Photoinduced Electron Transfer in Porphyrin-Quinone Cyclophanes, 5[1]

Quinone-Porphyrin-Quinone and Quinone-Porphyrin-Donor Cyclophanes: Syntheses, Structures and Electron-Transfer-Related Properties

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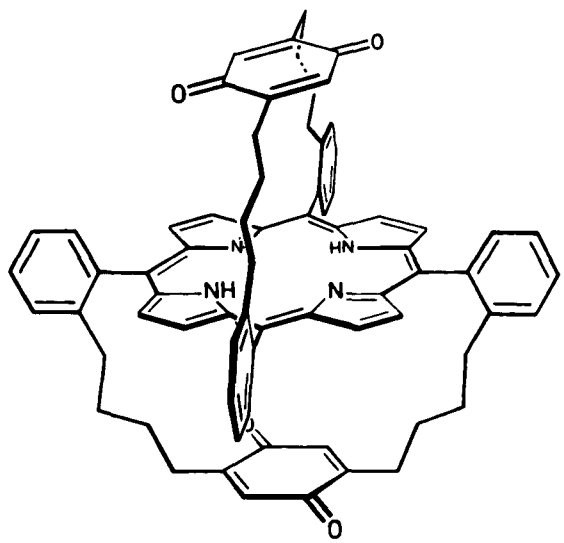
To study the structure dependence of photoinduced electron transfer between porphyrins and quinones the concept of a new family of porphyrin-quinone cyclophanes with vertical arrangements of porphyrin and quinone units is presented. The syntheses of the quinone-porphyrin-quinone cyclophane **1**, the prototype of this series, and of the quinone-porphyrin-donor cyclophanes **12** and **14** are described. Spectroscopic data are discussed with regard to the structures involved and in relation to electron-transfer reactions occurring in these systems.

With increasing progress in understanding the elementary process of biological photosynthesis[2] electon-transfer reactions occurring in synthetic prophyrin-quinone systems have found considerable interest in recent years[3]. So far in most of these synthetic systems the porphyrin and quinone units are connected with each other in a lateral arrangement and/or in a rather flexible way leaving considerable vagueness with regard to the specific mutual orientations and distances. In an attempt to better understand the structure dependence of photoinduced electron transfer from porphyrins to quinones we started in 1982 to synthesize porphyrin-quinone systems which were to meet the following criteria:

1) Porphyrin and quinone units should be linked in structural skeletons as rigid and well-defined as possible. 2) A vertical face-to-face arrangement of porphyrins and quinones was intended to complement the many lateral systems known already. 3) The structure should allow each of the parameters on which electron transfer depends (donor and acceptor strength, distance, orientation) to be varied systematically and separately while keeping constant the other parameters. 4) In order to reduce specific through-bond interactions in the electron-transfer process, the bridges between the porphyrin and quinone units should not contain heteroatoms with lone electron pairs as well as π-bonds but should consist of chains of methylene groups.

Under these aspects the structural concept represented by the quinone-porphyrin-quinone cyclophane **1** seemed to be of special interest. According to molecular models the four phenyl rings in the *meso*-positions of the porphyrin were expected to be approximately perpendicular to the porphyrin plane, thus providing a strong directive force for the *ortho*-bonds into which the tetramethylene chains are inserted. Within these tetramethylene chains the conformational mobility should be restricted. Thus, for the quinone rings in a first approximation a parallel face-to-face arrangement to the porphyrin plane was expected. The quinone units in **1** have two free ring positions left for the introduction of substituents by which the electron affinity can be varied. On the other hand, by converting one of the quinone units of **1** into an electron-donating aromatic ring a quinone-porphyrin-donor system with corresponding geometry should be obtained. Furthermore, by replacing the phenyl rings in the *meso*-positions of the porphyrin by naphthalene, biphenylene and anthracene spacers with the methylene chains in the respective 7-positions the otherwise unchanged bridges should be extended by a parallel shift, thus resulting in an increased porphyrin-quinone distance in a graduated way.



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The synthesis and structure determination of the quinone-porphyrin-quinone cyclophane **1** and results related to electron-transfer reactions proceeding in this system are reported in this paper as well as the preparation and properties of quinone-porphyrin-donor systems derived from **1**. The following publications of this series are dealing with the variations of **1** mentioned above and with the application of the underlying concept to the syntheses and electron-

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transfer properties of corresponding single-bridged quinone-porphyrine cyclophanes[4-6].

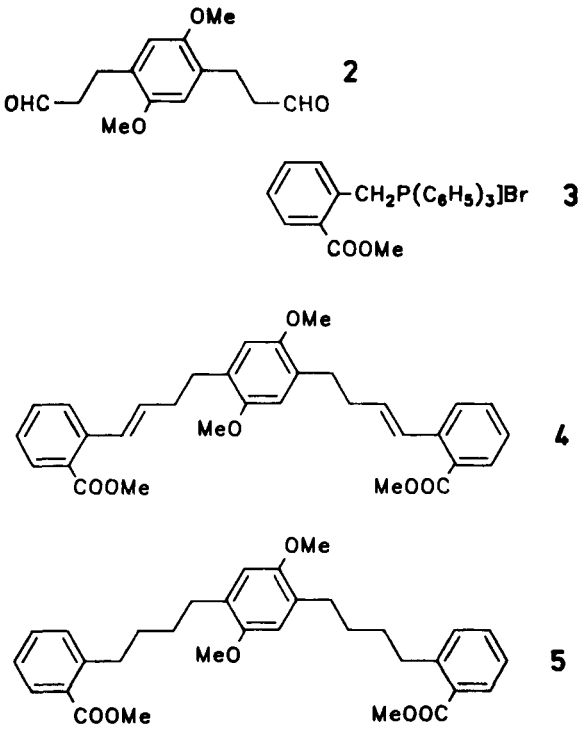
The application of the official nomenclature rules to **1** leads to a notation which does not at all reveal the basic subunits present in this porphyrin system sandwiched intramolecularly between two benzoquinone units. The Chemical Abstracts Index name of **1** is "15,16,17,18,23,24,25,26,41,42,43,44,49,50,51,52-hexadecahydro-19,22:48,45-diethanylylidene-6,9:32,35-diimino-5,31:10,36-di[2]pyrrolyl[5]ylidenetetrabenzo[*a,i,w,e1*]cyclotetratetracontene-21,46,53,67-tetrone". For deriving from this notation the real molecular structure quite some experience is required in puzzle-solving; furthermore, this name is unsuited for a coherent notation of *the various* modified systems related to **1**. Since the "phane nomenclature"[7] in this case also is not applicable, we suggest for **1** the semi-official name "5,15:10,20-bis[*p*-benzoquinone-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]porphyrin"[8] which can easily be modified to denote also the other members of this family[4-6].

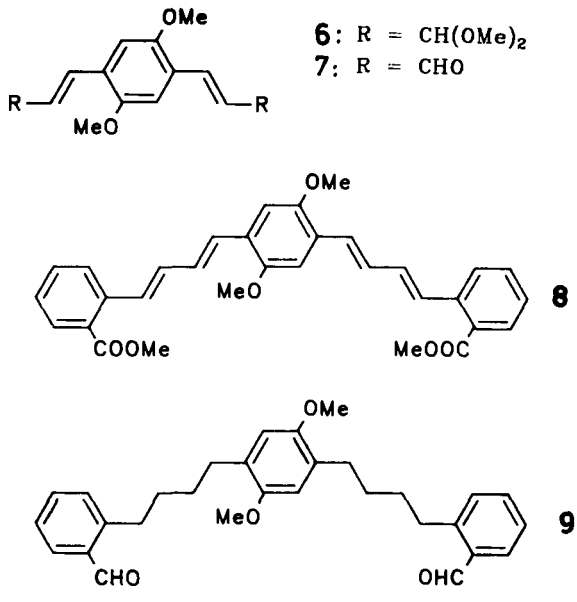
Synthesis, Structure and Electron-Transfer-Related Properties of Quinone-Porphyrin-Quinone Cyclophane 1

Synthesis of **1**: The first synthesis of **1**[9] started from 1,4-bis(3-hydroxypropyl)-2,5-dimethoxybenzene[10] which was oxidized with pyridinium chlorochromate (magnesium sulfate/celite, dichloromethane, 3 h, 20°C) to 1,4-bis(2-formylethyl)-2,5-dimethoxybenzene (**2**, m.p. 88–90°C; yield 68%). As the second component for the subsequent Wittig reaction (2-methoxycarbonylbenzyl)triphenylphosphonium bromide (**3**) was obtained by conventional procedures by bromination of 2-methylbenzoate with *N*-bromosuccinimide and reaction of the resulting methyl 2-(bromomethyl)benzoate with triphenylphosphane (m.p. 234–236°C; yield 65%). The double Wittig reaction of **2** with **3** (sodium methanolate, methanol, 60°C; yield 65%) led to 2,5-dimethoxy-1,4-bis[4-(2-methoxycarbonylphenyl)-3-butenyl]benzene (**4**, mixture with *Z* isomers) which was catalytically hydrogenated (Pd/C, methanol/ethyl acetate; yield 96%) to 2,5-dimethoxy-1,4-bis[4-(2-methoxycarbonylphenyl)butyl]benzene (**5**, m.p. 79–81°C).

