ (56), 772 $[M]^{\bullet+}$ (100), 728 $[M - C_2H_4O]^{\bullet+}$ (51), 716 $[M - C_4H_8]^{\bullet+}$ (49), 671 $[M - C_4H_9 - C_2H_4O]^{\bullet+}$ (94), 656 (55), 84 (52). − HRMS: calcd. for $C_{52}H_{44}O_3N_4$ 772.34134; found 772.34160.

3,6-Dimethyl-4-(10,15,20-triphenylporphyrin-5-yl)-1,2-benzoquinone (2): The dimethoxyporphyrin **12** (67 mg) was treated according to the general procedure. For complete oxidation the dried (Na_2SO_4) solution was stirred for 20 min with 500 mg of PbO_2.[40] − Yield: 37 mg (58%) of reddish brown crystals, m.p. 310−312 °C (dec.). − HPLC: *n*-hexane/diisopropyl ether = 85:15. − ^{1}H NMR ($CDCl_3$): δ = 9.23 (2 H, d, ^3J = 4.6 Hz, β-pyrrole), 9.00 (2 H, d, ^3J = 4.6 Hz, β-pyrrole), 8.87 (4 H, s, β-pyrrole), 8.29−8.25 (2 H, m, *o*-phenyl), 8.25−8.22 (1 H, m, *o*-phenyl), 8.22−8.16 (3 H, m, *o*-phenyl), 7.84−7.73 (9 H, m, *m*- and *p*-phenyl), 7.66 (1 H, q, ^4J = 1.8 Hz, quinoid), 2.15 (3 H, s, −Me), 1.82 (3 H, s, −Me), −2.68 (2 H, s, −NH). − ^{13}C NMR ($CDCl_3$): δ = 182.12, 181.03, 149.71, 142.56, 141.76, 141.56, 137.56, 134.48, 134.41, 132.79, ca. 131.6, 127.97, 127.92, 126.84, 126.80, 126.74, 121.58, 120.80, 113.71, 15.35, 14.45. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 414 (5.53), 512 (4.19), 550 (3.80), 593 (3.81), 654 nm (3.57). − MS; *m*/*z* (%): 675 $[M + 2H + 1]^{\bullet+}$ (47), 674 $[M + 2H]^{\bullet+}$ (100), 658 $[M - O]^{\bullet+}$ (4), 328 (7), 149 (93). − HRMS: calcd. for $C_{52}H_{44}O_3N_4$ 674.268177; found 674.268177.

3-Methyl-6-(10,15,20-triphenylporphyrin-5-yl)-1,2-benzoquinone (4): According to the general procedure 69 mg of the dimethoxy compound **14** was demethylated. After oxidation with 500 mg of active

PbO_2 and purification by column chromatography and preparative HPLC, the substituted 3-methyl-*o*-quinone **4** was obtained as red brown crystals. − Yield: 28 mg (43%), m.p. 293 °C (dec.). − HPLC: *n*-hexane/ethyl acetate = 88:12. − ^{1}H NMR ($CDCl_3$): δ = 8.98 (2 H, d, ^3J = 4.4 Hz, β-pyrrole), 8.87 (2 H, d, ^3J = 4.4 Hz, β-pyrrole), 8.82 (4 H, AB, ^3J = 4.5 Hz, β-pyrrole), 8.22−8.15 (6 H, m, *o*-phenyl), 7.78−7.68 (9 H, m, *m*- and *p*-phenyl), 7.50 (1 H, d, ^3J = 6.3 Hz, quinoid), 7.07 (1 H, dq, ^3J = 6.3 Hz, ^4J = 1.7 Hz, quinoid), 2.21 (3 H, s, −Me), −2.80 (2 H, s, −NH). − ^{13}C NMR ($CDCl_3$): δ = 181.07, 180.97, 142.54, 141.88, 141.85, 141.23, 140.66, 136.05, 134.55, 134.48, ca. 131.2, 129.3, 127.78, 126.78, 126.70, 126.63, 121.33, 120.55, 109.82, 15.93. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 416 (5.48), 512 (4.28), 545 (3.81), 589 (3.76), 646 nm (3.49). − MS; *m*/*z* (%): 661 [M + 2 H + 1]$^{\bullet+}$ (49), 660 [M + 2 H]$^{\bullet+}$ (100), 659 [M + 1]$^{\bullet+}$ (47), 658 [M]$^{\bullet+}$ (54), 330 [M]$^{\bullet++}$ (7), 156 (32). − HRMS: calcd. for $C_{45}H_{30}O_2N_4$ 658.23688; found 658.23624.

3-(10,15,20-Triphenylporphyrin-5-yl)-1,2-benzoquinone (5): For synthesis of the porphyrin-*o*-quinone 134 mg of the dimethoxy compound **15** was demethylated. As unsubstituted porphyrin-*o*-quinones are unstable compounds for characterization, the analogous porphyrin catechols were first isolated and analyzed spectroscopically. This is a purple, stable compound. Purification was achieved by column chromatography (dichloromethane/methanol = 20:1, v/v). The relatively low yield can be explained by formation of other polar products, which were not characterized further. The NMR studies on the catechol were performed in a sealed (Ar) NMR tube. Subsequently, the catechol formed was treated with Ag^{I} oxide in the NMR solvent according to the general procedure. Addition of water-free Na_2SO_4 ensured complete reaction. Column chromatographic purification (silica, CH_2Cl_2) was possible only on a small scale using a cooled column. NMR studies were performed at −20 °C.

