Photoinduced Electron-Transfer in Porphyrin-Quinone Cyclophanes, 17[◇]

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

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In continuation of previous syntheses of benzene-, naphthalene-, and anthracene-spacered porphyrin-quinone cyclophanes **1**, **2**, and **4**, biphenylene-spacered porphyrin-quinone cyclophanes of structure **3** as the "missing link" between **2** and **4** were prepared in multistep syntheses. These donor-acceptor systems are of interest since, with regard to electron-transfer rates, they complete the series of **1**, **2**, and **4.** As expected the electron-transfer of **3** proceeds between that of **2** and **4** in an especially steep region of distance dependences of electron-transfer rates.

To determine the distance dependence of photoinduced electron-transfer from porphyrins to quinones, a series of new intramolecular porphyrin-quinone compounds of well-defined sandwich-type cyclophane structures was synthesized. The distance variation was achieved by perpendicularly oriented arene "spacers" with the intention to keep the porphyrin and quinone structures in transannular face-to-face arrangements at well-defined distances. As such spacers 1,2-substituted benzene[2], 1,7-substituted naphthalene[3], and 1,7-substituted anthracene[1] so far have been used successfully for building up the porphyrin-quinone cyclophane structures **1**, **2**, and **4**, in which, due to the graduated extension of the spacers, a stepwise increase of the porphyrin-quinone distances was realized.

As discussed in the preceding papers[1][2][3], time-resolved fluorescence spectroscopy as a measure of photoinduced electron-transfer yielded approximated fluorescence lifetimes for **1** in the order of 1 *pico*second (ps); for **2** the lifetime is only slightly increased by a factor of about 2. For the anthracene-spacered **4** with the longest porphyrin-quinone distance, however, a fluorescence lifetime was found in the order of 10 *nano*seconds (e.g., 5.6 ns, in toluene)[4][10]. This remarkable difference of electron-transfer rates prompted us to try the synthesis of a cyclophane with a porphyrin-quinone distance in the critical region between the naphthalene- and the anthracene-spacered cyclophanes **2** and **4**.

The biphenylene-spacered analogue **3** with an intermediate transannular distance between **2** and **4**, with the same insertion angle to the arene spacers and an identical structure of the quinone-containing bridge as well as the same substitution pattern on the porphyrin part seemed to be a suitable system for studying the problem mentioned above. In fact, the biphenylene-spacered porphyrin-quinone cyclophane of structure **3** so far was a "missing link" in an especially interesting region with regard to the distance dependence of electron-transfer rates in porphyrin-quinone compounds.

Synthesis of Biphenylene-Spacered Porphyrin-Quinone Cyclophanes 3 and 19 and Related Cyclophanes

As described in the preceding papers on the syntheses of spacered porphyrin-quinone cyclophanes **1**, **2**, and **4**[1][2][3], the appropriate precursors for the preparation of these compounds were the corresponding dialdehydes consisting of the tetramethylene−2,5-dimethoxybenzene−tetramethylene bridges linked on both sides into the corresponding positions of the respective arene spacers. These arene spacers must be substituted in the *ortho*- or 1-positions by the terminal aldehyde groups which are essential for the cyclizing condensation with suitable pyrrole derivatives to form the porphyrin skeleton, thus completing the cyclophane structure. The demethylation of the two methoxy groups in the central aromatic ring of the bridge, and the subsequent oxidation to the quinones would then yield the desired arene-spacered porphyrin-quinone cyclophanes.

This general synthetic route, so far very successful and well-established in all our syntheses of compounds of the **1**-, **2**-, and **4**-series, had to be modified significantly, however, in the case of the synthesis of the biphenylene-spacered systems **3**. The reasons are that the tetramethylene−benzene−tetramethylene chains in the earlier syntheses were built up by twofold Wittig reactions with the aldehyde groups of the arene spacers; these reactions lead to double bonds

[◇] Part 16: Ref.[1].

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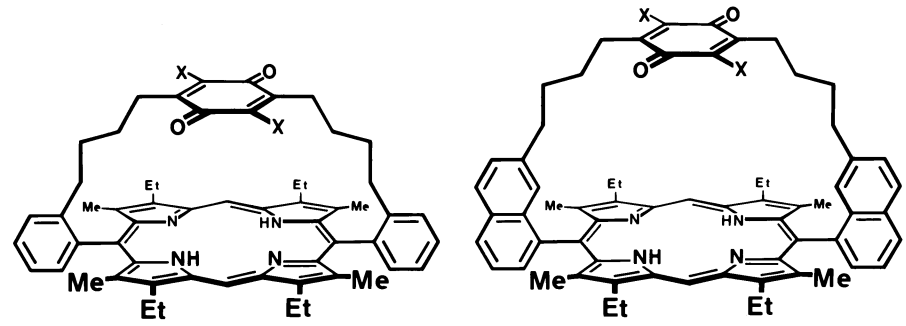
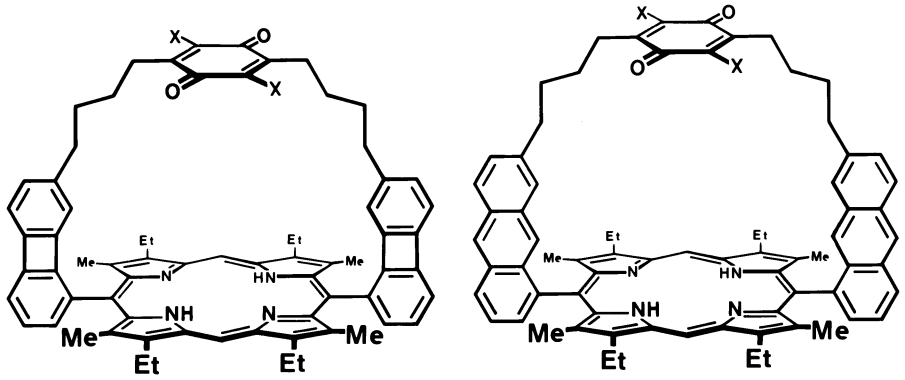


1 2

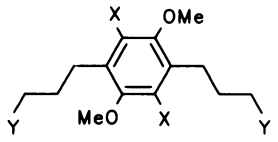


3 4

which must be hydrogenated to the tetramethylene chains. Since these hydrogenation steps might cleave, however, the four-membered rings of the two biphenylene units irreversibly, a different synthesis of the required dialdehydes **16** and **13** had to be worked out.

A second problem of the synthesis of **3** was the selective 1,7-disubstitution of the biphenylene by two different functional groups applicable for the further reactions in these two positions as needed for the preparation of the required dialdehydes. Fortunately, the metallation of biphenylene takes place preferably in the 1-position (*n*-butyllithium, *n*-hexane, potassium *tert*-butoxide, −50 to −55°C[5]; details see Experimental Section). A stream of carbon dioxide, dried by passing through concentrated sulfuric acid, was introduced into the reaction (1 h at −50°C, then 1 h without cooling). After purification of the product, biphenylene-1-carboxylic acid was esterified by diazomethane yielding after chromatography and drying the methyl ester (37% yield).

The tetramethylene−dimethoxybenzene−tetramethylene bridge in **3**, to be linked on both sides to the 7-positions of the two biphenylenes, was built up starting from 2,5-bis(3-bromopropyl)-1,4-dimethoxybenzene (**5**)[6] which with sodium cyanide−dimethyl sulfoxide yielded 2,5-bis(3-cyanopropyl)-1,4-dimethoxybenzene (**6**) (99% yield). For the conversion of the aforementioned dicyano compound into the corresponding 2,5-bis(3-methoxycarbonylpropyl)-1,4-dimethoxybenzene (**7**) the starting material was dissolved at room temperature in a mixture of equal amounts of methanol and dichloromethane, into which dried hydrochloride gas was introduced until saturation. After stirring, the solvents were distilled off, leaving **7** in 91% yield.

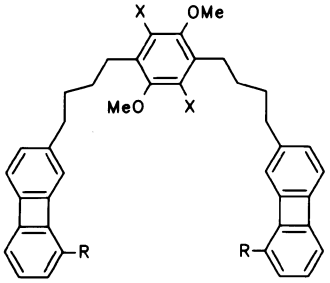


5: X = H, Y = Br
6: X = H, Y = CN
7: X = H, Y = CO-OMe
8: X = Br, Y = CO-OMe
9: X = Br, Y = CO-OH
10: X = Br, Y = CO-Cl

To prevent a twofold *intra*molecular cyclization reaction in the subsequent Friedel-Crafts reaction, the two unsubstituted positions in the aromatic ring of **7** were protected by bromination to 1,4-dibromo-2,5-dimethoxy-3,6-bis(3-methoxycarbonylpropyl)benzene (**8**). The basic hydrolysis of the ester groups in **8** was carried out by heating a methanol solution of the ester in potassium hydroxide in methanol/water under reflux yielding the dicarboxylic acid **9** which was converted into the corresponding dicarboxylic dichloride **10** by heating with excess oxalyl dichloride (95% yield).

With biphenylene-1-carboxylic ester and the dicarboxylic acid dichloride **10** the components were available for building up the carbon skeleton of **11**. It was known that biphenylenes with electron-attracting substituents in the 1-position react preferably with the C-7 position of the other aromatic ring, which is exactly what was needed in this synthesis. This regioselective direction of a second substituent into the 7-position of biphenylene-1-carboxylic ester was checked by

bromination and − in our case most important − by a Friedel-Crafts reaction with acetyl chloride to the 7-acetyl compound (see Experimental Section). The Friedel-Crafts reaction of **10** with methyl biphenylene-1-carboxylate was carried out by adding a solution of the two components in 1,2-dichloroethane under argon within 30 min to a suspension of aluminium chloride in 1,2-dichloroethane under ice/water cooling. Without isolation of the primary product, the keto groups introduced by the Friedel-Crafts reaction were reduced to methylene groups (trifluoroacetic acid in 1,2-dichloroethane, then triethylsilane; for details see Experimental Section). Since during the Friedel-Crafts reaction the two methoxy groups of the central aromatic ring were partially cleaved to hydroxy groups, these were remethylated by dimethyl sulfate in boiling acetone in the presence of potassium carbonate to yield **11** which already contains the carbon skeleton of the spacer-bridge-spacer system needed for the synthesis of the porphyrin-quinone cyclophane wanted.