An alternative route to **5** made use of the palladium(II) acetate/tri-*ortho*-tolylphosphane-catalyzed reaction of bromoarenes with acrolein dimethyl acetal which leads to a direct introduction of a C_3 side chain into the aromatic system. By use of this Heck reaction[11], here to our knowledge applied for the first time in a twofold version, 1,4-dibromo-2,5-dimethoxybenzene was converted in one step to (*E,E*)-1,4-bis(3,3-dimethoxy-1-propenyl)-2,5-dimethoxybenzene (**6**, m.p. 132–134°C; yield 62%). Acidic acetal cleavage yielded (*E,E*)-1,4-bis(2-formyl-1-ethenyl)-2,5-dimethoxybenzene (**7**, m. p. 238–242°C; yield 91%) which by a double Wittig reaction with **3** (sodium methanolate, methanol, 70°C) was transformed into 2,5-dimethoxy-1,4-bis[4-(2-methoxycarbonylphenyl)-1,3-butadienyl]benzene (**8**, yield 96%, *Z,E* isomers). By catalytic hydrogenation (Pd/C, ethyl acetate/methanol, 80°C; yield 94%) **5** was obtained.

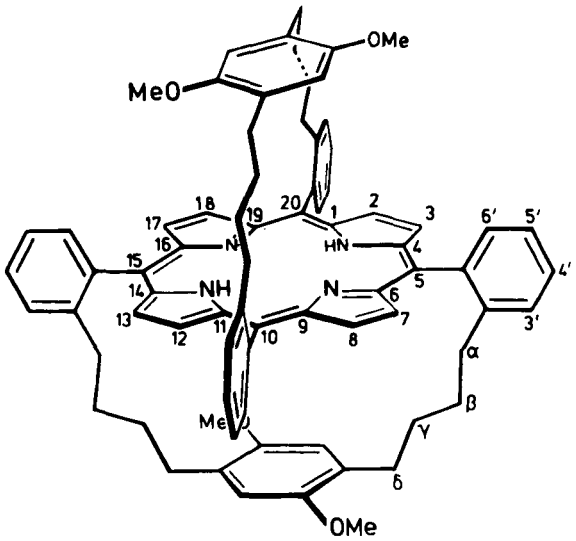
The reduction of dicarboxylic ester **5** with lithium aluminium hydride (tetrahydrofuran, at reflux for 3 h) afforded 1,4-bis[4-(2-hydroxymethylphenyl)butyl]-2,5-dimethoxybenzene (m.p. 128–130°C; yield 92%), the oxidation of which with pyridinium chlorochromate (dichloromethane, celite/magnesium sulfate, 3 h, 20°C) resulted in the formation of 1,4-bis[4-(2-formylphenyl)butyl]-2,5-dimethoxybenzene (**9**, m.p. 91–92°C; yield 90%). The dialdehyde **9** is the key intermediate not only for the synthesis of **1** but also for the preparation of the single-bridged analogues of **1** dealt with in the following paper[4].





By analogy to the preparation of tetraphenylporphyrin by acid-catalyzed condensation of benzaldehyde with pyrrole[12], **9** was treated with pyrrole (molar ratio 1:2) in boiling propionic acid for 4 h. Due to the bifunctionality of

9 the main products formed in this reaction were oligomers and polymers which, however, could easily be separated due to their insolubility or by chromatography (silica gel, toluene). Medium-pressure chromatography (silica gel, *n*-hexane/ethyl acetate) resulted in the separation of two porphyrin fractions: **A** (violet crystals, m.p. 267–269°C; yield 0.8%) and **B** (violet crystals, m.p. 296–297°C; yield 5.3%). For both compounds elemental analyses, electron spectra (which show the typical tetraphenylporphyrin bands), and mass spectra with molecular ions m/z = 1106 as base peaks strongly support the structure of doubly-bridged porphyrin cyclophanes.



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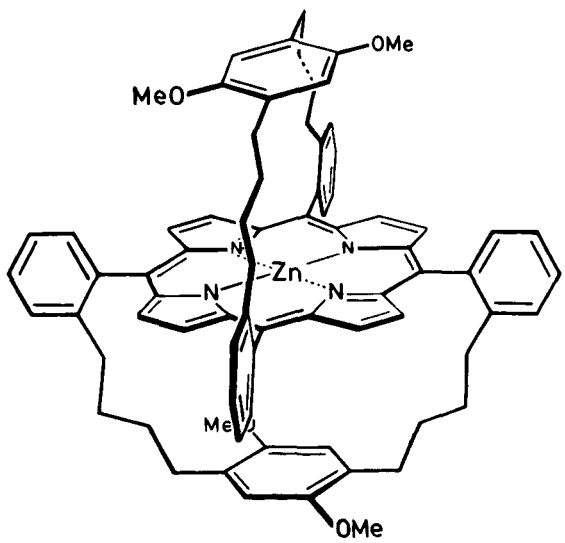
For **A** the highly symmetrical structure **10** with the two bridges on either side of the porphyrin plane linked to opposite *meso*-positions is clearly proved by the ^{1}H-NMR spectrum. The strong dominance of the ring-current effect of the porphyrin provides an internal reference with regard to the spatial localization of the different groups of protons. The four aromatic protons on the two central benzene rings of the bridges give rise to a singlet at δ = 4.31 which is upfield-shifted by $\Delta\delta$ = 2.33 compared to **9**; the four methoxy groups are also equivalent, and their singlet at δ = 1.97 shows an upfield shift of $\Delta\delta$ = 1.79 with reference to **9**; the groups of methylene protons which correspond to each other in the four C_4 chains are increasingly shielded by the porphyrin anisotropy when proceeding from the periphery to the aromatic rings above and below the porphyrin plane [δ = 2.07–2.09 (m, 8H, α-CH_2), 0.78–0.84 (m, 8H, β-CH_2), 0.40–0.47 (m, 8H, γ-CH_2), 0.09–0.14 (m, 8H, δ-CH_2)]; the eight porphyrin protons exhibit only one singlet at δ = 8.55, and a singlet for NH is found at δ = –2.79 (360 MHz, CD_2Cl_2).

In contrast to **A**, the ^{1}H-NMR spectrum of the isomer **B** indicates less symmetry and is in accordance with a structure where the two bridges do not cross-link diagonally two pairs of opposite *meso*-positions but are connected to adjacent *meso*-positions. Whether in isomer **B** the two bridges are on the same side of the porphyrin plane ("adjacent-*cis*") or on opposite sides ("adjacent-*trans*") cannot be decided conclusively by ^{1}H-NMR analysis. Obviously, both of these structures display a high conformational flexibility in the bridges and lack the ordered arrangement of **1**. Thus, in this paper, the preparation and properties of the **B**-derived structural isomer of **1** as well as the corresponding isomers of **11** and **12** are not discussed in detail.

Demethylation of **10** under mild conditions (boron tribromide, dichloromethane, 3 h, –40°C) and subsequent oxidation with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone in dichloromethane/methanol (1 h, 20°C) yielded **1** which, after chromatography (alumina, toluene), was obtained as metallic lustrous violet prisms (m.p. 281–282°C) in 85% yield. In the mass spectrum the molecular ion m/z = 1046 forms the base peak. The ^{1}H-NMR spectral data in analogy to the arguments in favour of structure **10**, strongly support the spatial structure of this quinone-porphyrin-quinone cyclophane as shown by formula **1** [^{1}H-NMR (360 MHz, CD_2Cl_2): δ = –2.82 (s, 2H, NH), 0.13–0.16 (m, 8H, γ-CH_2), 0.28–030 (m, 8H, δ-CH_2), 0.84–0.86 (m, 8H, β-CH_2), 2.29–2.31 (m, 8H, α-CH_2), 4.04 (s, 4H, quin-H), 7.55 (d, J = 6.8 Hz, 4H, ar-3′-H), 7.63 ("t", $J \approx$ 6.8 Hz, 4H, ar-5′-H), 7.69 ("t", $J \approx$ 6.8 Hz, 4H, ar-4′-H), 8.42 (d, J = 6.8 Hz, 4H, ar-6′-H), 8.64 (s, 8H, 2,3,7,8,12,13,17,18-H)].