5-(2,3-Dihydroxyphenyl)-10,15,20-triphenylporphyrin (25): HPLC: dichloromethane/ethyl acetate = 96:4. − Yield: 36 mg (28%), m.p. > 330 °C. − ^{1}H NMR ($CDCl_3$): δ = 8.86 (8 H, 2 AB, β-pyrrole), 8.24−8.17 (6 H, m, *o*-phenyl), 7.82−7.72 (9 H, m, *m*- and *p*-phenyl), 7.55 (1 H, dd, ^3J = 7.5 Hz, ^4J = 1.5 Hz, arom.), 7.25 (1 H, dd, ^3J = 8.3 Hz, ^4J = 1.5 Hz, arom.), 7.18 (1 H, dd, ^3J = 8.3 Hz, ^3J = 7.5 Hz, arom.), −2.81 (2 H, s, −NH). − ^{13}C NMR ($CDCl_3$): δ = 143.79, 143.23, 141.93, 141.76, 134.57, 134.55, 134.52, 131.5, 131.2, 128.09, 127.84, 126.75, 126.71, 121.10, 120.49, 119.62, 115.57, 111.31. − UV/Vis (CH_2Cl_2): λ_{max} (rel. int.) = 417 (1.000), 513 (0.053), 548 (0.021), 589 (0.017), 645 nm (0.013). − MS; *m*/*z* (%): 647 [M + 1]$^{\bullet+}$ (48), 646 [M]$^{\bullet+}$ (100), 323 [M]$^{\bullet++}$ (12), 86 (44). − HRMS: calcd. for $C_{44}H_{30}O_2N_4$ 646.23688; found 646.23632.

3-(10,15,20-Triphenylporphyrin-5-yl)-1,2-benzoquinone (5): Brown crystals, m.p. 230−235 °C (dec.). − ^{1}H NMR ($CDCl_3$): δ = 8.94 (2 H, d, ^3J = 4.6 Hz, β-pyrrole), 8.83 (2 H, d, ^3J = 4.6 Hz, β-pyrrole), 8.76 (4 H, AB, ^3J = 4.4 Hz, β-pyrrole), 8.17−8.09 (6 H, m, *o*-phenyl), 7.74−7.65 (9H, m, *m*- and *p*-phenyl), 7.75 (1 H, d, quinoid), 7.58 (1 H, dd, ^3J = 10.2 Hz, ^3J = 6.1 Hz, quinoid), 6.87 (1 H, dd, ^3J = 10.2 Hz, ^3J = 1.5 Hz, quinoid), −2.87 (2 H, s, −NH). − ^{13}C NMR ($CDCl_3$): δ = 180.93, 180.62, 144.15, 141.84, 141.79, 141.27, 140.35, 134.57, 134.49, 131.17, 127.83, 126.80, 126.66, 121.12, 120.68, 109.50. − UV/Vis (CH_2Cl_2): λ_{max} (rel. int.) = 417 (1.000), 512 (0.052), 544 (0.023), 589 (0.019), 649 nm (0.015).

4-(10,15,20-Triphenylporphyrin-5-yl)-1,2-benzoquinone (3): As described for **5** 134 mg of **13** was demethylated with BBr_3 followed by a similar purification procedure. The porphyrin pyrocatechol **24** is an extremly air-sensitive substance. NMR investigations were possible only under Ar in sealed tubes. Compound **38** was oxidized with 500 mg of Ag^{I} oxide for 3 d at −20 °C to the unsubstituted porphyrin-*o*-quinone **3**; water formed during the reaction was bound with Na_2SO_4. After an initial purification step (silica, CH_2Cl_2) the porphyrin was purified by preparative HPLC. In solid form the *o*-quinone is stable at room temperature, while a solution in dichloromethane can be stored at −20 °C for several weeks.

5-(3,4-Dihydroxyphenyl)-10,15,20-triphenylporphyrin (24): HPLC: *n*-hexane/ethyl acetate = 88:12. − Yield: 59 mg (46%) of purple crystals, m.p. > 330 °C. − ^{1}H NMR ([D]$_6$acetone): δ = 9.01 (2 H, d, β-pyrrole), 8.84 (6 H, s, β-pyrrole), 8.26−8.21 (6 H, m, *o*-phenyl), 7.86−7.78 (9 H, m, *m*- and *p*-phenyl), 7.74 (1 H, d, ^4J = 2.2 Hz, arom.), 7.56 (1 H, dd, ^3J = 8.2 Hz, ^4J = 2.2 Hz, arom.), 7.26 (1 H, d, ^3J = 8.2 Hz, arom.), −2.74 (2 H, s, −NH). − ^{13}C NMR ([D]$_6$acetone): δ = 146.15, 144.22, 142.74, 142.71, 135.10, 135.03, 134.94, 134.21, 131.2, 130.9, 128.62, 127.54, 122.83, 121.45, 120.75, 120.59, 114.46. − UV/Vis (CH_2Cl_2): λ_{max} (rel. int.) = 418 (1.000), 515 (0.043), 550 (0.020), 588 (0.015), 647 nm (0.011). − MS; *m*/*z* (%): 647 [M + 1]$^{\bullet+}$ (48), 646 [M]$^{\bullet+}$ (100), 323 [M]$^{\bullet++}$ (7), 110 (4). − HRMS: calcd. for $C_{44}H_{30}O_2N_4$ 646.23688; found 646.23691.

