Photoinduced Electron Transfer in Porphyrin-Quinone Cyclophanes, 6[1]

Porphyrin-Quinone Cyclophanes with Gradually Varied Acceptor Strength: Syntheses and Characterizations

Heinz A. Staab*, Jürgen Weiser, Michael Futscher, Guido Voit, Andreas Rückemann, and Christine Anders

Abteilung Organische Chemie, Max-Planck-Institut für medizinische Forschung, Jahnstraße 29, W-6900 Heidelberg, F.R.G.

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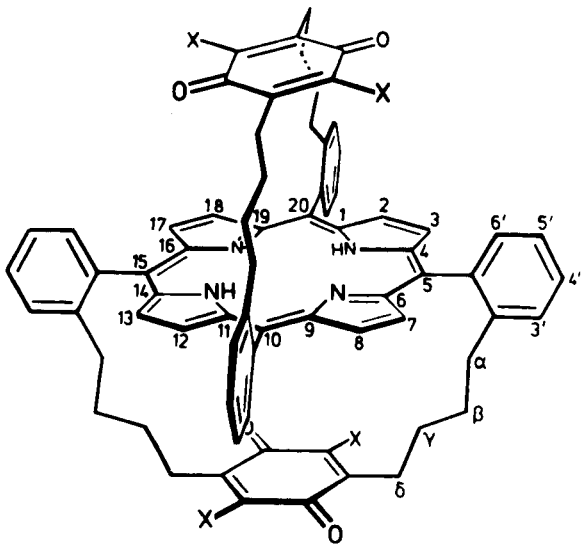
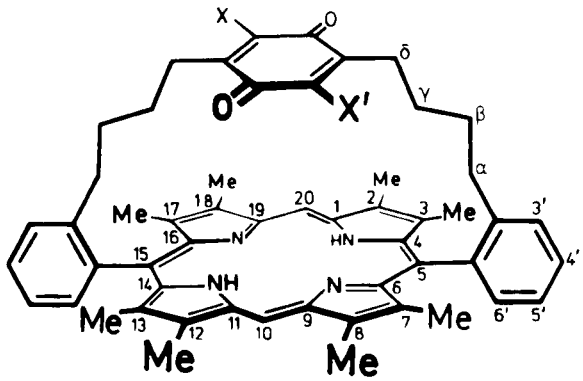
For studying intramolecular electron-transfer reactions, three groups of double- and single-bridged porphyrin-quinone cyclophanes **1** – **4**, **5** – **9**, and **11** – **14**, resp., with gradual variation of quinone acceptor strengths were synthesized. As key intermediates for building up the porphyrin-cyclophane skeleton the correspondingly 3,6-substituted 1,4-bis[4-(2-formylphenyl)-butyl]-2,5-dimethoxybenzenes **15** – **20** were synthesized. Condensation with pyrrole yielded the doubly bridged porphyrin cyclophanes **42** – **45**; via the bis(dipyrrolylmethyl) derivatives **46** – **51** and **64** – **67** the single-bridged porphyrin cyclophanes **58** – **63** and **72** – **75** were obtained by acidic condensation with triethyl formate. Cleavage of the methoxy groups and oxidation yielded the corresponding porphyrin-quinone systems. Some magnesium and zinc complexes of these cyclophanes are described. Spectroscopic data (MS, ^{1}H NMR) are reported in support of the proposed structures.

In the preceding paper[1], synthesis, structure, and spectroscopic properties related to intramolecular photoinduced electron transfer of cyclophane **3** with vertical quinone-porphyrin-quinone arrangement were described. Based on the concept discussed there, the intention of the studies reported in the present paper and in the following contributions[2-4] was to achieve a controlled variation of structural parameters on which electron-transfer rates depend. As one of these parameters the electron affinity of the quinone units was varied while keeping constant the other structural parameters. In the series of porphyrin-quinone cyclophanes the variation of the acceptor strength can be achieved by modification of the quinone units by appropriate electron-donating and electron-withdrawing substituents. Thus, the compounds **1**, **2**, and **4** containing methyl-, methoxy-, and chloro-substituted quinones, together with the unsubstituted parent compound **3**[1], represent a series of intramolecular porphyrin-quinone systems with gradually increasing electron-acceptor strength.

Complementary to this series, as further models for intramolecular electron transfer, porphyrin-quinone cyclophanes with only one quinone bridge were of interest. Due to the same type and length of the cyclophane bridges the



1 : X = Me
2 : X = OMe
3 : X = H
4 : X = Cl



5 : X, X' = Me
6 : X, X' = OMe
7 : X, X' = H
8 : X=Cl, X'= H
9 : X, X' = Cl
10 : X, X' = CN

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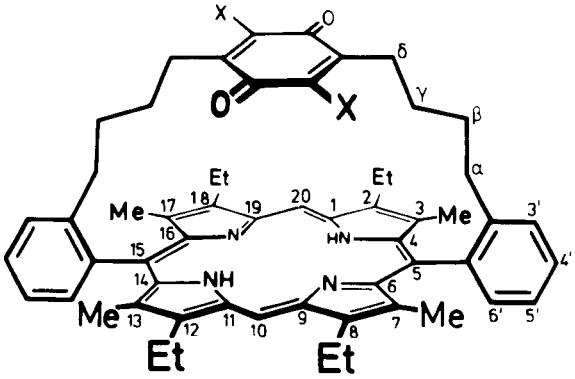
spatial arrangement of the quinone and porphyrin units was expected to be similar to the doubly quinone-bridged systems[1,5]. On the other hand, besides the fact that only one neighbouring electron acceptor is present, the electron transfer should show a different solvent-dependence as compared to the series **1**–**4** because in the latter the sterically shielded porphyrin units are not expected to participate significantly in the solvation of the charge-separated zwitterionic state. Of the single-bridged porphyrin-quinone cyclophanes, compounds **5** to **10** would form another sequence with increasing acceptor strength vis-á-vis the octamethylporphyrin unit as a stronger electron donor than present in the series **1**–**4**.

Finally, as a consequence of solubility problems which were experienced during spectroscopic investigations on the last-mentioned group of compounds, the syntheses of porphyrin-quinone cyclophanes were of interest whose octamethylporphyrin unit is replaced by tetramethyltetraethylporphyrin. The porphyrin-quinone compounds **11** to **14**, thus, represent a third series of compounds with gradually varied acceptor strength.

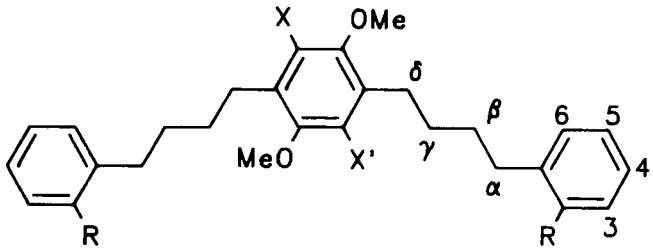


11 : X = Me
12 : X = OMe
13 : X = H
14 : X = Cl

In the present paper the syntheses and characterizations of the porphyrin-quinone cyclophanes **1**, **2**, **4**–**9**, and **11**–**14**, are deseribed; not yet completed attempts to synthesize **10** are reported. In the following paper[2] absorption and emission spectra as well as cyclovoltammetrically determined oxidation and reduction potentials of these compounds are reported with reference to photoinduced electron transfer as determined by time-resolved spectroscopy[6]. Finally, the detailed sterical structure of these compounds and possible conformational processes are dealt with based on X-ray structure analyses and temperature-dependent ^{1}H-NMR spectra[3].