With regard to electron-transfer processes, metal complexes of **1** were of interest. Normally, the zinc porphyrins which may be easily prepared and handled were obtained by short heating of the porphyrin with zinc acetate in pyridine. In the case of **10** it took 14 h in boiling dimethyl formamide in the presence of a great excess of zinc acetate to obtain in good yield the zinc complex **11** (m.p. 308–310°C, for analytical data see Experimental). Under such drastic conditions, however, the zinc complex of **1** was not obtainable due to decomposition of the quinoid system. The failure in preparing metal complexes of **1** is obviously due to the strong sterical shielding of the central porphyrin part by the two bridges on both sides. Zinc as well as mag-



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nesium complexes can easily be obtained from the corresponding single-bridged quinone-porphyrin cyclophanes dealt with in the following paper[4].

Structure of **1**: An X-ray structure analysis of **1** has been reported in an earlier communication[13] to which reference is made with regard to crystallographic data, data collection, structure solution and refinement. Only structural features with relevance to electron-transfer processes, like the mutual orientations and distances of quinone and porphyrin units, are summarized here again.

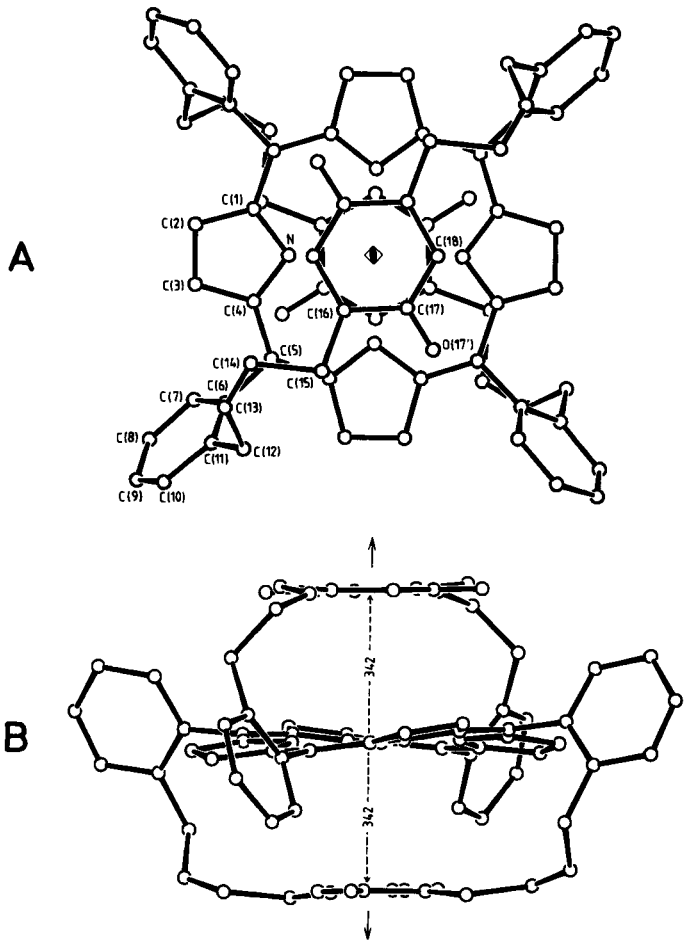


Figure 1. Molecular structure of **1** in a top-view (**A**) and in a side-view (**B**)[13]

According to the structure analysis of **1** the molecule shows S_4 symmetry with the two quinone rings being parallel to each other and to the least-squares plane of the porphyrin unit. As can be seen from the top-view of the molecule (Figure 1, A) the centres of the three rings are exactly superposed along the S_4 axis. The transannular distance between the porphyrin ring and the benzoquinone units on either side is 342 pm. As the side-view (Figure 1, B) indicates, the porphyrin ring deviates from planarity which results mainly from an inclination of the pyrrole rings by 9° against the least-squares plane of the porphyrin; the pyrrole rings themselves are nearly planar. The planes of the phenyl substituents in the *meso*-positions deviate further than expected from the perpendicular orientation with respect to the porphyrin plane (angle 67°). Bond lengths and bond angles of **1** do not differ significantly from normal values.

In the crystal the molecules form stacks with the stacking axis perpendicular to the ring planes along the fourfold rotary inversion axis which is the crystallographic *c*-axis (Figure 2). As a consequence of this symmetry, neighbouring cyclophanes within these stacks are oriented in such a way that the axes of the two quinone rings facing each other are crossed at 90°. The intermolecular distance between these quinone units is slightly shorter (337 pm) than the intramolecular distance between quinone and porphyrin planes. Whether this crystal structure has implications with regard to photoinduced electron transfer in the crystalline state has still to be studied.

The X-ray structure analysis of **1** confirms for the crystalline state the highly symmetrical structure which is in accordance with the ^{1}H-NMR data mentioned above. In principle, however, there is the possibility of a less symmetrical isomeric structure which is derived from **1** by a rotation of 180° of one of the two quinone rings around the axis through the two bridgehead atoms. The problem whether in solution conformations of **1** exist, which differ from the structure in the crystalline state and interconvert rapidly in spite of the obvious sterical hindrance, will be discussed on the basis of low-temperature ^{1}H-NMR data of **1** and related porphyrin-quinone cyclophanes[5].

Electron-Transfer-Related Properties of **1**: The absorption spectrum in the visible range shows for **1** the typical porphyrin pattern of the Soret band [λ_{max} = 421 nm (ε = 3.8 · 10^5)] and the four Q-bands [516 nm (ε = 1.7 · 10^4), 549 (4.4 · 10^3), 593 (4.8 · 10^3) and 650 (1.9 · 10^3), in trichloromethane]. As compared to tetraphenylporphyrin (TPP) [418 nm (ε = 4.9 · 10^5), 515 (1.9 · 10^4), 551 (7.8 · 10^3), 590 (5.4 · 10^3) and 647 (4.4 · 10^3), in trichloromethane] small red shifts and a reduction of the extinction coefficients are observed for **1**. In this context it is interesting that the absorption spectrum of **1** is virtually congruent to that of **10** [421 nm (ε = 3.8 · 10^5), 516 (1.8 · 10^4), 549 (4.9 · 10^3), 592 (4.7 · 10^3), 649 (2 · 10^3), in trichloromethane]. The fact that **10** contains no quinone units as electron acceptors means that in **1** the porphyrin chromophore is unaffected by donor-acceptor interactions (the undetectability of charge-transfer absorptions might, however, be due to the overlap caused by the strong porphyrin absorptions). The marked similarity of the absorption spectra of **1** and **10**, on the other hand, suggests that the difference to TPP may be attributed to the deviation of the porphyrin system from planarity as discussed above for these porphyrin cyclophanes on the basis of the molecular structure of **1**.

In contrast to the absorption spectra, the fluorescence shows striking differences between the two porphyrin cyclophanes **1** and **10**. For **10** the emission bands are found at about the same wavelengths and with similar intensities as for TPP whereas for **1** in benzene solution a nearly complete quenching of the fluorescence is observed (Figure 3). With reference to the fluorescence quantum yield of TPP ($\Phi_{fl.}$ = 0.13[14]) the integration of the emission spectra leads for **10**