4-(10,15,20-Triphenylporphyrin-5-yl)-1,2-benzoquinone (3): HPLC: *n*-hexane/ethyl acetate = 92:8. − M.p. 295−300 °C (dec.). − ^{1}H NMR ($CDCl_3$): δ = 9.22 (2 H, d, ^3J = 4.8 Hz, β-pyrrole), 8.95 (2 H, d, ^3J = 4.8 Hz, β-pyrrole), 8.81 (4 H, s, β-pyrrole), 8.22−8.16 (6 H, m, *o*-phenyl), 8.09 (1 H, dd, ^3J = 10.0 Hz, ^4J = 2.0 Hz, quinoid), 7.82−7.70 (9 H, m, *m*- and *p*-phenyl), 7.14 (1 H, d, ^4J = 2.0 Hz, quinoid), 6.61 (1 H, d, ^3J = 10.0 Hz, quinoid), −2.59 (2 H, s, −NH). − ^{13}C NMR ($CDCl_3$): δ = 180.23, 179.86, 153.35, 145.36, 141.57, 140.66, 134.49, 133.38, 131.6, 128.6, 128.06, 126.86, 126.80, 126.10, 122.36, 121.52, 113.24. − UV/Vis (CH_2Cl_2): λ_{max} (rel. int.) = 415 (1.000), 512 (0.049), 544 (0.023), 591 (0.020), 651 nm (0.015). − MS; *m*/*z* (%): 647 [M + 2 H + 1]$^{\bullet+}$ (33), 646 [M + 2 H]$^{\bullet+}$ (63), 644 [M]$^{\bullet+}$ (13.8), 628 [M − O]$^{\bullet+}$ (7), 323 [M]$^{\bullet++}$ (9), 247 (16), 157 (100), 91 [C_7H_7]$^+$ (60).

Preparation of the (Porphyrinato)zinc(II) Complexes

General Procedure: In all dimethoxy-protected porphyrin pyrocatechols and in the porphyrin-quinone **1**, insertion of zinc(II) was achieved by Method A. Free base porphyrins with more than one proton on the quinone fragment were converted into the metalloporphyrins by Method B.

Insertion of Zinc with Zinc(II) Acetate (Method A): For preparation of the zinc(II) complexes 0.05 mmol of the free base porphyrins was dissolved in 20 mL of dried dichloromethane and treated with 10 mL of a saturated solution of zinc(II) acetate. After 60 min, excess zinc acetate and acetic acid were extracted with water. After drying with Na_2SO_4, the solvent was removed in vacuo and the product purified by column chromatography and HPLC. The reaction is quantitative.

Insertion of Zinc with Zinc(II) Oxide and Trifluoroacetic Acid (Method B): In this case 0.05 mmol of the free base porphyrins was dissolved in 20 mL of dried dichloromethane and treated with 200 mg of zinc oxide. After the addition of 4 drops of TFA, the reaction mixture turned green. A color change back to red indicated completion of the reaction. The product was separated from ZnO and most of the TFA by filtration through a short silica column. Further purification was performed according to Method A.

{5-(2,5-Di-*tert*-butyl-3,4-dimethoxyphenyl)-10,15,20-triphenylporphyrinato}zinc(II) (16): Using Method A 39 mg of the free base **11** was converted into the zinc(II) complex. − HPLC: dichlorome-

thane/*n*-hexane = 70:30. Purple crystals, m.p. > 330 °C. − ^{1}H NMR ($CDCl_3$): δ = 8.92 (4 H, AB, ^3J = 4.6 Hz, β-pyrrole), 8.89 (2 H, d, ^3J = 4.7 Hz, β-pyrrole), 8.85 (2 H, d, ^3J = 4.7 Hz, β-pyrrole), 8.33−8.29 (2 H, m, *o*-phenyl), 8.28−8.25 (1 H, m, *o*-phenyl), 8.19−8.13 (3 H, m, *o*-phenyl), 7.78−7.69 (9 H, m, *m*- and *p*-phenyl), 7.59 (1 H, s, arom.), 4.14 (3 H, s, −OMe), 4.13 (3 H, s, −OMe), 1.39 (9 H, s, *t*Bu), 0.72 (9 H, s, *t*Bu). − ^{13}C NMR ($CDCl_3$): δ = 153.50, 153.19, 151.26, 150.08, 150.00, 149.99, 142.88, 142.83, 142.81, 136.92, 134.78, 134.50, 134.45, 134.36, 134.28, 132.16, 131.82, 131.72, 129.83, 127.42, 126.52, 126.50, 124.64, 120.96, 120.76, 59.80, 59.54, 37.73, 34.67, 32.38, 30.69. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 422 (5.59), 513 (3.41), 551 (4.27), 591 nm (3.50). − MS; *m*/*z* (%): 850 [M + 2]$^{\bullet+}$ (83), 849 [M + 1]$^{\bullet+}$ (73), 848 [M]$^{\bullet+}$ (100), 791 [M − Zn]$^{\bullet+}$ (6), 57 [C_4H_9]$^+$ (9). − HRMS: calcd. for $C_{54}H_{48}O_2N_4Zn$ 848.30687; found 848.30662.

{5-(2,5-Dimethyl-3,4-dimethoxyphenyl)-10,15,20-triphenylporphyrinato}zinc(II) (17): Free base porphyrin **12** (35 mg) was treated according to Method A and yielded the zinc(II) complex as red-purple crystals. − HPLC: *n*-hexane/ethyl acetate = 92:8, m.p. > 330 °C. − ^{1}H NMR ($CDCl_3$): δ = 8.92 (4 H, AB, β-pyrrole), 8.90 (2 H, d, ^3J = 4.7 Hz, β-pyrrole), 8.84 (2 H, d, ^3J = 4.7 Hz, β-pyrrole), 8.25−8.17 (6 H, m, *o*-phenyl), 7.78−7.70 (9 H, m, *m*- and *p*-phenyl), 7.60 (1 H, q, ^4J = 1.9 Hz, arom.), 4.14 (3 H, s, −OMe), 4.06 (3 H, s, −OMe), 2.44 (3 H, s, −Me), 1.89 (3 H, s, −Me). − ^{13}C NMR ($CDCl_3$): δ = 151.19, 150.42, 150.22, 150.16, 150.14, 150.12, 142.80, 142.75, 138.14, 134.43, 134.37, 132.11, 131.91, 131.83, 131.65, 131.55, 127.45, 127.04, 126.52, 120.10, 120.94, 119.73, 60.51, 60.49, 15.92, 14.63. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 419 (5.69), 510 (3.46), 548 (4.32), 584 nm (3.52). − MS; *m*/*z* (%): 766 [M + 2]$^{\bullet+}$ (73), 765 [M + 1]$^{\bullet+}$ (59), 764 [M]$^{\bullet+}$ (100), 749 [M − CH_3]$^{\bullet+}$ (6), 719 [M − 3 CH_3]$^{\bullet+}$ (10), 662 (20), 530 (23), 382 (9), 57 (45). − HRMS: calcd. for $C_{48}H_{36}O_2N_4Zn$ 764.21297; found 764.21557.