Syntheses and Characterizations

3,6-Disubstituted 1,4-bis[4-(2-formylphenyl)butyl]-2,5-dimethoxybenzenes **15**, **16**, **17**, **18**, **19**, *and* **20**: For the three families of porphyrin-quinone cyclophanes mentioned above the common key intermediates are the dialdehydes **15**–**20** with the appropriate substituents in the 3- and 6-positions of the central aromatic rings. These dialdehydes were prepared by reduction of the correspondingly substituted 2,5-dimethoxy-1,4-bis[4-(2-methoxycarbonylphenyl)-butyl]benzenes **21**–**25** to the bis(hydroxymethyl) compounds **26**–**31** and subsequent oxidation of the latter. Generally, the substituents on the central aromatic rings, which later were to be converted into the quinone units, must be introduced in the first stages of the multistep reaction sequences leading to **21**–**25**, respectively. For this reason the syntheses of the individual members of the three porphyrin-quinone cyclophane families comprise a considerable number of new compounds (>80); this requires that more than usually details for their preparation and characterization must be given in the experimental part.

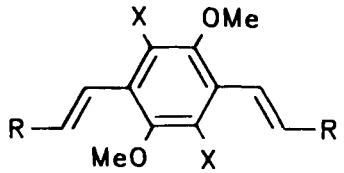


R = CHO	R = COOMe	R = CH_2OH
15:X,X'=Me	**21**:X,X'=Me	**26**:X,X'=Me
16:X,X'=OMe	**22**:X,X'=OMe	**27**:X,X'=OMe
17:X,X'=H	**23**:X,X'=H	**28**:X,X'=H
18:X=Cl, X'=H	———	**29**:X=Cl, X'=H
19:X,X'=Cl	**24**:X,X'=Cl	**30**:X,X'=Cl
20:X,X'=CN	**25**:X,X'=CN	**31**:X.X'=CN

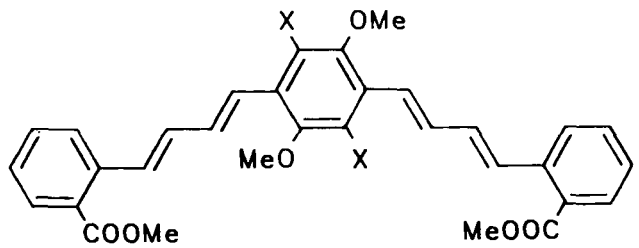
1,4-Bis[4-(2-formylphenyl)butyl]-2,5-dimethoxy-3,6-dimethylbenzene (**15**): In the synthesis of **17** it had been shown[1] that for building up the side chains starting from the central aromatic ring the simultaneous introduction of two C_3 units by palladium-catalyzed vinylation[7] of 1,4-dibromo-2,5-dimethoxybenzene was most successful. Even in the case of sixfold substituted benzenes this "Heck reaction", in spite of the steric hindrance, works excellently. Thus, 1,4-dibromo-2,5-dimethoxy-3,6-dimethylbenzene[8] in the presence of palladium(II) acetate and tri-*ortho*-tolylphosphane in triethylamine/acetonitrile was converted into (*E*,*E*)-2,5-dimethoxy-1,4-bis(2-methoxycarbonylethenyl)-3,6-dimethylbenzene (**32**; yield 86%). By reduction of **32** with diisobutylaluminium hydride (yield 92%) the corresponding bis(hydroxypropenyl) compound **33** was obtained which was oxidized with barium manganate(VI)[9] to the dialdehyde **34** (yield 78%). A twofold Wittig reaction of **34** with (2-methoxycarbonylbenzyl)triphenylphosphonium bromide[1] resulted in the formation of **35** (*Z*,*E* isomers, 93%) which were catalytically hydrogenated to **21** (Pd/C, ethyl acetate/methanol; 88%). By reduction of **21** to **26** (lithium aluminium hydride, tetrahydrofuran, at reflux for 3 h; yield 98%) and subsequent oxidation with pyridinium chlorochromate (yield 93%) **15** was obtained.

1,4-Bis[4-(2-formylphenyl)butyl]-2,3,5,6-tetramethoxybenzene (**16**): For the twofold Heck reaction in this sterically especially hindered case it was preferable to use the more reactive diiodobenzene instead of the dibromo compound.

1,4-Diiodo-2,3,5,6-tetramethoxybenzene[10] was obtained by metalation of 1,2,4,5-tetramethoxybenzene with excess *n*-butyllithium and subsequent reaction with iodine (yield 35%, besides 24% of the monoiodo compound). The palladium(II) acetate catalyzed reaction with methyl acrylate, performed analogously to the preparation of **32**, resulted in the formation of (*E,E*)-2,3,5,6-tetramethoxy-bis(2-methoxycarbonylethenyl)benzene (**36**; yield 98%). Reduction of **36** with diisobutylaluminium hydride to **37** (85%), oxidation of **37** with barium manganate(VI) to **38** (90%), and the twofold Wittig reaction of the dialdehyde **38** with (2-methoxycarbonylbenzyl)triphenylphosphonium bromide[1] to **39** (*Z,E* isomers, 94%) were performed in close analogy to the corresponding steps in the synthesis of **35**. Catalytic hydrogenation of **39** yielded **22** (93%) which was reduced with lithium aluminium hydride to 1,4-bis[4-(2-hydroxymethylphenyl)-butyl]-2,3,5,6-tetramethoxybenzene (**27**; 88%). Oxidation of **27** with pyridinium chlorochromate afforded the dialdehyde **16** (92%).



R = COOMe	R = CH_2OH	R = CHO
32 : X=Me	**33** : X=Me	**34** : X=Me
36 : X=OMe	**37** : X=OMe	**38** : X=OMe
		40 : X=Cl



35 : X = Me
39 : X = OMe
41 : X = Cl

1-Chloro-2,5-bis[4-(2-formylphenyl)butyl]-3,6-dimethoxybenzene (**18**) *and 1,4-dichloro-2,5-bis[4-(2-formylphenyl)-butyl]-3,6-dimethoxybenzene* (**19**): The synthesis of **18** and **19** started from 2,5-dimethoxyterephthalaldehyde which by iodine-catalyzed chlorination yielded 2,5-dichloro-3,6-dimethoxyterephthalaldehyde (yield 58%). This dialdehyde was converted in a twofold Wittig reaction with (1,3-dioxolan-2-ylmethyl)triphenylphosphonium bromide[11] into (*E,E*)-1,4-dichloro-2,5-bis(2-formylethenyl)-3,6-dimethoxybenzene (**40**; 52%). A double Wittig reaction of **40** with (2-methoxycarbonylbenzyl)triphenylphosphonium bromide[1], yielded **41** (*Z,E* isomers) which was converted by catalytic hydrogenation into **24** (67%, based on **40**). A second reaction sequence leading, however, to a lower yield of **24** started from 2,5-dimethoxy-1,4-bis(2-methoxycarbonylethyl)benzene which in the presence of iodine was chlorinated to 1,4-dichloro-3,6-dimethoxy-2,5-bis(2-methoxycarbonylethyl)-benzene. Reduction with lithium aluminium hydride yielded the corresponding bis(hydroxypropyl) compound which was oxidized with pyridinium chlorochromate to 1,4-dichloro-2,5-bis(2-formylethyl)-3,6-dimethoxybenzene. A twofold Wittig reaction with (2-methoxycarbonylbenzyl)triphenylphosphonium bromide[1] and subsequent catalytic hydrogenation afforded **24**[13].

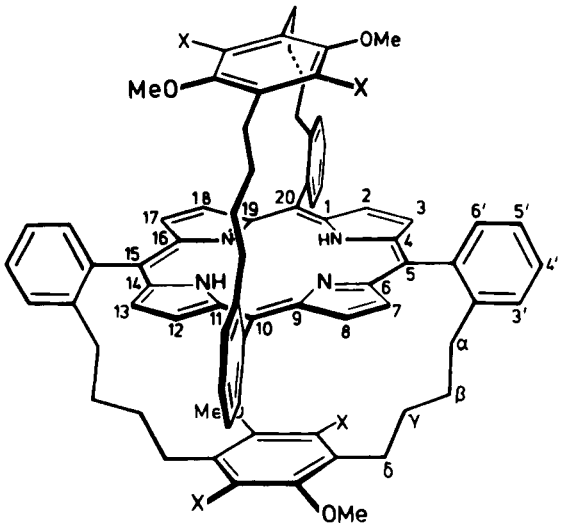
In an attempt to reduce the two ester groups in **24** by lithium aluminium hydride in addition to the expected product **30** the corresponding monochloro compound **29** was obtained by reductive elimination of a chloro substituent. After oxidation with pyridinium chlorochromate the mono- and dichloro-substituted dialdehydes **18** and **19** were separated by medium-pressure chromatography (yield 20% and 31%, resp., relative to **24**). The isolation of **18** provided an unintended access to porphyrin-quinone cyclophanes with a monochloroquinone unit as an interesting acceptor in this series of gradually varied acceptor strengths. By using lithium borohydride[14] instead of lithium aluminum hydride, however, we achieved a selective reduction of the ester groups of **24** with **30** as the only product (yield 82%) which was oxidized with pyridinium chlorochromate to the dialdehyde **19** in 85% yield.