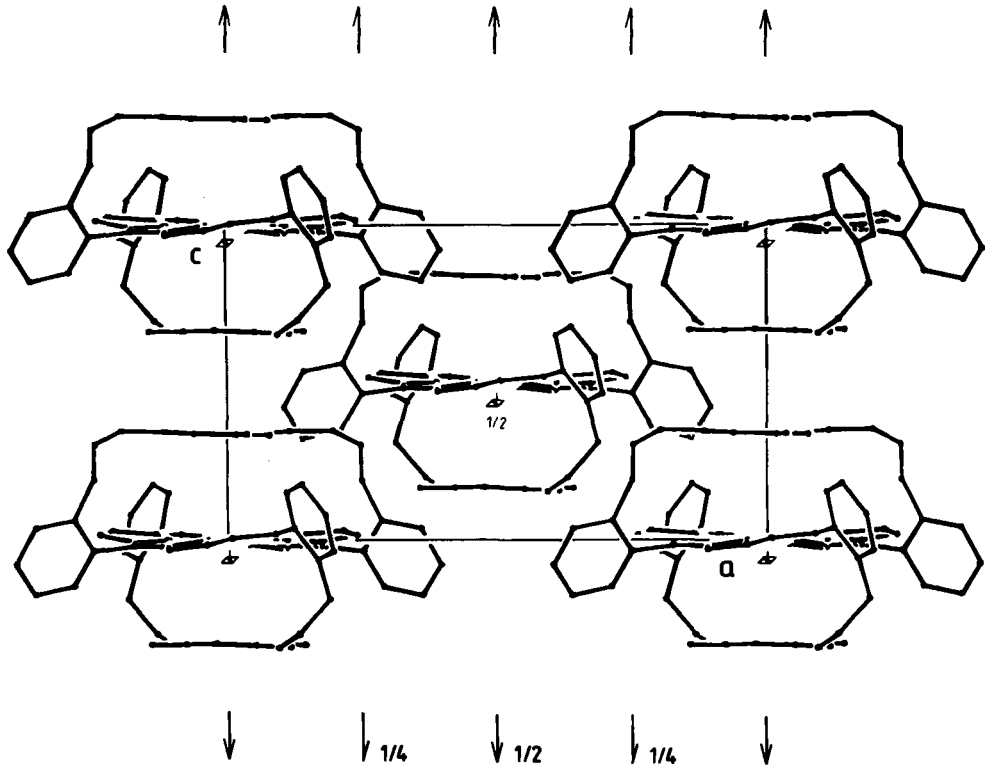


Figure 2. Crystal packing of **1**

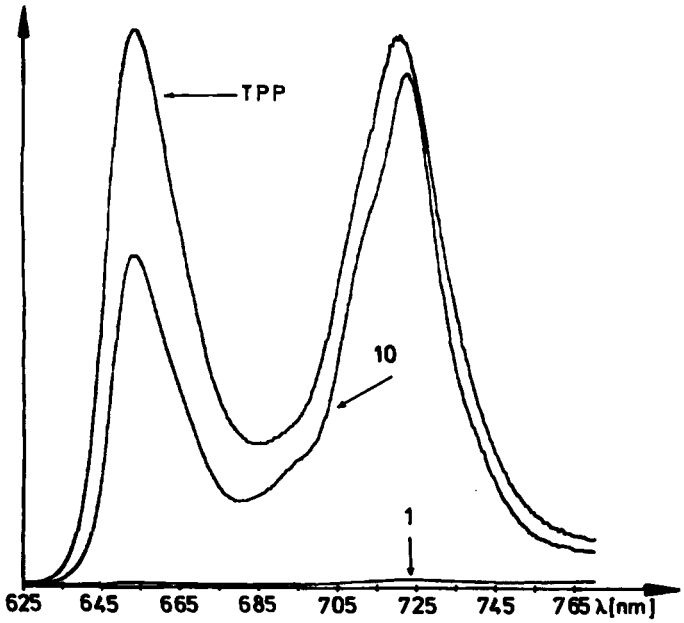


Figure 3. Fluorescence spectra of **1** in comparison with **10** and TPP (10^{-6} M solutions in benzene degassed by argon, excitation at 420 nm)

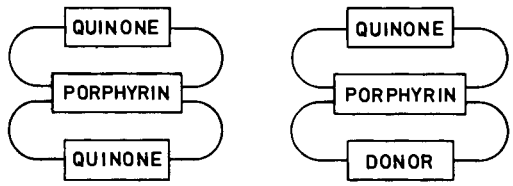
to an approximated quantum yield of 0.07, and for **1**, however, to less than 10^{-4}. This result is explained, as in the case of other porphyrin-quinone systems[3], by assuming that in **1** an electron transfer occurs from the first excited singlet state of the porphyrin to the quinone unit. This photoinduced charge separation leading to a zwitterionic state obviously competes successfully with the fluorescence emission $S_1 \rightarrow S_0$. Whereas fluorescence lifetimes of the normal order of about 10 ns are found for **10**, depending only slightly on the polarity of solvents, short-time resolved emission spectroscopy of **1** leads to strongly solvent-dependent fluorescence lifetimes in the picosecond range. Absorption spectroscopy with pico- and femtosecond laser pulses demonstrates for the charge recombination a time range between 5 and 40 ps. Further experimental details about these measurements and their results were published in separate papers[15,16].

Since the electron-transfer rates depend on the free energy ΔG of the electron-transfer reactions, oxidation and reduction potentials of **1** have been measured cyclovoltammetrically. These data will be discussed in the context of the potentials of other members of this porphyrin-quinone cyclophane family in one of the following publications[4b].

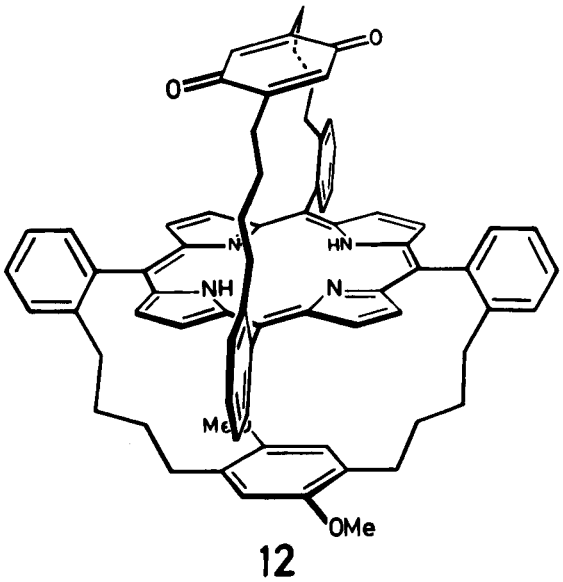
Quinone-Porphyrin-Donor Cyclophanes: Synthesis and Properties

Whereas **1** corresponds to the schematic pattern **A**, in systems of type **B** one of the quinone units is replaced by an electron donor. Since the specific topology of the vertical stacking is maintained, such triads are of interest in comparison with **1** because here the question is raised to what an extent the photoinduced charge separation caused by electron transfer from the porphyrin to the quinone unit will be supported by an electron-donating effect. With rather strong donors the charge-separated state of such systems can be expected to carry the positive charge on this donor instead of the porphyrin unit, which leads to photoinduced

charge separation over a longer distance. In this context, compounds of type **B** have been synthesized where the donor consists of a 1,4-dimethoxybenzene unit as a rather weak donor and of a 1,4-bis(dimethylamino)benzene (TMPD) unit as a very strong donor.



Syntheses: The preparation of the quinone-porphyrin-donor system **12** from **10** by selective cleavage of the two methoxy groups in one of the two equivalent cyclophane bridges was not possible by using a variety of methods for ether cleavage. The synthesis of **12** succeeded, however, in two steps the first of wich involved cleavage of just one of the four methoxy groups by *B*-bromo-9-borabicyclo-[3.3.1]nonane (dichloromethane, 40 min, 20°C)[17] to the corresponding monohydroxy compound (m.p. 115–118°C; yield 56%). Oxidative demethylation with cerium(IV) ammonium hexanitrate (acetonitrile/water, 30 min, 20°C) yielded **12** as violet microcrystals (m.p. 111–115°C; yield 70%). The structure of **12** was conclusively established by its ^{1}H-NMR spectrum which combines the features of the spectra of **1** and **10** of which **12** can be considered to be a hybrid (for data see Experimental).



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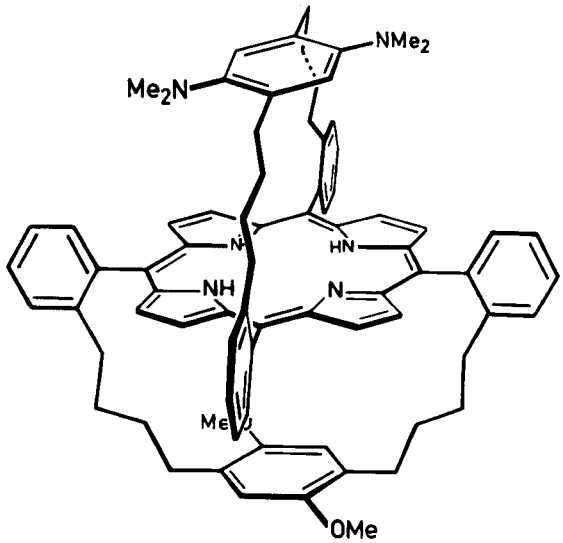
Compound **12** represents not only the first example of quinone-porphyrin-donor cyclophanes of type **B** but it is also a suitable precursor for preparing the quinone-porphyrin-donor system with TMPD as a strong donor unit: By reaction of **12** with *O*-benzylhydroxylamine hydrochloride (methanol, 5 d, reflux) the bis(*O*-benzyloxime) of **12** was obtained (m.p. 135–140°C; yield 90%). Catalytic hydrogenation (Pd/C, methanol/ethyl acetate, 2 h, 20°C) yielded the diamino compound which without isolation was methylated with iodomethane (potassium carbonate, trichloromethane/methanol, 17 h, 20°C) to the bis(dimethylamino) compound **13** (violet needles, m.p. >300°C; 77% yield; for analytical data see Experimental).