{5-(3,4-Dimethoxyphenyl)-10,15,20-triphenylporphyrinato}zinc(II) (18): The zinc(II) complex was prepared using 34 mg of the dimethoxyporphyrin **13** and following Method A. HPLC: *n*-hexane/ethyl acetate = 84:16. Purple crystals, m.p. > 330 °C. − ^{1}H NMR ($CDCl_3$): δ = 8.92 (2 H, AB, ^3J = 4.7 Hz, β-pyrrole), 8.89−84 (6 H, AB, s, β-pyrrole), 8.16−8.10 (6 H, m, *o*-phenyl), 7.72 (1 H, d, ^3J = 2.0 Hz, arom.), 7.70−7.62 (9 H, m, *m*- and *p*-phenyl), 7.69 (1 H, arom.), 7.13 (1 H, d, ^3J = 8.1 Hz, arom.), 4.06 (3 H, s, −OMe), 3.87 (3 H, s, −OMe). − ^{13}C NMR ($CDCl_3$): δ = 150.44, 150.18, 150.15, 148.55, 146.80, 142.75, 135.36, 134.38, 131.98, 127.47, 127.16, 126.53, 121.12, 121.10, 120.88, 118.09, 109.23, 56.08, 56.04. − UV/Vis (CH_2Cl_2): λ_{max} (rel. int.) = 420 (1.000), 511 (0.008), 547 (0.050), 586 nm (0.010). − MS; *m*/*z* (%): 738 [M + 2]$^{\bullet+}$ (72), 737 [M + 1]$^{\bullet+}$ (51), 736 [M]$^{\bullet+}$ (100), 721 [M − CH_3]$^{\bullet+}$ (5), 368 [M]$^{\bullet++}$ (8). − HRMS: calcd. for $C_{46}H_{32}O_2N_4Zn$ 736.18167; found 736.18153.

{5-(2,3-Dimethoxy-4-methylphenyl)-10,15,20-triphenylporphyrinato}zinc(II) (19): The substituted dimethoxyporphyrin (34 mg) was treated with zinc(II) acetate according to Method A. − HPLC: *n*-hexane/ethyl acetate = 90:10. Red-purple crystals, m.p. > 330 °C. − ^{1}H NMR ($CDCl_3$): δ = 8.95 (8 H, AB, β-pyrrole), 8.26−8.21 (3 H, m, *o*-phenyl), 8.21−8.17 (3 H, m, *o*-phenyl), 7.75−7.66 (9 H, m, *m*- and *p*-phenyl), 7.76 (1 H, d, arom.), 7.20 (1 H, d, ^3J = 7.6 Hz, arom.), 4.01 (3 H, s, −OMe), 3.20 (3 H, s, −OMe), 2.55 (3 H, s, −Me). − ^{13}C NMR ($CDCl_3$): δ = 153.29, 150.81, 150.45, 150.22, 150.19, 150.06, 142.80, 134.82, 134.42, 134.40, 132.65, 132.23, 131.95, 131.91, 131.67, 130.25, 127.46, 126.52, 123.84, 121.27, 121.03, 116.57, 60.76, 60.47, 16.30. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 419 (5.76), 511 (3.46), 547 (4.34), 585 nm (3.52). − MS; *m*/*z* (%): 752 [M + 2]$^{\bullet+}$ (1), 751 [M + 1]$^{\bullet+}$ (1), 750 [M]$^{\bullet+}$ (1), 44 [C_2H_4O]$^+$ (100). − HRMS: calcd. for $C_{47}H_{34}O_2N_4Zn$ 750.19732; found 750.19744.

{5-(2,3-Dimethoxyphenyl)-10,15,20-triphenylporphyrinato}zinc(II) (20): Free base **15** (34 mg) was treated according to Method A and gave red-purple crystals. − HPLC: *n*-hexane/ethyl acetate = 85:15. − M.p. > 330 °C. − ^{1}H NMR ($CDCl_3$): δ = 8.95, 8.92 (8 H, AB, β-pyrrole), 8.28−8.18 (6 H, m, *o*-phenyl), 7.80−7.71 (9 H, m, *m*- and *p*-phenyl), 7.67 (1 H, dd, ^3J = 7.5 Hz, ^4J = 1.5 Hz, arom.), 7.38 (1 H, dd, ^3J = 8.4 Hz, ^3J = 7.5 Hz, arom.), 7.32 (1 H, dd, ^3J = 8.4 Hz, ^4J = 1.5 Hz, arom.), 4.09 (3 H, s, −OMe), 3.21 (3 H, s, −OMe). − ^{13}C NMR ($CDCl_3$): δ = 152.20, 150.24, 150.16, 149.98, 149.46, 142.85, 142.81, 136.88, 134.45, 134.42, 132.16, 131.92, 131.84, 131.66, 127.86, 127.41, 126.50, 121.92, 121.24, 120.96, 116.25, 112.44, 60.80, 56.02. − UV/Vis (CH_2Cl_2): λ_{max} (rel. int.) = 419 (1.000), 511 (0.006), 547 (0.039), 584 nm (0.007). − MS; *m*/*z* (%): 738 [M + 2]$^{\bullet+}$ (68), 737 [M + 1]$^{\bullet+}$ (50), 736 [M]$^{\bullet+}$ (100), 721 [M − CH_3]$^{\bullet+}$ (7). − HRMS: calcd. for $C_{46}H_{32}O_2N_4Zn$ 736.18167; found 736.18196.

