Photoinduced Electron Transfer in Porphyrin−Quinone Cyclophanes, 16[◇]

Distance Dependence of Photoinduced Electron Transfer: Syntheses and Properties of Anthracene-Spacered Porphyrin−Quinone Cyclophanes

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In our previous work on benzene- and naphthalene-spacered porphyrin−quinone cyclophanes[1][2], the dependence of electron-transfer rates on reduction potentials of the acceptors and oxidation potentials of the porphyrins was studied. The present paper, dealing with the distance dependence of electron transfer, reports on the synthesis of anthracene-spacered analogues and on the electron-transfer rates, which are found to be drastically reduced.

Photoinduced electron-transfer processes in biological photosynthetic reaction centres involve a sequence of electron-transfer steps between porphyrin units, and from porphyrines to quinones as electron acceptors. In this chain of electron transfers most of the individual electron-transfer rates are not yet completely understood, since they depend on a multitude of independent factors like oxidation and reduction potentials of the interacting donors and acceptors, influence of the surrounding media, as well as the distances and the mutual orientation of the porphyrin and quinone subunits. These problems were partially solved by synthesizing series of porphyrins linked in rather well-defined structures to various quinones and other electron acceptors with a broad range of reduction potentials[2].

The driving force of electron-transfer reactions depends on the difference ($E^1_{red} - E^1_{ox}$) between the first reduction potential of the acceptors and the first oxidation potential of the porphyrins. The donor strength of the porphyrins was varied by substitution on the porphyrin periphery, as well as by metallation in the porphyrin centre. Our aim was to systematically change the factors influencing electron-transfer reactions one by one, keeping the other parameters as constant as possible. To this end, the compounds first synthesized and studied extensively with regard to structure, conformation, and the determination of electron-transfer rates, were the binary porphyrin−quinone cyclophanes[2][3]. Based on these experiments, porphyrin−quinone systems were recently included, which allow in analogy to the natural systems, a sequence of electron transitions rather than just one electron-transfer step. For example, porphyrin−quinone(1)−quinone(2)[4], porphyrin(1)−porphyrin(2)−quinone triads[5], as well as corresponding tetrads[6], have been synthesized, all with well-defined and usually rigid structures.

To understand the interaction between porphyrins and quinones in our models as well as in a biological centre, the dependence of electron-transfer rates on the porphyrin−quinone distance is especially important. For this reason, in the preceding paper[1], the series of compounds of types **1**, **2**, **3**, and **4** with gradually increasing porphyrin−quinone distances was suggested. As spacers for keeping the porphyrin and quinone units apart, the series with phenyl, 1-naphthyl, 1-biphenylenyl, and 1-anthryl in the 5,15-positions of the porphyrins was used. The planes of these spacers, due to the substituents in the β-positions of the pyrroles, are fixed in positions orthogonal to the porphyrin planes. The tetramethylene−quinone−tetramethylene bridges in **1**−**4** are inserted by C−C bonds parallel to each other in the *ortho*-phenyl, 7-naphthyl, 7-biphenylenyl, and 7-anthryl spacers, suggesting a parallel insertion of the bridges, with a gradual increase in the distance between the quinones and the porphyrin plane. The aromatic spacers neither interfere significantly with the quinone, due to the separating saturated tetramethylene chains on both sides, nor is there any substantial interaction between the π-systems of the spacers and the porphyrin, due to the fact that the spacers are fixed in an orientation perpendicular to the porphyrin plane, as demonstrated by a series of X-ray analyses[1][2]. On the basis of these arguments, for the sequence **1**-**2**-**3**-**4**, a well-defined increase of the porphyrin−quinone distance from about 350 pm to about 900 pm seemed possible.

The comparison of **1** and **2** in the preceding papers[1][2], however, showed that the tetramethylene−quinone−tetramethylene chain in **2** in its central part is not exactly parallel-shifted in spite of the parallel insertion of the bridges

[◇] Part 15: Ref.[1].

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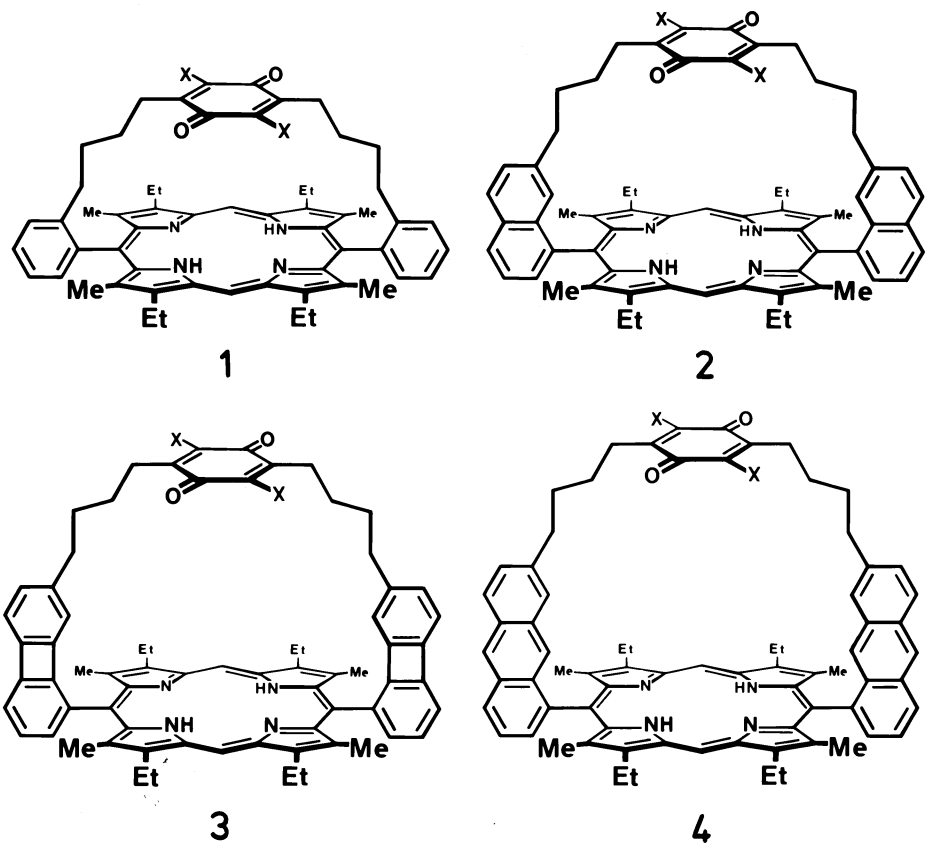


into the corresponding positions of the spacers. In fact, naphthyl-spacered porphyrin−quinone cyclophanes of type **2** were compared with their phenyl analogues **1** by X-ray analyses, with the result that the quinone-containing bridge shows a considerably less symmetrical conformation, with the tetramethylene chain on one side of the quinone bent towards the porphyrin plane, whereas the other tetramethylene part of the bridge is turned away from the porphyrin. As a consequence of this conformation, the quinone ring is not in a position parallel and centred to the porphyrin unit; the distance to the porphyrin plane from the quinone centre is about 500 pm, and from the most distant carbon of the quinone 600 pm[1].

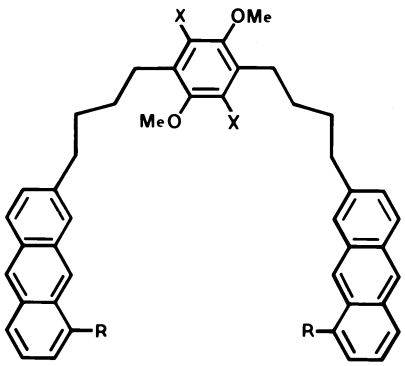
Based on these results from the naphthalene-spacered porphyrin−quinone cyclophanes **2**, conformational and structural considerations led to the expectation that for the anthracene-spacered systems **4** an analogous approach of the quinone towards the porphyrin plane should not be possible, since the more extended spacers should keep quinones and porphyrins distinctly apart. By comparison of these differently spacered porphyrin−quinone systems, molecular dynamics calculations predicted for **4**, as the "lowest energy conformation found", an extended structure with a vertical distance from the quinone centre to the porphyrin plane of about 950 pm[7].

Syntheses of Anthracene-Spacered Porphyrin−Quinone Cyclophanes

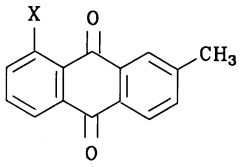
In analogy of the syntheses of naphthalene-spacered porphyrin−quinone cyclophanes (**2**)[1], the corresponding dialdehyde **7** was the essential intermediate for the preparation of the anthracene-spacered porphyrin−quinone cyclophanes **4**. In **7**, the two anthracene units are linked together by the tetramethylene−arene−tetramethylene chain via their 7-positions. Each of the two anthracene units also contains in its 1-position the aldehyde groups needed for condensation with the β-substituted pyrroles, leading finally to the anthracene-spacered porphyrin−cyclophanes. Demethylation of the dimethoxy groups on the central arene, and oxidation to the quinone should then yield the porphyrin−quinone cyclophane **4** containing the longest porphyrin−quinone distance in this series.

Thus, in principle, the synthesis of the dialdehyde **7** was designed according to its naphthalene analogue[1]. In the synthesis of the anthracene structures, however, due to the sensitive 9,10-positions of anthracene, unwanted side-reactions (e.g. during hydrogenation or bromination steps) might occur. In the building up of the carbon skeleton of **7**, it was therefore essential to bypass such critical stages by using correspondingly substituted anthraquinones instead of the anthracene units, which later should be obtained by reduction of the anthraquinones[8].

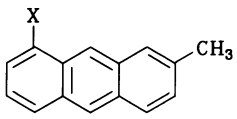
A further problem in the synthesis of **7** was the specific 1,7-substitution of the anthracene. Substituents R in the 1-positions had to be suitable to be converted to the aldehyde groups at a later stage. Substituents that allowed us to build up the tetramethylene chains to the central aromatic ring were needed in the 7-positions, such as, for example, a methyl group which can be brominated to the 7-bromomethyl substituent. These conditions are fulfilled by 1-



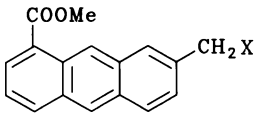
	R	X
5	–COOMe	H
6	$-CH_2OH$	H
7	–CHO	H
8	–COOMe	Br
9	$-CH_2OH$	Br
10	–CHO	Br



11 : X = Cl
12 : X = CN
13 : X = COOH



14 : X = COOH
15 : X = COOMe



16 : X = Br
17 : X = $P(C_6H_5)_3^{\oplus}$ $Br^{\ominus}$

methoxycarbonyl-7-methylanthracene (**15**), which was prepared in a multistep synthesis starting from 3-chlorophthalic anhydride[9].