Ether cleavage by boron tribromide (dichloromethane, 2 h, 20°C) yielded **14** (m.p. 259–261°C, from methanol/trichloromethane, yield 84%). Elemental analysis, mass spectrum (FAB) as well as the fully assigned ^{1}H-NMR spectrum (500 MHz, COSY) confirm the structure (see Experimental).



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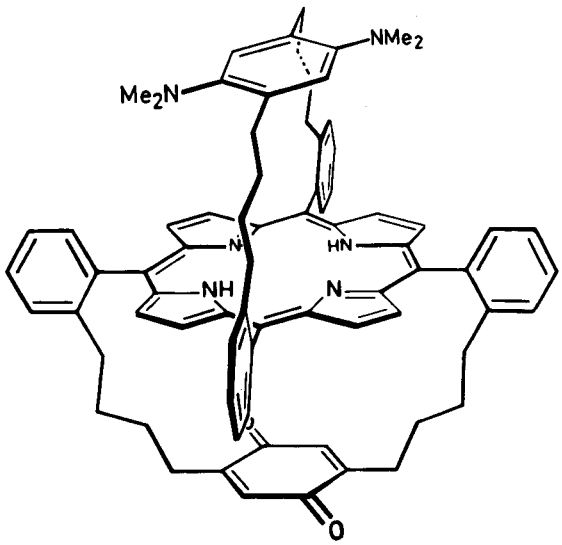

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Electron-Transfer-Related Properties: In complete agreement with the results obtained for **1** and **10**, the absorption spectra of **12**, **13** and **14** correspond closely to that of tetraphenylporphyrin (TPP) as well as for the Soret band and for the Q-bands. This means that the porphyrin chromophore is not perceptibly influenced by transannular interactions with the cyclophane-bridged π-systems – neither in

the case of the quinone unit as an acceptor nor in the case of donors like TMPD.

The emission spectra of **12** and **14**, on the other hand, show a very strong quenching of the fluorescence from which a reduction of the quantum yield in the order of two powers of ten as compared to TPP can be derived. The fluorescence quenching increases with increasing polarity of the solvent; for example, the relative quantum yields of **12** in the respective solvents are 0.017 in *n*-hexane, 0.006 in toluene and 0.0012 in acetonitrile (measured with reference to TPP).

With these observations preliminary results of time-resolved emission and absorption measurements agree rather well[16]. In polar solutions fluorescence lifetimes in the order of several picoseconds are found for **12**, whereas in nonpolar solvents fluorescence decay times of several hundreds of picoseconds are observed. These results, however, are not significantly different from those observed for **1**. A quantitative comparison on the basis of rather small differences so far is limited by the methods available for measuring precise rate constants for these "ultra-fast" electron-transfer reactions. For the especially interesting quinone-porphyrin-TMPD system **14**, time-resolved spectroscopic data are not yet available. In this compound the electron transfer is expected to be very fast since it shows the strongest quenching of fluorescence in this series of compounds. The specific question whether in the charge-separated state of **14** the positive charge is located at the porphyrin or at the TMPD unit could only be answered by transient absorption measurements. Surprisingly, even for **13**, where no quinone acceptor is present at all, considerable fluorescence quenching is observed indicating electron donation from TMPD to the porphyrin in the S_1 state. This problem will be discussed elsewhere on the basis of a new synthetic model[18] and in the light of approximated ΔG values for such electron-transfer reactions based on redox potentials[4b].

To sum up, it can be stated that the combination of complex syntheses of "tailor-made" porphyrin-quinone model systems with the new potential of short-time resolved emission and absorption spectroscopy certainly will contribute to a more comprehensive understanding of photoinduced electron-transfer processes as a function of molecular structure. For the series of porphyrin-quinone cyclophanes, in which structural parameters can be varied well-defined and one at a time, the following papers[4-6,15] will present further examples.

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Experimental

Melting points: Büchi SMP 20 and 512; Bock Monoskop M (m.p. > 240°C). – IR: Beckman IR-4240 (KBr). – UV/Vis: Varian Cary 17 and 2300. – Fluorescence: SLM Instruments 8000 (10^{-6} M solutions in benzene or toluene, degassed; 20–21°C). – MS: Du Pont CEC 21-492; Finnigan MAT 212 (ionization potential 70 eV, only peaks with I_{rel} > 10% are listed); FAB spectra (LSI-MS: Liquid Secondary Ion MS, positive; 3-nitrobenzylic alcohol/1% trifluoroacetic acid): VG Analytical ZAB 2E/SE. – ^{1}H NMR: Bruker WP-80, HX-360, AM-500 (internal reference tetramethylsilane). – Microanalysis: Elemental Analyzer 1106 Carlo Erba. – MPLC: Labomatic.

1,4-Bis(2-formylethyl)-2,5-dimethoxybenzene (**2**): 2.54 g (10 mmol) of 1,4-bis(3-hydroxypropyl)-2,5-dimethoxybenzene[10] and 6.45 g (30 mmol) of pyridinium chlorochromate together with 6 g of Celite/magnesium sulfate (1:1) in 50 ml of dichloromethane were stirred at 20°C for 3 h. After the addition of 50 ml of diethyl ether and filtration over a silica gel column (h = 30 cm, d = 4 cm; toluene/ethyl acetate) the solution was washed with 2 N hydrochloric acid, aqueous sodium hydrogen carbonate solution and water, then dried with magnesium sulfate. After distilling off the solvent, 1.7 g (68%) of **2** was obtained as white crystal powder, m.p. 88–90°C. – MS: m/z (%) = 250 (100) [M^+], 207 (58), 194 (42), 177 (24), 163 (20), 91 (28). – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 2.53–3.15 (m, 8H), 3.73 (s, 6H), 6.65 (s, 2H), 9.77 (t, J = 1.5 Hz, 2H).

$C_{14}H_{18}O_4$ (250.3) Calcd. C 67.18 H 7.25 Found C 67.11 H 7.28

(2-Methoxycarbonylbenzyl)triphenylphosphonium Bromide (**3**): 30 g (200 mmol) of methyl 2-methylbenzoate was treated with 35.6 g (200 mmol) of *N*-bromosuccinimide in 200 ml of tetrachloromethane in the usual way (at reflux for 2 h, 100-W lamp). The precipitated succinimide was filtered off and washed with 450 ml of tetrachloromethane; to the combined solution 157.2 g (600 mmol) of triphenylphosphane was added. After heating at reflux for 1 h the solution was cooled, the precipitate formed was filtered off and washed with acetone; **3** was obtained as a white microcrystalline product, m.p. 234–236°C; yield 64.5 g (65%).

$C_{27}H_{24}BrO_2P$ (491.4)
Calcd. C 66.00 H 4.92 Br 16.26 P 6.30
Found C 66.15 H 4.84 Br 16.22 P 6.02

2,5-Dimethoxy-1,4-bis[4-(2-methoxycarbonylphenyl)butyl]benzene (**5**): Through a solution of 1.62 g (6.5 mmol) of dialdehyde **2** and 13.2 g (26.9 mmol) of phosphonium salt **3** in 200 ml of dry methanol nitrogen was passed at 20°C for 30 min. After warming the solution to 60°C, 50 ml of a methoxide solution (from 0.42 g of sodium and 50 ml of methanol) was added under nitrogen within 30 min. After the yellow solution had been kept at 60°C for 12 h it was poured into 250 ml of water and extracted with dichloromethane; the extract was washed with water, dried, and the solvent distilled off in vacuo. Column chromatography (silica gel 60, toluene/ethyl acetate, 9:1) of the residue yielded as the second fraction (TLC: silica gel, dichloromethane, $R_f \approx$ 0.27) 2.22 g (65%) of a mixture of **4** and *Z*/*E* isomers as a colourless oil. Without further separation and characterization this mixture was dissolved in 120 ml of methanol/ethyl acetate (1:1) and hydrogenated in the presence of 1 g of palladium catalyst (on charcoal, 5%) until the calculated amount of hydrogen had been absorbed. After filtration the solvent was distilled off in vacuo, and the residue was crystallized by the addition of methanol. Recrystallization from methanol yielded 2.15 g (96%) of **5** as fine white needles of m.p. 79–81°C. – MS: m/z (%) = 518 (100) [M^+], 414 (16), 91 (12). – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 1.55–1.80 (m, 8H), 2.40–2.70 (m, 4H), 2.80–3.10 (m, 4H), 3.75 (s, 6H), 3.86 (s, 6H), 6.65 (s, 2H), 7.00–7.48 (m, 6H), 7.70 (dd, $J \approx$ 8 and 2 Hz, 2H).