Synthesis of the Zinc(II) Complexes of the Demethylation Products of 11: For preparation of larger amounts of the zinc(II) complexes of the *tert*-butylated porphyrin-*o*-quinone **1** and its decomposition products **32** and **33**, the mixture resulting from the demethylation of **11** was treated with zinc(II) acetate according to Method A. As all products were stable compounds, the individual zinc(II) complexes could be separated from each other by HPLC. − The zinc(II) complexes could also be prepared from the individual free base porphyrins. During metallation of the diketone **32** two different metal complexes [the (*E*) and (*Z*) stereoisomers] were formed (1:3.2 ratio). The (*Z*) isomer **43** could be obtained in its pure form by treating the mixture with light for 2 d.[41] HPLC: *n*-hexane/ethyl acetate = 90:10.

{5-(3,6-Di-*tert*-butyl-1,2-dioxocyclohexa-3,5-dien-4-yl)-10,15,20-triphenylporphyrinato}zinc(II) (6): Reddish brown crystals, m.p. 183−185 °C. − ^{1}H NMR ($CDCl_3$): δ = 9.30 (2 H, d, ^3J = 4.5 Hz, β-pyrrole), 9.05 (2 H, d, ^3J = 4.5 Hz, β-pyrrole), 8.94 (4 H, AB, ^3J = 4.5 Hz, β-pyrrole), 8.34−8.29 (2 H, m, *o*-phenyl), 8.28−24 (1 H, m, *o*-phenyl), 8.18−8.10 (3 H, m, *o*-phenyl), 7.83−7.70 (9 H, m, *m*- and *p*-phenyl), 7.58 (1 H, s, quinoid), 1.22 (9 H, s, *t*Bu), 0.69 (9 H, s, *t*Bu). − ^{13}C NMR ($CDCl_3$): δ = 185.26, 181.80, 150.61, 150.56, 150.32, 148.72, 148.67, 147.01, 143.47, 142.44, 142.33, 142.32, 134.42, 134.35, 134.26, 133.21, 132.39, 129.72, 127.71, 127.64, 126.69, 126.64, 126.61, 121.98, 121.57, 118.73, 37.82, 34.70, 30.98, 29.16. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 418 (5.42), 553 (3.99), 597 nm (3.42). − MS; *m*/*z* (%): 820 [M + 2]$^{\bullet+}$ (6), 819 [M + 1]$^{\bullet+}$ (1), 818 [M]$^{\bullet+}$ (2), 792 [M − CO]$^{\bullet+}$ (22), 708 [M − 2 CO −C_4H_8]$^{\bullet+}$ (12), 191 (100). − HRMS: calcd. for $C_{52}H_{42}O_2N_4Zn$ 818.25992; found 818.25968.

{5-(3,6-Di-*tert*-butyl-2,7-dihydro-2,7-dioxooxepin-4-yl)-10,15,20-triphenylporphyrinato}zinc(II) (39): Purple crystals, m.p. > 330 °C. − ^{1}H NMR ($CDCl_3$): δ = 9.20 (2 H, br. s, β-pyrrole), 9.04 (2 H, d, ^3J = 4.7 Hz, β-pyrrole), 8.94 (4 H, AB, ^3J = 4.7 Hz, β-pyrrole), 8.35−8.30 (2 H, m, *o*-phenyl), 8.30−8.26 (1 H, m, *o*-phenyl), 8.15−8.09 (3 H, m, *o*-phenyl), 7.84−7.69 (9 H, m, *m*- and *p*-phenyl), 7.26 (1 H, s, olef.), 1.23 (9 H, s, *t*Bu), 0.71 (9 H, s, *t*Bu). − ^{13}C NMR ($CDCl_3$): δ = 163.97, 162.35, 150.51, 150.34, 150.13, 146.91, 142.45, 142.30, 141.13, 137.36, 134.44, 134.41, 134.35, 134.35, 134.25, 133.24, 132.36, 132.25, 130.09, 127.69, 127.63, 126.65, 126.59, 122.13, 121.50, 113.67, 37.53, 36.14, 30.31, 29.01. − UV/Vis (CH_2Cl_2): λ_{max} (rel. int.) = 421 (1.000), 513 (0.006), 549 (0.041), 588 nm (0.007). − MS; *m*/*z* (%): 836 [M + 2]$^{\bullet+}$ (1), 835 [M

+ 1]$^{\bullet+}$ (1), 834 [M]$^{\bullet+}$ (2), 806 [M − CO]$^{\bullet+}$ (2), 790 [M − CO −O]$^{\bullet+}$ (100), 733 [M − CO − O − C_4H_9]$^{\bullet+}$ (96), 718 [M − 2 C_4H_9]$^{\bullet+}$ (56). − HRMS: calcd. for $C_{52}H_{42}O_3N_4Zn$ 834.25484; found 834.25478.