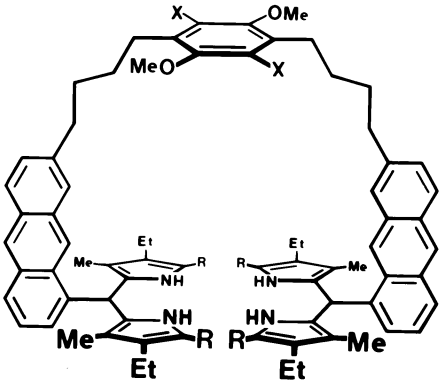
3-Chlorophthalic anhydride by reaction with 4-methylphenylmagnesium bromide yielded an isomer mixture of which the wanted 6-chloro-2-(4′-methylbenzoyl)benzoic acid could be separated from the corresponding 3-chloro-2-(4′-methylbenzoyl)benzoic acid. Conversion to 6-chloro-2-(4′-methylbenzoyl)benzoyl chloride with thionyl chloride, and subsequent intramolecular Friedel-Crafts acylation, yielded 1-chloro-7-methyl-9,10-anthraquinone (**11**). Reaction with copper cyanide in *N,N*-dimethylacetamide yielded the 1-cyano analogue **12**. Basic hydrolysis (sodium hydroxide, ethanol/water, 10 h reflux) after acidification by hydrochloric acid yielded 7-methyl-9,10-anthraquinone-1-carboxylic acid (**13**). Anthraquinone **13** was converted into anthracene **14**, containing the required substitution pattern in the 1- and 7-positions, using zinc dust/aqueous ammonia. Esterification led to the corresponding methyl 7-methylanthracene-1-carboxylate (**15**) (see Experimental Section for the detailed syntheses of these compounds).

The 1,7-disubstituted anthracene **15** meets all the essential requirements for the completion of the synthesis: The 7-methyl substituent by bromination led to the 7-bromomethyl group (**16**), and the phosphonium salt **17** derived therefrom is essential for building up the tetramethylene–quinone–tetramethylene chain, by use of the Wittig reaction. The reduction of the carboxylic function in the 1-position was later important for the formation of the dialdehyde **7**. Thus, from this stage on, the synthesis of the anthracene-spacered porphyrin–quinone cyclophane was closely analogous to that of the recently reported benzene- and naphthalene-spacered cyclophanes[1][2].

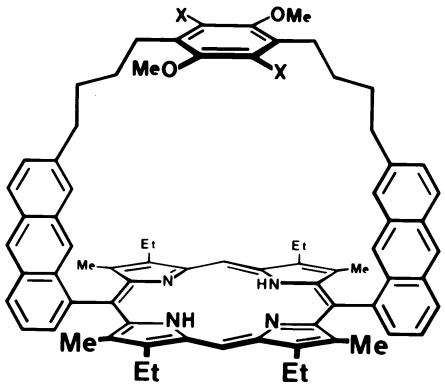
The twofold Wittig reaction of **17** with the dialdehyde 1,4-bis(2-formylethyl)-2,5-dimethoxybenzene[10], prepared by oxidation of 1,4-bis(3-hydroxypropyl)-2,5-dimethoxybenzene with pyridinium chlorochromate, gave 2,5-dimethoxy-1,4-bis[4-(8-methoxycarbonyl-2-anthryl)but-3-enyl]-benzene as mixture of *E*/*Z* isomers. Mild hydrogenation [Pd (10%)/charcoal, 5 h under normal hydrogen pressure, room temperature] led to **5**, which already contains the central tetramethylene–dimethoxybenzene–tetramethylene bridge with the anthracene spacers on both sides. The methoxycarbonyl groups in the 8-position of anthracene were now reduced to the corresponding 8-hydroxymethyl groups (compound **6**) which by mild oxidation yielded the dialdehyde **7** to be treated with 2-benzyloxy-3-ethyl-4-methylpyrrole[11] to give **18**. Mild hydrogenation removed the benzyl groups, yielding **19** (according to ^1H NMR some hydrogenation at the 9,10-positions of the anthracene units occurred even under the mild hydrogenation conditions used). Reacting **19** by the conventional procedure[2] with trichloroacetic acid and triethyl orthoformate, followed by a dehydrogenation with chloranil, yielded the bridged anthracene-spacered porphyrin cyclophane **20** as dark-violet microcrystals (for details of the synthesis and of the analytical data see Experimental Section).

Cleavage of the methoxy groups on the central benzene ring in **20** was achieved by a 1 M boron tribromide solution in dichloromethane. In the last step, the oxidation to the benzoquinone with chloranil in dichloromethane yielded the anthracene-spacered benzoquinone–porphyrin cyclophane in dark-violet microcrystals (m.p. > 380°C). The high-resolution MS data, as well as the completely assigned ^1H-NMR data (360 MHz, CD_2Cl_2) confirm the structure of the wanted anthracene-spacered porphyrin–quinone cyclophane **4** (see below).

Since the zinc complexation in the porphyrin centres, like the magnesium complexes of chlorophylls in nature, increase the donor strength of the porphyrin part, the zinc complex **24** of the anthracene-spacered porphyrin–quinone cyclophane **4** has been prepared. For comparison, the zinc complex **25** of the related porphyrin cyclophane **20**, the im-

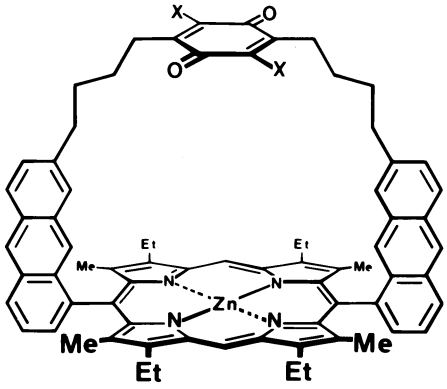


18: R = COOBz, X = H **21**: R = COOBz, X = Br
19: R = COOH; X = H **22**: R = COOH, X = Br

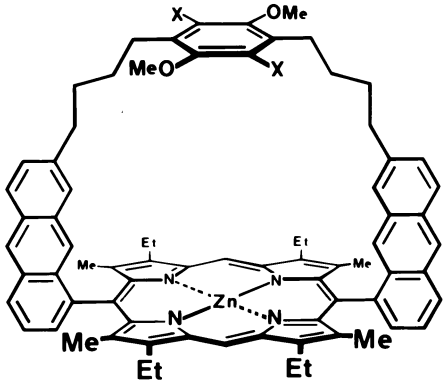


20: X = H, **23**: X = Br

mediate, yet non-quinoid precursor of the anthracene-spacered porphyrin cyclophane **4**, has also been synthesized (for the characterization data see Experimental Section).



24: (X = H)
26: (X = Br)



25: (X = H)
27: (X = Br)

The synthesis of the dibromoquinone porphyrin analogue **4**, **X = Br** was very similar to the preparation of **4**, **X = H**. In building up the lateral anthracene parts of the potential bridge across the porphyrin, the synthesis was identical up to the stage of the Wittig reaction. Now **17** was allowed to react with the dialdehyde 2,5-dibromo-1,4-bis(2-formylethyl)-3,6-dimethoxybenzene (**8**), which via **9** and **10** yielded the porphyrin cyclophane **23**, in which the central aromatic ring of the bridge contains in addition to the two methoxy groups two bromo substituents. Cleavage of **23** with boron tribromide and oxidation with chloranil yielded **4**, **X = Br**. From this dibromoquinone–porphyrin cyclophane and its non-quinoid precursor, the corresponding zinc complexes **26** and **27** were also obtained (for details of the syntheses of the bromo-substituted cyclophanes see Experimental Section).

It should be mentioned that compound **10**, the precursor for the preparation of **4**, **X = Br**, is of special interest, since it can be converted into a new type of anthracene-spacered porphyrin–acceptor system, namely the fourfold anthracene-spacered porphyrin–quinone cyclophanes by use of Heck and Wittig reactions. In these new type of cyclophanes, the quinone is linked by *four* perpendicularly oriented anthracene units to the four *meso* positions of the porphyrin, keeping these "cage"-type compounds in a much more rigid and precisely fixed structure than in the bridged porphyrin–quinone cyclophanes prepared so far. We have already reported on the first example of this series, the fourfold benzene-spacered porphyrin–quinone cyclophane[12]. The synthesis of the corresponding fourfold naphthalene-spacered system was recently completed[13] and shall be published soon together with the results on electron-transfer rates, which were not yet available.

Physical Properties Related to Electron Transfer in Anthracene-Spacered Porphyrin–Quinone Cyclophanes

^{1}H Nuclear Magnetic Resonance

In contrast to the analogous benzene- and naphthalene-spacered porphyrin cyclophanes, X-ray structure analyses are not yet available for the anthracene-spacered compounds. Convincing information about the distance dependence of the interaction in porphyrin–quinone systems like **1**, **2**, and **4**, however, can be obtained by ^{1}H NMR (360 MHz, CD_2Cl_2, 303 K). The ring-current effect of the cyclic conjugated π system of the porphyrins on the protons at the central aromatic and the quinoid rings in the bridges across the porphyrins is of value with regard to the geometry and rigidity of these porphyrin–quinone systems.

In the open-chained precursor **7**, carrying at the central benzene ring, in addition to the two methoxy groups the two 7-anthryl-tetramethylene units, the two protons in the 3,6-position of the central ring show a singlet at δ = 6.64. Exactly the same chemical shift is observed for the corresponding ring protons in the bis(phenyl-tetramethylene) analogue[2] and the corresponding naphthyl compounds[1]. As soon as the open-chained systems are closed to the porphyrin cyclophane, however, these two-proton signals are shifted from δ = 6.64 to δ = 4.15 for the benzene-spacered cyclophane, and to δ = 4.41 for the naphthalene-spacered system. The relatively small difference between the latter compounds indicates that the average distance of the central aromatic ring to the porphyrin plane is only slightly longer for the naphthalene-spacered compound than for the benzene-spacered analogue. This is in agreement with the results of X-ray structure analyses[1][2]. The ring-current effect of the porphyrin on the hydrogen atoms of the central arene ring in the bridge is somewhat smaller for the naphthalene-spacered system than for the benzene analogue. Similar results are found if the dimethoxybenzene ring in the centre of the bridge across the porphyrin is converted to the corresponding quinone. The protons in this case show singlets at δ = 4.15 and 4.92 for the benzene- and naphthalene-spacered systems, respectively.

The situation becomes very different as soon as the series is extended to the anthracene-spacered systems. The distance between the attachment positions of the cyclophane bridges, i.e. between the *ortho*-phenyl positions and the 7-naphthyl positions, is the same as the distance from the latter to the attachment at the 7-positions of the anthracene spacer. Thus, we have in this series of porphyrin−quinone cyclophanes a system of cyclophanes with a stepwise increase in the distance between the ring system, which should be reflected by the ring-current effect of the porphyrin. In contrast to **1** and **2** (see above), the chemical shift of the quinone protons in the anthracene-spacered **4**, δ = 6.06 (s), is strongly shifted to a value very close to those of the open-chained systems. This strong reduction of the ring-current effect of the porphyrin is a clear indication of the elongation of the average transannular distance between porphyrin and quinone in the anthracene-spacered cyclophanes. The consequences for the porphyrin−quinone interaction and for the electron-transfer rates will be discussed below.