1,4-Dicyano-2,5-bis[4-(2-formylphenyl)butyl]-3,6-dimethoxybenzene (**20**): The preparation of the dicyano-substituted dialdehyde **20** started from 1,4-dicyano-2,5-bis[4-(2-methoxycarbonylphenyl)butyl]-3,6-dimethoxybenzene (**25**) which had previously been synthesized in a different context[15]. **25** was reduced with lithium borohydride to the corresponding bis(hydroxymethyl) compound **31** (77% yield) which was oxidized with pyridinium chlorochromate to **20** (yield 74%).

Quinone-Porphyrin-Quinone Cyclophanes **1**, **2**, *and* **4**: For the syntheses of the 5,15:10,20-bis[*p*-benzoquinone-1,4-diyl-bis(4,1-butanediyl-2,1-benzeno)]porphyrins[16] the bottle-neck is, of course, the building up of the complete carbon skeleton of these cyclophanes including the specific substituents on the central aromatic rings as well as the four methoxy groups which are required for the conversion of these rings into quinone units. Compounds **42**, **43**, and **45** which meet these criteria were obtained, like **44** from **17**[1], in a single step by the reaction of the dialdehydes **15**, **16** and **19**, respectively, with pyrrole in boiling propionic acid[17]; the yields of the porphyrin cyclophanes are, however, rather poor (0.5 to 1%). Due to the bifunctionality of the reactants the main products of this reaction are oligomers. In the case of **42**, as shown for **44**[1], an isomer was isolated in which the two bridges are inserted into two adjacent methine positions of the porphyrin.

For the porphyrin cyclophanes **42**, **43**, and **45** the structure of 3,6-disubstituted 5,15:10,20-bis[2,5-dimethoxybenzene-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]porphyrins with the two cyclophane bridges on either side of the porphyrin plane cross-linking opposite methine positions is clearly proven by ^{1}H-NMR spectrometry. The proton resonance spectra, completely assigned by COSY, show the

high molecular symmetry discussed already for **44**[1]. The most prominent feature of these spectra in the dominant ring-current effect of the porphyrin which acts as an internal reference system for the localization of the different groups of protons in these cyclophanes (for data see Experimental).

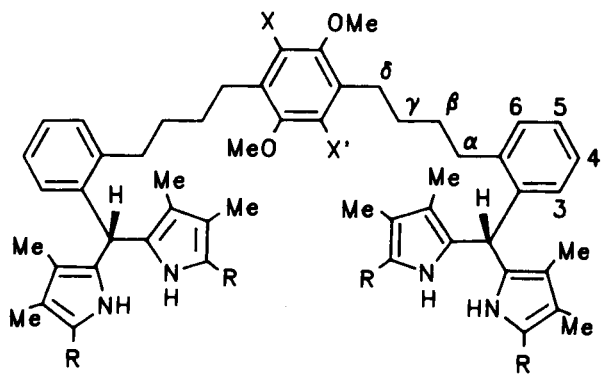


42 : X = Me
43 : X = OMe
44 : X = H
45 : X = Cl

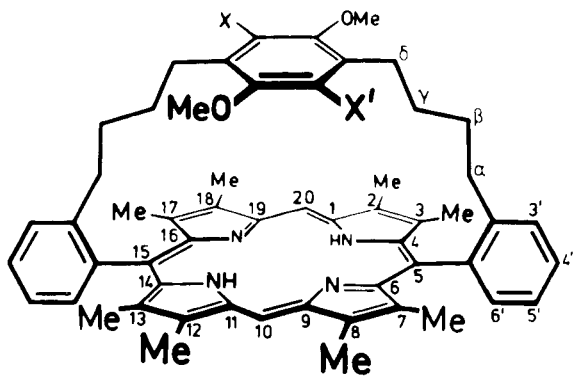
Ether cleavage of the four methoxy groups by boron tribromide and subsequent oxidation with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) yielded **1** from **42** (yield 73%) and **4** from **45** (72%). Selective demethylation of **43** containing the two tetramethoxybenzene units and subsequent oxidation with cerium(IV) ammonium nitrate afforded **2** (yield 63%). For the quinone-porphyrin-quinone cyclophanes the ^{1}H-NMR spectra of **1**, **2**, and **4** correspond closely to that of **3** the structure of which has been confirmed by an X-ray analysis[1,18]; rather small deviations of certain chemical shifts can be ascribed to the effect of the different substituents X in **1**, **2**, and **4** (for details see Experimental).

Porphyrin-Quinone Cyclophanes **5**, **6**, **7**, **8**, *and* **9**: The porphyrin-quinone cyclophanes **5**–**9**, in which only a single quinone bridge cross-links two opposite methine carbons of an octamethylporphyrin, were expected to be accessible by starting again from the dialdehydes **15**–**20**. These aldehydes were treated with 2-benzyloxycarbonyl-3,4-dimethylpyrrole[19] (prepared by transesterification of 2-ethoxycarbonyl-3,4-dimethylpyrrole[20]) to furnish the bis(dipyrrolylmethyl) compounds **46**, **47**, **49**–**51** (yield 90–99%). Compound **48** was obtained by condensation of **17** with 2-ethoxycarbonyl-3,4-dimethylpyrrole to the respective bis(dipyrrolylmethyl) compound and subsequent transesterification of the latter (yield relative to **17**: 82%). By catalytic hydrogenation (Pd/C) the benzyl groups of **46**–**51** were split off resulting in the formation of the tetracarboxylic acids **52**–**57**, respectively, in excellent yields.

In these tetracarboxylic acids the cyclophane bridge with the appropriate substituents on the central aromatic ring as well as the four pyrrole rings and two of the four methine carbon atoms are already present. For building up the porphyrin system the next steps should be the decarboxylation and the ring-closing condensation by which the missing two carbon atoms were to be inserted. Porphyrin syntheses of this type have been reported before by using triethyl orthoformate and trichloroacetic acid in dichloromethane[21]. Due to the bifunctionality of the aldehyde component in the present case, it was rather difficult to reach optimum reaction conditions with regard to yield and reproducibility. Sufficient and reliable yields were eventually obtained by the procedure described in detail in the experimental part. Besides the concentration of the tetracarboxylic acids (≈1 mmol in 500 ml of dichloromethane) and the tetracarboxylic acid/orthoformate ratio (1:10) the order and the rate in which the components were added turned out to be essential. The dihydroporphyrins formed in this ring-closing conden-



R = COOBz	R = COOH
46 : X, X' = Me	**52** : X, X' = Me
47 : X, X' = OMe	**53** : X, X' = OMe
48 : X, X' = H	**54** : X, X' = H
49 : X=Cl, X'=H	**55** : X=Cl, X'=H
50 : X, X' = Cl	**56** : X, X' = Cl
51 : X, X' = CN	**57** : X, X' = CN



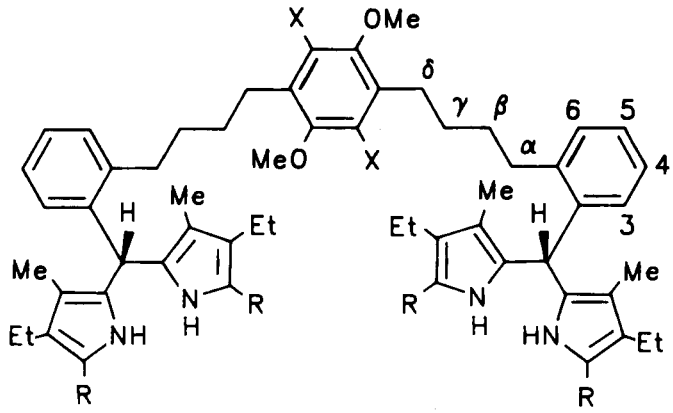
58 : X, X' = Me
59 : X, X' = OMe
60 : X, X' = H
61 : X=Cl, X'=H
62 : X, X' = Cl
63 : X, X' = CN

sation were dehydrogenated by DDQ to the bridged porphyrin cyclophanes **58**–**63**, which after separation and purification were obtained in yields up to 20%.