[5-{(*E*)-2,2,7,7-Tetramethyl-3,6-dioxooct-4-en-4-yl}-10,15,20-triphenylporphyrinato]zinc(II) (43): ^{1}H NMR ($CDCl_3$): δ = 9.70 (2 H, d, ^3J = 4.7 Hz, β-pyrrole), 9.03 (2 H, d, ^3J = 4.7 Hz, β-pyrrole), 8.93 (4 H, AB, ^3J = 4.6 Hz, β-pyrrole), 8.38−8.34 (2 H, m, *o*-phenyl), 8.17−8.13 (1 H, m, *o*-phenyl), 8.12−8.05 (3 H, m, *o*-phenyl), 7.82−7.69 (9 H, m, *m*- and *p*-phenyl), 7.53 (1 H, s, olef.), 1.45 (9 H, s, *t*Bu), 0.81 (9 H, s, *t*Bu). − ^{13}C NMR ($CDCl_3$): δ = 213.28, 205.65, 157.43, 150.51, 150.16, 149.06, 142.66, 142.42, 135.37, 134.42, 134.25, 132.90, 132.41, 132.13, 131.48, 127.67, 126.64, 126.52, 122.39, 121.72, 114.19, 45.65, 43.72, 27.03, 26.37.

[5-{(*Z*)-2,2,7,7-Tetramethyl-3,6-dioxooct-4-en-4-yl}-10,15,20-triphenylporphyrinato]zinc(II) (44): Purple crystals, m.p. > 330 °C. − ^{1}H NMR ($CDCl_3$): δ = 9.32 (2 H, d, ^3J = 4.7 Hz, β-pyrrole), 8.95 (2 H, d, ^3J = 4.7 Hz, β-pyrrole), 8.89 (4 H, AB, ^3J = 4.5 Hz, β-pyrrole), 8.30−8.24 (3 H, m, *o*-phenyl), 8.17−8.13 (2 H, m, *o*-phenyl), 8.12−8.05 (1 H, m, *o*-phenyl), 8.08 (1 H, s, olef.), 7.83−7.69 (9 H, m, *m*- and *p*-phenyl), 1.16 (9 H, s, *t*Bu), 0.78 (9 H, s, *t*Bu). − ^{13}C NMR ($CDCl_3$): δ = 209.63, 204.98, 154.03, 150.33, 150.03, 149.97, 148.77, 142.66, 142.42, 134.48, 134.35, 132.72, 132.06, 131.89, 130.65, 130.54, 127.48, 126.52, 126.48, 121.92, 121.26, 112.87, 45.90, 44.63, 27.75, 26.16. − UV/Vis (CH_2Cl_2): λ_{max} (rel. int.) = 422 (1.000), 518 (0.014), 553 (0.060), 594 nm (0.016). − MS; *m*/*z* (%): 796 [M + 2]$^{\bullet+}$ (20), 795 [M + 1]$^{\bullet+}$ (15), 794 [M]$^{\bullet+}$ (26), 778 [M − O]$^{\bullet+}$ (11), 709 [M − CO −C_4H_9]$^{\bullet+}$ (18), 624 [M − 2 CO − 2 C_4H_9]$^{\bullet+}$ (31), 149 (100), 57 [C_4H_9]$^+$ (29). − HRMS: calcd. for $C_{50}H_{42}O_2N_4Zn$ 794.25992; found 794.25972.

{5-(3,6-Dimethyl-1,2-dioxocyclohexa-3,5-dien-4-yl)-10,15,20-triphenylporphyrinato}zinc(II) (7): 34 mg of the free base was treated in dichloromethane with a methanol solution of zinc(II) acetate. − HPLC: *n*-hexane/diisopropyl ether = 80:20. Reddish brown crystals, m.p. 320 °C (dec.). − ^{1}H NMR ($CDCl_3$): δ = 9.20 (2 H, d, ^3J = 4.6 Hz, β-pyrrole), 8.97 (2 H, d, ^3J = 4.6 Hz, β-pyrrole), 8.86 (4 H, s, β-pyrrole), 8.18−8.14 (2 H, m, *o*-phenyl), 8.14−8.07 (4 H, m, *o*-phenyl), 7.73−7.62 (9 H, m, *m*- and *p*-phenyl), 7.57 (1 H, q, ^4J = 1.4 Hz, quinoid), 2.02 (3 H, s, −Me), 1.70 (3 H, s, −Me). − ^{13}C NMR ($CDCl_3$): δ = 182.22, 181.09, 150.69, 150.56, 150.43, 150.41, 146.58, 142.69, 142.36, 142.27, 137.11, 134.35, 134.31, 133.42, 132.54, 132.39, 132.39, 129.35, 127.73, 127.68, 126.69, 126.65, 126.61, 122.44, 121.73, 114.82, 15.31, 14.55. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 415 (5.62), 488 (sh), 548 (4.14), 620 nm (3.61). − MS; *m*/*z* (%): 737 [M + 2 H + 1]$^{\bullet+}$ (53), 736 [M + 2 H]$^{\bullet+}$ (100), 694 [M − CO, − CH_3]$^{\bullet+}$ (33), 207 (82), 156 (68), 156 (78). − HRMS: calcd. for $C_{46}H_{32}O_2N_4Zn$ 736.18167; found 736.16638 as pyrocatechol.

{5-(3-Methyl-1,2-dioxocyclohexa-3,5-dien-6-yl)-10,15,20-triphenylporphyrinato}zinc(II) (8): For the synthesis of the zinc(II) complex 33 mg of the respective free base porphyrin-*o*-quinone **4** was treated according to Method B. − HPLC: dichloromethane/ethyl acetate = 98:2. Reddish brown crystals, m.p. 305−308 °C (dec.). − ^{1}H NMR ($CDCl_3$): δ = 9.13 (2 H, AB, ^3J = 4.6 Hz, β-pyrrole), 8.98 (2 H, AB, ^3J = 4.6 Hz, β-pyrrole), 8.92 (4 H, AB, ^3J = 4.6 Hz, β-pyrrole), 8.24−8.14 (6 H, m, *o*-phenyl), 7.80−7.68 (9 H, m, *m*- and *p*-phenyl), 7.72 (1 H, quinoid), 7.36 (1 H, dq, ^3J = 6.6 Hz, ^4J = 1.6 Hz, quint), 2.33 (3 H, s, −Me). − ^{13}C NMR ($CDCl_3$): δ = 181.34, 181.24, 150.50, 150.17, 150.15, 149.40, 142.54, 142.52, 142.03, 142.01, 140.60, 136.32, 134.51, 134.41, 134.33, 134.29, 132.90, 132.32, 132.07, 130.14, 127.59, 126.66, 126.59, 126.50, 122.24, 121.53, 110.75, 16.09. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 419 (5.46), 510 (3.57), 547 (4.22), 585 nm (3.52). − MS; *m*/*z* (%): 724 [M + 2 H + 2]$^{\bullet+}$ (3), 723 [M + 2 H + 1]$^{\bullet+}$ (2), 722 [M + 2 H]$^{\bullet+}$ (4), 157 (48), 44 [C_2H_4O]$^+$ (100). − HRMS: calcd. for $C_{45}H_{30}O_2N_4Zn$ 722.16602; found 722.16766 as pyrocatechol.