$C_{32}H_{38}O_6$ (518.6) Calcd. C 74.10 H 7.39 Found C 74.11 H 7.60

(E,E)-1,4-Bis(3,3-dimethoxy-1-propenyl)-2,5-dimethoxybenzene (**6**): Under argon 44.4 g (150 mmol) of 1,4-dibromo-2,5-dimethoxybenzene, 720 mg (3.0 mmol) of palladium(II) acetate, 3.78 g (12.0 mmol) of tri-*o*-tolylphosphane, and 45.9 g (450 mmol) of acrolein dimethyl acetal in 150 ml of triethylamine were heated in a bomb tube with stirring at 110°C for 60 h. After cooling the reaction mixture, 500 ml of trichloromethane was added, then it was washed four times with 400 ml of water each. After drying the solution over magnesium sulfate the solvent was removed on a rotary evaporator, and the residue was suspended in 200 ml of methanol. By filtration 31.3 g (62%) of **6** was obtained: yellow platelets, m.p. 132–134°C (from methanol). – MS: m/z (%) = 338 (65) [M^+], 323 (13), 307 (100), 233 (22). – ^{1}H NMR (360 MHz, $CDCl_3$): δ = 3.39 (s, 12H), 3.82 (s, 6H), 4.94 (dd, J_{AM} = 5.2 Hz, J_{AX} = 0.8 Hz, 2H), 6.18 (dd, J_{MX} = 16.2 Hz, J_{AM} = 5.2 Hz, 2H), 6.96 (s, 2H), 7.00 (dd, J_{MX} = 16.2 Hz, J_{AX} = 0.8 Hz, 2H).

$C_{18}H_{26}O_6$ (338.4) Calcd. C 63.88 H 7.74 Found C 63.73 H 7.81

(E,E)-1,4-Bis(2-formyl-1-ethenyl)-2,5-dimethoxybenzene (**7**): To a solution of 31.3 g (92.5 mmol) of **6** in 1 l of acetone 5 ml of 2 N hydrochloric acid was added with stirring. The precipitate was filtered off, washed with acetone and recrystallized from trichloromethane: yield 20.6 g (91%) **7**, bright yellow needles, m.p. 238–242°C. – MS: m/z (%) = 246 (82) [M^+], 215 (100), 187 (11). – ^{1}H NMR (360 MHz, $CDCl_3$): δ = 3.92 (s, 6H), 6.80 (dd, J_{AM} = 16.1 Hz,

J_{AX} = 7.8 Hz, 2H), 7.09 (s, 2H), 7.82 (d, J_{AM} = 16.1 Hz, 2H), 9.73 (d, J_{AX} = 7.8 Hz, 2H).

$C_{14}H_{14}O_4$ (246.3) Calcd. C 68.28 H 5.73 Found C 68.39 H 5.61

2,5-Dimethoxy-1,4-bis[4-(2-methoxycarbonylphenyl)butyl]benzene (**5**): Under argon a methoxide solution was prepared from 7.17 g (312 mmol) of sodium in 750 ml of dry methanol. Then 153.4 g (312 mmol) of **3** was added. After stirring at 70°C for 30 min and the addition of a suspension of 19.3 g (78.0 mmol) of 7 in 500 ml of tetrahydrofuran the reaction mixture was kept with stirring at 70°C for 2 h. The orange precipitate then formed was filtered off, and the filtrate was concentrated in a rotary evaporator. After washing with methanol these two product fractions (38.0 g, 96%) consisting of **8** and its *Z,E* isomers were used without further purification for the following catalytic hydrogenation. 36.0 g (69.0 mmol) of **8** (and isomers) was suspended in 600 ml of ethyl acetate/methanol (1:1) and the suspension was heated with stirring to 80°C. Under argon 4 g of palladium/charcoal (10%) was added, and hydrogen was passed through the resulting suspension. After 3 h the catalyst was filtered off and the solvent removed in vacuo from the filtrate. Crystallization of the residue from methanol yielded 33.8 g (94%) of **5**, identical with the product obtained by catalytic hydrogenation of **4**.

1,4-Bis[4-(2-hydroxymethylphenyl)butyl]-2,5-dimethoxybenzene: A solution of 1.55 g (3 mmol) of **5** in 50 ml of dry tetrahydrofuran was added dropwise to 0.6 g (15 mmol) of lithium aluminium hydride in 50 ml of tetrahydrofuran. After heating at reflux for 3 h, water was added cautiously; the precipitate formed was filtered off and extracted several times with boiling tetrahydrofuran. From these extracts tetrahydrofuran was distilled off, and the residue was crystallized from ethyl acetate: yield 1.28 g (92%), m.p. 128–130°C.

$C_{30}H_{38}O_4$ (462.6) Calcd. C 77.89 H 8.28 Found C 77.66 H 8.21

1,4-Bis[4-(2-formylphenyl)butyl]-2,5-dimethoxybenzene (**9**): 462 mg (1.0 mmol) of the product of the preceding reaction, 645 mg (3.0 mmol) of pyridinium chlorochromate and 1 g of Celite/magnesium sulfate (1:1) in 10 ml of dichloromethane were stirred at 20°C for 3 h. After the addition of 10 ml of diethyl ether the reaction mixture was filtered through a silica gel column with dichloromethane. The filtrate was washed with 2 N hydrochloric acid, sodium hydrogen carbonate solution and with water. After drying over magnesium sulfate and evaporation of the solvent in vacuo a colourless oil was obtained which crystallized upon the addition of methanol. Recrystallization from methanol/water yielded 410 mg (90%) of **9**, colourless needles, m.p. 91–92°C. – MS: *m/z* (%) = 458 (100) [M^+], 165 (12). – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 1.42–1.95 (m, 8H, β- and γ-CH_2), 2.45–2.82 (m, 4H, δ-CH_2), 2.86–3.35 (m, 4H, α-CH_2), 3.76 (s, 6H, ar-OCH_3), 6.64 (s, 2H, ar-H, central ring), 7.10–7.68 (m, 6H, ar-4,5,6-H), 7.79 (dd, J = 7.5 and 1.75 Hz, 2H, ar-3-H), 10.31 (s, 2H, CHO).

$C_{30}H_{34}O_4$ (458.6) Calcd. C 78.57 H 7.47 Found C 78.63 H 7.69

5,15: 10,20-Bis[2,5-dimethoxybenzene-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]porphyrin (**10**) *and 5,10:15,20-bis[2,5-dimethoxybenzene-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]porphyrin:* 9.16 g (20 mmol) of **9** and 2.68 g (40 mmol) of freshly distilled pyrrole were added to 2 l of boiling propionic acid and the mixture was heated at reflux for 4 h. After cooling the propionic acid was distilled off in vacuo. The black residue was dissolved in 300 ml of dichloromethane and the solution extracted three times with 200 ml of a saturated sodium hydrogen carbonate solution. After drying of the organic phase over magnesium sulfate the dichloromethane was evaporated in vacuo. To separate the products from polymeric material the black residue was taken up in toluene and the solution filtered through a silica gel column (h = 9 cm, d = 5 cm). The toluene was evaporated from the violet filtrate in a rotary evaporator, and the remaining mixture of porphyrin isomers, dissolved in 3 ml of toluene, was separated by medium-pressure chromatography on a silica gel column (eluent: toluene; h = 40 cm, d = 5 cm, flow rate 50 ml/min). – The first porphyrin fraction (**A**) with $R_f \approx 0.64$ (silica gel, toluene) was dissolved in boiling dichloromethane and crystallized by slow addition of methanol: yield 89 mg (0.8%) of **10**, violet crystals, m.p. 267–269°C. – MS: *m/z* (%) = 1106 (100) [M^+], 1078 (19), 553 (40) [M^{++}]. – ^{1}H NMR (360 MHz, CD_2Cl_2; assignment by COSY): signals mentioned above, in addition: δ = 7.53 (d, J = 7 Hz, 4H, ar-3′-H), 7.59 ("t", $J \approx$ 7 Hz, 4H, ar-5′-H), 7.69 ("t", $J \approx$ 7 Hz, 4H, ar-4′-H), 8.19 (d, J = 7 Hz, 4H, ar-6′-H).