The ^{1}H-NMR spectra of these porphyrin cyclophanes at room temperature with regard to the cyclophane bridge and the central aromatic ring closely resemble those of the correspondingly substituted quinone-porphyrin-quinone cyclophanes **1**–**4**. The high symmetry thus pretended for these cyclophanes is, however, the result of fast conformational interconversions which will be discussed on the basis of temperature-dependent ^{1}H-NMR measurements in a separate paper[3]. In this context the results of an X-ray structure analysis of **59** will also be reported.

Ether cleavage of the methoxy groups by boron tribromide and subsequent oxidation of the hydroquinones with DDQ resulted in the formation of **5** from **58** (67%), **7** from **60** (74%), **8** from **61** (63%), and **9** from **62** (54%). The selective demethylation of the tetramethoxy compound **59** and the oxidation to **6** was achieved with cerium(IV) ammonium nitrate (yield 50%). So far, all attempts to demethylate **63** and oxidize the hydroquinone to the corresponding quinone **10** failed. The reaction of **10** with boron tribromide led to decomposition as did the reaction with cerium(IV) ammonium nitrate as well as with silver(II) oxide, pyridinium hydrochloride and other demethylating and/or oxidizing agents under various conditions.

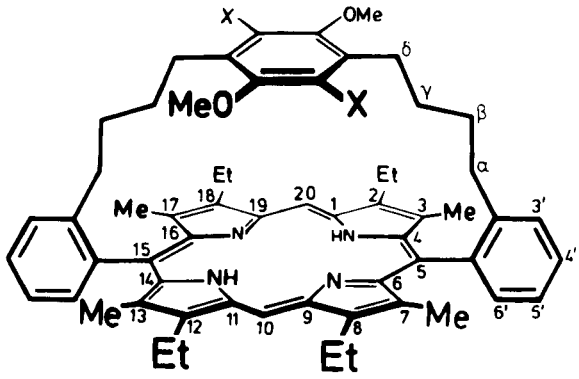
The ^{1}H-NMR spectra and other analytical data for **5**, **6**, **7**, **8**, and **9** (see Experimental) are well in accordance with the structures suggested. A specific steric situation is indicated by the ^{1}H-NMR spectrum of the monochloroquinone system **8**: here the single proton on the quinone ring with $\delta = 3.12$ is considerably more shielded by the ring-current effect of the porphyrin than the two corresponding protons in **7** ($\delta = 4.06$). Probably in the most favoured conformation of **8** the quinone ring with the sterically less hindered side is especially tilted towards the porphyrin plane bringing the aromatic proton closer into the shielding region of the porphyrin system.



X	R = COOBz	R = COOH
Me	**64**	**68**
OMe	**65**	**69**
H	**66**	**70**
Cl	**67**	**71**

Porphyrin-Quinone Cyclophanes **11**, **12**, **13**, and **14**: These porphyrin-quinone cyclophanes which contain the tetraethyltetramethylporphyrin system were synthesized in analogy to the synthesis of **5**–**9**. Acid-catalyzed condensation of the dialdehydes **15**, **16**, **17**, and **19**, resp., with 2-benzyloxycarbonyl-3-ethyl-4-methylpyrrole resulted in the formation of 1,4-bis{4-[2-(bis⟨5-benzyloxycarbonyl-4-ethyl-3-methyl-2-pyrrolyl⟩methyl)phenyl]butyl}-2,5-dimethoxybenzenes with the respective substitution in the 3- and 6-positions of the central aromatic ring [**64** (94%), **65** (90%), **66** (99%), **67** (91%)]. By catalytic hydrogenation (Pd/C) the benzyl groups were split off resulting in the nearly quantitative formation of the tetracarboxylic acids **68**, **69**, **70**, and **71**.

The cyclization to the porphyrin cyclophanes by acid-catalyzed condensation with triethyl orthoformate and the dehydrogenation with DDQ were carried out analogously to the syntheses of **58**–**63** (see above): **72** (17%), **73** (8.3%), **74** (12%), **75** (13%). Spectroscopic properties and analytical data correspond to those of the octamethylporphyrin analogues. The structures were especially confirmed by the ^{1}H-NMR spectra, completely assigned by COSY (for data see Experimental).

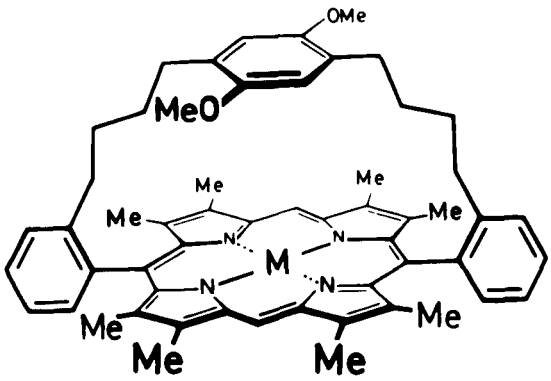


72 : X = Me
73 : X = OMe
74 : X = H
75 : X = Cl

Demethylation by boron tribromide and subsequent oxidation of the hydroquinones to the respective quinones yielded **11** from **72** (74%), **13** from **74** (86%) and **14** from **75** (66%). The preparation of **12** from **73**, was achieved by oxidative demethylation with cerium(IV) ammonium nitrate (yield 60%) as in the case of the conversion of **59** into **6** (see above). Again the structures of these porphyrin-quinone cyclophanes were confirmed by elemental analysis, mass spectra, the complete assignment of ^{1}H-NMR spectra and other spectroscopic data (see Experimental and ref.[2]). An X-ray structure analysis of **12** will be discussed in the context of conformational studies on these porphyrin-quinone cyclophanes[3].

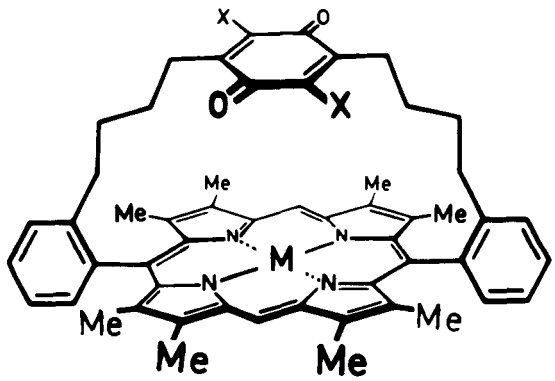
Metalloporphyrin-Quinone-Cyclophanes and Reference Compounds: For a comparison with the porphyrin cyclo-

phanes mentioned so far, the corresponding metalloporphyrins were of interest because of the expected considerable change in the oxidation potentials of the porphyrin units in these compounds[2]. As reported in the preceding paper[1] attempts to convert the doubly quinone-bridged porphyrin cyclophane into its zinc complex failed. Due to the sterical shielding of the porphyrin from both sides the complexation needs drastic reaction conditions which the quinone compound cannot tolerate. By boiling of the nonquinoid **44** in dimethyl sulfoxide with excess zinc acetate for 14 h a zinc complex was obtained. From single-bridged porphyrin cyclophanes, however, metal complexes should be obtainable under normal conditions. In fact, **60** reacted with excess zinc acetate in trichloromethane/methanol (1:1) to give the zinc complex **76**, and under similar conditions also from the porphyrin-quinone cyclophanes **7** and **5** the zinc complexes **77** *and* **78**, *resp.*, were obtained in high yields. Their absorption spectra, ^{1}H-NMR and other analytical data proved that complexation was complete.