Absorption Spectra

In the whole series of porphyrin cyclophanes, the absorption spectra in the visible part are dominated by the typical porphyrin chromophore. Even if there are quinones or other strong electron acceptors in close proximity to the porphyrin, there is no indication of a charge-transfer absorption, which might have been expected. Table 1 shows the absorption maxima for the anthracene-spacered quinone−porphyrin cyclophane **4**, **X = H** in comparison to the non-quinoid precursor cyclophane **20**, in toluene and in the more polar solvent dichloromethane.

Table 1 contains the typical absorption bands of porphyrins with the Soret band at shorter wavelength and with strongest intensity, and the typical Q-bands which dominate the visible region at longer wavelength. The porphyrin−quinone cyclophane **4**, **X = H** and the non-quinoid precursor **20** are very similar with regard to wavelengths and intensities, and with regard to the dependence on solvent polarity.

Obviously there is no interference of the porphyrin with the anthracene spacers due to their orthogonal orientation to the porphyrin plane. The anthracene units absorb at much shorter wavelength with a maximum at about 250 nm. Thus, the separation of the chromophoric parts of the anthracene-spacered porphyrin−quinone cyclophanes and the consistency of the absorption pattern are of great value for the interpretation of absorption-dependent properties like fluorescence emission and photoinduced electron-transfer processes.

Fluorescence Spectroscopy

Fluorescence measurements were performed for 10^{-5} M concentrations in toluene as well as dichloromethane (Fluorolog F 112 XE spectrometer). For excitation of the porphyrin−quinone cyclophanes, the maxima of the Soret band and the third Q-band Q_x (1/0) were used. The emission spectra were recorded between 600 and 750 nm. The spectra consist of two emission bands of which one is assigned to the transition from the vibration ground state of the first electronically excited state S_1 into the vibration ground state of S_0, and the second emission band is caused by the transition from the vibration ground state of S_1 into the first vibrationally excited state of S_0. For all porphyrin−quinone cyclophanes **1**, **2**, and **4** with different spacers, the two emission maxima are within the narrow ranges of 630 to 633 and 696 to 701 nm respectively, demonstrating that the porphyrin system is not significantly affected by the different spacers and the transannular interaction with the quinones.

With regard to the fluorescence intensity, however, a strong dependence on the size of the spacers is observed: the shorter the quinone−porphyrin distance, the more the

Table 1. Absorption maxima [nm] and intensities [log ε] of quinone−porphyrin cyclophane **4**, **X = H** in comparison to the non-quinoid precursor **20** ($c = 10^{-5}$ mol/l)

	Solvent	Soret band	Q_y (1/0)	Q_y (0/0)	Q_x (1/0)	Q_x (0/0)
20	toluene	419 (19.3)	508 (1.84)	540 (0.58)	578 (0.68)	629 (0.17)
20	CH_2Cl_2	416 (17.5)	508 (1.66)	541 (0.54)	575 (0.66)	626 (0.15)
4, **X = H**	toluene	419 (18.4)	509 (1.68)	540 (0.50)	578 (0.63)	630 (0.16)
4, **X = H**	CH_2Cl_2	416 (17.5)	508 (1.58)	541 (0.49)	577 (0.64)	630 (0.14)

quenching of the fluorescence dominates. This fluorescence quenching is obviously the result of the competing electron transfer from the excited porphyrin to the quinone, which occurs more easily as the porphyrin−quinone distance is decreased. As a measure of this process, we use the ratio of the integrated fluorescence intensities of the quinone−porphyrine cyclophanes to the corresponding precursors, the dimethoxybenzene−porphyrin cyclophanes, in which an electron transfer by excitation of the porphyrin chromophore is not possible at all. These ratios may be considered as approximated "relative fluorescence yields" of the porphyrin−quinone cyclophanes with reference to the non-quinoid porphyrin−dimethoxybenzene cyclophanes. The only structural difference is that the electron-acceptor quinone is replaced by the dimethoxybenzene unit, which is not an electron acceptor at all.

Using this rather simple concept, reasonable results were obtained with regard to the distance dependence of electron-transfer reactions. From benzene- to naphthalene- and finally to anthracene-spacered porphyrin−quinone cyclophanes, the "relative fluorescence yield" increases from about 0.26, to 0.50, to 40.1% (toluene; excitation at 577−579 nm). This means that for shorter porphyrin−quinone distances the competing effect of photoinduced electron transfer differs less and is much more efficient than for the respective longer distances. For other solvents like dichloromethane, a similar trend was observed. An interesting result is that from benzene to naphthalene spacers in the porphyrin−quinone cyclophanes, the fluorescence quenching was reduced by a factor of only 2 to 4 (depending upon solvents and excitation wavelengths), whereas the corresponding change from naphthalene to anthracene (which formally represents a spacer elongation of the same amount) results in a drastic increase of the fluorescence by a factor in the order of 100. This means that in the anthracene-spacered porphyrin−quinone cyclophanes the electron transfer, which for the shorter porphyrin−quinone cyclophanes competes successfully with the fluorescence, is now strongly reduced due to the longer donor−acceptor distance.

The conclusions discussed above are supported, in principle, by time-resolved fluorescence spectroscopy performed in the laboratory of Michel-Beyerle, Heitele, Pöllinger and co-workers (Technical University of Munich). In cooperation with our group they measured the rate constants of electron transfer of the differently spacered porphyrin−quinone cyclophanes in comparison with the non-quinoid analogues (with dimethoxybenzene in place of the quinone). An approximate measure of the electron-transfer rate is the fluorescence lifetime, which for the benzene-spacered system **1** is about 1 ps. The lifetime for **2** is also in the *pico*second range, whereas for the anthracene-spacered **4** a lifetime of 10.4 *nano*seconds (87%; 1 ns, 13%) was observed (all measurements in dichloromethane). In this context it was extremely interesting to synthesize a porphyrin−quinone cyclophane with a spacer length between that of naphthalene and anthracene. For this critical range, biphenylene **3** was the spacer of choice. The porphyrin−quinone cyclophane with biphenylene spacers has recently been synthesized in our group[14]; its synthesis and electron-transfer properties will be published as soon as the spectroscopic measurements are completed.

We thank Prof. *M. E. Michel-Beyerle*, Dr. *H. Heitele*, Dr. *F. Pöllinger* and their co-workers (Institut für Physikalische und Theoretische Chemie, Technische Universität München) for an excellent cooperation in this field.

Experimental Section

Melting points: Büchi SMP 512; m.p. > 240°C Bock Monoskop. − Elemental analysis: Elemental Analyzer 1106 Carlo Erba. − IR: Perkin-Elmer FT-IR 1760X. − UV/Vis: Varian Cary 2300. − MS: DuPont CEC 21-492; Finnigan MAT 212 (only the most prominent peaks are listed, usually with I_{rel} > 15%). − FAB spectra (LSIMS, positive): VG Analytical ZAB 2E/SE (I_{rel} > 15%). − ^{1}H NMR: Bruker HX 360 and AM 500 {internal reference tetramethylsilane or solvent signals C*H*Cl$_3$ (δ = 5.52), [D$_5$*H*]DMSO (δ = 2.50)}. − Analytical TLC: DC Microcards Polygram SILG/UV$_{254}$, Macherey-Nagel. − CC: Silica gel SiliTech 63−200 μm, ICN Biomedicals. − MPLC: Kronwald, column 48 × 3.7 cm; silica gel 20−45 μm, 60 Å.

3-Chloro-2-(4′-methylbenzoyl)benzoic Acid and 6-Chloro-2-(4′-methylbenzoyl)benzoic Acid (Isomer Mixture): A solution of 4-methylphenylmagnesium bromide, prepared from 8.7 g (0.35 mol) of magnesium chips and 57 g (0.34 mol) of 4-bromotoluene in 150 ml of diethyl ether, after separation by a reverse frit, was added at 40°C within 60 min to a solution of 60 g (0.33 mol) of 3-chlorophthalic anhydride[9] in 400 ml of tetrahydrofuran. After 15 h at 40°C, the organic solvent was removed, and at the same time ca. 500 ml of water was carefully added. The reaction mixture was acidified by 3 N hydrochloric acid , the precipitate formed was dissolved in 200 ml of diethyl ether, and the aqueous solution was extracted three times with 100 ml each of diethyl ether. The combined ethereal extracts were washed with 100 ml of 1 N hydrochloric acid and subsequently with 5% sodium carbonate solution (7 × 80 ml). The aqueous extracts, acidified by 3 N hydrochloric acid to pH = 3, were decanted from the oily precipitate, twice extracted with 80 ml each of diethyl ether, and added to the solution of the oily precipitate in 300 ml of diethyl ether. The combined ethereal solutions were dried with magnesium sulfate; the solvent was removed leaving a brown oil which slowly solidified on standing: 40 g (44%; in later preparations the yield was increased to 78%) of the isomer mixture, which was used without further purification for the esterification (see below). The isolation of 3-chloro-2-(4′-methylbenzoyl)benzoic acid from the isomer mixture was possible by dissolving 1 g (3.6 mmol) of the isomer mixture in 10 ml of boiling toluene. On cooling to room temp. the white precipitate formed was filtered and dried in vacuo at 60°C to give 180 mg (18%), m.p. 184°C. − MS; *m*/*z* (%): 274 (13, M$^+$), 183 (14), 119 (100), 91 (27). − ^{1}H NMR (360 MHz, [D$_6$]DMSO, 303 K): δ = 2.37 (s, 3 H, CH$_3$), 7.31 (d, *J* = 8.0 Hz, 2 H, 3′,5′-H), 7.55 (d, *J* = 8.1 Hz, 2 H, 2′,6′-H), 7.65 ("t", *J* ≈ 8.0 Hz, 1 H, 5-H), 7.83 (d, *J* = 7.7 Hz, 1 H, 4-H), 8.02 (d, *J* = 7.7 Hz, 1 H, 6-H), 13.42 (s, 1 H, COOH). − C$_{15}$H$_{11}$ClO$_3$ (274.70): calcd. C 65.59, H 4.00, Cl 12.91; found C 65.49, H 4.14, Cl 13.00.

Methyl 3-Chloro-2-(4′-methylbenzoyl)benzoate and Methyl 6-Chloro-2-(4′-methylbenzoyl)benzoate (Isomer Mixture): 40 g (0.15 mol) of the above-mentioned isomer mixture of the correspondingly substituted benzoic acid was dissolved in 300 ml of anhydrous methanol, and under stirring 20 ml (0.28 mol) of acetyl chloride was carefully added. After 10 h, a further 5 ml of acetyl chloride

was added; after another 10 h, the solution was concentrated in vacuo to about 100 ml, and added to 300 ml of water. The reaction mixture was extracted five times by 100 ml each of diethyl ether. The combined ethereal solutions were washed twice with 100 ml of 5% sodium hydrogen carbonate solution, followed by 100 ml of water. After drying on magnesium sulfate, the solvent was removed, and 30 g (71% yield) of the isomer mixture was obtained as a white solid.