11: R = CO-OMe, X = Br
12: R = CH_2OH, X = Br
13: R = CHO, X = Br
14: R = CO-OMe, X = H
15: R = CH_2OH, X = H
16: R = CHO, X = H

Reduction of **11** by lithium tetrahydridoborate in tetrahydrofuran yielded **12** with the two 8-hydroxymethylbiphenylene units, 96%). **12** was oxidized by barium manganate in boiling dichloromethane to yield the dialdehyde **13** (84% yield). As will be shown below, this dialdehyde was used as the precursor of the biphenylene-spacered 2,5-dibromoquinone-porphyrin cyclophane **19**, containing a stronger electron acceptor than the cyclophane **3(X=H)**.

For the synthesis of this parent porphyrin-quinone cyclophane, however, the two bromo substituents of the central aromatic ring of **12** were to be removed by lithiation (*n*-butyllithium, *n*-hexane), followed by hydrolysis to **15** which was oxidized by barium manganate in dichloromethane to the dialdehyde **16** (75%).

The dialdehydes **13** and **16**, containing the biphenylene units linked to the central aromatic ring by the two tetramethylene chains with all the substituents in the right places, represent the essential partial structures for building up the wanted biphenylene-spacered porphyrin cyclophanes. In the next step the condensation of the aldehyde groups of **16** with 2-benzyloxycarbonyl-3-ethyl-4-methylpyrrole[7], carried out earlier with good results in the syntheses of other porphyrine cyclophanes[1][2][3], in this specific case resulted in unsatisfactory yields since the hydrogenolytic removal of the benzyl groups also led to a partial cleavage of the four-membered rings of the biphenylenes, and to other side-reactions. The basic hydrolysis of the benzyl esters in ethanol by sodium hydroxide/water according to ref.[8] succeeded in the first step to the tetracarboxylic acids; the ring closure to the porphyrin, however, was not achieved in satisfactory yields.

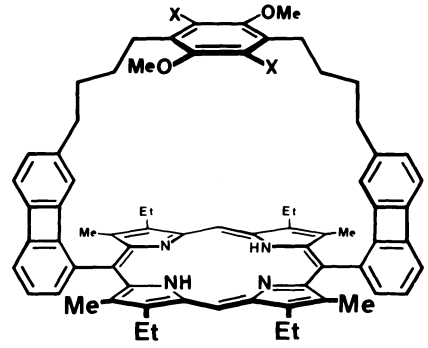
The desired cyclization linking the two aldehyde groups of **16** to form a porphyrin system was eventually achieved by condensation of **16** with bis(3-ethyl-4-methyl-2-pyrrolyl)-methane[9] in dichloromethane in the presence of trichloroacetic acid, followed by the oxidation of the porphyrinogene by chloranil in the presence of sodium acetate. After chromatography on aluminium oxide and crystallization from dichloromethane/methanol, the cyclophane was obtained as violet microcrystals in 30% yield. All analytical and spectroscopic data are in full agreement with the structure of the arene-porphyrin cyclophane **17**, where the appropriately substituted central arene is connected to the porphyrin by two tetramethylene−biphenylene units linked to the opposite 5,15-positions of the porphyrin.

The corresponding biphenylene-spacered porphyrin-arene cyclophane **18** with the two bromo substituents in the arene ring was obtained from the dialdehyde **13** according to the procedure described for the preparation of **17** (see above). The cyclophane **18** was purified by flash chromatography and recrystallization from dichloromethane/methanol (violet microcrystals; 8% yield; for further analytical data see Experimental Section.)

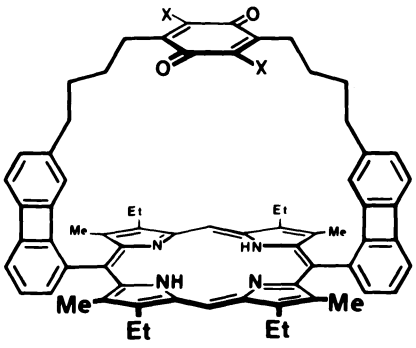
With **17** and **18** the carbon skeleton of the desired products with the porphyrins, the two biphenylene spacers, and the two tetramethylene bridges to the central arene ring on top were achieved. The last remaining steps were the cleavage of the methoxy to hydroxy groups, and the oxidation to the quinones. The demethylation of the methoxy substituents by boron tribromide in dichloromethane and the oxidation by 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) yielded, after recrystallization in the case of **17**, the corresponding quinone-porphyrin cyclophane **3(X=H)** (92%). The corresponding reaction sequence for **18** (demethylation by boron tribromide and oxidation by DDQ) yielded the dibromoquinone analogue **19** (in 77% yield).

Since for a variety of porphyrin-quinone cyclophanes containing zinc complexation in the porphyrin centre ultrafast charge separations were observed on photoinduction[4][10], the zinc complex of **3** was also of interest. The earlier studies dealing with zinc−porphyrin complexes of the cyclophane type **1** and **2** showed by X-ray structure analyses[3][6][11], and in agreement with molecular dynamics calculations[12], that the quinones in the cyclophane bridges are inclined towards the porphyrin plane leading to short contacts between the carbonyl oxygen atoms and the zinc centre (ca. 255 pm). The rigidly extended biphenylene spacers in the porphyrin-quinone cyclophanes **3**, of course, would prevent such a close interaction between the quinone part and the zinc ion in the porphyrin centre. Thus, from **3(X=H)** and **17** with zinc(II) acetate in trichloromethane/methanol (5:1) the zinc complexes of the biphenylene-spacered cyclophanes **20** and **21** were obtained in about 80% yield.

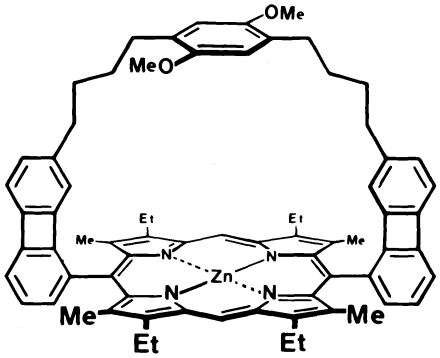
For **17**, **3(X=H)** and their zinc complexes **20** and **21**, all analytical data are in accordance with the structures sug-



17 : X = H
18 : X = Br



3 : X = H
19 : X = Br



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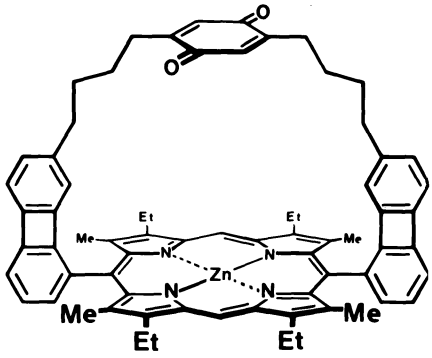

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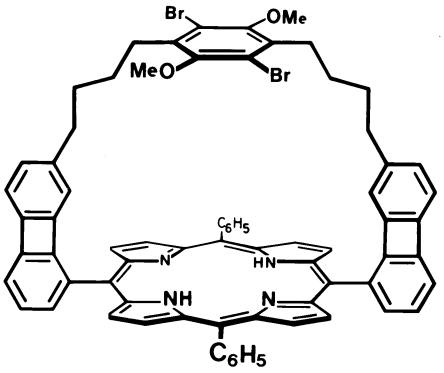
gested (see Experimental Section). Physical properties confirming the biphenylene-spacered porphyrin-quinone cyclophane structure as well as preliminary results related to electron-transfer reactions are dealt with in the following sections.

As an additional type of biphenylene-spacered porphyrin-quinone cyclophanes, corresponding cyclophanes with phenyl substituents in the 10- and 20-positions of the porphyrin were of interest with regard to conformational and electronic effects on the cyclophane structure. For this reason, the dialdehyde **13** by acid-catalyzed condensation with pyrrole (*p*-toluene sulfonic acid, toluene) and subsequent reaction with benzaldehyde in propionic acid yielded cyclophane **22** with 10,20-diphenylporphyrin as the porphyrin component of the cyclophane. Demethylation of the dimethoxy groups of the central arene ring in the bridge with boron triiodide and oxidation by DDQ yielded a further biphenylene-spacered porphyrin-quinone cyclophane **23**, differing from the precedingly described biphenylene-spacered porphyrin-quinone cyclophanes by the two phenyl substituents in the 10- and 20-positions and the missing alkyl groups in the β-pyrrole positions at the periphery of the porphyrin, making the porphyrin in **23** a weaker electron-donor.

Physical Measurements on Biphenylene-Spacered Porphyrin-Quinone Cyclophanes

^{1}H-NMR Investigations of Biphenylene-Spacered Porphyrin-Quinone Cyclophanes

The ^{1}H-NMR data of the biphenylene-spacered cyclophanes are in accordance with the structures suggested. Chemical shifts and coupling constants are in general in the normal range. Of special interest, however, are the ^{1}H-NMR signals of those protons for which a significant dependence on the porphyrin−quinone distances was to be expected. Such distance dependences of ^{1}H-NMR data in the series **1**, **2**, **3**, **4** (all **X=H**) result from the porphyrin which as a cyclic conjugated ring system exerts an anisotropic ring-current effect leading to a shielding of those hydrogen atoms located inside the conjugated π-system of the porphyrin. Since the steric arrangement of the bridges with respect to the porphyrin plane is primarily determined by



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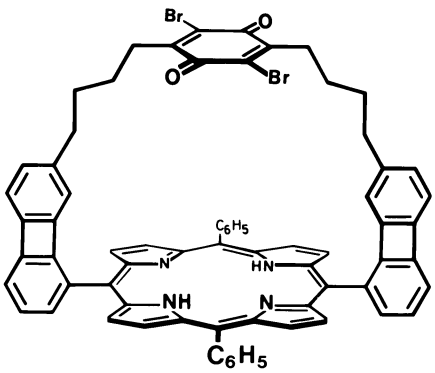

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the length of the arene-spacers in **1** to **4**, the increasing distances should lead to decreasing shielding of the protons in the central parts of the bridges. These are especially the hydrogen atoms of the central benzene rings as well as of the quinoid rings of the quinone-porphyrin cyclophanes, as we discussed already for **4**[1].