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[1] [1a] D. Gust, T. A. Moore, *Adv. Photochem.* **1991**, *16*, 1−65. − [1b] M. R. Wasielewski, *Chem. Rev.* **1992**, *92*, 435−461. − [1c] H. Kurreck, M. Huber, *Angew. Chem.* **1995**, *107*, 929−947; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 849−866. − [1d] J. S. Connolly, J. R. Bolton, in: *Photoinduced Electron Transfer Part D* (Eds.: M. A. Fox, M. Chanon), Elsevier, Amsterdam, **1988**, p. 303−393.

[2] [2a] J. L. Y. Kong, P. A. Loach, *J. Heterocycl. Chem.* **1980**, *17*, 737−744. − [2b] D. Gust, T. A. Moore, P. A. Liddell, G. A. Nemeth, L. R. Makings, A. L. Moore, D. Barrett, P. J. Pessiki, R. V. Bensasson, M. Rougée, C. Chachaty, F. C. De Schryver, M. van der Auweraer, A. R. Holzwarth, J. S. Connolly, *J. Am. Chem. Soc.* **1987**, *109*, 846−856.

[3] [3a] J. von Gersdorff, M. Huber, H. Schubert, D. Niethammer, B. Kirste, M. Plato, K. Möbius, H. Kurreck, R. Eichberger, R. Kietzmann, F. Willig, *Angew. Chem.* **1990**, *102*, 690−692; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 670−672. − [3b] H. A. Staab, J. Weiser, M. Futscher, G. Voit, A. Rückemann, C. Anders, *Chem. Ber.* **1992**, *125*, 2285−2301.

[4] [4a] J. Dalton, L. R. Milgrom, *J. Chem. Soc., Chem. Commun.* **1979**, 609−610. − [4b] R. A. Cormier, M. R. Posey, W. L. Bell, H. N. Fonda, J. S. Connolly, *Tetrahedron* **1989**, *45*, 4831−4843. − [4c] J. L. Sessler, M. R. Johnson, *Recl. Trav. Chim. Pays-Bas* **1987**, *106*, 222.

[5] S. Runge, M. O. Senge, *Z. Naturforsch.* **1998**, *53b*, 1021−1030.

[6] [6a] H. Dieks, M. O. Senge, B. Kirste, H. Kurreck, *J. Org. Chem.* **1997**, *62*, 8666−8680. − [6b] R. A. Cormier, M. R. Posey, W. L. Bell, H. N. Fonda, J. S. Connolly, *Tetrahedron* **1989**, *45*, 4831−4843. − [6c] M. R. Wasielewski, M. P. Niemczyk, D. G. Johnson, W. A. Svec, D. W. Minsek, *Tetrahedron* **1989**, *45*, 4785−4806.

[7] K. M. Giangiacomo, P. L. Dutton, *Proc. Natl. Acad. Sci. USA* **1989**, *86*, 2658−2662.

[8] T. Nagaoka, S. Okazaki, T. Fujinaga, *J. Electroanal. Chem.* **1982**, *133*, 89−99.

[9] [9a] H. Kurreck, S. Aguirre, S. N. Batchelor, H. Dieks, J. von Gersdorff, C. V. M. Kay, H. Mößler, H. Newman, D. Niethammer, J. Schlüpmann, J. Sobek, M. Speck, T. Stabingis, L. Sun, P. Tian, A. Wiehe, K. Möbius, *Sol. Energy Mat. Sol. Cells* **1995**, *38*, 91−110. − [9b] M. Speck, M. O. Senge, A. Schäfer, H. Kurreck, *Bioorg. Med. Chem. Lett.* **1997**, *7*, 2589−2592.

[10] G. R. Deviprasad, B. Keshavan, F. D'Souza, *J. Chem. Soc., Perkin Trans. 1* **1998**, 3133−3135.

[11] J. von Gersdorff, B. Kirste, H. Kurreck, *Liebigs Ann. Chem.* **1993**, 897−903.

[12] J. S. Lindsey, I. C. Schreiman, H. C. Hsu, P. C. Kearney, A. M. Marguerettaz, *J. Org. Chem.* **1987**, *52*, 827−836.

[13] A. Rieche, H. Gross, E. Höft, *Chem. Ber.* **1960**, *93*, 88−94.

[14] [14a] H. Fischer, W. Neumann, *Justus Liebigs Ann. Chem.* **1932**, *494*, 225−245. − [14b] J. W. Buchler, L. Puppe, *Justus Liebigs Ann. Chem.* **1970**, *740*, 142−163.

[15] R. Hollenstein, W. von Philipsborn, *Helv. Chim. Acta* **1973**, *56*, 320−322.