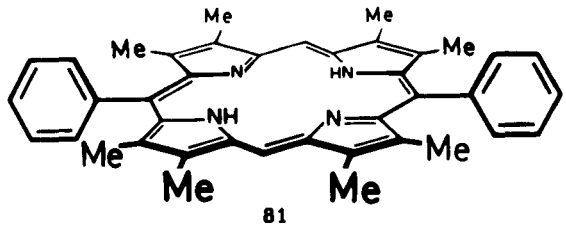


76 : M = Zn
79 : M = Mg

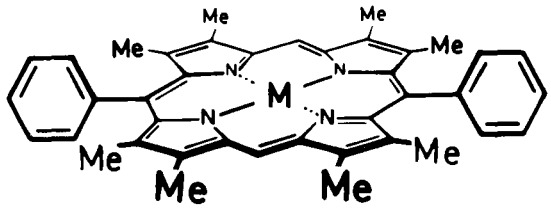
It was also possible to prepare the magnesium complexes of the single-bridged porphyrin cyclophanes, for example **79** by reaction of **60** with methylmagnesium iodide in dioxane (yield 94%) and **80** by treatment of **7** with the magnesium



77 : M = Zn, X = H
78 : M = Zn, X = Me
80 : M = Mg, X = H



81



82 : M = Zn
83 : M = Mg

salt of 3,5-di-*tert*-butyl-4-hydroxytoluene[23] in diethyl ether (yield 76%).

As references for the spectroscopic studies on the porphyrin-quinone cyclophane systems[2] 2,3,7,8,12,13,17,18-octamethyl-5,15-diphenyl-porphyrin (**81**)[24] and its zinc and magnesium complexes **82** and **83** were of interest. **81** was obtained as described in ref.[25] by cyclization of bis(3,4-dimethyl-2-pyrrolyl)methane[26] with benzaldehyde and subsequent dehydrogenation with DDQ (yield 91%). Treatment with zinc acetate in pyridine resulted in the formation of the zinc complex **82** (92%). The reaction of **83** with magnesium perchlorate in pyridine yielded **83** (94%) (for details and analytical data supporting the structures see Experimental).

Experimental

Melting points: Büchi SMP 20 and 512; Bock Monoskop M (m.p. > 240°C). – IR: Beckman IR-4240 (KBr). – UV/Vis: Varian Cary 2300. – Fluorescence: SLM 8000, Fa. SLM Instruments; Fluorolog F 112, Fa. Spex. – MS: DuPont CEC 21-492; Finnigan MAT 212 (ionization potential 70 eV; only the most prominent peaks are listed, usually with I_{rel} > 10%), FAB spectra (LSI-MS: Liquid Secondary Ion MS, positive; 3-nitrobenzylic alcohol/1% trifluoroacetic acid): VG Analytical ZAB 2E/70SE. – ^{1}H NMR: Hitachi Perkin-Elmer R 24B; Bruker Physik HX-360, AM 500 (internal reference tetramethylsilane). – Microanalysis: Elemental Analyzer 1106 Carlo Erba. – Analytical TLC: DC Micro Cards Polygram SIL G/UV$_{254}$, Macherey-Nagel. – CC: Silica gel SiliTech 63-200μ, ICN Biomedicals. – MPLC: Labomatic; Silica gel 60, 20–45 μm.

(E,E)-2,5-Dimethoxy-1,4-bis(2-methoxycarbonylethenyl)-3,6-dimethylbenzene (**32**): In a bomb tube (h = 45 cm, d = 5 cm) 40.0 g (123 mmol) of 1,4-dibromo-2,5-dimethoxy-3,6-dimethylbenzene[8], 1.65 g (7.38 mmol) of palladium(II) acetate and 13.5 g (44.4 mmol) of tri-*ortho*-tolylphosphane were suspended in 180 ml of triethylamine/acetonitrile (2:1), then 33.0 ml (369 mmol) of methyl acrylate was added. The bomb tube was closed under argon and heated with stirring to 80°C for 65 h. After cooling the reaction mixture was added into 600 ml of trichloromethane and washed four times with 400 ml of water each. The aqueous solution was extracted several times with 200 ml of trichloromethane, and the combined extracts were dried with magnesium sulfate. After distilling off the solvent the residue was washed with 700 ml of methanol and sucked off: yield 35.7 g (86%) of **32** as yellow microcrystals sufficiently pure to be used in the following reaction. Recrystalli-

zation from methanol: m.p. 176°C. – MS: *m/z* (%) = 334 (74) [M^+], 303 (100) [$M^+ - OCH_3$], 229 (25), 186 (15), 185 (12). – ^{1}H NMR (360 MHz, $CDCl_3$): δ = 2.32 (s, 6H), 3.61 (s, 6H), 3.83 (s, 6H), 6.58 (d, *J* = 16.3 Hz, 2H), 7.84 (d, *J* = 16.3 Hz, 2H).

$C_{18}H_{22}O_6$ (334.4) Calcd. C 64.66 H 6.63 Found C 64.56 H 6.69

(E,E)-1,4-Bis(3-hydroxy-1-propenyl)-2,5-dimethoxy-3,6-dimethylbenzene (**33**): To a stirred solution of 30.1 g (90.0 mmol) of **32** in 500 ml of dichloromethane under argon at −30°C within 15 min by means of a syringe 450 ml of a 1 M solution of diisobutylaluminium hydride in dichloromethane was added. After warming up to 0°C the reaction mixture was transferred in small portions into 600 ml of ice-water with vigorous shaking. The precipitate formed was dissolved by the addition of 2 N sulfuric acid, and the aqueous solution was then extracted three times with 400 ml of dichloromethane each. The united extracts were washed twice with 400 ml of a sodium carbonate solution (10%) and twice with 400 ml of water each. After drying with magnesium sulfate and distilling off the solvent *in vacuo*, **33** was obtained analytically pure as a colourless crystal powder: yield 23.0 g (92%) of **33**, m.p. 104–105°C. – MS: *m/z* (%) = 278 (100) [M^+], 189 (22), 175 (12), 156 (16), 128 (11). – ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.73 (br. t, *J* = 5.6 Hz, 2H), 2.25 (s, 6H), 3.60 (s, 6H), 4.35 (m_c, 4H), 6.27 (dt, *J* = 16.2 and 5.6 Hz, 2H), 6.64 (dt, *J* = 16.2 and 1.5 Hz, 2H).

$C_{16}H_{22}O_4$ (278.3) Calcd. C 69.04 H 7.97 Found C 68.77 H 8.20

(E,E)-1,4-Bis(formylethenyl)-2,5-dimethoxy-3,6-dimethylbenzene (**34**): 22.3 g (80.1 mmol) of **33** and 205 g (800 mmol) of freshly prepared barium manganate(VI)[9] in 700 ml of dichloromethane were heated with vigorous stirring at reflux for 3 h. The reaction mixture cooled down to 20°C was filtered through Celite which was washed with dichloromethane until the filtrate became colourless. Evaporation of the solvent from the filtrate afforded pure **34**: yield 17.2 g (78%), yellow powder, m.p. 139–140°C. – MS: *m/z* (%) = 274 (29) [M^+], 243 (100) [$M^+ - OCH_3$]. – ^{1}H NMR (360 MHz, $CDCl_3$): δ = 2.37 (s, 6H), 3.65 (s, 6H), 6.87 (dd, *J* = 16.3 and 7.7 Hz, 2H), 7.67 (d, *J* = 16.3 Hz, 2H), 9.75 (d, *J* = 7.6 Hz, 2H).