For the central benzene rings in the open-chained precursors before closing the cycle to the porphyrine−arene−cyclophanes, the chemical shifts of these arene protons are in the normal range of $\delta = 6.6-6.7$ like, for example, the aromatic protons in 1,4-dimethyl-2,5-dimethoxybenzene (δ = 6.65, $CDCl_3$). As soon as the porphyrin rings are closed, however, we note for these protons of the central benzene rings in the bridge a strong shielding by the porphyrin ring-current depending on the transannular distances between the porphyrin unit and the central aromatic ring of the bridge. For the benzene- and naphthalene-spacered cyclophanes with the shortest transannular distances, the δ values for the two hydrogen atoms on the central benzene ring are dramatically reduced from the normal value of $\delta \approx 6.65$ to $\delta = 4.15$ for the benzene-spacered compound, and to $\delta = 4.41$ for the naphthalene-spacered analogue as a result of the porphyrin ring-current (all s, 2 H, $CDCl_3$). For the biphenylene- and anthracene-spacered systems due to the longer transannular distances from porphyrin to the benzene units of the bridges the chemical shifts of the two protons on these benzene rings are reduced only to $\delta = 5.71$ (s, 2 H; $CDCl_3$), and $\delta = 5.96$ (s, 2 H; CD_2Cl_2), respectively, and thus are approaching the normal chemical shifts of the corresponding protons of the open-chain precursor rather closely.

For the porphyrin-quinone cyclophanes the trend of the ^{1}H-NMR data in relation to the porphyrin−quinone distances is very similar. Whereas the chemical shift for the ring protons of 2,5-dimethyl-1,4-quinone is observed at δ = 6.69 (s, 2 H, $CDCl_3$), for the quinoid protons of the benzene-spacered porphyrin-quinone cyclophane **1** the δ value for these protons is reduced to $\delta = 4.15$ (CD_2Cl_2) as a consequence of the shielding ring-current in the porphyrin. For the naphthalene-spacered analogue **2(X=H)** the δ value of the protons on the quinone is still significantly reduced to $\delta = 4.92$ (s, 2 H, $CDCl_3$), whereas for the more extended biphenylene- and anthracene-spacered porphyrin-quinone cyclophanes **3** and **4** the shifts of the quinone protons, as compared to 2,5-dimethylquinone, with $\delta = 5.81$ (s, 2 H, $CDCl_3$) for **3(X=H)** and to $\delta = 5.96$ (s, 2 H, CD_2Cl_2) for **4(X=H)** move considerably closer to the normal δ value.

These ^{1}H-NMR data give significant information with regard to mean electron-donor−acceptor distances in porphyrin-quinone cyclophanes which are, of course, of interest for electron-transfer processes. Certainly different conformational processes still exist, like the ring rotation of the central ring around the axis through the bridge-head atoms or the "swinging bridge" process[3], or the N−H tautomerization in the porphyrin part. Obviously, however, the energy barriers in these systems are low, since they could not be determined by low-temperature ^{1}H-NMR measurements down to 143 K ($CD_2Cl_2/CFCl_3$, 1:4).

Of further interest are the high-field shifts which are observed for the quinone protons of the zinc complexes of the benzene- and naphthalene-spacered systems ($\Delta\delta$ = 0.47 and 3.76, respectively), which most likely are due to an attractive interaction between the zinc ion and the carbonyl oxygen atoms of the quinones[3][10][11]. This high-field shift is not observed for the zinc complexes of the biphenylene- and anthracene-spacered porphyrin-quinone cyclophanes, where obviously the distances between the porphyrin-complexed zinc ion and the quinone carbonyl oxygen atoms are too long.

Molecular dynamics (MD) calculations[12] led to "lowest energy conformations" with vertical distances from the centre of the quinones to the porphyrin plane of 515 pm for **2**, 625 pm for **3**, and 862 pm for **4**.

Absorption Spectra

The absorption spectra of the porphyrin-quinone cyclophanes are dominated by the porphyrin chromophor with the typical set of Soret band and the four Q-bands. Besides a very small shift to longer wavelengths from **1** to **4** there is no characteristic difference between porphyrin-quinone cyclophanes which would be related to the porphyrin-quinone distance. Table 1 shows the wavelengths and the molar extinction coefficients of the series **1** to **4** in dichloromethane and in toluene as solvents. A very similar agreement

between the absorption spectra of the Zn complexes of **1** to **4** was observed.

Table 1. Absorption data of the series **1**−**4** with increasing quinone−porphyrin distances (wavelength in nm, in parentheses extinction coefficients in 10^4 l·mol^{-1}·cm^{-1})

	Solvent	Soret	$Q_y(1/0)$	$Q_y(0/0)$	$Q_x(1/0)$	$Q_x(0/0)$
1	CH_2Cl_2	409(21.4)	507(1.5)	540(0.5)	576(0.6)	631(0.2)
	toluene	411(21.5)	508(1.6)	539(0.5)	578(0.7)	631(0.3)
2	CH_2Cl_2	411(21.8)	508(1.6)	541(0.5)	575(0.6)	627(0.1)
	toluene	413(19.5)	507(1.5)	539(0.5)	577(0.6)	629(0.2)
3	CH_2Cl_2	412(21.4)	508(1.7)	541(0.5)	574(0.7)	630(0.1)
	toluene	415(21.2)	508(1.8)	540(0.6)	578(0.7)	631(0.2)
4	CH_2Cl_2	416(17.5)	508(1.6)	541(0.5)	575(0.6)	626(0.1)
	toluene	419(18.4)	509(1.7)	540(0.5)	578(0.6)	630(0.2)

Fluorescence Spectra

Of much more interest with regard to electron-transfer reactions are the fluorescence data of **1** to **4** since for the deactivation of the excited state the electron-transfer from the porphyrin as donor to the quinone as acceptor competes with the fluorescence emission. Thus, from the fluorescence quenching the electron-transfer rates can be approximately derived. In Table 2 the two fluorescence bands with maxima around 630 and 700 nm [excitation by Soret and $Q_x(1/0)$ bands] are listed for dichloromethane and toluene as solvents. The relative quantum yields Φ_{rel} were obtained by dividing the integrated fluorescence bands by those of the corresponding porphyrin-dimethoxybenzene cyclophanes which for **1** to **4** are the appropriate precursors without, however, the capability of an intramolecular electron-transfer. For the porphyrin-zinc complexes of **1**, **2**, **3** and **4**, a rather similar trend of the relative quantum yields of fluorescence is observed.

Table 2. Relative quantum yield Φ [± 30%] of fluorescence (in parentheses excitation wavelengths)

	Dichloromethane	Toluene
1	0.001(410)	0.0008(410)
	0.001(579)	0.0026(579)
2	0.002(411)	0.003(413)
	0.004(575)	0.005(577)
3	0.068(412)	0.093(415)
	0.046(574)	0.136(578)
4	0.070(416)	0.425(419)
	0.109(575)	0.477(577)

The data of Table 2 show − so far only roughly − the decrease of fluorescence quenching as a result of the competing electron-transfer from the porphyrin to the quinone units. This competitive electron-transfer in the series of the porphyrin-quinone cyclophanes **1** − **2** − **3** − **4** decreases due to the increasing porphyrin−quinone distances which in our cyclophane series are rather well-controlled by the size of the specific arene spacers used.

The electron-transfer between porphyrin and quinone depends, of course, upon the difference between the first oxidation potential E_{ox}^1 of the electron donor and the first reduction potential E_{red}^1 of the electron acceptor. For the porphyrin-quinone systems with different spacers separating donor and acceptor, a significant distance dependence of the redox potentials was not to be expected. In fact, for **1**, **2**, and **3** very similar redox potentials were observed: E_{ox}^1 = +0.36 (**1**), +0.39 (**2**), +0.40 (**3**) V, and E_{red}^1 = −1.25 (**1**), −1.17 (**2**), −1.15 (**3**) V (±0.02 V, dichloromethane, 0.1 M tetrabutylammonium hexafluorophosphate). For the corresponding zinc complexes, however, a stronger dependence on donor−acceptor distances can be observed especially for the reduction potential: E_{ox}^1 = +0.16 (**1**), +0.19 (**2**), +0.21 (**3**), and E_{red}^1 = −0.93 (**1**), −0.93 (**2**), −1.09 (**3**). Here, obviously the direct spatial interaction of the quinone with the zinc atom leads to a stabilizing effect on the quinone radical anion which with increasing distance between porphyrin and quinone is no longer possible. This result is in agreement with earlier electron-transfer rate determinations[10] including X-ray structure elucidations of zinc porphyrin-quinone cyclophanes[3][11].

The syntheses and structure of **3** complete the preceding series **1**, **2**, and **4**[1][2][3] of our program on the distance dependence of electron-transfer processes in porphyrin acceptor systems. The physical part of this work needs further experimental and theoretical clarification which we hope to obtain from our fruitful cooperation with our physics partners at the Technical University of Munich[4][10].

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Experimental Section

Melting points: Büchi SMP 512; for m.p. > 220°C Bock Monoscop, m.p. not corrected. − Elemental analyses: Elemental Analyzer 1106 Carlo Erba. − IR: Perkin Elmer FT-IR 1760 X. − UV/Vis: Cary 2300, Varian. − MS: MAT 212 Finnigan (70 eV); high resolution: JEOL JMS-SX 102A. − ^{1}H NMR: Bruker HX 360 and AM 500; internal standard tetramethylsilane. − Fluorescence spectra: Fluorolog F 112 XE, Spex. − Thin-layer chromatography: DC Polygram SIL G/UV_{254}, Macherey-Nagel. − Column chromatography: SiliTech (63−200 μm) ICN Biochemicals or aluminium oxide 90 (activity II−III, 63−200 μm) Merck. − Medium-pressure chromatography: Abimed column (d = 3.7, h = 48 cm; silica 60 Å, 25−45 μm; Kronwald), flowing rate 40 ml/min, detection at 333

nm. − GC/MS: HP 5890 Ser. II coupled to MS detector HP 5972, Hewlett-Packard; capillary column: Optima-5, 30 m × 0.25 mm, 94% methyl silicone, 5% phenyl silicone, 1% vinyl silicone; Macherey-Nagel.