6-Chloro-2-(4′-methylbenzoyl)benzoic Acid: 30 g (0.1 mol) of the above isomer mixture of methyl esters in 300 ml of concentrated sulfuric acid was stirred at room temp. for 6 h. The reaction mixture then was poured onto 300 ml of ice water and extracted five times with 80 ml each of diethyl ether. The combined extracts were washed with 100 ml of water and extracted four times with 100 ml each of 5% aqueous sodium carbonate. After washing with 100 ml of diethyl ether, the solution was carefully acidified with 60 ml of 6 N hydrochloric acid and then extracted four times with 100 ml each of diethyl ether. The combined organic phases were dried with magnesium sulfate, and after distilling off the solvents the 6-chloro-2-(4′-methylbenzoyl)benzoic acid was obtained as an analytically pure beige powder of m.p. 128−129°C in a yield of 20 g (70%). − MS; *m*/*z* (%): 274 (15, M^+), 195 (19), 183 (11), 119 (100), 91 (29). − ^{1}H NMR (500 MHz, [D$_6$]DMSO, 303 K): δ = 2.38 (s, 3 H, CH_3), 7.33 (d, J = 7.8 Hz, 2 H, 3′,5′-H), 7.44 (d, J = 7.6 Hz, 1 H, 5-H), 7.58−7.61 (m, 3 H, 2′,6′,4-H), 7.72 (d, J = 8.1 Hz, 1 H, 3-H), 13.38 (s, 1 H, COOH). − $C_{15}H_{11}ClO_3$ (274.70): calcd. C 65.59, H 4.00, Cl 12.91; found C 65.55, H 4.03, Cl 13.08.

Methyl 6-Chloro-2-(4′-methylbenzoyl)benzoate: The esterification was very similar to the preparation of the esters of the isomer mixture of the corresponding 3-chloro- and 6-chlorobenzoic acids (see above): 1 g (3.6 mmol) of the 6-chloro-2-(4′-methylbenzoyl)benzoic acid in 20 ml of dry methanol were allowed to react, with stirring, with 1.7 g (21 mmol) of acetyl chloride. After 20 h, 100 ml of water was added, and the solution was extracted three times with 100 ml each of diethyl ether. The combined ethereal phases were washed twice with 100 ml each of 5% sodium hydrogen carbonate solution, and then with 100 ml of water. The organic phase was dried on magnesium sulfate, and the solvent was removed to give 880 mg (84%) of a pale-yellow oil, which slowly crystallized to a white solid of m.p. 81−82°C. − MS; *m*/*z* (%): 288 (29, M^+), 257 (20), 179 (21), 119 (100), 91 (18). − ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ = 2.43 (s, 3 H, CH_3), 3.79 (s, 3 H, OCH_3), 7.27 (d, J = 7.4 Hz, 2 H, 3′,5′-H), 7.42−7.43 (m, 2 H, 4,5-H), 7.58 (dd, ^3J = 6.4 Hz, ^4J = 2.9 Hz, 1 H, 3-H), 7.67 (d, J = 8.1 Hz, 2 H, 2′,6′-H). − $C_{16}H_{13}ClO_3$ (288.73): calcd. C 66.56, H 4.54, Cl 12.28; found C 66.34, H 4.63, Cl 12.04.

6-Chloro-2-(4′-methylbenzoyl)benzoyl Chloride: To 10 g (36 mmol) of 6-chloro-2-(4′-methylbenzoyl)benzoic acid 5 ml (58 mmol) of thionyl chloride was added, and the reaction mixture was heated under reflux for 30 min. Excess thionyl chloride was removed in vacuo leaving the product analytically pure as a white powder of m.p. 145−146°C; nearly quantitative yield. − MS; *m*/*z* (%): 257 [100, $(M - Cl)^+$], 165 (13), 119 (11), 91 (14). − ^{1}H NMR (360 MHz, [D$_6$]DMSO, 303 K): δ = 2.40 (s, 3 H, CH_3), 7.36 (d, J = 8.0 Hz, 2 H, 3′,5′-H), 7.46 (d, J = 7.6 Hz, 1 H, 5-H), 7.57 (m, 3 H, 2′,6′,4-H), 7.75 (d, J = 8.0 Hz, 1 H, 3-H). − $C_{15}H_{10}Cl_2O_2$ (293.15): calcd. 61.46, H 3.44, Cl 24.19; found C 61.24, H 3.58, Cl 24.39.

1-Chloro-7-methyl-9,10-anthraquinone (**11**): To a suspension of 10.7 g (36 mmol) of 6-chloro-2-(4′-methylbenzoyl)benzoyl chloride under ice cooling, a suspension of 11.5 g (86 mmol) of anhydrous aluminium chloride in 40 ml of carbon disulfide was added. After 17 h of heating to 50°C, the reaction mixture was cooled down to room temp. After careful hydrolysis with 10 ml of concentrated hydrogen chloride in 200 ml of ice water, carbon disulfide was removed leaving a pale-yellow precipitate which was filtered, washed with 50 ml of water, twice with 50 ml each of 2 N sodium hydroxide solution, and again twice with 50 ml each of water. The precipitate was dried to give 6.4 g (68%) yield. For analysis, a small sample was further purified by bulb tube distillation. − M.p. 180−184°C. − MS; *m*/*z* (%): 256 (100, M^+), 255 (11), 241 (17), 228 (43), 227 (11), 221 (14), 200 (14), 199 (18), 195 (18), 165 (90), 164 (29), 163 (39), a.o. − ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ = 2.53, (3 H, CH_3), 7.57 (dd, ^3J = 7.9 Hz, ^4J = 1.4 Hz, 1 H, 6-H), 7.66 ("t", $J \approx$ 7.7 Hz, 1 H, 3-H), 7.78 (dd, ^3J = 8.0 Hz, ^4J = 1.3 Hz, 1 H, 2-H), 8.07 (s, 1 H, 8-H), 8.14 (d, J = 7.9 Hz, 1 H, 5-H), 8.29 (dd, ^3J = 7.9 Hz, ^4J = 1.3 Hz, 1 H, 4-H). − $C_{15}H_9ClO_2$ (256.69): calcd. C 70.19, H 3.53, Cl 13.81; found C 70.31, H 3.55, Cl 13.79.

1-Cyano-7-methyl-9,10-anthraquinone (**12**): 6 g (23 mmol) of **11** and 3 g (33 mmol) of copper cyanide were heated under reflux in 70 ml of *N*,*N*-dimethylacetamide for 4 h. Subsequently the hot mixture was poured into 300 ml of water under vigorous stirring. The brown precipitate was sucked off, washed with 80 ml of water, and suspended in 100 ml of water. Slowly, a solution of 40 ml of 65% nitric acid in 60 ml of water was added. The resulting mixture was slowly heated to boiling, and kept under reflux for 2 h, while strong gas evolution occurred. The product was washed with water, dried and chromatographed with dichloromethane on silica [R_f (starting material) = 0.55; R_f (product) = 0.28]. Yield 3.8 g (66%), m.p. 260−264°C. − MS; *m*/*z* (%): 247 (100, M^+), 246 (15), 232 (11), 219 (74), 190 (44), 165 (13), a.o. − ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ = 2.57 (s, 3 H, CH_3), 7.65 (dd, ^3J = 7.9 Hz, ^4J = 1.2 Hz, 1 H, 6-H), 7.91 ("t" $J \approx$ 7.9 Hz, 1 H, 3-H), 8.13 (dd, ^3J = 7.9 Hz, ^4J = 1.2 Hz, 1 H, 2-H), 8.17 (s, 1 H, 8-H), 8.21 (d, J = 7.9 Hz, 1 H, 5-H), 8.57 (dd, ^3J = 7.9 Hz, ^4J = 1.2 Hz, 1 H, 4-H). − $C_{16}H_9NO_2$ (247.25): calcd. C 77.72, H 3.67, N 5.67; found C 77.70, H 3.64, N 5.48.

7-Methyl-9,10-anthraquinone-1-carboxylic Acid (**13**): 3.0 g (12 mmol) of **12** suspended in 50 ml of ethanol and 50 ml of 10% sodium hydroxide solution was heated under reflux for 10 h. The hot dark solution was then poured into 200 ml of hot water and was filtered immediately. To the filtrate at about 80°C, 20 ml of concentrated hydrochloric acid was added, and the brown precipitate was filtered, washed with 50 ml of water, and dried. An analytically pure product was obtained by recrystallizations from glacial acetic acid in the presence of activated charcoal, and then from ethanol, m.p. 296°C (dec.), yield 3 g (68%). − MS; *m*/*z* (%): 266 (7, M^+), 222 (100, $M - CO_2$), 221 (10), 207 (10), 194 (37), 193 (10), 166 (23), 165 (54), 164 (10), 163 (13). − ^{1}H NMR (360 MHz, [D$_6$]DMSO, 303 K): δ = 2.52 (s, 3 H, CH_3), 7.76 (dd, ^3J = 8.0 Hz, ^4J = 1.4 Hz, 1 H, 6-H), 7.83 (dd, ^3J = 7.3 Hz, ^4J = 1.0 Hz, 1 H, 2- or 4-H), 7.94 − 7.98 (m, 2 H, 3,8-H), 8.12 (d, J = 7.9 Hz, 1 H, 5-H), 8.28 (dd, ^3J = 7.8 Hz, ^4J = 1.0 Hz, 1 H, 4- or 2-H), 13.25 (s, 1 H, COOH). − $C_{16}H_{10}O_4$ (266.25): calcd. C 72.18, H 3.79; found C 72.19, H 3.84.

7-Methylanthracene-1-carboxylic Acid (**14**): 3.0 g (11 mmol) of **13** in 140 ml of 20% aqueous ammonia was stirred in the presence of 10 g (0.15 mol) of zinc dust and 200 mg of copper sulfate for 4 h at 70°C. The hot suspension was filtered, and the cooled filtrate was acidified by concentrated hydrochloric acid. The bright yellow precipitate was filtered, washed with 50 ml of water, and dried. An analytically pure product was obtained by dissolving the product in 20% aqueous ammonia and precipitating with concentrated hydrochloric acid. Yield 2.15 g (81%), m.p. 249°C. − MS; *m*/*z* (%):

236 (100, M^+), 191 (16), 189 (10). − ^{1}H NMR (500 MHz, [D$_6$]DMSO, 303 K): δ = 2.52 (s, 3 H, CH$_3$), 7.41 (dd, ^3J = 8.2 Hz, ^4J = 1.5 Hz, 1 H, 6-H), 7.56 (dd, ^3J = 7.0 Hz, ^3J = 8.4 Hz, 1 H, 3-H), 7.89 (s, 1 H, 8-H), 8.01 (d, J = 8.6 Hz, 1 H, 5-H), 8.24 (dd, ^3J = 7.0 Hz, ^4J = 1.1 Hz, 1 H, 2-H), 8.30 (d, J = 8.6 Hz, 1 H, 4-H), 8.61 (s, 1 H, 9-H), 9.48 (s, 1 H, 10-H), 13.19 (s, 1 H, COOH). − $C_{16}H_{12}O_2$ (236.27): calcd. C 81.34, H 5.12; found C 81.06, H 5.37.