$C_{16}H_{18}O_4$ (274.3) Calcd. C 70.05 H 6.61 Found C 70.01 H 6.81

2,5-Dimethoxy-1,4-bis[4-(2-methoxycarbonylphenyl)-1,3-butadienyl]-3,6-dimethylbenzene (**35**, *Z,E* isomers): To a solution of sodium methanolate in methanol, prepared by adding cautiously 6.80 g (296 mmol) of sodium to 750 ml of methanol under argon, 145 g (296 mmol) of (2-methoxycarbonylbenzyl)triphenylphosphonium bromide[1] was added. After stirring at 70°C for 30 min a suspension of 20.3 g (74.0 mmol) of **34** in 500 ml of tetrahydrofuran was slowly added, and the reaction mixture was stirred at 70°C for a further 2 h. The residue obtained by evaporation of the solvents was suspended in 100 ml of cold methanol and sucked off on a frit: yield 19.0 g (48%) of **35**, according to TLC (silica gel, toluene/ethyl acetate, 25:1) a homogeneous product with $R_f \approx 0.21$. The filtrate was concentrated by evaporation of the methanol and the residue subjected to chromatography on silica gel (*h* = 18 cm, *d* = 19.5 cm, eluent toluene/ethyl acetate, 25:1) to yield further 18.0 g (45%) of analytically pure **35** (mixture of *Z,E* isomers): m.p. 125–145°C. – MS: *m/z* (%) = 538 (100) [M^+], 375 (20). – ^{1}H NMR (360 MHz, CD_2Cl_2) indicated the presence of all three *Z,E* isomers (signals of two double bonds introduced by the Wittig reaction).

$C_{34}H_{34}O_6$ (538.6) Calcd. C 75.82 H 6.36 Found C 75.69 H 6.36

2,5-Dimethoxy-1,4-bis[4-(2-methoxycarbonylphenyl)butyl]-3,6-dimethylbenzene (**21**): After having passed argon for 30 min through a solution of 8.50 g (15.8 mmol) of **35** (*Z,E* isomers) in 300 ml of ethyl acetate/methanol (1:1) it was heated to 80°C; then 1.5 g of palladium catalyst (10% on charcoal) in 40 ml of ethyl acetate was added. Hydrogen was passed through the solution at 80°C for 5 h. For the isolation, the products of four such hydrogenation reactions were combined, the catalyst was separated by filtration over a glass frit (D4) and washed with 400 ml of ethyl acetate. The solvents were distilled off, and the residue was crystallized from methanol: 30.2 g (88%) of **21**, colourless needles, m.p. 110–111°C. – MS: *m/z* (%) = 546 (100) [M^+]. – ^{1}H NMR (360 MHz, CD_2Cl_2, complete assignment by COSY and NOE): δ = 1.48–1.57 (m, 4H, γ-CH_2), 1.65–1.73 (m, 4H, β-CH_2), 2.18 (s, 6H, ar-CH_3), 2.62 (t, *J* = 8.0 Hz, 4H, δ-CH_2), 2.98 (t, *J* = 7.8 Hz, 4H, α-CH_2), 3.63 (s, 6H, ar-OCH_3), 3.85 (s, 6H, $COOCH_3$), 7.24 ("td", *J* ≈ 7.6 and 1.3 Hz, 2H, ar-4-H), 7.28 (dd, *J* = 7.6 and 0.8 Hz, 2H, ar-6-H), 7.41 ("td", *J* ≈ 7.5 and 1.5 Hz, 2H, ar-5-H), 7.82 (dd, *J* = 7.7 and 1.4 Hz, 2H, ar-3-H).

$C_{34}H_{42}O_6$ (546.7) Calcd. C 74.70 H 7.74 Found C 74.63 H 7.82

1,4-Bis[4-(2-hydroxymethylphenyl)butyl]-2,5-dimethoxy-3,6-dimethylbenzene (**26**): To a suspension of 4.16 g (110 mmol) of lithium aluminium hydride in 550 ml of tetrahydrofuran 15.1 g (27.6 mmol) of **21** in 270 ml of tetrahydrofuran was added under argon within 30 min at 20°C. The reaction mixture was heated at reflux for 3 h, then cooled down to 0°C and hydrolyzed by slowly adding a solution of 16 ml of water and 100 ml of tetrahydrofuran with stirring at 20°C for 12 h. The precipitate was sucked off and washed four times with 150 ml of boiling tetrahydrofuran each. The united filtrates were dried with magnesium sulfate, and the solvent was distilled off: yield 13.3 g (98%) of **26** which was directly used in the following reaction step. For characterization the product was crystallized from ethyl acetate: m.p. 102–104°C. – MS: *m/z* (%) = 490 (30) [M^+], 179 (32), 145 (100), 143 (27), 133 (25), 131 (40), 129 (20), 119 (32), 117 (23), 105 (98), 91 (50). – ^{1}H NMR (360 MHz, CD_2Cl_2): δ = 1.53–1.59 (m, 4H, γ-CH_2), 1.65–1.72 (m, 6H, β-CH_2 and OH), 2.18 (s, 6H, ar-CH_3), 2.63 (t, *J* = 7.9 Hz, 4H, δ-CH_2), 2.71 (t, *J* = 7.8 Hz, 4H, α-CH_2), 3.62 (s, 6H, ar-OCH_3), 4.69 (d, *J* = 5.7 Hz, 4H, ar-CH_2OH), 7.18–7.22 (m, 6H, ar-H), 7.36 (d, *J* = 6.6 Hz, 2H, ar-H).

$C_{32}H_{42}O_4$ (490.7) Calcd. C 78.33 H 8.63 Found C 78.27 H 8.90

1,4-Bis[4-(2-formylphenyl)butyl]-2,5-dimethoxy-3,6-dimethylbenzene (**15**): 13.5 g (27.5 mmol) of **26** and 17.6 g (81.6 mmol) of pyridinium chlorochromate together with 13.5 g of Celite and 13.5 g of magnesium sulfate in 380 ml of dichloromethane were stirred at 20°C for 3 h. Filtration through a silica gel column (h = 18 cm, d = 19.5 cm; toluene/ethyl acetate, 16:1) and evaporation of the solvents yielded 12.5 g (93%) of **15**; m.p. 104–106°C (from diethyl ether). – MS: *m/z* (%) = 486 (100) [M^+], 193 (11), 179 (11), 133 (11), 131 (17), 117 (12), 91 (23). – ^{1}H NMR (360 MHz, CD_2Cl_2; complete assignment by COSY and NOE): δ = 1.53–1.60 (m, 4H, γ-CH_2), 1.68–1.74 (m, 4H, β-CH_2), 2.18 (s, 6H, ar-CH_3), 2.63 (t, *J* = 8.0 Hz, 4H, δ-CH_2), 3.08 (t, *J* = 7.8 Hz, 4H, α-CH_2), 3.62 (s, 6H, ar-OCH_3), 7.31 (dd, *J* = 7.7 and 0.9 Hz, 2H, ar-6-H), 7.36 ("td", *J* ≈ 7.6 and 0.9 Hz, 2H, ar-4-H), 7.51 ("td", *J* ≈ 7.4 and 1.5 Hz, 2H, ar-5-H), 7.82 (dd, *J* = 7.7 and 1.4 Hz, 2H, ar-3-H), 10.30 (s, 2H, CHO).

$C_{32}H_{38}O_4$ (486.6) Calcd. C 78.98 H 7.87 Found C 79.13 H 8.01

1,4-Diido-2,3,5,6-tetramethoxybenzene: To a solution of 10.0 g (50.5 mmol) of 1,2,4,5-tetramethoxybenzene in 1600 ml of tetrahydrofuran/diethyl ether (1:1) 75.0 ml (120 mmol) of a 1.6 N solution of *n*-butyllithium in *n*-hexane was added slowly under argon by means of a syringe. After stirring for 4 h at 20°C and cooling down to 0°C a solution of 20.3 g (80.0 mmol) of iodine in 100 ml of tetrahydrofuran was added within 30 min. The reaction mixture then was extracted with 400 ml of 10% sodium thiosulfate solution and twice with 1 l of water each, the organic phase dried with magnesium sulfate, and the solvents were evaporated. To separate the diiodo compound from the monoiodo byproduct the raw material of six such reactions was collected and chromatographed on a silica gel column (*h* = 18 cm, *d* = 19.5 cm; eluent: cyclohexane/ethyl acetate, 16:1). The fraction with $R_f \approx 0.44$ afforded 41.2 g (35%) of pure product, m.p. 133–135°C (ref.[10]: yield 8.9%, m.p. 136°C).