Methyl Biphenylene-1-carboxylate: From a solution of 39.6 ml (98.4 mmol) of *n*-butyllithium (2.5 M solution) in *n*-hexane the major part of the solvent was evaporated within about 40 min. After cooling down to −60°C (acetone, dry ice), 750 ml of dry tetrahydrofuran at −78°C was added. Then 10.0 g (65.6 mmol) of biphenylene[5] was dissolved in this solution, and 11.1 g (98.4 mmol) of potassium *tert*-butoxide was added. The deep-violet reaction mixture obtained was stirred at −50 to −55°C for 30 min. Then a stream of carbon dioxide, dried by passing through concentrated sulfuric acid, was introduced over 1 h at −50°C. The carbon dioxide introduction was continued for 50 min without cooling, the solvents were distilled off in a rotary evaporator, and the suspension of the residue in 600 ml of diethyl ether was extracted with 500 ml of 1 M aqueous sodium hydroxide solution. The aqueous phase was separated and extracted once more with 300 ml of diethyl ether. Acidification by concentrated hydrochloric acid to pH ≈ 1 precipitated the carboxylic acid as a yellow solid. A suspension of this product in 50 ml of ether was esterified by diazomethane (from *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide). After stirring with silica gel the solvent was distilled off, and the viscous oil obtained was purified by flash chromatography (silica gel, dichloromethane/gasoline, 1:1; $R_f \approx 0.40$), and crystallization from *n*-hexane yielded after drying methyl biphenylene-1-carboxylate (5.1 g, 36%; m.p.79−81°C). − MS; *m/z* (%): 210 (100) [M^+], 179 (20), 151 (74). − ^{1}H NMR (360 MHz, $CDCl_3$): δ = 3.92 (3 H, s, $COOCH_3$), 6.66−6.70 (1 H, m, ar-H), 6.71 (1 H, dd, ^3J = 6.7 Hz, ^4J = 0.7 Hz, ar-H), 6.78 (1 H, d, ^3J = 8.6 Hz, ar-H), 6.78−6.93 (3 H, m, ar-H), 7.22 (1 H, dd, ^3J = 8.6, ^4J = 0.7 Hz, ar-H). − $C_{14}H_{10}O_2$ (210.23): calcd. C 79.99, H 4.79; found C 79.92, H 4.94.

Methyl 7-Bromobiphenylene-1-cyarboxylate: 300 mg (1.43 mmol) of biphenylene-1-carboxylate in 10 ml of dichloromethane was adsorbed on 1.5 g of aluminium oxide (activity II−III); also 342 mg (2.14 mmol) of bromine was adsorbed on 1.5 g of aluminium oxide (activity II−III), and by intensive stirring the two components on aluminium oxide were mixed in the solid phase, to which three times in intervals of 1 h each time 37 µl (altogether 2.14 mmol) of bromine on 0.5 g of aluminium oxide was added. After stirring overnight, the aluminium oxide phase was extracted with dichloromethane and chromatographed on silica gel. The red solution obtained was washed with water and concentrated sodium sulfite solution. The organic phase was washed with water and dried with magnesium sulfate. After distilling off the solvents in a rotary evaporator, the raw product was purified by flash chromatography on silica gel from *n*-hexane/toluene (95:5) ($R_f \approx 0.55$, silica gel, *n*-hexane/toluene, 6:4), and separation from insoluble material by dichloromethane yielded (besides varied amounts of the spectroscopically identified 6-bromo isomer) the 7-bromo compound (yield 20−40%; m.p. 88−91°C). − MS; *m/z* (%): 290 (99), 289 (16), 288 (100) [M^+], 259 (27), 257 (26), 231 (28), 229 (27), 150 (57), 75 (35). − HR-MS; *m/z* [M^+]: calcd. 287.9786, found 287.9787. − ^{1}H NMR (360 MHz, $CDCl_3$): δ = 3.90 (s, 3 H, $COOCH_3$), 6.52 (m, 1 H, H-5), 6.71 (d, ^3J = 6.8 Hz, 1 H, H-4), 6.83 (dd, ^3J = 6.8 Hz, ^3J = 8.5 Hz, 1 H, H-3), 6.97 (s, 1 H, H-8), 6.97-7.00 (m, 1 H, H-6), 7.35 (d, ^3J = 8.5 Hz, 1 H, H-2); assignment of signals by ^{1}H-^{13}C correlation spectra.

Methyl 7-Acetylbiphenylene-1-carboxylate: 200 mg (0.95 mmol) of methyl biphenylene-1-carboxylate was dissolved together with 157 mg (2 mmol) of acetyl chloride in 10 ml of 1,2-dichloromethane. Under ice cooling 456 mg (4.2 mmol) of anhydrous aluminium chloride was added in portions; the reaction mixture was stirred overnight and then poured into ice water. The precipitate was dissolved by acidification with concentrated hydrochloric acid. After phase separation, the organic phase was washed twice with concentrated sodium chloride solution and then dried with magnesium sulfate. The raw product was filtered through silica gel (cyclohexane/methyl acetate, 70:30) and crystallized from cyclohexane: fine yellow needles of m.p. 114−118°C (yield 85%). − MS; *m/z* (%): 252 (87), 238 (11), 237 (100), 209 (18). − ^{1}H-NMR (360 MHz, $CDCl_3$): δ = 2.52 (s, 3 H, CH_3CO), 3.96 (s, 3 H, $COOCH_3$), 6.71 (d, ^3J = 7.3 Hz, 1 H, H-5), 6.79 (dd, ^3J = 6.9 Hz, ^4J = 0.8 Hz, 1 H, H-4), 6.85 (dd, ^3J = 8.4 Hz, ^3J = 6.9 Hz, 1 H, H-3), 7.30 (dd, ^3J = 8.4 Hz, ^4J = 0.8 Hz, 1 H, H-2), 7.36 (m, 1 H, H-8), 7.51 (dd, ^3J = 7.3 Hz, ^4J = 1.4 Hz, 1 H, H-6). The assignment of the signals are based on a ^{1}H-^{13}C correlation spectrum. − $C_{16}H_{12}O_3$ (252.27): calcd. C 76.18, H 4.79; found C 76.39, H 4.96.

1,4-Bis(3-cyanopropyl)-2,5-dimethoxybenzene (**6**): To a suspension of 10.0 g (195 mmol) sodium cyanide in 75 ml of dimethyl sulfoxide 28.3 g (74.0 mmol) of 2,5-bis(3-bromopropyl)-1,4-dimethoxybenzene (**5**)[6] was added in portions. The reaction mixture was stirred for 3 h at 55−60°C and then for 10 min at 80−90°C. After cooling to 50°C, the mixture was poured into 200 ml of ice/water leading to a solid precipitate which was filtered off, washed with water and dried in vacuo over phosphorus pentaoxide: 19.6 g (97% yield) of **6**, m.p. 79−82°C. − MS; *m/z* (%): 273 (12), 272 (100) [M^+], 218 (38). − ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.95 (quint, ^3J = 7.25 Hz, 4 H, CH_2-CH_2-CH_3), 2.32 (t, ^3J = 7.12 Hz, 4 H, Ph-CH_2), 2.74 (t. ^3J = 7.32 Hz, 4 H, CH_2-CN), 3.78 (s, 6 H, OCH_3), 6.66 (s, 2 H, ar-H). − $C_{16}H_{20}N_2O_2$: HR-MS; *m/z* [M^+]: calcd. 272.1524, found 272.1532.

1,4-Dimethoxy-2,5-bis(3-methoxycarbonylpropyl)benzene (**7**): 10.9 g (40.0 mmol) of **6** in 700 ml of a 1:1 mixture of methanol and dichloromethane was cooled to 5°C. Hydrogen chloride, dried by concentrated sulfuric acid, was passed into this solution below 15°C. After about 1 h, the solution was HCl saturated (formation of gas bubbles), and the HCl stream was discontinued. Under stirring the reaction was kept for 1 h at room temperature and then for 3 h at 35°C. After the solvents had been distilled off, the white product was stirred in 400 ml of water for 1 h at 80°C. By cooling to 0°C and addition of a small amount of ice **7** was precipitated, filtered off, washed with water and dried in vacuo at 40°C over phosphorus pentaoxide: 12.3 g (86% yield) of **7**, m.p. 57−59°C (crystallized from methanol). − MS; *m/z* (%): 338 (100) [M^+], 275 (16), 264 (42), 251 (39), 231 (14), 190 (16), 177 (55), 147 (19), 91 (18). − ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.91 (quint, ^3J = 7.6 Hz, 4 H, γ-H), 2.33 (t, ^3J = 7.6 Hz, 4 H, β- or γ-H), 2.61 (t, ^3J = 7.6 Hz, 4 H, γ- or β-H), 3.66 (s, 6 H, OCH_3), 3.76 (s, 6 H, -CO-OMe), 6.63 (s, 2 H, ar-H). − $C_{18}H_{26}O_6$ (338.4): calcd. C 63.89, H 7.74; found C 64.08, H 7.87.

1,4-Dibromo-2,5-dimethoxy-3,6-bis(3-methoxycarbonylpropyl)-benzene (**8**): To a solution of 7 g (21 mmol) of **7** in 50 ml of dichloromethane, after addition of 350 mg of iodine as catalyst, 3.2 ml (10.1 g, 63 mmol) of bromine dissolved in 25 ml of dichloromethane was added within 5 min. The reaction mixture was heated for 30 min under reflux and then after cooling was poured into 100 ml of water. After 2 min of vigorous shaking, the phases were separated; the aqueous phase was extracted with 20 ml of dichloromethane, and the combined organic phases were stirred with 50 ml of concentrated aqueous sodium sulfite solution until the colour changed from red to yellow. The separated organic phase was washed with 30 ml of saturated sodium hydrogen carbonate solu-

tion and subsequently with 30 ml of water. After drying with magnesium sulfate, the solvent was distilled off in a rotary evaporator. The raw product obtained was recrystallized from methanol yielding analytically pure yellow needles (yield 3.5 g, 91%; m.p. 114−121°C, slowly deliquescent). − MS; *m/z* (%): 496 (100) $[M]^+$, 494 (53), 422 (35), 386 (26), 385 (39), 384 (26), 383 (41), 336 (100), 304 (100), 295 (32), 272 (24), 115 (24), 101 (40). − ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.91 ("quint", ^3J = 7.6 Hz, 4 H, γ-H), 2.41 (t, ^3J = 7.5 Hz, 4 H, β- or δ-H), 2.84−2.88 (m, 4 H, δ- or β-H), 3.68 (s, 6 H, O-CH_3), 3.80 (s, 6 H, O-CH_3). − $C_{18}H_{24}Br_2O_6$ (496.2): calcd. C 43.57, H 4.88, Br 32.21; found C 43.71, H 4.69, Br 32.42.