[16] The complete assignment of all resonances can be found in: M. Speck, *Synthese, Reaktionen und Strukturanalyse kovalent verknüpfter Porphyrin-o-chinone als Modellverbindungen für die Photosynthese*, Shaker Verlag, **1999**, p. 334, ISBN 3-8265-4600-8.

[17] The dihedral angles were determined from a single crystal X-ray structure analysis of the the protected porphyrin catechols. M. O. Senge, M. Speck, A. Wiehe, S. Aguirre, H. Dieks, H. Kurreck, *Photochem. Photobiol.* **1999**, *70*, 206−216.

[18] [18a] M. E. Peover, *J. Chem. Soc.* **1962**, 4540−4549. − [18b] O. Ryba, J. Pilar, J. Petránek, *Coll. Czech. Chem. Commun.* **1968**, *33*, 26−34.
[19] [19a] D. Rehm, A. Weller, *Ber. Bunsenges. Phys. Chem.* **1969**, *73*, 834−839. − [19b] D. Rehm, A. Weller, *Isr. J. Chem.* **1970**, *8*, 259−271.
[20] [20a] M. R. Wasielewski, M. P. Niemczyk, *J. Am. Chem. Soc.* **1984**, *106*, 5043−5045. − [20b] H. A. Staab, G. Voit, J. Weiser, M. Futscher, *Chem. Ber.* **1992**, *125*, 2303−2310.
[21] Oriel Corporation, 1-kW Hg(Xe) lamp type 977B0010.
[22] T. Funabiki, "Oxygenases in Model Systems" in: *Catalysis by Metal Complexes Series* (Ed.: T. Funabiki), Kluwer Academic Publishers, Norwell, **1996**, p. 408.
[23] [23a] C. Kashima, A. Tomotake, Y. Omote, *J. Heterocycl. Chem.* **1987**, *24*, 785−788. − [23b] T. Funabiki, M. Ishikawa, Y. Nagai, J. Yorita, S. Yoshida, *J. Chem. Soc., Chem. Commun.* **1994**, 1951−1952. − [23c] L. S. White, E. J. Hellman, L. Que, Jr., *J. Org. Chem.* **1982**, *47*, 3766−3769.
[24] A comprehensive overview about possible oxidation products of pyrocatechol is given in: [24a] Y. Tatsuno, C. Nakamura, T. Saito, *J. Mol. Catal.* **1987**, *42*, 57−66. − [24b] T. Funabiki, A. Mizoguchi, T. Sugimoto, S. Yoshida, *Chem. Lett.* **1983**, 917−920.
[25] T. Funabiki, T. Yamazaki, A. Fukui, T. Tanaka, S. Yoshida, *Angew. Chem.* **1998**, *110*, 527−530; *Angew. Chem. Int. Ed.* **1998**, *37*, 513−515.
[26] L. Que, Jr., in: *Iron Carriers and Iron Proteins* (Ed.: T. M. Loehr), VCH, New York, **1989**, p. 467.
[27] H. Tomioka, H. Fukao, Y. Izawa, *Bull. Chem. Soc. Jpn.* **1978**, *51*, 540−543.
[28] [28a] O. Hayaishi, M. Katagiri, S. Rothberg, *J. Am. Chem. Soc.* **1955**, *77*, 5450−5451. − [28b] O. Hayaishi, M. Katagiri, S. Rothberg, *J. Biol. Chem.* **1957**, *229*, 905−920.
[29] G. Speier, Z. Tyeklar, *Chem. Ber.* **1979**, *112*, 389−391.
[30] [30a] G. O. Schenck, K. G. Kinkel, H.-J. Mertens, *Justus Liebigs Ann. Chem.* **1953**, *584*, 125−155. − [30b] C. S. Foote, Y. C. Chang, R. W. Denny, *J. Am. Chem. Soc.* **1970**, *92*, 5216−5218.
[31] H. H. Wasserman, J. R. Scheffer, *J. Am. Chem. Soc.* **1967**, *89*, 3073−3075.
[32] [32a] H. H. Wasserman, J. L. Ives, *Tetrahedron* **1981**, *37*, 1825−1852. − [32b] W. Adam, *Chem.-Ztg.* **1975**, *99*, 142−155. − [32c] D. R. Kearns, *Chem. Rev.* **1971**, *71*, 395−427.
[33] C. F. Wilcox, M. P. Stevens, *J. Am. Chem. Soc.* **1962**, *84*, 1258−1262.
[34] [34a] G. A. Russell, R. L. Blankespoor, J. Mattox, P. R. Whittle, D. Symalla, J. R. Dodd, *J. Am. Chem. Soc.* **1974**, *96*, 7249−7254. − [34b] V. Jayathirtha, V. Ramamurthy, E. Schaumann, H. Nimmesgern, *J. Org. Chem*. **1984**, *49*, 615−621.
[35] R. Ramasseul, A. Rassat, *Bull. Soc. Chim. Fr.* **1963**, 2218−2219.
[36] J. Weinstock, D. L. Ladd, J. W. Wilson, C. K. Brush, N. C. F. Yim, G. Gallagher, M. E. McCarthy, Jr., J. Silvestri, H. M. Sarau, K. E. Flaim, D. M. Ackerman, P. E. Setler, A. J. Tobia, R. A. Hahn, *J. Med. Chem.* **1986**, *29*, 2315−2325
[37] The original procedure of Lindsey was modified to assure complete neutralization of the reaction mixture. The higher basicity had no negative influence on the overall yield of the porphyrin.
[38] D. L. Comins, J. D. Brown, *J. Org. Chem.* **1984**, *49*, 1078−1083.
[39] To investigate compound **1** immediately after demetalation, the reaction was performed in deuterated chloroform.
[40] R. Kuhn, I. Hammer, *Chem. Ber.* **1950**, *83*, 413−414.
[41] The assignment of the isomers was confirmed by non broadband decoupled NMR spectra.

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