(E,E)-2,3,5,6-Tetramethoxy-1,4-bis(2-methoxycarbonylethenyl)benzene (**36**): In analogy to the preparation of **32**, in a bomb tube sealed under argon 41.0 g (91.1 mmol) of 1,4-diiodo-2,3,5,6-tetramethoxybenzene, 1.27 g (5.67 mmol) of palladium(II) acetate, 3.63 g (11.9 mmol) of tri-*ortho*-tolylphosphane, and 24.5 ml (65.0 mmol) of methyl acrylate in 100 ml of triethylamine and 50 ml of acetonitrile were allowed to react at 70°C for 70 h. After cooling to room temp. and addition of 1 l of trichloromethane, the solution was extracted four times with 400 ml of water each; the aqueous extracts were washed twice with 200 ml of trichloromethane each, and the combined organic solutions were dried with magnesium sulfate. Evaporation of the solvents in a rotary evaporator yielded crude **36** which was crystallized from 1.3 l of methanol: 29.6 g (89%) of **36**, needles of m.p. 169–170°C. – MS: *m/z* (%) = 366 (100) [M^+], 335 (35) [$M^+ - OCH_3$]. – ^{1}H NMR (360 MHz, $CDCl_3$): δ = 3.82 (s, 6H), 3.84 (s, 12H), 6.98 (d, *J* = 16.4 Hz, 2H), 7.88 (d, *J* = 16.4 Hz, 2H).

$C_{18}H_{22}O_8$ (366.4) Calcd. C 59.01 H 6.05 Found C 59.25 H 6.04

(E,E)-1,4-Bis(3-hydroxy-1-propenyl)-2,3,5,6-tetramethoxybenzene (**37**): In analogy to the reduction of **32**, under argon and at −30°C to a solution of 22.0 g (60.1 mmol) of **36** in 400 ml of dichloromethane within 15 min 300 ml of a 1 M solution of diisobutyl aluminium hydride in dichloromethane was added. The isolation of **37** was performed exactly according to the procedure used for the separation of **33**: yield 15.8 g (85%) of **37**, m.p. 136°C. – MS: *m/z* (%) = 310 (100) [M^+]. – ^{1}H NMR (360 MHz, CD_2Cl_2): δ = 1.47 (br. t, *J* = 6 Hz, 2H), 3.80 (s, 12H), 4.36 (m, 4H), 6.73 (dt, *J* = 16.2 and 1.4 Hz, 2H), 6.86 (dt, *J* = 16.2 and 5.5 Hz, 2H).

$C_{16}H_{22}O_6$ (310.3) Calcd. C 61.92 H 7.15 Found C 61.76 H 7.07

(E,E)-1,4-Bis(formylethenyl)-2,3,5,6-tetramethoxybenzene (**38**): 20.0 g (64.5 mmol) of **37** and 143 g (558 mmol) of freshly prepared barium manganate(VI)[9] in 700 ml of dichloromethane were heated at reflux for 2.5 h. The oxidation product was isolated according to the procedure mentioned for **34**: yield 17.7 g (90%) of **38**, m.p. 164–166°C. – MS: *m/z* (%) = 306 (19) [M^+], 275 (100) [$M^+ - OCH_3$]. – ^{1}H NMR (360 MHz, CD_2Cl_2): δ = 3.86 (s, 12H), 7.19 (dd, *J* = 16.4 and 8.0 Hz, 2H), 7.71 (d, *J* = 16.4 Hz, 2H), 9.71 (d, *J* = 8.0 Hz, 2H).

$C_{16}H_{18}O_6$ (306.3) Calcd. C 62.74 H 5.92 Found C 62.52 H 6.20

2,3,5,6-Tetramethoxy-1,4-bis[4-(2-methoxycarbonylphenyl)-1,3-butadienyl]benzene (**39**, mixture of *Z,E* isomers): From a methanolate solution, prepared from 5.30 g (230 mmol) of sodium in 750 ml of methanol, and 113 g (230 mmol) (2-methoxycarbonylbenzyl)triphenylphosphonium bromide the ylide was prepared as for the synthesis of **35**. To this solution a suspension of 17.7 g (57.8 mmol) of **38** in 500 ml of tetrahydrofuran was added within 30 min. After stirring at 70°C for 2 h the solution was concentrated to 200 ml, and the yellow precipitate formed was filtered off and washed with methanol. The solvents were evaporated from the filtrate, and the residue was purified by chromatography (silica gel, toluene/ethyl acetate, 25:1). From the eluate a TLC-homogeneous fraction ($R_f \approx 0.26$) was separated. Including the product precipitated from solution 30.9 g (94%) of a mixture of **39** and *Z,E* isomers was obtained which was used without further purification for the hydrogenation to **22**. – MS: *m/z* (%) = 570 (100) [M^+], 544 (12), 222 (11), 189 (16), 179 (11), 91 (14).

$C_{34}H_{34}O_8$ (570.6) Calcd. C 71.56 H 6.01 Found C 71.60 H 6.00

2,3,5,6-Tetramethoxy-1,4-bis[4-(2-methoxycarbonylphenyl)butyl]benzene (**22**): Through a solution of 10.0 g (17.5 mmol) of **39** (*Z,E* isomers) in 400 ml of ethyl acetate/methanol (1:1) argon was passed for 30 min. After heating to 80°C, 2 g of palladium catalyst (10% on charcoal) was added, and hydrogen was passed through the solution at 80°C for 5 h. TLC (silica gel, toluene/ethyl acetate, 8:1) showed the presence of only **22** ($R_f \approx 0.63$; fluorescent intermediates were no longer detected). The catalyst was filtered off and washed with 400 ml of ethyl acetate. The filtrate was dried with magnesium sulfate, and the solvents were evaporated in a rotary evaporator to leave a residue which was crystallized from 300 ml of methanol: yield 9.45 g (93%), colourless needles, m.p. 100°C. – MS: *m/z* (%) = 578 (100) [M^+]. – ^{1}H NMR (360 MHz, CD_2Cl_2, complete assignment by COSY and NOE): δ = 1.54–1.60 (m, 4H, γ-CH_2), 1.63–1.71 (m, 4H, β-CH_2), 2.60 (t, *J* = 7.7 Hz, 4H, δ-CH_2), 2.98 (t, *J* = 7.6 Hz, 4H, α-CH_2), 3.76 (s, 12H, ar-OCH_3), 3.85 (s, 6H, $COOCH_3$), 7.23 ("td", *J* ≈ 7.5 and 1.2 Hz, 2H, ar-4-H), 7.29 (dd, *J* = 7.4 and 0.9 Hz, 2H, ar-6-H), 7.41 ("td", *J* ≈ 7.5 and 1.3 Hz, 2H, ar-5-H), 7.81 (dd, *J* = 7.8 and 1.3 Hz, 2H, ar-3-H).

$C_{34}H_{42}O_8$ (578.7) Calcd. C 70.56 H 7.32 Found C 70.55 H 7.13

1,4-Bis[4-(2-hydroxymethylphenyl)butyl]-2,3,5,6-tetramethoxybenzene (**27**): The reduction of 19.1 g (33.0 mmol) of **22** in 350 ml of tetrahydrofuran by a suspension of 5.0 g (132 mmol) of lithium aluminium hydride in 700 ml of tetrahydrofuran and the isolation of the product were carried out as described for **26**: yield 17.0 g of **27** (99%; m.p. 124–125°C) which was directly used in the following reaction. By crystallization from ethyl acetate **27** was obtained as a colourless microcrystalline powder, m.p. 125–127°C (yield 88%). – MS: *m/z* (%) = 522 (100) [M^+], 145 (12), 131 (11), 105 (24), 91 (11). – ^{1}H NMR (360 MHz, CD_2Cl_2): δ = 1.56–1.70 (m, 10H, β- and γ-CH_2, OH), 2.61 (t, *J* = 7.6 Hz, 4H, δ-CH_2), 2.72 (t, *J* = 7.7 Hz, 4H, α-CH_2), 3.75 (s, 12H, ar-OCH_3), 4.70 (d, *J* = 5 Hz, 4H, CH_2OH), 7.17–7.23 (6H, ar-H), 7.36 (d, *J* = 6.6 Hz, 2H, ar-H).