$C_{76}H_{74}N_4O_4$ (1107.5) Calcd. C 82.43 H 6.74 N 5.06
Found C 82.70 H 6.71 N 5.29

The second fraction (**B**) of the above-mentioned medium-pressure chromatography with $R_f \approx 0.46$ (silica gel, toluene) was recrystallized from dichloromethane/methanol (1:1): violet crystals of 5,10:15,20-bis[2,5-dimethoxybenzene-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]porphyrin, m.p. 296 to 297°C, 585 mg (yield 5.3%). – MS: *m/z* (%) = 1106 (100) [M^+], 553 (30) [M^{++}]. – ^{1}H NMR (360 MHz, CD_2Cl_2): δ = –2.81 (s, 2H), 0.78–1.44 (m, 14H), 1.73–1.89 (m, 4H), 2.24 (s, 3H), 2.28 (s, 3H), 2.40–2.52 (m, 2H), 2.56–2.73 (m, 10H), 2.75–2.85 (m, 2H), 3.67 (s, 6H), 5.38 (s, 1H), 5.44 (s, 1H), 6.23 (s, 2H), 7.68–7.80 (m, 12H), 7.44 ("t", $J \approx$ 7 Hz, 4H), 8.48 (s, 4H), 8.49 (s, 4H).

$C_{76}H_{74}N_4O_4$ (1107.5) Calcd. C 82.43 H 6.74 N 5.06
Found C 82.39 H 6.70 N 5.23

5,15: 10,20-Bis[p-benzoquinone-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]porphyrin (**1**): 30 mg (0.027 mmol) of **10** and 125 mg (0.5 mmol) of boron tribromide in 15 ml of dichloromethane were kept with stirring at –40°C for 5 h. After warming up to 20°C within 2 h, the solution was washed twice with 20 ml of a saturated sodium hydrogen carbonate solution, 20 ml of water and 20 ml of a saturated sodium chloride solution, then dried with magnesium sulfate; subsequently, 113.5 mg (0.50 mmol) of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone and 15 ml of methanol were added, and the reaction mixture was stirred at 20°C for 1 h. After the addition of 15 ml of dichloromethane the solution was extracted twice with 20 ml each of a saturated sodium hydrogen carbonate solution, 20 ml each of water and a saturated sodium chloride solution. Drying with magnesium sulfate and removal of the solvent in a rotary evaporator resulted in a brown residue which was dissolved in toluene. The solution was filtered through aluminium oxide the solvent was distilled off in vacuo from the filtrate, and the product crystallized from *n*-hexane/toluene (2:1): yield 24 mg (85%) of **1**, violet needles, m.p. 281–282°C. – MS: *m/z* (%) = 1046 (100) [M^+], 522 (20), 444 (26), 395 (12), 356 (28), 334 (45), 284 (80), 258 (50), 231 (70), 193 (70), 192 (70), 189 (45), 164 (80), 149 (70), 137 (50), 128 (50), 123 (80). – ^{1}H NMR (360 MHz, $CDCl_3$): See above.

$C_{72}H_{62}N_4O_4$ (1047.3) Calcd. C 82.57 H 5.97 N 5.35
Found C 82.61 H 6.11 N 5.36

5,15: 10,20-Bis[2,5-dimethoxybenzene-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]porphyrinzinc (**11**): 8 mg (0.007 mmol) of **10** and 366 mg (2 mmol) of zinc acetate in 10 ml of dimethylformamide were heated under argon at reflux for 14 h. The solvent was distilled off in vacuo; the solution of the residue in 50 ml toluene was extracted three times with 50 ml each of water and 50 ml of a saturated ammonium chloride solution. After drying of the organic phase over magnesium sulfate the toluene was removed in a rotary evaporator and the residue crystallized from dichloromethane/methanol (1:1): yield 8 mg (94%) of **11**, violet needles, m.p. 308–310°C. – MS: *m/z* (%) = 1168 (100), [M^+, Zn isotopic pattern], 584 (22) [M^{++}]. – ^{1}H NMR (360 MHz, CD_2Cl_2): δ = 0.05–0.09 (m, 8H, δ-CH_2), 0.48–0.51 (m, 8H, γ-CH_2), 0.99–1.02 (m, 8H, β-CH_2), 1.54 (s, 12H, ar-OCH_3), 2.06–2.10 (m, 8H, α-CH_2), 4.25 (s, 4H, central arom. ring), 7.51–7.55 (m, 8H, ar-3′,5′-H), 7.67 ("t", $J \approx$ 7 Hz, 4H, ar-4′-H), 8.19 (d, J = 7 Hz, 4H, ar-6′-H), 8.56 (s, 8H, 2,3,7,8,12,13,17,18-H).

$C_{76}H_{72}N_4O_4Zn$ (1170.8) Calcd. C 77.97 H 6.20 N 4.79
Found C 78.20 H 6.40 N 4.67

5,15-[p-Benzoqinone-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-10,20-[2,5-dimethoxybenzene-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]porphyrin (**12**): To a solution of 17.2 mg (0.0155 mmol) of **10** in 5 ml of dichloromethane 0.4 ml of a 1 M solution of *B*-bromo-9-borabicyclo[3.3.1]nonane[17] in dichloromethane was added under argon. After stirring for 40 min at 20°C 10 ml of water was added, and the organic phase was separated, washed with 20 ml of water, 20 ml of a saturated sodium carbonate solution and again with 20 ml of water. After drying over magnesium sulfate and evaporation of the solvent, the obtained product mixture was separated by medium-pressure chromatography (silica gel 100, 16–24 μm; toluene/*n*-hexane, 3:2). The first fraction contained the starting compound **10**, the second fraction ($R_f \approx 0.4$, silica gel, toluene) consisted of the monodemethylated product (9.6 mg, 56%). Without further purification 4.1 mg (0.00375 mmol) of this product was dissolved in 2 ml of acetonitrile. To this solution 60 mg (0.011 mmol) of cerium(IV) ammonium nitrate, dissolved in 0.5 ml of water, was added. After 30 min the violet precipitate formed was isolated by filtration, then dissolved in 5 ml of dichloromethane; the filtrate to which 10 ml of water was added was three times extracted with 5 ml each of dichloromethane. The combined dichloromethane solutions were washed with 20 ml of water, 20 ml of a saturated sodium hydrogen carbonate solution and again with 20 ml of water. Drying with magnesium sulfate, evaporation of the solvent and medium-

pressure chromatography (silica gel 60, 20–45 μm; h = 40 cm, d = 5 cm; flow rate 50 ml/min; eluent toluene) resulted in the separation of the starting compound (first fraction) and **12** (second fraction: $R_f \approx 0.25$). By dissolving in acetonitrile and by the addition of water to the hot solution **12** (2.8 mg, 70%) was obtained as violet microcrystals of m.p. 169–172°C. (For the syntheses of **13** and **14**, **12** had to be prepared on a larger scale; by using essentially the preparation mentioned above yields up to 90% were obtained.) – MS: m/z (%) = 1076 (100) [M^+], 538 (50) [M^{++}]. – ^{1}H NMR (500 MHz, $CDCl_3$; assignment by COSY): δ = –2.82 (s, 2H), 0.01–0.05 (m, 4H), 0.05–0.10 (m, 4H), 0.30–0.38 (m, 4H), 0.40–0.50 (m, 4H), 0.76–0.86 (m, 8H), 1.93 (s, 6H), 2.03–2.06 (m, 4H), 2.21–2.24 (m, 4H), 4.19 (s, 2H), 4.29 (s, 2H), 7.53–7.55 (m, 4H), 7.61–7.62 (m, 4H), 7.69–7.70 (m, 4H), 8.14 (d, J = 7 Hz, 2H), 8.49 (d, J = 7 Hz, 2H), 8.58 (d, J = 4.5 Hz, 4H), 8.61 (d, J = 4.5 Hz, 4H).