1,4-Dibromo-2,5-dimethoxy-3,6-bis(3-carboxypropyl)benzene (**9**): To a solution of 9.4 g of the diester **7** in 150 ml of methanol/water (2:1) 3.7 g (66 mmol) of potassium hydroxide was added, and the reaction mixture was heated at reflux for 2 h while a deep-violet colour developed. After cooling, the methanol was distilled off in a rotary evaporator, and on addition of concentrated hydrochloric acid (to pH = 1) the product precipitated as a white sediment which was filtered off and dried in a vacuum dry box at 40°C. Compound **9** was obtained as white powder analytically pure (2.5 g, yield 77%, m.p. 211−212°C). − MS; *m/z* (%): 468 (130), 466 (100) $[M^+]$, 408 (68), 371 (86), 369 (89), 308 (88), 290 (75), 284 (73). − ^{1}H NMR (360 MHz, [D$_6$]DMSO): δ = 1.70−1.78 ("quint" centered at 1.74, 4 H, γ-H), 2.29 (t, ^3J = 7.3 Hz, 4 H, β- or δ-H), 2.77−2.81 (m, 4 H, δ- or β-H), 12.06 (br. s, 2 H, COOH). − $C_{16}H_{20}Br_2O_6$ (468.15): calcd. C 41.05, H 4.31, Br 34.14; found C 41.25, H 4.44, Br 33.91.

1,4-Dibromo-2,5-dimethoxy-3,6-bis(3-chloroformylpropyl)-benzene (**10**): Under argon 2.50 g (5.38 mmol) of the dicarboxylic acid **9** was added to 32.0 ml of oxalic acid dichloride, and the suspension obtained was heated under reflux. From 40°C on, the reaction started under vigorous gas evolution, while the starting material slowly dissolved. The temperature was raised from 45 to 60°C and the mixture was kept stirring for 15 h. Excess oxalic acid dichloride was removed under oil pump vacuum. The yellow solid obtained was dried in vacuo. Because of its hygroscopic sensivity the product could not be further purified and stored only for very short periods (2.6 g, yield 96%, m.p. after washing with cyclohexane and drying 118−121°C). − MS; *m/z* (%): 506 (55), 504 (67), 502 (19), 409 (44), 390 (44), 299 (67), 297 (100), 295 (44). − ^{1}H-NMR (360 MHz, [D$_6$]DMSO): δ = 1.69−1.84 (m, 4 H, γ-H), 2.29 (t, ^3J = 7.3 Hz, 4 H, β-H or δ-H), 2.78−2.85 (m, 4 H, δ-H or β-H), 3.75 (s, 6 H, OCH_3); the ^{1}H-NMR spectrum shows additional signals which cannot be assigned to **10** obviously due to decomposition products. − $C_{16}H_{18}Br_2Cl_2O_4$ (505.6): calcd. C 38.05, H 3.59; found C 37.99, H 3.60.

1,4-Dibromo-2,5-dimethoxy-3,6-bis[4-(8-methoxycarbonylbiphenylenyl-2)butyl]benzene (**11**): Under argon 14.6 g (110 mmol) of aluminium trichloride was suspended in 90 ml of 1,2-dichloromethane. To this suspension a solution of 5.55 g (11.0 mmol) of **10** and 5.78 (27.5 mmol) of methyl biphenylene-1-carboxylate in 150 ml of 1,2-dichloroethane was added within 30 min (temperature below 5°C). The reaction mixture was stirred at room temperature for 7.5 h (reaction TLC-controlled, cyclohexane/ethyl acetate, 6:4). 75 ml of trifluoroacetic acid in 90 ml of 1,2-dichloroethane was added within 30 min; to this reaction mixture 11.0 ml (132 mmol) of triethylsilane was added immediately. After 1 h of stirring at room temperature, 200 ml of water and subsequently 100 ml of 2 M hydrochloric acid was added under ice/water cooling. After 10 min of stirring at room temperature, the phases were separated. The aqueous phase was extracted twice with 300 ml each of 1,2-dichloroethane, and the combined organic phases were washed twice with 300 ml of 2 M hydrochloric acid each. The organic phase was dried with magnesium sulfate, and the solvent was removed in a rotary evaporator. Since under the above conditions the methoxy groups of the central aromatic ring were partially split off, a remethylation step was necessary for the preparation of **11**. For this purpose the residue was dissolved in 250 ml of acetone, and 7.60 g (55.0 mmol) of potassium carbonate and 5.0 ml (55.0 mmol) of dimethyl sulfate were added to the solution under ice/water cooling. After heating the suspension for 6 h at reflux, further 3.04 g (22.0 mmol) of potassium carbonate and 2.0 ml (22.0 mmol) of dimethyl sulfate were added, and the reaction was stirred under reflux for further 11 h and then cooled to room temperature. To destroy excess of dimethyl sulfate the reaction mixture was stirred for 1 h with 20 ml of concentrated ammonia solution at room temperature. After addition of 75 ml of water, the acetone was removed, and the precipitated solid was dissolved in 250 ml of dichloromethane. The aqueous phase was extracted twice with 100 ml of dichloromethane each, and the combined organic phases were washed with 150 ml of saturated ammonium chloride solution and dried with magnesium sulfate. The solvents were evaporated and the residue was purified by chromatography on silica gel (dichloromethane, $R_f \approx 0.53$). The combined product fractions were dried in vacuo, and the raw product was flash-chromatographed on silica gel with cyclohexane/ethyl acetate (9:1) yielding a yellow solid: 6.94 g, 76% yield; m.p. 179−180°C. − MS (LSIMS positive, *m*-nitrobenzyl alcohol, 1% trifluoroacetic acid); *m/z* (%): 827 (51), 826 (51), 825 (81), 824 (100), 823 (51) $[MH^+]$, 822 (50) $[M^+]$. − ^{1}H NMR (500 MHz, $CDCl_3$); δ = 1.58−1.67 ("quint" centered at 1.62, 4 H, γ−H), 1.67−1.75 ("quint" centered at 1.70, 4 H, β-H), 2.48−2.55 (t, ^3J = 7.5 Hz, 4 H, α-H), 2.80−2.90 (t, ^3J = 7.8 Hz, 4 H, δ-H), 3.80 (s, 6 H, OCH_3), 3.92 (s, 6 H, OCH_3), 6.59 (d, ^3J = 7.0 Hz, 2 H, H-5), 6.66−6.68 (m, 4 H, H-4,6), 6.76 (dd, ^3J = 8.5 Hz, ^3J = 8.3 Hz, 2 H, H-3), 6.81 (s, 2 H, H-8), 7.18 (d, ^3J = 8.5 Hz, 2 H, H-2); assignment of signals by COSY and ^{1}H-^{13}C correlation spectra. − $C_{44}H_{40}Br_2O_6$: HR-MS (LSIMS positive, *m*-nitrobenzyl alcohol, 1% trifluoroacetic acid); *m/z* $[M^+]$: calcd. 822.1192, found 822.1136.

1,4-Dibromo-3,6-bis[4-(8-hydroxymethylbiphenylenyl-2)butyl]-2,5-dimethoxybenzene (**12**): To 4.12 g (5.0 mmol) of **11**, under argon dissolved in 200 ml of tetrahydrofuran, 2.2 g (100 mmol) of lithium tetrahydridoborate was added in portions. The solution was refluxed for 3 h, then further 1.1 g (50 mmol) of lithium tetrahydridoborate was added, and the reflux was continued for further 2 h to complete the reaction (TLC, cyclohexane/ethyl acetate, 7:3). The reaction mixture was cooled to room temperature, and with ice/water cooling 100 ml of water and subsequently 100 ml of 2 M hydrochloric acid was carefully added, followed twice by extraction with 100 ml of dichloromethane each. The combined organic phases were washed with 50 ml each of 2 M hydrogen chloride and 50 ml of sodium chloride solutions. Drying with magnesium sulfate, removal of the solvents by distillation, and drying in vacuo at room temperature yielded the product which was washed with cold dichloromethane for the analytical data: 3.70 g (96% yield, m.p. 174−176°C). − MS (LSIMS positive, *m*-nitrobenzyl alcohol, 1% trifluoroacetic acid); *m/z* (%): 770 (65). 769 (46), 767 (37) $[MH^+]$, 766 (62) $[M^+]$. − ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.55−1.75 (m, 8 H, β- and γ-H), 2.42−2.50 ("t" centered at 2.46, 4 H, α-H), 2.78−2.88 ("t" centered at 2.81, 4 H, δ-H), 3.76 (s, 6 H, OCH_3), 4.55 (s, 4 H, CH_2OH), 6.51 (d, ^3J = 6.7 Hz, 2 H, H_{Biph}), 6.55 (s, 2 H, 8-H), 6.56 (d, ^3J = 6.7 Hz, 4 H, H_{Biph}), 6.62 (d, ^3J = 8.3 Hz, 2 H, H_{Biph}), 6.72 (dd, ^3J = 8.3 Hz, ^3J = 6.7 Hz, 2 H, H_{Biph}). − $C_{42}H_{40}Br_2O_4$ (768.6): calcd. C 65.63, H 5.25, Br 20.79; found C 65.41, H 5.36, Br 20.78. − HR-MS; *m/z* $[M^+]$: calcd. 767.1372, found 767.1409.