Methyl 7-Methylanthracene-1-carboxylate (**15**): To 2 g (8.5 mmol) of **14** dissolved in 60 ml of anhydrous methanol, 3 ml of acetyl chloride were carefully added, and the reaction mixture was stirred at room temp. for 3 d. After addition of 150 ml of water, the solution was extracted twice with 70 ml each of dichloromethane. The combined organic phases were dried with magnesium sulfate, and the solvent was removed. The crude product for further purification was filtered through silica, with dichloromethane yielding 1.44 g (68%) of the ester as a pale-yellow powder of m.p. 132°C. − MS; *m/z* (%): 250 (100, M^+), 219 (21), 191 (31), 189 (15). − ^{1}H NMR (360 MHz, CDCl$_3$, 303 K): δ = 2.53 (s, 3 H, CH$_3$), 4.03 (s, 3 H, OCH$_3$), 7.31 (d, J = 8.6 Hz, 1 H, 6-H), 7.39 ("t", $J \approx$ 7.7 Hz, 1 H, 3-H), 7.82 (s, 1 H, 8-H), 7.86 (d, J = 8.7 Hz, 1 H, 5-H), 8.11 (d, J = 8.4 Hz, 1 H, 2-H), 8.19 (d, J = 7.0 Hz, 1 H, 4-H), 8.36 (s, 1 H, 9-H), 9.44 (s, 1 H, 10-H). − $C_{17}H_{14}O_2$ (250.30): calcd. C 81.58, H 5.64; found C 81.52, H 5.68.

Methyl 7-Bromomethylanthracene-1-carboxylate (**16**): To 10 g (40 mmol) of methyl 7-methylanthracene-1-carboxylate (**15**), suspended in 400 ml of tetrachloromethane, was added 4.7 g (26 mmol) of *N*-bromosuccinimide in 100 ml of tetrachloromethane. The reaction mixture was irradiated with a 300-W lamp and heated to boiling. After 1 h, a further 2.0 g (11 mmol) of *N*-bromosuccinimide in 100 ml of tetrachloromethane was added, and after 45 min the reaction was stopped. After cooling the solution, the succinimide formed was filtered off, and the filtrate was concentrated in a rotary evaporator to dryness, leaving the crude 7-bromomethyl compound **16** (still containing about 20% of the starting material). The product was used for the next step without further purification.

[(8-Methoxycarbonyl-2-anthryl)methyl]triphenylphosphonium Bromide (**17**): To 12.0 g of the above-mentioned crude product in 300 ml of toluene, 30 g (114 mmol) of triphenylphosphane in 100 ml of toluene was added, and the reaction mixture was stirred for 6 h at 100°C. After cooling down, the bright-yellow precipitate was filtered off (14.5 g, yield 61% for the two steps), m.p. 260−263°C (dec.). − ^{1}H NMR (360 MHz, [D$_6$]DMSO, 303 K): δ = 3.97 (s, 3 H, OCH$_3$), 5.40 (d, ^2J = 16.0 Hz, 2 H, CH$_2$), 7.08 (d, ^3J = 8.8 Hz, 1 H, 3-H), 7.62 (dd, ^3J = 8.2 Hz, ^3J = 7.3 Hz, 1 H, 6-H), 7.71−7.94 (m, 17 H, 15 Ph-H, 2-anthr.-H), 7.98 (d, ^3J = 8.8 Hz, 1 H, anthr.-H), 8.25 (d, ^3J = 6.4 Hz, 1 H, anthr.-H), 8.68 (s, 1 H, 9- or 10-H), 9.18 (s, 1 H, 10- or 9-H). − $C_{35}H_{28}BrO_2P$ (591.49): calcd. C 71.07, H 4.77, Br 13.51, P 5.24; found C 70.89, H 4.74, Br 13.75, P 5.15.

1,4-Bis[4-(8-methoxycarbonyl-2-anthryl)-3-butenyl]-2,5-dimethoxybenzene (E/Z Isomer Mixture): 18.2 g (31 mmol) of the phosphonium salt **17** and 400 mg of 18-crown-6 were dissolved in 500 ml of dichloromethane, and 12.5 g (90 mmol) of pulverized potassium carbonate was added. The dark-red mixture was heated under argon to 50°C, and 3.1 g (12.4 mmol) of 1,4-bis(2-formylethyl)-2,5-dimethoxybenzene[9] was added. After 24 h, a further 5 g (36 mmol) of pulverized potassium carbonate and 0.25 g (0.4 mmol) of the phosphonium salt were added, and the reaction was kept at 50°C for further 24 h. The cooled reaction mixture was then poured into 400 ml of 1 N hydrochloric acid. After separating the organic phase, the aqueous phase was extracted twice with 100 ml dichloromethane, and the combined organic phases were dried with magnesium sulfate and after addition of 40 g florisil (magnesium silicate gel) were concentrated in a rotary evaporator. The *E*/*Z*-isomer mixture of the product of the double Wittig reaction was obtained as a yellow powder, 7.1 g (80%) by chromatography (silica gel, cyclohexane/ethyl acetate, R_f = 0.18−0.28). − MS; *m/z* (%): 714 (20, M^+), 439 (30), 275 (94), 243 (100), 215 (87), 165 (15) a.o. − ^{1}H NMR (360 MHz, CDCl$_3$, 303 K): The signals are in agreement with the structure, although due to the mixture of *E*/*Z* isomers, a detailed assignment was not possible.

1,4-Bis[4-(8-methoxycarbonyl-2-anthryl)butyl]-2,5-dimethoxybenzene (**5**): 5.2 g (7.3 mmol) of the preceding diene isomers in 500 ml of tetrahydrofuran, was stirred for 5 h under normal hydrogen pressure in the presence of 1 g palladium (10%)/charcoal. Filtering off the catalyst followed by evaporation of the solvent yielded 5.2 g (99%) of the product, crystallized from toluene, m.p. 153°C. − MS; *m/z* (%): 718 (100, M^+), 686 (15), 654 (18), 441 (23), 411 (39), 359 (16), 290 (38), 249 (50), 231 (21), 205 (16), 191 (31), 151 (15) a.o. − ^{1}H NMR (360 MHz, CDCl$_3$, 303 K): δ = 1.67−1.73 (m, 4 H, γ-H), 1.78−1.84 (m, 4 H, β-H), 2.65 (t, ^3J = 7.6 Hz, 4 H, δ-H), 2.86 (t, ^3J = 7.4 Hz, 4 H, α-H), 3.74 (s, 6 H, OCH$_3$), 4.05 (s, 6 H, COOCH$_3$), 6.65 (s, 2 H, centr. Ar-H), 7.33 (dd, ^3J = 8.7 Hz, ^4J = 1.5 Hz, 2 H, 3-H), 7.43 (dd, ^3J = 7.1 Hz, ^3J = 8.4 Hz, 2 H, 6-H), 7.85 (s, 2 H, 1-H), 7.90 (d, ^3J = 8.7 Hz, 2 H, 4-H), 8.16 (d, ^3J = 8.5 Hz, 2 H, 7-H), 8.21 (dd, ^3J = 7.0 Hz, ^4J = 1.1 Hz, 2 H, 5-H), 8.40 (s, 2 H, 9-H), 9.46 (s, 2 H, 10-H). − $C_{48}H_{46}O_6$ (718.89): calcd. C 80.20, H 6.45; found C 80.41, H 6.70.

1,4-Bis[4-(8-hydroxymethyl-2-anthryl)butyl]-2,5-dimethoxybenzene (**6**): To a suspension of 2 g (53 mmol) lithium aluminium hydride in 400 ml of tetrahydrofuran under argon, a solution of 5.2 g (7.2 mmol) of the diester **5** in 300 ml of tetrahydrofuran was slowly added (over about 1.5 h). After complete addition, the reaction mixture was stirred for 4 h. The reaction was stopped by the dropwise addition of 5 ml of water. The batch was then poured into 400 ml of 0.5 N aqueous hydrochloric acid. In a rotary evaporator the tetrahydrofuran was removed, and the remaining mixture was extracted with 400 ml of ethyl acetate. The organic phase was dried with magnesium sulfate and concentrated to dryness. The pale-yellow powder (yield 4.8 g, quantitative) was used for the following step without further purification. For analysis, a sample was chromatographed on silica with cyclohexane/ethyl acetate (1.4:1; R_f = 0.3). − MS; *m/z* (%): 644 (16, M − H_2O), 630 (39), 412 (20), 398 (41), 384 (18), 315 (17), 242 (18), 232 (24), 220 (28), 205 (100), 191 (36), 165 (23), 151 (17), a.o. − ^{1}H NMR (360 MHz, CDCl$_3$, 303 K): δ = 1.57−1.63 (m, 4 H, γ-H), 1.71−1.75 (m, 4 H, β-H), 2.58 (t, ^3J = 7.5 Hz, 4 H, δ-H), 2.81 (t, ^3J = 7.3 Hz, 4 H, α-H), 3.66 (s, 6 H, OCH$_3$), 5.08 (d, ^3J = 5.3 Hz, 4 H, CH$_2$), 5.31 (t, ^3J = 5.5 Hz, 2 H, OH), 6.72 (s, 2 H, centr. Ar-H), 7.37 (dd, ^3J = 8.7 Hz, ^4J = 1.4 Hz, 2 H, 3-H), 7.44 (dd, ^3J = 8.4 Hz, ^3J = 6.8 Hz, 2 H, 6-H), 7.53 (d, ^3J = 6.4 Hz, 2 H, 7-H), 7.84 (s, 2 H, 1-H), 7.95 (d, ^3J = 6.7 Hz, 2 H, 5-H), 7.97 (d, ^3J = 8.4 Hz, 2 H, 4-H), 8.49 (s, 2 H, 10-H), 8.57 (s, 2 H, 9-H). − $C_{46}H_{46}O_4$ (662.87): calcd. C 83.35, H 7.00; found C 83.14, H 7.20.