$C_{74}H_{68}N_4O_4$ Calcd. 1076.5240 Found 1076.5379 (MS)

Bis(O-benzyloxime) of **12**: 51.7 mg (0.05 mmol) of **12** and 257 mg (1.6 mmol) of *O*-benzylhydroxyammonium chloride in 250 ml of methanol were heated at reflux for 5 d. After evaporation of the solvent the residue was dissolved in 50 ml of trichloromethane, and the solution was washed with 50 ml each of a saturated sodium hydrogen carbonate solution and water. Drying with magnesium sulfate and evaporation of the solvent in vacuo afforded a product which was purified by medium-pressure chromatography (silica gel 60, 20–45 μm; h = 40 cm, d = 5 cm; flow rate 50 ml/min; *n*-hexane/ethyl acetate, 95:5). Crystallization from methanol/trichloromethane (3:1) yielded: 56.0 mg (90%) of the bis(*O*-benzyloxime), violet microcrystals, m.p. 135–140°C. – MS (LSI-MS): m/z (%) = 1291 (12), 1290 (33), 1289 (70), 1288 (100) [MH^+], 1287 (71) [M^+], 1286 (32).

$C_{88}H_{82}N_6O_4$ (1287.66) Calcd. C 82.08 H 6.42 N 6.53
Found C 82.27 H 6.37 N 6.48

5,15-[2,5-Bis(dimethylamino)benzene-1,4-diylbis(4,1-butandiyl-2,1-benzeno)]-10,20-[2,5-dimethoxybenzene-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]porphyrin (**13**): 25.5 mg (0.02 mmol) of the bis(*O*-benzyloxime) of **12** was dissolved in 5 ml of trichloromethane. After the addition of 20 ml of methanol/ethyl acetate (1:1) and 40 mg of palladium (10%)/charcoal catalyst to the solution the hydrogenation was carried out at 4 bar hydrogen pressure (2 h, 20°C). After evaporation of the solvents the crude diamino compound was dissolved in 2 ml of trichloromethane and 10 ml of methanol, then methylated with 2.00 ml (21.6 mmol) of iodomethane in the presence of potassium carbonate (17 h, 20°C). The solvents were distilled off in vacuo, and the solution of the residue in 10 ml of trichloromethane was washed twice with 20 ml each of water and dried with magnesium sulfate. Medium-pressure chromatography (silica gel 60, 20–45 μm; h = 40 cm, d = 5 cm; flow rate 50 ml/min; *n*-hexane/ethyl acetate, 9:1) and recrystallization from methanol/trichloromethane (3:1) yielded 17.2 mg (77%) of **13**, violet needles, m.p. >300°C. – MS (LSI-MS): m/z (%) = 1136 (33), 1135 (83), 1134 (100) [MH^+], 1133 (31) [M^+], 1132 (12). – ^{1}H NMR (500 MHz, CD_2Cl_2; assignment by COSY and NOE): δ = –2.82 (s, 2H, NH), –0.18 to –0.15 (m, 4H, δ_{TMPD}-CH_2), 0.16–0.19 (m, 4H, δ_{DMB}-CH_2), 0.41–0.44 (m, 4H, γ_{DMB}-CH_2), 0.60–0.63 (m, 4H, γ_{TMPD}-CH_2), 0.76–0.86 (m, 8H, β-CH_2), 1.03 [s, 12H, $N(CH_3)_2$], 1.95 (s, 6H, ar-OCH_3), 1.96–1.99 (m, 4H, α_{TMPD}-CH_2), 2.01–2.05 (m, 4H, α_{DMB}-CH_2), 4.34 (s, 2H, ar_{DMB}-H), 4.67 (s, 2H, ar_{TMPD}-H), 7.52 (d, J = 7.7 Hz, 4H, ar-3′-H), 7.57–7.62 (m, 4H, ar-5′-H), 7.67–7.70 (m, 4H, ar-4′-H), 8.19 (dd, J = 7.6 and 1.1 Hz, 2H, ar_{DMB}-6′-H), 8.25 (dd, J = 7.9 and 1.0 Hz, 2H, ar_{TMPD}-6′-H), 8.53 (br. s, 8H, 2,3,7,8,12,13,17,18-H).

$C_{78}H_{80}N_6O_2$ (1133.54) Calcd. C 82.65 H 7.11 N 7.41
Found C 82.72 H 6.92 N 7.23

5,15-[2,5-Bis(dimethylamino)benzene-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-10,20-[p-benzoquinone-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]porphyrin (**14**): To 11.4 mg (0.01 mmol) of **13** in 10 ml of dichloromethane 0.2 ml of a 1 M boron tribromide solution in dichloromethane was added under argon and the mixture was stirred at 20°C for 2 h. After the addition of 10 ml of water the dichloromethane phase was separated, washed with 20 ml each of a saturated sodium carbonate solution and water and dried with magnesium sulfate. The solvent was distilled off in vacuo, and the violet residue was dissolved in 10 ml of diethyl ether. Then 40 mg (0.32 mmol) of silver(I) oxide was added, and the reaction mixture was stirred at 20°C for 1 h. The residue, obtained after filtration and evaporation of the solvent from the filtrate, was crystallized from methanol/trichloromethane (4:1) to afford 9.7 mg (84%) of **14**, violet crystals, m.p. 259–261°C; **14** crystallized in 1:1 ratio with methanol. – MS (LSI-MS): m/z (%) = 1109 (13), 1108 (36), 1107 (72), 1106 (100), 1105 (66), 1104 (24) [MH^+], 1103 (6) [M^+]. – ^{1}H NMR (500 MHz, CD_2Cl_2; assignment by COSY): δ = –2.82 (s, 2H, NH), –0.17 to –0.14 (m, 4H, δ_{TMPD}-CH_2), 0.08–0.12 (m, 4H, γ_Q-CH_2), 0.44–0.47 (m, 4H, δ_Q-CH_2), 0.61–0.64 (m, 4H, γ_{TMPD}-CH_2), 0.75–0.90 (m, 8H, β-CH_2), 1.03 [s, 12H, $N(CH_3)_2$], 1.94–1.97 (m, 4H, α_{TMPD}-CH_2), 2.13–2.16 (m, 4H, α_Q-CH_2), 4.30 (s, 2H, qu-H), 4.69 (s, 2H, ar_{TMPD}-H), 7.53 (d, J = 7.3 Hz, 4H, ar-3′-H), 7.62–7.65 (m, 4H, ar-5′-H), 7.68–7.72 (m, 4H, ar-4′-H), 8.25 (d, J = 7.0 Hz, 2H, ar_{TMPD}-6′-H), 8.51 (d, J = 6.9 Hz, 2H, ar_Q-6′-H), 8.57–8.61 (m, 8H, 2,3,7,8,12,13,17,18-H).

$C_{76}H_{74}N_6O_2$ (1103.47) Calcd. C 82.72 H 6.76 N 7.62
$C_{76}H_{74}N_6O_2 \cdot CH_3OH$ (1135.51) Calcd. C 81.45 H 6.92 N 7.40
Found C 81.41 H 6.88 N 7.35

[1] Part 4: ref.[15]. – Part 1: ref.[9]; part 2: ref.[13]; part 3: J. Weiser, H. A. Staab, *Tetrahedron Lett.* **1985**, *26*, 6059–6062.

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1: 91295-89-5 / **2**: 91295-93-1 / **3**: 60494-73-7 / **4** (isomer 1): 91295-95-3 / **4** (isomer 2): 91295-94-2 / **4** (isomer 3): 142397-52-2 / **5**: 91295-91-9 / **6**: 142397-44-2 / **7**: 142397-45-3 / **8** (isomer 1): 142397-46-4 / **8** (isomer 2): 142436-35-9 / **8** (isomer 3): 142397-53-3 / **9**: 91295-90-8 / **10**: 104182-02-7 / **10** (monodemethyl): 142397-50-0 / **11**: 142397-47-5 / **11** (dezinc): 104182-02-7 / **12**: 124901-63-9 / **12** [bis(*O*-benzyloxime)]: 142397-51-1 / **13**: 142397-48-6 / **14**: 142397-49-7 / 1,4-bis(3-hydroxypropyl)-2,5-dimethoxybenzene: 5628-27-3 / 1,4-dibromo-2,5-dimethoxybenzene: 2674-34-2 / 1,4-bis[4-(2-hydroxymethylphenyl)butyl]-2,5-dimethoxybenzene: 91295-92-0 / methyl 2-methylbenzoate: [89-71-4] / acrolein dimethylacetal: [6044-68-4] / pyrrole: [109-97-7] / benzyloxyoxime hydrochloride: [2687-43-6]