1,4-Dibromo-3,6-bis[4-(8-formylbiphenylenyl-2-)butyl]-2,5-dimethoxybenzene (**13**): To 800 g (1.04 mmol) of **12** in 80 ml of dichloromethane 3.5 g (13.5 mmol) of barium manganate was added, and the reaction mixture was heated to 40°C for 24 h. To complete the reaction, the mixture was heated with additional 600 mg (2.34 mmol) of barium manganate for further 3 h at 40°C. The manganate was filtered off using a 1-cm layer of Celite on a D4 frit and washed with 150 ml of dichloromethane. Removal of the solvent in a rotary evaporator yielded an intensively yellow-coloured raw product which was purified by flash chromatography (dichloromethane/cyclohexane, 9:1). The product fraction ($R_f \approx 0.47$) was concentrated to dryness: yellow solid (130 mg, 84% yield, m.p. 143−145°C). − MS (LSIMS positive, *m*-nitrobenzyl alcohol, 1% trifluoroacetic acid); *m/z* (%): 766 (100), 765 (73), 764 (71), 763 (49) [MH^+], 762 (29) [M^+], a.o. − ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.55−1.75 (m, 8 H, β- and γ-H), 2.50 (t, ^3J = 7.6 Hz, 4 H, α-H), 2.85 (t, ^3J = 7.6 Hz, 4 H, δ-H), 3.79 (s, 6 H, OCH_3), 6.62 (d, ^3J = 7.0 Hz, 2 H, 5-H), 6.54-6.76 (m, 4 H, 4,6-H), 6.84 ("t", 2 H, 3-H, and s, 2 H, 8-H), 7.09 (d, ^3J = 8.5 Hz, 2 H, 2-H), 9.91 (s, 2 H, CHO). − $C_{42}H_{36}Br_2O_4$: HR-MS; *m/z* [M^+]: calcd. 762.098, found 762.101.

2,5-Bis[4-(8-hydroxymethylbiphenylenyl-2)butyl]-1,4-dimethoxybenzene (**15**): Under argon in 20.0 ml of anhydrous diethyl ether, 196 mg (0.25 mmol) of **12** was dissolved, and the solution was cooled to −65°C. To this solution 1.30 ml (3.06 mmol) of *n*-butyllithium in *n*-hexane was added. The reaction mixture was slowly warmed to room temperature. At about 3°C 1.0 ml of water was added, and at room temperature further 20.0 ml was added under stirring for 30 min. The aqueous phase was extracted three times with diethyl ether. The combined organic phases were dried with magnesium sulfate. The solvents were evaporated by rotary evaporation to yield a yellow product, which was purified by flash chromatography on silica gel (cyclohexane/ethyl acetate, 6:4; $R_f \approx 0.30$). After removal of the solvents in a rotary evaporator, **15** was obtained as yellow solid: 151 mg (99% yield). For spectroscopic data **15** was recrystallized from ethyl acetate: m.p. 157−159°C. − MS; *m/z* (%): 612 (15), 611 (54), 610 (100) [M^+], 195 (47), a.o. − ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.55−1.70 (m, 8 H, β- and γ-H), 2.44 (t, ^3J = 6.6 Hz, 4 H, α-H), 2.58 (t, ^3J = 6.7 Hz, 4 H, δ-H), 3.76 (s, 6 H, OCH_3), 4.53 (d, ^3J = 5.8 Hz, 4 H, CH_2OH), 6.51 (d, ^3J = 6.7 Hz, 2 H, H_{Biph}), 6.54−6.62 (m, 10 H, biphen-H, ar-3′,6′-H), 6.72 (dd, ^3J = 6.8 Hz, ^3J = 6.7 Hz, 2 H, H_{Biph}).− $C_{42}H_{42}O_4$: HR-MS; *m/z* [M^+]: calcd. 610.3083, found 610.3077.

2,5-Bis[4-(8-formylbiphenylenyl-2)butyl]-1,4-dimethoxybenzene (**16**): To 155 mg of **14**, dissolved in 20.0 ml of dichloromethane, 653 mg (2.50 mmol) of barium manganate was added at room temperature, and the suspension was heated under reflux (TCL reaction control, cyclohexane/ethyl acetate, 7:3). After 23 h of heating, further 111 mg (0.43 mmol) of barium manganate was added, and heating to 50°C was continued for 4 h under stirring. After cooling, the barium manganate was removed by filtration through 1 cm Celite (D4 frit), and the solution was concentrated in a rotary evaporator leaving an oily yellow-brown residue which was purified by flash chromatography with dichloromethane on silica gel (*d* = 3 cm, *h* = 19 cm; $R_f \approx 0.30$). From the product fractions the dichloromethane was removed by rotary evaporation, and the product was dried in vacuo: yellow solid (130 mg, 84% yield) of which a sample was crystallized from ethyl acetate: m.p. 142−144°C. − MS; *m/z* (%): 608 (14), 607 (46), 606 (100) [M^+], 193 (27). − ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.58 (m, 8 H, β-, γ-H), 2.48 (t, ^3J = 6.9 Hz, 4 H, α-H), 2.60 (t, ^3J = 7.0 Hz, 4 H, δ-H), 3.77 (s, 6 H, OCH_3), 6.60−6.70 (m, 8 H, biphen-3,4,5-H, ar-3′,6′-H), 6.81 (s, 2 H, 1-H), 6.84 (t, ^3J = 6.8 Hz, 2 H, 6-H), 7.08 (d, ^3J = 8.3 Hz, 2 H, 7-H), 9.91 (s, 2 H, CHO). − $C_{42}H_{38}O_4$: HR-MS; *m/z* [M^+]: calcd. 606.2770, found 606.2773.

5,15-[2,5-Dimethoxybenzene-1,4-diylbis(1,4-butanediyl-1,7-biphenyleno)]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (**17**): In a three-neck flask through a suspension of 6 g of magnesium sulfate in 300 ml of dichloromethane during 30 min an argon stream was passed. Then, under strong stirring and exclusion of oxygen, at room temperature 200 mg (0.87 mmol) of bis(3-ethyl-4-methyl-2-pyrrolyl)methane[13] was added, after the complete dissolution of which 5.70 g of trichloroacetic acid and immediately thereafter 188 mg (0.31 mmol) of the dialdehyde **16**, dissolved in a small amount of dichloromethane, were added. The dark-brown reaction mixture was vigorously stirred for 30 min at room temperature and under exclusion of light and oxygen. 6 g of sodium acetate and 450 mg of *p*-chloranil were introduced, and the mixture was stirred again under exclusion of light and oxygen for another 20 min. The reaction mixture with 100 ml of saturated sodium hydrogen carbonate solution was vigorously stirred, and the organic phase was separated after 20 min. The dark organic phase was washed eight times with 100 ml each of saturated sodium hydrogen carbonate solution and finally twice with 100 ml each of water. The combined aqueous phases were washed twice with 100 ml of dichloromethane each. After drying of the combined organic phases with magnesium sulfate, the solvents were distilled off. For purification a solution of the residue in toluene/ethyl acetate (20:1) was immediately filtered through aluminium oxide (D3 frit, *d* = 9, *h* = 10 cm). The first fractions of thin-layer chromatograms (toluene/ethyl acetate, 20:1) were combined, and the solvents were distilled off. The crude product obtained was flash-chromatographed on aluminium oxide using cyclohexane/ethyl acetate (30:1). The solvents were removed from the combined fractions to yield the product which for crystallization was dissolved in 7 ml of dichloromethane and covered by a layer of 70 ml of methanol. After 3 d at 5°C, a dark-violet microcrystalline sediment was formed from which the solvents were decanted. After washing the microcrystalline product with methanol at room temperature, the product was dried in vacuo: 95.4 mg (30% yield), m.p. > 300°C (crystallized from methanol/dichloromethane, 10:1). − MS (FAB positive, *m*-nitrobenzyl alcohol/1% trifluoroacetic acid); *m/z* (%): 307 (63), 1025 (26) [M^+], 1026 (100) [$MH]^+$. − ^{1}H NMR (360 MHz, $CDCl_3$): δ = −2.51 (s, 2 H, NH), 0.87−0.91 (m, 4 H, β-H), 1.03-1.07 (m, 4 H, γ-H), 1.78 (t, ^3J = 7.6 Hz, 12 H, CH_2CH_3), 1.87 (t, ^3J = 7.6 Hz, 4 H, α-H), 1.94 (t, ^3J = 6.9 Hz, 4 H, δ-H), 2.50 (s, 6 H, O-CH_3), 3.07 (s, 12 H, CH_3), 4.05 (q, ^3J = 7.5 Hz, 8 H, CH_2-CH_3), 5.01 (s, 2 H, biphen-8-H), 5.71 (s, 2 H, central arene-H), 6.45 (d, ^3J = 7.0 Hz, 2 H, biphen-6-H), 6.70 (d, ^3J = 7.0 Hz, 2 H, biphen-5-H), 7.00 (d, ^3J = 6.9 Hz, 2 H, biphen-4-H), 7.17 (dd, ^3J = 7.0 Hz, ^3J = 6.9 Hz, 2 H, biphen-3-H), 7.52 (d, ^3J = 8.2 Hz, 2 H, biphen-2-H), 10.22 (s, 2 H, methine-H). − $C_{72}H_{72}N_4O_2$: HR-MS; *m/z* [M^+]: calcd. 1024.5655, found 1024.5642.