1,4-Bis[4-(8-formyl-2-anthryl)butyl]-2,5-dimethoxybenzene (**7**): 4.8 g (7.2 mmol) of the above mentioned bis(hydroxymethyl) compound **6** in 700 ml of dichloromethane was stirred under argon. After addition of 15 ml of dimethyl sulfoxide the mixture was cooled down to −75°C, and slowly 11 ml (16 g, 126 mmol) of oxalyl dichloride was added (during 2.5 h). After stirring for two more hours, 40 ml (29.2 g, 0.27 mol) triethylamine was added slowly. After a further hour, the reaction mixture was warmed up to room temp. and then poured into 400 ml of water. The organic phase was separated, washed with 300 ml of saturated aqueous

sodium hydrogen carbonate, then dried with magnesium sulfate, and the organic solvent was removed in a rotary evaporator. The yellow powder obtained (5.1 g, quantitative yield) was used for the next step without further purification. For analysis, a sample was chromatographed on silica with cyclohexane/ethyl acetate (3:1) and recrystallized from toluene, m.p. 184−186°C. − MS; *m/z* (%): 658 (100, M^+), 454 (36), 438 (17), 411 (30), 260 (69), 233 (28), 219 (95), 205 (43), 191 (97), 177 (38), 165 (54), 149 (40), 91(36). − ^{1}H NMR (360 MHz, $CDCl_3$, 303 K): δ = 1.66−1.73 (m, 4 H, γ-H), 1.78−1.86 (m, 4 H, β-H), 2.65 (t, ^3J = 8.1 Hz, 4 H, δ-H), 2.86 (t, ^3J = 7.4 Hz, 4 H, α-H), 3.73 (s, 6 H, OCH_3), 6.64 (s, 2 H, centr. Ar-H), 7.39 (dd, ^3J = 8.6 Hz, ^4J = 1.5 Hz, 2 H, 3-H), 7.54 (dd, ^3J = 8.5, ^3J = 6.9 Hz, 2 H, 6-H), 7.89−7.96 (m, 6 H, anthr.-H), 8.21 (d, ^3J = 8.5 Hz, 2 H, anthr.-H), 8.40 (s, 2 H, 10-H), 9.81 (s, 2 H, 9-H), 10.38 (s, 2 H, CHO). − $C_{46}H_{42}O_4$ (658.84): calcd. C 83.86, H 6.43; found C 83.98, H 6.67.

1,4-Bis(4-{8-[bis(5-benzyloxycarbonyl-4-ethyl-3-methyl-2-pyrryl)methyl]-2-anthryl}butyl)-2,5-dimethoxybenzene (**18**): 1.56 g (2.37 mmol) of the dialdehyde **7**, 2.31 g (9.5 mmol) of 2-benzyloxycarbonyl-3-ethyl-4-methylpyrrole[11], and 0.5 g of *p*-toluenesulfonic acid in 400 ml of benzene were refluxed under argon for 48 h. After cooling to room temp., 100 ml of ethyl acetate was added. The solution was washed with 400 ml of saturated sodium hydrogen carbonate, the organic phase was dried with magnesium sulfate, and after adding 10 g of florisil the solvent was concentrated. Chromatography on silica gel with cyclohexane/ethyl acetate (5:1) yielded **18** as orange oil which solidified on drying in vacuo, to give 2.0 g (53%), m.p. 106−109°C. − MS (LSIMS positive, *m*-nitrobenzyl alcohol/1% trifluoroacetic acid); *m/z* (%): 1596 (16), 1594 (45, M^+), 1506 (23), 1505 (56), 1504 (100), 1503 (83), 1488 (20), 1487 (21), 1459 (21), 1353 (29), 1352 (40), 1351 (36), 91 (100) a.o. − ^{1}H NMR (360 MHz, [D$_6$]DMSO, 303 K): δ = 0.99 (t, ^3J = 7.4 Hz, 12 H, CH_2CH_3), 1.56−1.67 (m, 8 H, β,γ-H), 1.89 (s, 12 H, pyrryl-CH_3), 2.55 (t, ^3J = 7.3 Hz, 4 H, δ-H), 2.63−2.72 (m, 8 H, CH_2CH_3), 2.76 (t, ^3J = 7.0 Hz, 4 H, α-H), 3.62 (s, 6 H, OCH_3), 5.20 (s, 8 H, OCH_2Ph), 6.44 (s, 2 H, methine-H), 6.68 (s, 2 H, Ar-H), 7.09 (d, ^3J = 6.9 Hz, 2 H, 7-H), 7.26−7.36 (m, 22 H, Ph-H, 3-H), 7.42 ("t", $^3J \approx$ 7.8 Hz, 2 H, 6-H), 7.57 (s, 2 H, 1-H), 7.95 (d, ^3J = 8.8 Hz, 2 H, 4-H), 7.99 (d, ^3J = 8.6 Hz, 2 H, 5-H), 8.28 (s, 2 H, 10-H), 8.51 (s, 2 H, 9-H), 10.81 (s, 4 H, NH). − $C_{106}H_{106}N_4O_{10}$ (1596.03): calcd. C 79.77, H 6.69, N 3.51; found C 79.93, H 6.88, N 3.61.

1,4-Bis(4-{8-[bis(5-carboxy-4-ethyl-3-methyl-2-pyrryl)methyl]-2-anthryl}butyl)-2,5-dimethoxybenzene (**19**): 1.2 g (0.75 mmol) of the above mentioned benzyl ester in 300 ml of tetrahydrofuran was stirred for 24 h under standard hydrogen pressure, in the presence of 1.3 g palladium (10%)/carbon. Then the catalyst was filtered off, and the filtrate was concentrated to dryness, leaving a red oil, which solidified on further drying. Under these conditions, the 9,10-position of the anthracenes were also partially hydrogenated (according to ^{1}H NMR). Yield 670 mg (72%), m.p. 144°C (dec.). − ^{1}H NMR (360 MHz, [D$_6$]DMSO, 303 K): δ = 1.02 (t, ^3J = 7.4 Hz, 12 H, CH_2CH_3), 1.47−1.67 (m, 8 H, β,γ-H), 1.98 (s, 12 H, pyrryl-CH_3), 2.54−2.78 (m, 16 H, α,β-H, CH_2CH_3), 3.65 (s, 6 H, OCH_3), 6.36 (s, 2 H, methine-H), 6.71 (s, 2 H, centr. Ar-H), 7.15 (d, ^3J = 6.9 Hz, 2 H, 7-H), 7.35−7.43 (m, 4 H, 3,6-H), 7.59 (s, 2 H, 1-H), 7.94−7.98 (m, 4 H, 4,5-H), 8.30 (s, 2 H, 10-H), 8.50 (s, 2 H, 9-H), 10.71 (s, 4 H, NH), 11.97 (s, 4 H, COOH). − $C_{78}H_{82}N_4O_2$ (1235.53): calcd. C 75.83, H 6.69, N 4.53; found C 75.59, H 7.03, N 4.03.

5,15-{2,5-Dimethoxy-1,4-benzenediyl[bis(4,1-butanediyl-7,1-anthraceno)]}-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (**20**): To 300 ml of dichloromethane under argon (dried by stirring with 6 g of magnesium sulfate for 15 min at room temp., with the exclusion of light) was added, in the following order: 0.68 g (0.55 mmol) of **19**, 5.7 g (35 mmol) of trichloroacetic acid, and 0.9 ml (5.4 mmol) of triethyl orthoformate. After 22 h at room temp., 0.6 g (7.3 mmol) of sodium acetate and 0.45 g (1.8 mmol) of *p*-chloranil were added. After further 3.5 h, 175 ml of saturated aqueous sodium hydrogen carbonate solution was added, and the mixture was vigorously stirred. The organic phase was separated and washed twice with 100 ml each of saturated sodium hydrogen carbonate solution and twice with 100 ml each of water. After separation and drying with magnesium sulfate, 7 g florisil was added, and the solvent was removed in a rotary evaporator. The remaining reaction mixture was flash-chromatographed on silica gel with toluene/ethyl acetate (20:1) and purified by MPLC on silica gel with cyclohexane/ethyl acetate (20:1) (R_f: product: 0.60; over-hydrogenated by-product: 0.74). The product was dissolved in a small amount of dichloromethane, covered with a methanol layer and left at 4°C for 2 d; dark blue-violet microcrystals were obtained in 5−13% yield, m.p. 272−275°C. − MS (LSIMS, *m*-nitrobenzyl alcohol/1% trifluoroacetic acid); *m/z* (%): 1081.6 (13), 1080.6 (26), 1079.6 (54), 1078.6 (87), 1077.6 (100), 1076.6 (27, M^+). − HR-MS for 1078 [MH^+]: $C_{76}H_{77}N_4O_2$, calcd. 1077.6047, found 1077.6078. − ^{1}H NMR (360 MHz, CD_2Cl_2, 303 K): δ = 2.17 (s, 2 H, NH), 1.26−1.30 (m, 8 H, β,γ-H), 1.71 (t, ^3J = 7.5 Hz, 12 H, CH_2CH_3), 2.12−2.19 (m, 16 H, pyrrole-CH_3, δ-H), 2.42−2.44 (m, 4 H, α-H), 2.98 (s, 6 H, OCH_3), 3.89−4.05 (m, 8 H, CH_2CH_3), 6.06 (s, 2 H, Ar-H), 6.74 (s, 2 H, 8-H), 7.19 (d, ^3J = 8.7 Hz, 2 H, 6-H), 7.28 (s, 2 H, 9-H), 7.93−7.99 (m, 4 H, 3,5-H), 8.35 (d, ^3J = 6.7 Hz, 2 H, 2-H), 8.52 (d, ^3J = 8.6 Hz, 2 H, 4-H), 8.69 (s, 2 H, 10-H), 10.29 (s, 2 H, methine-H).

5,15-{2,5-Benzoquinone-1,4-diyl[bis(4,1-butanediyl-7,1-anthraceno)]}-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (**4**): To 8 mg (7.4 μmol) of the dimethoxybenzene-bridged porphyrin cyclophane **20** in 20 ml of dichloromethane under argon and at room temp., 1 ml (1 mmol) of a 1 M solution of boron tribromide in dichloromethane was added. After 2 h, 20 ml of saturated aqueous sodium hydrogen carbonate solution was added, and the deep-green solution was vigorously stirred. After stirring, the now red organic phase was separated and washed with 20 ml of saturated sodium hydrogen carbonate solution and then with 20 ml of water. After the separation of the organic phase, 20 mg (80 μmol) of *p*-chloranil was added, and the reaction mixture was stirred for 5 min and then added to 20 ml of saturated sodium hydrogen carbonate solution. The organic phase was separated, washed with 20 ml of saturated sodium hydrogen carbonate solution and 20 ml of water, dried with magnesium sulfate and chromatographed [MPLC, toluene/ethyl acetate (30:1), on silica gel]. The product was dissolved in a small amount of dichloromethane, covered with a layer of methanol and allowed to stand for 2 d at 4°C. 1.5 mg (19%) of **4** was obtained as a violet powder; the yield was very variable reaching 81% of dark-violet microcrystals identical in MS and ^{1}H NMR to the previously mentioned sample (m.p. > 380°C). − MS (LSIMS positive, *m*-nitrobenzyl alcohol/1% trifluoroacetic acid); *m/z* (%): 1051.5 (31), 1050.6 (53), 1049.5 (100), 1048.5 (83), 1047.5 (92, MH^+), 1046.5 (14, M^+). − ^{1}H NMR (360 MHz, CD_2Cl_2, 303 K): δ = −2.19 (s, 2 H, NH), 1.26−1.31 (m, 8 H, β,γ-H), 1.72 (t, ^3J = 7.5 Hz, 12 H, CH_2CH_3), 1.99−2.04 (m, 4 H, δ-H), 2.18 (s, 12 H, pyrrole-CH_3), 2.47−2.50 (m, 4 H, α-H), 3.87−4.05 (m, 8 H, CH_2CH_3), 5.96 (s, 2 H, quinone-H), 6.79 (s, 2 H, 8-H), 7.20 (d, ^3J = 8.7 Hz, 2 H, 6-H), 7.42 (s, 2 H, 9-H), 7.92−8.00 (m, 4 H, 3,5-H), 8.29 (d, ^3J = 6.5 Hz, 2 H, 2-H), 8.52 (d, ^3J = 8.6 Hz, 2 H, 4-H),

8.70 (s, 2 H, 10-H), 10.28 (s, 2 H, methine-H). − HR-MS (MH^+): $C_{74}H_{71}N_4O_2$: calcd. 1047.5577; found 1047.5604.