5,15-[p-Benzoquinone-1,4-diylbis(1,4-butanediyl-1,7-biphenyleno)]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (**3,X= H**): Under argon to the solution of 30.0 mg (0.03 mmol) of porphyrin cyclophane **17** in 25 ml of dichloromethane 2.50 ml (ca. 2.5 mmol) of boron tribromide (1 M in dichloromethane) was added and the mixture stirred for 1.5 h at room temperature. After addition of 25 ml of a saturated aqueous solution of sodium hydrogen carbonate, the violet organic phase was separated and washed with 25 ml of water. The combined water phases were extracted with 25 ml of dichloromethane, the organic phases were dried with magnesium sulfate, and the solvent was distilled off. The residue was dissolved in a mixture of 25 ml of dichloromethane and 7 ml of methanol, and oxidized by addition of 13.6 mg (0.06 mmol) of 2,3-

dichloro-5,6-dicyano-*p*-benzoquinone. The reaction mixture was stirred at room temperature for 2.5 h, and then 25 ml of saturated sodium hydrogen carbonate was added. After 5 min of stirring, the phases were separated, the organic phase was washed with 25 ml of water and dried with magnesium sulfate. The product obtained was crystallized by solution in 2 ml of dichloromethane which was covered with a layer of 20 ml of methanol. After 3 d of standing at 5°C, violet microcrystals were obtained by decantation of the solvents, washing with methanol and drying in an oil pump vacuum: 27.0 mg (92%) of **3,X=H**, m.p. > 300°C (from methanol/dichloromethane, 10:1). − MS (FAB positive, *m*-nitrobenzyl alcohol/1% trichloroacetic acid); *m/z* (%): 995 (12) $[M]^+$, 996 (41) $[MH]^+$, 997 (59) $[MH_2]^+$, 998 (100) $[MH_3]^+$. − ^{1}H NMR (360 MHz, $CDCl_3$): δ = −2.58 (s, 2 H, NH), 0.88−0.94 (m, 4 H, β-H), 0.98−1.04 (m, 4 H, γ-H), 1.78 (t, ^3J = 7.5 Hz, 12 H, CH_2-CH_3), 1.82 (t, ^3J = 6.3 Hz, 4 H, δ-H), 1.92 (t, ^3J = 7.4 Hz, 4 H, α-H), 3.06 (s, 12 H, CH_3), 4.01−4.11 (m, 8 H, CH_2-CH_3), 5.03 (s, 2 H, biphen-8-H), 5.81 (s, 2 H, quin-H), 6.46 (d, ^3J = 6.8 Hz, 2 H, biphen-6-H), 6.71 (d, ^3J = 7.1 Hz, 2 H, biphen-5-H), 7.01 (d, ^3J = 6.8 Hz, 2 H, biphen-4-H), 7.16 (dd, ^3J = 8.2 Hz, ^3J = 6.9 Hz, 2 H, biphen-3-H), 7.47 (d, ^3J = 8.2 Hz, 2 H, biphen-2-H), 10.22 (s, 2 H, methine-H). − $C_{70}H_{66}N_4O_2$ (995.32): calcd. C 84.47, H 6.68, N 5.63; found C 84.32, H 6.87, N 5.79. − HR-MS; *m/z*: calcd. 997.5264, found 997.5426 $[(M + 3 H)^+, C_{70}H_{69}N_4O_2]$.

5.15-[2,5-Dimethoxybenzene-1,4-diylbis(1,4-butanediyl-1,7-biphenyleno)]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrinato-zinc(II) (**20**): 10.0 mg (9.75 μmol) of **3,X=H** was dissolved under argon in 30 ml of trichloromethane/methanol (5:1). To this solution 167 mg (760 μmol) of zinc acetate dihydrate was added, and the reaction mixture was heated to reflux for 1.5 h and then cooled to room temperature. After washing with 50 ml of water, then with 50 ml of saturated aqueous sodium hydrogen carbonate solution, and again with 50 ml of water, the organic phase was dried with magnesium sulfate. Then the solvents were distilled off, the remaining residue was dissolved in 1 ml of dichloromethane, and covered with a layer of 10 ml of methanol. After 3 d at 5°C, a pale-violet microcrystalline precipitate had formed which by decanting of the solvents, washing with methanol and drying in vacuo at room temperature was isolated: 8.6 mg (81%) of **20**, m.p. > 300°C. − MS (FAB positive, *m*-nitrobenzyl alcohol/1% trifluoroacetic acid); *m/z* (%): 1025 (55), 1026 (100), 1027 (67), 1087 (37) $[M^+]$, 1088 (50) $[MH^+]$. − ^{1}H NMR (360 MHz, $CDCl_3$): δ = 0.86−0.92 (m, 4 H, β-H), 1.02−1.06 (m, 4 H, γ-H), 1.78 (t, ^3J = 7.5 Hz, 12 H, CH_2CH_3), 1.86−1.94 (m, 8 H, α-, β-H), 2.54 (s, 6 H, O-CH_3), 3.07 (s, 12 H, CH_3), 4.04 (q, ^3J = 7.5 Hz, 8 H, CH_2-CH_3), 4.95 (s, 2 H, biphen-8-H), 5.71 (s, 2 H, central arene-H), 6.46 (d, ^3J = 7.0 Hz, 2 H, biphen-6-H), 6.71 (d, ^3J = 7.1 Hz, 2 H, biphen-5-H), 7.00 (d, ^3J = 6.8 Hz, 2 H, biphen-4-H), 7.16 (dd, ^3J = 8.1 Hz, ^3J = 6.9 Hz, 2 H, biphen-3-H), 7.52 (d, ^3J = 8.2 Hz, 2 H, biphen-2-H), 10.18 (s, 2 H, methine-H). − $C_{72}H_{70}N_4O_2Zn$: HR-MS; *m/z*: calcd. 1086.4790, found 1086.4824 $[M]^+$.

5,15-[p-Benzoquinone-1,4-diylbis(1,4-butanediyl-1,7-biphenyleno)]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrinato-zinc(II) (**21**): Under argon 36.0 mg (36.2 μmol) of **20** was dissolved in 60 ml of trichloromethane/methanol (5:1). To this solution 500 mg (2.28 mmol) of zinc(II) acetate dihydrate was added at room temperature, and the mixture was heated for 1.5 h under reflux. After cooling to room temperature, the solution was washed with 100 ml of water, 100 ml of saturated aqueous sodium hydrogen carbonate solution, and once more with 100 ml of water. The organic phase was dried with magnesium sulfate and then the solvent was evaporated, leaving crystalline **21** which was dissolved in 3 ml of dichloromethane. This solution was covered with a layer of 30 ml of methanol. After 3 d of standing at 5°C, pale-violet microcrystals were formed which after decanting of the solvents were washed with methanol and dried in vacuo at room temperature: 29.7 mg (77%) yield, m.p. (decomp.) ca. 288°C. − MS (FAB positive, *m*-nitrobenzyl alcohol/1% trifluoroacetic acid); *m/z* (%): 998 (100), 999 (70) 1000 (30), 1056 (15) $[M^+]$, 1057 (2) $[MH]^+$, 1058 (6) $[M + 2 H]^+$. − ^{1}H NMR (360 MHz, $CDCl_3$): δ = 0.87−0.89 (m, 4 H, β-H), 1.01−1.06 (m, 4 H, γ-H), 1.80 (t, ^3J = 7.6 Hz, 12 H, CH_2CH_3), 1.82−1.89 (m, 8 H, α-, δ-H), 3.09 (s, 12 H, CH_3), 4.01−4.09 (m, 8 H, CH_2-CH_3), 4.93 (s, 2 H, biphen-8-H), 5.83 (s, 2 H, quin-H), 6.45 (d, ^3J = 6.9 Hz, 2 H, biphen-6-H), 6.71 (d, ^3J = 7.0 Hz, 2 H, biphen-5-H), 7.02 (d, ^3J = 6.8 Hz, 2 H, biphen-4-H), 7.16 (dd, ^3J = 7.9 Hz, ^{3}J = 6.9 Hz, 2 H, biphen-3-H), 7.48 (d, ^3J = 8.0 Hz, 2 H, biphen-2-H), 10.20 (s, 2 H, methine-H). − $C_{70}H_{64}N_4O_2Zn$: HR-MS; *m/z*: calcd. 1056.4320, found 1056.4293 $[M]^+$.

5,15-[2,5-Dibromo-3,6-dimethoxybenzene-1,4-diylbis(1,4-butanediyl-1,7-biphenyleno)]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (**18**): Through a suspension of 6 g magnesium sulfate in 300 ml of dichloromethane an argon stream was passed for 30 min to remove oxygen traces. Under vigorous stirring 200 mg (0.87 mmol) of bis(3-ethyl-4-methyl-2-pyrrolyl)methane[13] was dissolved to which 5.7 g of trichloroacetic acid and immediately thereafter 236 mg (0.31 mmol) of the dialdehyde **13**, dissolved in a small amount of dichloromethane, were added. The reaction mixture then was stirred at room temperature under exclusion of light and oxygen. The reaction was terminated by the addition of 100 ml of saturated sodium hydrogen carbonate solution. After 20 min of stirring, the organic phase was separated and washed eight times with 100 ml each of saturated sodium hydrogen carbonate solution and finally twice with 100 ml each of water. The combined aqueous extracts were extracted twice with 100 ml each of dichloromethane. After drying the combined organic phases with magnesium sulfate, the solvent was distilled off, leaving a black residue which immediately was filtered with toluene/ethyl acetate (20:1) through an alumina frit (D3). The first fractions, of which the TLC with toluene/acetic acid (20:1) showed strong fluorescence (λ ≈ 366 nm), were combined, and the solvent was evaporated. This raw product was further purified by flash chromatography on alumina with cyclohexane/ethyl acetate (15:1) (R_f = 0.32); after removal of the solvents, the product was dissolved in 1 ml of dichloromethane and covered with a layer of 10 ml of methanol. Within 3 d at 5°C, violet microcrystals had formed which by decantation, washing with methanol, and drying at room temperature in vacuo were obtained pure: 30.1 mg (8%), m.p. > 300°C (from methanol/dichloromethane, 10:1). − MS (FAB positive, *m*-nitrobenzyl alcohol/1% trifluoroacetic acid); *m/z* (%): 1180 (15), 1181 (50) $[M]^+$, 1182 (55) $[MH]^+$, 1183 (100) $[M + 2 H]^+$, 1184 (80) $[M + 3 H]^+$, 1185 (65) $[M + 4 H]^+$. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = −2.47 (s, 2 H, N-H), 0.95−0.98 (m, 4 H, β-H), 1.04−1.07 (m, 4 H, γ-H), 1.80 (t, ^3J = 7.6 Hz, 12 H, CH_2-CH_3), 1.98 (t, ^3J = 6.8 Hz, 4 H, α-H), 2.06 (t, ^3J = 7.3 Hz, 4 H, δ-H), 2.26 (s, 6 H, OCH_3), 3.08 (s, 12 H, CH_3), 4.06 (q, ^3J = 7.5 Hz, 8 H, CH_2-CH_3), 5.23 (s, 2 H, biphen-8-H), 6.49 (d, ^3J = 7.1 Hz, 2 H, biphen-6-H), 6.74 (d, ^3J = 7.1 Hz, 2 H, biphen-5-H), 7.01 (d, ^3J = 6.8 Hz, 2 H, biphen-4-H), 7.18 (dd, ^3J = 8.1 Hz, ^3J = 6.9 Hz, 2 H, biphen-3-H), 7.46 (d, ^3J = 8.0 Hz, 2 H, biphen-2-H), 10.23 (s, 2 H, methine-H). − $C_{72}H_{70}Br_2N_4O_2$: HR-MS; *m/z*: calcd. 1180.3865, found 1180.3942 $[M^+]$.

5,15-[2,5-Dibromo-p-benzoquinone-1,4-diylbis(1,4-butanediyl-1,7-biphenyleno)]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (**19**): To 15 mg (12.7 μmol) of **18** in 25 ml of dichloromethane under argon 1.05 ml (1.05 mmol) of boron tribromide (1 M

solution in dichloromethane) was added and the mixture was kept at room temperature under stirring for 1.5 h. Then 25 ml of a saturated aqueous solution of sodium hydrogen carbonate was added, and the reaction mixture was vigorously stirred until the colour of the solution turned to violet. The phases were separated, and the organic phase was washed with 25 ml of water. Then the combined aqueous phases were extracted with 25 ml of dichloromethane. After drying of the organic phases with magnesium sulfate, the solvent was removed in a vacuum evaporator. The residue obtained was dissolved in 25 ml of dichloromethane and 7 ml of methanol. After addition of 5.10 mg (22.5 μmol) of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), this solution was stirred for 2.5 h, and subsequently 25 ml of saturated sodium hydrogen carbonate solution was added. The phases were separated after 5 min of stirring, and the organic phase was washed with 25 ml of water, then dried with magnesium sulfate, and the solvents were distilled off, yielding **19** which for crystallization was dissolved in 1.5 ml of dichloromethane. Then this solution was covered with a layer of 15 ml of methanol. After 3 d at 5°C, the violet microcrystals formed were purified after decanting the solvents by washing with methanol and drying in vacuo at room temperature: 11.3 mg (77% yield) of **19**, m.p. > 300°C. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = −2.53 (s, 2 H, N-H), 0.97−1.01 (m, 8 H, β-,γ-H), 1.79 (t, ^3J = 7.6 Hz, 12 H, CH_2-CH_3), 1.92 (t, ^3J = 6.2 Hz, 4 H, α-H), 2.08 (t, ^3J = 6.2 Hz, 4 H, δ-H), 3.07 (s, 12 H, CH_3), 4.03−4.07 (m, 8 H, CH_2-CH_3), 5.03 (s, 2 H, biphen-8-H), 6.46 (d, ^3J = 7.3 Hz, 2 H, biphen-6-H), 6.71 (d, ^3J = 7.2 Hz, 2 H, biphen-5-H), 7.01 (d, ^3J = 7.1 Hz, 2 H, biphen-4-H), 7.17 (dd, ^3J = 8.1 Hz, ^3J = 7.0 Hz, 2 H, biphen-3-H), 7.51 (d, ^3J = 8.2 Hz, 2 H, biphen-2-H), 10.23 (s, 2 H, methine-H). − $C_{70}H_{65}Br_2N_4O_2$: HR-MS; *m/z* [MH^+]: calcd. 1151.3471, found 1151.3456.

5,15-[2,5-Dibromo-3,6-dimethoxybenzene-1,4-diylbis(1,4-butanediyl-1,7-biphenyleno)]-10,20-diphenylporphyrin (**22**): a) 1,4-Dibromo-2,5-dimethoxy-3,6-bis{4-[8-(2,2′-dipyrrylmethyl)biphenylene-2]butylbenzene: To a suspension of 663 mg (0.867 mmol) of the dialdehyde **16** in 35 ml of toluene, 582 mg (8.67 mmol) of freshly distilled pyrrole and 45 mg of *p*-toluenesulfonic acid were added. For 10 min a stream of argon was passed through the reaction mixture, and subsequently the mixture was heated under reflux (oil bath). After cooling, the solvent was distilled off in a rotary evaporator, and the residue was immediately purified by flash chromatography on silica gel (cyclohexane/ethyl acetate, 60:1). The product was identified by TLC (development with iodine), and from the product fraction (R_f ≈ 0.21) the solvents were distilled off. The remaining oily product was dissolved in a few ml of dichloromethane, and the solvent was removed in vacuo, leaving a green solid which was immediately used for the following step (38% raw yield).

b) 328 mg (0.208 mmol) of the precedingly described compound was dissolved in 40 ml of propionic acid (distilled from potassium permanganate), and 240 mg (2.26 mmol) of benzaldehyde was added. The reaction mixture was stirred at room temperature for 30 min, and subsequently within 45 min the temperature was raised for 90 min to 90°C and then again for 90 min to 110°C. After cooling down the dark reaction mixture during 15 min, the propionic acid was distilled off in a rotary evaporator. The remaining product was flash-chromatographed (cyclohexane/ethyl acetate, 10:1) on silica gel. Of the first porphyrin-containing fraction of R_f ≈ 0.53 the solvents were evaporated, and the residue was dissolved in a small amount of dichloromethane. This solution was covered by a layer of cold methanol. After 3 d at 4°C, the product was obtained as violet microcrystals (3.6%, m.p. > 330°C). − MS (LSIMS positive, *m*-nitrobenzyl alcohol, 1% trifluoroacetic acid); *m/z* (%): 1164 (21) $[M]^+$, 1165 (50) $[MH]^+$, 1166 (73), 1167 (100), 1168 (82), 1169 (55). − ^{1}H NMR (360 MHz, CD_2Cl_2): δ = −2.72 (s, 2 H, N-H), 0.75−0.87 ("quint", 4 H, γ-H), 1.12 ("quint", ^3J = 6.6 Hz, 4 H, β-H), 1.91 (s, 6 H, OCH_3), 1.94 (t, ^3J = 7.2 Hz, 4 H, δ-H), 2.11 (t, ^3J = 6.6 Hz, 4 H, α-H), 5.29 (s, 2 H, biphen-1-H), 6.53 (d, ^3J = 6.8 Hz, 2 H, biphen-6-H), 6.75 (d, ^3J = 6.6 Hz, 2 H, biphen-5-H), 6.99 (d, ^3J = 6.8 Hz, 2 H, biphen-4-H), 7.20 (dd, ^3J = 8.2 Hz, ^3J = 6.8 Hz, 2 H, biphen-3-H), 7.73 (d, ^3J = 8.2 Hz, 2 H, biphen-2-H), 7.73−7.85 (m, centered at 7.79, 6 H, phenyl-3,4,5-H), 8.20−8.27 (m, centered at 8.24, 4 H, phenyl-2,6-H), 8.91 (d, ^3J = 4.5 Hz, 4 H, pyrrole-β-H), 9.27 (d, ^3J = 4.5 Hz, 4 H, pyrrole-α-H). − $C_{72}H_{54}Br_2N_4O_2$: HR-MS; *m/z*: calcd. 1164.2613, found 1164.2627 $[M^+]$.

5,15-[2,5-Dibromo-p-benzoquinone-1,4-diylbis(1,4-butanediyl-1,7-biphenyleno)]-10,20-diphenylporphyrin (**23**): To 7.2 mg (6.85 μmol) of **22** in 10 ml of dichloromethane under argon 320 mg (0.82 mmol) of boron tribromide was added. After 15 min at room temperature, 15 ml of a saturated sodium hydrogen carbonate solution was added dropwise to this mixture, and the reaction mixture was stirred for 15 min. After separation of the phases, the organic one was washed with 15 ml of saturated sodium hydrogen carbonate solution, and three times with 25 ml of water each. The aqueous phase was extracted several times with 10 ml of dichloromethane each, and then was concentrated to a volume of 20 ml to which under argon 500 mg of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was added. After 15 min of stirring at room temperature, the solution was extracted with 40 ml of saturated sodium hydrogen carbonate solution, washed three times with 40 ml of water, and then dried with magnesium sulfate. After removal of the solvent by distillation, the deep-violet residue was flash-chromatographed on silica gel (*h* = 15 cm, *d* = 1.5 cm) with cyclohexane/ethyl acetate (20:1). Of the product fractions with R_f ≈ 0.38 (cyclohexane/ethyl acetate, 10:1) the solvents were distilled off in a rotary evaporator. The product was dissolved in a small quantity of dichloromethane, and by covering with cold methanol after 3 d at 4°C, the dark-violet microcrystals were filtered off. For further purification the product was subjected twice to preparative thin-layer chromatography (cyclohexane/toluene/ethyl acetate/2-propanol, 20:3:1:3). The product with R_f ≈ 0.63 was eluted from silica gel with dichloromethane which then was distilled off (90% yield, m.p. > 330°C). − MS (LSIMS positive, *m*-nitrobenzyl alcohol, 1% trifluoroacetic acid); *m/z* (%): 1136 (41) $[MH_2]^+$, 1137 (54), 1138 (93), 1139 (100) $[MH_5]^+$. − ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 2.80 (s, 2 H, NH), 0.85 (center of "quint", ^3J = 7.3 Hz, 4 H, γ-H), 1.05 (center of "quint", ^3J = 7.3 Hz, 4 H, β-H), 1.99 (t, ^3J = 7.3 Hz, 4 H, δ-H), 2.04 (t, ^3J = 7.3 Hz, 4 H, α-H), 5.03 (s, 2 H, biphen-8-H), 6.50 (d, ^3J = 7.0 Hz, 2 H, biphen-6-H), 6.75 (d, ^3J = 7.0 Hz, 2 H, biphen-5-H), 7.00 (d, ^3J = 7.0 Hz, 2 H, biphen-4-H), 7.23 (dd, ^3J = 8.1 Hz, ^3J = 7.0 Hz, 2 H, biphen-3-H), 7.78−7.88 (m, 8 H, phen-3,4,5-H, biphen-2-H), 8.20 (br. d, 2 H, phen-2-H), 8.36 (br. d, 2 H, phen-6-H), 8.93 (d, ^3J = 4.7 Hz, 4 H, pyrrole-β-H), 9.27 (d, ^3J = 4.7 Hz, 4 H, pyrrole-α-H). − $C_{70}H_{48}Br_2N_4O_2$: HR-MS; *m/z*: calcd. 1134.2144, found 1134.2233 $[M]^+$; calcd. 1135.2222, found 1135.2291.

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