5,15-{2,5-Dimethoxybenzene-1,4-diyl[bis(4,1-butanediyl-7,1-anthraceno)]}-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrinatozinc (**25**): To a solution of 24 mg (22 μmol) of **20** in 50 ml of trichloromethane/methanol (4:1) was added 220 mg (1.2 mmol) of zinc acetate, and the mixture was heated under reflux for 2 h. 300 ml of trichloromethane was added to the reaction, and the solution was washed with 200 ml of water, then with 200 ml of half-concentrated sodium hydrogen carbonate solution and again with 200 ml of water. The organic phase was dried with magnesium sulfate, and the solvents were removed. Thin-layer chromatography (aluminium oxide, toluene/ethyl acetate 20:1) showed the product spot exclusively. Recrystallization from dichloromethane/methanol yielded the zinc complex **25** as violet platelets: 22 mg (86%), m.p. > 370°C. − MS (FAB positive, *m*-nitrobenzyl alcohol/1% trifluoroacetic acid); *m/z*: 1142 (8), 1141 (7), 1140 (8, MH^+), 1139 (8, M^+), 1077 (100, M−Zn). − HR-MS (MH^+): calcd. for $C_{76}H_{75}O_2N_4Zn$: 1139.5181, found 1139.5129. − ^{1}H NMR (360 MHz, CD_2Cl_2, 303 K): δ = 1.22−1.31 (m, 8 H, β-CH_2, γ-CH_2), 1.68 (t, ^3J = 7.6 Hz, 12 H, CH_2CH_3), 2.11−2.14 (m, 16 H, pyrrole-CH_3, δ-CH_2), 2.40−2.43 (m, 4 H, α-CH_2), 2.88 (s, 6 H, OCH_3), 3.86−4.02 (m, 8 H, CH_2CH_3), 6.00 (s, 2 H, Ar-H), 6.70 (s, 2 H, 8-H), 7.19 (dd, ^4J = 1.4 Hz, ^3J = 8.8 Hz, 2 H, 6-H), 7.24 (s, 2 H, 9-H), 7.92−7.99 (m, 4 H, 3,5-H), 8.32 (d, ^3J = 5.5 Hz, 2 H, 2-H), 8.58 (d, ^3J = 8.7 Hz, 2 H, 4-H), 8.69 (s, 2 H, 10-H), 10.22 (s, 2 H, methine-H).

5,15-{p-Benzoquinone-1,4-diyl[bis(4,1-butanediyl-7,1-anthraceno)]}-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrinatozinc (**24**): To a solution of 20 mg (19 μmol) of the porphyrin−quinone cyclophane **4** in trichloromethane/methanol (4:1), was added 200 mg (1.1 mmol) of zinc acetate. After refluxing the reaction mixture for 2 h, the solution was diluted with 300 ml of dichloromethane, washed with 200 ml of water, with 200 ml of half-concentrated sodium hydrogen carbonate solution, and again with 200 ml of water. The organic phase was separated and dried with magnesium sulfate. The solvents were then removed; the residue [only one spot by DC (aluminium oxide, toluene/ethyl acetate, 20:1)] was crystallized from dichloromethane/methanol yielding, after standing at 4°C, black-violet microcrystals, 15 mg (72%), m.p. > 370°C. − ^{1}H NMR (360 MHz, CD_2Cl_2, 303 K): δ = 1.24−1.40 (m, 8 H, β- and γ-CH_2), 1.69 (t, ^3J = 7.6 Hz, 12 H, CH_2CH_3), 2.02 (m, 4 H, δ-CH_2), 2.13 (s, 12 H, pyrrole-CH_3), 2.46 (m, 4 H, α-CH_2), 3.86−4.02 (m, 8 H, CH_2CH_3), 5.95 (s, 2 H, Ar-H), 6.75 (s, 2 H, 8-H), 7.18 (dd, ^4J = 1.5 Hz, ^3J = 8.8 Hz, 2 H, 6-H), 7.35 (s, 2 H, 9-H), 7.92−8.00 (m, 4 H, 3,5-H), 8.27 (d, ^3J = 6.5 Hz, 2 H, 2-H), 8.52 (d, ^3J = 8.6 Hz, 2 H, 4-H), 8.70 (s, 2 H, 10-H), 10.23 (s, 2 H, methine-H). − MS (FAB positive, *m*-nitrobenzyl-alcohol/1% trifluoroacetic acid); *m/z* (%): 1116 (26), 1115 (46), 1114 (70), 1113 (82), 1112 (100), 1111 (98), 1110 (99, MH^+), 1109 (52, M^+), 1108 (40) a.o. − HR-MS (MH^+): $C_{74}H_{69}O_2N_4Zn$: calcd. 1109.4712, found 1109.4774.

1,4-Dibromo-3,6-dimethoxy-2,5-bis[4-(8-methoxycarbonyl-2-anthryl)-3-butenyl]benzene (Z/E Isomer Mixture): To 3.62 g (6.12 mmol) of [(8-methoxycarbonyl-2-anthryl)methyl]triphenylphosphonium bromide (**17**) and 80 mg of 18-crown-6 in 300 ml of dichloromethane, was added 2.50 g (18.0 mmol) of powdered potassium carbonate. To the dark-coloured solution under argon at 50°C, was added 1.00 g (2.45 mmol) of 2,5-dibromo-1,4-bis(2-formylethyl)-3,6-dimethoxybenzene, and after 24 h a further 1.0 g (7.2 mmol) of potassium carbonate and 50 mg (84 μmol) of phosphonium bromide. After an additional 24 h, the solution was cooled and poured into 200 ml of 1 N hydrochloric acid. The organic phase was separated, and the aqueous phase was extracted twice with 100 ml each of dichloromethane. The combined organic phases were dried with magnesium sulfate, and after addition of 10 g of florisil were concentrated to dryness in a rotary evaporator. The *E*/*Z* mixture was obtained as yellow powder, 2.1 g (98%), m.p. 155−160°C by chromatography (silica gel, cyclohexane/ethyl acetate, 5:1). − $C_{48}H_{40}Br_2O_6$ (872.65): calcd. C 66.07, H 4.62, Br 18.31; found C 65.83, H 4.83, Br 18.23.

1,4-Dibromo-3,6-dimethoxy-2,5-bis[4-(8-methoxycarbonyl-2-anthryl)butyl]benzene (**8**): 1.85 g (2.12 mmol) of the above mentioned *E*/*Z* mixture was hydrogenated in 250 ml of tetrahydrofuran over palladium (10%)/carbon under normal hydrogen pressure for 4.5 h. The catalyst was removed by filtration through Celite, and the solvents were removed in vacuo to give 1.87 g (≈ quant.) .For analysis, the product was dissolved in dichloromethane, filtered through silica gel, and crystallized from dichloromethane/*n*-hexane, m.p. 183°C. − MS; *m/z* (%): 876 (11, M^+), 250 (20), 249 (100), 223 (15), 191 (12), 190 (23), 189 (18). − ^{1}H NMR (360 MHz, $CDCl_3$, 303 K): δ = 1.61−1.69 (m, 4 H, γ-CH_2), 1.84−1.90 (m, 4 H, β-CH_2), 2.85−2.90 (m, 8 H, α,δ-CH_2), 3.77 (s, 6 H, OCH_3), 4.05 (s, 6 H, $COOCH_3$), 7.38 (dd, ^3J = 8.6 Hz, ^4J = 1.3 Hz, 2 H, 3-H), 7.41 (dd, ^3J = 8.3 Hz, ^3J = 8.4 Hz, 2 H, 6-H), 7.87 (s, 2 H, 1-H), 7.92 (d, ^3J = 8.7 Hz, 2 H, 4-H), 8.17 (d, ^3J = 8.5 Hz, 2 H, 7-H), 8.21 (d, ^3J = 7.1 Hz, 2 H, 5-H), 8.41 (s, 2 H, 9-H), 9.47 (s, 2 H, 10-H). − $C_{48}H_{44}Br_2O_6$ (876.68): calcd. C 65.76, H 5.06, Br 18.23; found C 65.64, H 5.23, Br 18.36.

1,4-Dibromo-2,5-bis[4-(8-hydroxymethyl-2-anthryl)butyl]-3,6-dimethoxybenzene (**9**): 2.50 g (2.85 mmol) of **8** was dissolved under argon in 300 ml of dry tetrahydrofuran, and 550 mg (25.0 mmol) of lithium tetrahydridoborate was added in two portions. After 6 h of heating under reflux, a further 550 mg (25.0 mmol) of lithium tetrahydridoborate was added, and the reaction mixture was heated for further 12 h under reflux. After cooling, a few ml of water were added dropwise for hydrolysis, and the solvent was evaporated. The residue was dissolved in dichloromethane, washed twice with 100 ml each of 2 N hydrochloric acid and once with 100 ml of water. The organic phase was dried with magnesium sulfate, and the solvent was removed in vacuo to give 2.04 g (87%, m.p. 127°C) of a white powder, which was immediately used for the next reaction.

1,4-Dibromo-2,5-bis[4-(8-formyl-2-anthryl)butyl]-3,6-dimethoxybenzene (**10**): 2.04 g (2.50 mmol) of **9** was dissolved in 150 ml of dichloromethane, to which 5.0 ml (70 mmol) of dry dimethyl sulfoxide was added. Under argon, the mixture was cooled to −75°C and during 1.5 h, 3.8 ml (44 mmol) of oxalyl dichloride was added dropwise. The reaction was kept stirring at this temp. for 2 h, and then 11.2 ml (82 mmol) of triethylamine was added, and kept at −75°C for another 1 h. The reaction mixture was warmed up to room temp. over 2 h, and then was poured into 200 ml of water. The organic phase was separated, washed with saturated sodium hydrogen carbonate solution, dried with magnesium sulfate, and the solvent removed in vacuo, leaving a yellow oil which crystallized slowly at 4°C. This product was used immediately for the next step. For the analysis a sample was dissolved in dichloromethane, filtered through silica gel and crystallized from dichloromethane/*n*-hexane to give yellow crystals, m.p. 89°C. − MS (FAB); *m/z* (%): 820 (26), 819 (59), 818 (83), 817 (99, MH^+), 816 (100, M^+), 815 (52), 814 (39). − ^{1}H NMR (360 MHz, $CDCl_3$, 303 K): δ = 1.63−1.71 (m, 4 H, γ-CH_2), 1.84−1.93 (m, 4 H, β-CH_2), 2.83−2.91 (m, 8 H, α-CH_2, δ-CH_2), 3.77 (s, 6 H, Ar-OCH_3), 7.41 (dd, ^3J = 8.7 Hz, ^4J = 1.6 Hz, 2 H, 3-H), 7.55 (dd, ^3J = 8.5 Hz, ^3J = 6.8 Hz, 2 H, 6-H), 7.92−7.97 (m, 6 H, 1-H, 4-H, 7-H), 8.23 (d, ^3J = 8.4 Hz, 2 H, 5-H), 8.43 (s, 2 H, 10-H), 9.83 (s, 2 H, 9-H), 10.38 (s,

2 H, CHO). − $C_{46}H_{40}Br_2O_4$ (816.59): calcd. C 67.66, H 4.94, Br 19.57; found C 67.71, H 5.08, Br 19.53.

5,15-{1,4-Dibromo-3,6-dimethoxy-2,5-benzenediyl[bis(4,1-butanediyl-7,1-anthraceno)]}-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (**23**): 7.0 g of magnesium sulfate in 350 ml of dichloromethane was stirred under argon for 30 min, and then 0.24 g (0.87 mmol) of 2,2′-bis(3-ethyl-4-methylpyrryl)methane, 5.70 g of trichloroacetic acid, and the above-mentioned dialdehyde **10** dissolved in small amounts of dichloromethane, were added in quick succession. The solution was vigorously stirred at room temp. and with exclusion of light. 600 mg of sodium acetate and 0.45 g (1.8 mmol) of chloranil were then added, and the reaction mixture was stirred for a further 15 min. To the reaction mixture 100 ml of saturated aqueous sodium hydrogen carbonate was added, the organic phase was separated and washed three times with 300 ml each of saturated aqueous sodium hydrogen carbonate solution as well as six times with 300 ml of water. After drying with magnesium sulfate and removing the solvent by distillation, the obtained black residue was filtered from a toluene/ethyl acetate (20:1) solution through aluminium oxide. The solvents were evaporated from the porphyrin-containing fractions, and the residue was purified by flash-chromatography (silica gel, toluene/ethyl acetate, 20:1) and subsequent MPLC (silica gel, cyclohexane/ethyl acetate, 97:3). The combined product fractions were concentrated to dryness, dissolved in a small amount of dichloromethane, layered with 10 ml of methanol, and keeping at 4°C to give 19−24 mg (5−7%) of **23**, m.p. > 370°C. − MS (FAB positive, *m*-nitrobenzyl alcohol/1% trifluoroacetic acid); *m/z* (%): 1238 (27), 1237 (50), 1236 (79), 1235 (83), 1234 (100, MH^+), 1233 (56, M^+), 1232 (47) o.a. − ^{1}H NMR (360 MHz, CD_2Cl_2, 303 K): δ = −2.14 (s, 2 H, NH), 1.27−1.31 (m, 4 H, β-CH_2), 1.37−1.42 (m, 4 H, γ-CH_2), 1.71 (t, ^3J = 7.5 Hz, 12 H, CH_2CH_3), 2.19 (s, 12 H, CH_3), 2.37−2.45 (m, 8 H, α-,δ-CH_2), 2.81 (s, 6 H, OCH_3), 3.92−4.00 (m, 8 H, CH_2CH_3), 6.79 (s, 2 H, 8-H), 7.20 (d, ^3J = 7.9 Hz, 2 H, 6-H), 7.36 (s, 2 H, 9-H), 7.92−8.00 (m, 4 H, 3-and 5-H), 8.31 (d, ^3J = 5.6 Hz, 2 H, 2-H), 8.51 (d, ^3J = 8.6 Hz, 2 H, 4-H), 8.69 (s, 2 H, 10-H), 10.30 (s, 2 H, methine-H). − $C_{76}H_{75}Br_2O_2N_4$: calcd. 1233.4257 (M^+), found 1233.4296.

5,15-{1,4-Dibromo-3,6-dimethoxy-2,5-benzenediyl[bis(4,1-butanediyl-7,1-anthraceno)]}-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrinatozinc (**27**): To a solution of 21 mg (17 μmol) of **23** in 50 ml of trichloromethane/methanol (4:1), 200 mg (1.1 mmol) of zinc acetate was added, and the reaction mixture was heated under reflux for 2 h. After dilution with 300 ml of dichloromethane, the solution was washed with 200 ml of water, 200 ml of half-concentrated sodium hydrogen carbonate solution, and again with 200 ml of water. The organic phase was dried with magnesium sulfate, and the solvents were evaporated. Thin-layer chromatography (TLC) (aluminium oxide, toluene/ethyl acetate, 20:1) showed only the product spot. Recrystallization (dichloromethane/methanol, 4°C) yielded 14 mg (63%) of the product, m.p. 321°C. − MS (FAB positive, *m*-nitrobenzyl alcohol); *m/z* (%): 1300 (10, MH^+), 1299 (13, M^+), 1298 (14), 1297 (15), 279 (32), 149 (100), 136 (84) a.o. − ^{1}H NMR (500 MHz, CD_2Cl_2, 303 K): δ = 1.91−1.51 (m, 4 H, β-,γ-CH_2), 1.69 (t, ^3J = 7.5 Hz, 12 H, CH_2CH_3), 2.11 (s, 12 H, CH_3), 2.27−2.35 (m, 8 H, α-,δ-CH_2), 2.79 (s, 6 H, OCH_3), 3.90−4.02 (m, 8 H, CH_2CH_3), 6.76 (s, 2 H, 8-H), 7.19 (d, ^3J = 7.5 Hz, 2 H, 6-H), 7.53 (s, 2 H, 9-H), 7.93−7.98 (m, 4 H, 3,5-H), 8.25 (d, ^3J = 6.0 Hz, 2 H, 2-H), 8.51 (d, ^3J = 8.5 Hz, 2 H, 4-H), 8.68 (s, 2 H, 10-H), 10.22 (s, 2 H, methine-H).

5,15-{1,4-Dibromo-p-benzoquinone-2,5-diyl[bis(4,1-butanediyl-7,1-anthraceno)]}-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (**4**, **X = Br**): To 32 mg (26 μmol) of **23** in 50 ml of dichloromethane under argon, was added in portions over 1 h, 1 ml of boron tribromide, dissolved in 10 ml of dichloromethane. After stirring for a further 2 h at room temp., 40 ml of saturated aqueous sodium hydrogen carbonate solution and 200 ml of dichloromethane were added. The phases were separated, and the aqueous phase was extracted twice with 100 ml each of dichloromethane. The combined organic phases were washed twice with 50 ml each of water, then dried with magnesium sulfate and concentrated in vacuo to a volume of 150 ml. This solution, together with 80 mg (6.1 mmol) of chloranil was stirred for 10 min at room temp. and with exclusion of light. The solution was again washed three times with 100 ml each of saturated aqueous sodium hydrogen carbonate solution as well as three times with 100 ml each of water. The organic solution was dried with magnesium sulfate, and the solvents were evaporated. The residue was purified by MPLC (silica gel, cyclohexane/ethyl acetate, 97:3). The product fractions were concentrated to dryness, dissolved in a small amount of dichloromethane, and covered with a fourfold amount of methanol. At 4°C within 24 h, violet microcrystals were formed, yield 24 mg (77%), m.p. > 370°C. − MS (FAB positive, *m*-nitrobenzyl alcohol/1% trifluoroacetic acid); *m/z* (%): 1206 (6), 1205 (8, MH^+), 1204 (6, M^+). − ^{1}H NMR (360 MHz, CD_2Cl_2, 303 K): δ = −2.17 (s, 2 H, NH), 1.31−1.40 (m, 8 H, β-,γ-CH_2), 1.71 (t, ^3J = 7.6 Hz, 12 H, CH_2CH_3), 2.19 (s, 12 H, CH_3), 2.32−2.37 (m, 4 H, δ-CH_2), 2.39−2.44 (m, 4 H, α-CH_2), 3.89−4.06 (m, 8 H, CH_2CH_3), 6.78 (s, 2 H, 8-H), 7.20 (d, ^3J = 8.4 Hz, 2 H, 6-H), 7.31 (s, 2 H, 9-H), 7.92−8.00 (m, 4 H, 3-,5-H), 8.32 (d, ^3J = 6.7 Hz, 2 H, 2-H), 8.52 (d, ^3J = 8.6 Hz, 2 H, 4-H), 8.70 (s, 2 H, 10-H), 10.30 (s, 2 H, methine-H).

5,15-{1,4-Dibromo-p-benzoquinone-2,5-diyl[bis(4,1-butanediyl-7,1-anthraceno)]}-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrinatozinc (**26**): To 25 mg (21 μmol) of the quinone-porphyrin cyclophane **4**, **X = Br** in 50 ml of trichloromethane/methanol (4:1), was added 200 mg (1.1 mmol) of zinc acetate, and the reaction mixture was refluxed for 2 h. 300 ml of dichloromethane was then added, and the solution was washed with 200 ml of water, followed by 200 ml of half-saturated sodium hydrogen carbonate solution, and once again with 200 ml of water. The organic phase was dried with magnesium sulfate, and then the solvents were removed by distillation. TLC (aluminium oxide, toluene/ethyl acetate, 20:1) showed only one product spot. Recrystallization from dichloromethane/methanol at 4°C yielded 23 mg (88%) of the product as black-violet microcrystals (m.p. > 365°C). − ^{1}H NMR (500 MHz, CD_2Cl_2, 303 K): δ = 1.24−1.30 (m, 8 H, β-CH_3), 1.42−1.48 (m, 8 H, γ-CH_2), 1.68 (t, ^3J = 7.6 Hz, 12 H, CH_2CH_3), 2.13 (s, 12 H, CH_3), 2.36−2.43 (m, 4 H, δ-CH_2), 2.43−2.48 (m, 4 H, α-CH_2), 3.85−3.93 (m, 8 H, CH_2CH_3), 6.74 (s, 2 H, 8-H), 7.17 (d, ^3J = 8.8 Hz, 2 H, 6-H), 7.24 (s, 2 H, 9-H), 7.92−7.98 (m, 4 H, 3-,5-H), 8.30 (d, ^3J = 6.8 Hz, 2 H, 2-H), 8.51 (d, ^3J = 8.9 Hz, 2 H, 4-H), 8.69 (s, 2 H, 10-H), 10.22 (s, 2 H, methine-H).

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