$C_{32}H_{42}O_6$ (522.7) Calcd. C 73.53 H 8.10 Found C 73.26 H 7.90

1,4-Bis[4-(2-formylphenyl)butyl]-2,3,5,6-tetramethoxybenzene (**16**): In analogy to the preparation of **15**, 17.0 g (32.5 mmol) of **27**, 21.0 g (97.1 mmol) of pyridinium chlorochromate, 18 g of Celite and 18 g of magnesium sulfate in 750 ml of dichloromethane were stirred at 20°C for 2 h. Isolation (same procedure as used for the separation of **15**) yielded 15.5 g (92%) of **16** of m.p. 96–97°C; recrystallized from diethyl ether: m.p. 98°C. – MS: *m/z* (%) = 518 (100) [M^+], 131 (12), 129 (11), 91 (23). – ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 1.55–1.62 (m, 4H, γ-CH_2), 1.67–1.73 (m, 4H, β-CH_2), 2.61 (t, *J* = 7.8 Hz, 4H, δ-CH_2), 3.08 (t, *J* = 7.7 Hz, 4H, α-CH_2), 3.75 (s, 12H, ar-OCH_3), 7.32 (d, *J* = 7.8 Hz, 2H, ar-6-H), 7.35 ("t", *J* ≈ 7.5 Hz, 2H, ar-4-H), 7.50 ("t", *J* ≈ 7.5 Hz, 2H, ar-5-H), 7.82 (d, *J* = 7.9 Hz, 2H, ar-3-H), 10.31 (s, 2H, CHO).

$C_{32}H_{38}O_6$ (518.6) Calcd. C 74.10 H 7.39 Found C 73.95 H 7.48

1,4-Dichloro-2,5-diformyl-3,6-dimethoxybenzene: Through a solution of 10.0 g (51.5 mmol) of 2,5-dimethoxyterephthalaldehyde and 2.60 g (10.3 mmol) of iodine in 750 ml of dichloromethane at 20°C chlorine, dried with concentrated sulfuric acid, was passed through a D1 glass frit. After 30 min excess chlorine was expelled by a strong stream of argon; the solvent was evaporated, and the residue was twice recrystallized from ethyl acetate to yield 7.80 g (58%) of the pure product, yellow needles, m.p. 150°C. – MS: *m/z* (%) = 262 (100) [M^+], 247 (42) [$M^+ - CH_3$]. – ^{1}H NMR (360 MHz, $CDCl_3$): δ = 3.98 (s, 6H), 10.40 (s, 2H).

$C_{10}H_8Cl_2O_4$ (263.1) Calcd. C 45.66 H 3.07 Cl 26.95
Found C 45.53 H 2.96 Cl 26.98

(E,E)-1,4-Dichloro-2,5-bis(2-formylethenyl)-3,6-dimethoxybenzene (**40**): Into a suspension of 9.78 g (22.8 mmol) of (1,3-dioxolan-2-yl-methyl)triphenylphosphonium bromide[11] in 100 ml of dry tetrahydrofuran 15.2 ml (22.8 mmol) of a 1.5 M solution of *n*-butyllithium in *n*-hexane was injected with a syringe within 10 min. After heating to reflux 2.0 g (7.6 mmol) of 1,4-dichloro-2,5-diformyl-3,6-dimethoxybenzene in 50 ml of tetrahydrofuran was added within 30 min; the reaction mixture was kept under reflux for 6 h, then cooled down to room temp., poured on 400 ml of water, and extracted twice with 200 ml of dichloromethane each. From the combined extracts the solvent was evaporated in a rotary evaporator, and to the residue 50 ml of acetone and 5 ml of concentrated hydrochloric acid were added with stirring to achieve cleavage of the acetal. After 2 h the precipitated **40** was sucked off, washed with a small amount of acetone and crystallized from toluene: yield 1.32 g (55%) of **40**, m.p. 202°C. – MS: *m/z* (%) = 314 (16) [M^+], 279 (100) [M^+ – Cl], 248 (15). – ^{1}H NMR (360 MHz, CD_2Cl_2): δ = 3.79 (s, 6H), 7.13 (dd, *J* = 16.3 and 7.5 Hz, 2H), 7.72 (d, *J* = 16.2 Hz, 2H), 9.77 (d, *J* = 7.4 Hz, 2H).

$C_{14}H_{12}Cl_2O_4$ (315.2) Calcd. C 53.36 H 3.84 Cl 22.50
Found C 53.62 H 3.95 Cl 22.70

1,4-Dichloro-3,6-dimethoxy-2,5-bis[4-(2-methoxycarbonylphenyl)-1,3-butadienyl]benzene (**41** and *Z,E* isomers): Under argon 1.64 g (71.4 mmol) of sodium was dissolved in 300 ml of dry methanol, then 35.1 g (71.4 mmol) of (2-methoxycarbonylbenzyl)triphenylphosphonium bromide[11] was added to the solution. The ylide solution was heated to reflux, and 7.50 g (23.8 mmol) of **40** in 100 ml of dry tetrahydrofuran was added in portions within 2 h. The reaction mixture was heated for 2 h at reflux and then, after cooling to 20°C, concentrated to half of its volume by distilling off the solvents; the precipitate formed was sucked off, washed with methanol and dried at 50°C in vacuo: yield 13.8 g of **41** and its isomers which were used without further purification in the following reaction.

1,4-Dichloro-3,6-dimethoxy-2,5-bis[4-(2-methoxycarbonylphenyl)butyl]benzene (**24**): To a suspension of 14.7 g (25.0 mmol) of the mixture of **41** and *Z,E* isomers in 600 ml of ethyl acetate/methanol (1:1) 3 g of palladium catalyst (5% on charcoal) was added. After passing argon through the hydrogenation apparatus the reaction mixture was heated to reflux and a strong stream of hydrogen was passed through the latter for 2 h. Then a further 2 g of catalyst was added, and the hydrogenation was continued for another 30 min until the solution became colourless. According to the usual procedure the hydrogenation was completed, the catalyst was filtered off, and the solution concentrated to about 20% of its original volume by use of a rotary evaporator: the precipitate of **24** formed consisted of colourless plates, m.p. 112–114°C (from methanol); yield 9.40 g (67%, relative to **40**). – MS: *m/z* (%) = 586 (63) [M^+], 487 (20), 455 (30), 357 (38), 241 (25), 259 (20), 233 (75), 219 (20), 199 (26), 189 (25), 175 (30), 157 (45), 149 (65), 145 (95), 131 (85), 117 (75), 103 (25), 91 (100). – ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.64–1.72 (m, 8H, β- and γ-CH_2), 2.79 (t, *J* = 7.8 Hz, 4H, δ-CH_2), 3.00 (t, *J* = 7.5 Hz, 4H, α-CH_2), 3.79 (s, 6H, ar-OCH_3), 3.88 (s, 6H), CO-OCH_3), 7.22–7.86 (m, 8H, ar-H).

$C_{32}H_{36}Cl_2O_6$ (587.5) Calcd. C 65.42 H 6.18 Cl 12.07
Found C 65.43 H 6.33 Cl 12.02

1-Chloro-2,5-bis[4-(2-hydroxymethylphenyl)butyl]-3,6-dimethoxybenzene (**29**) *and 1,4-dichloro-2,5-bis[4-(2-hydroxymethylphenyl)butyl]-3,6-dimethoxybenzene* (**30**): To a suspension of 2.97 g (78.3 mmol) of lithium aluminium hydride in 400 ml of dry tetrahydrofuran a solution of 9.22 g (15.7 mmol) of

24 in 150 ml of tetrahydrofuran was added under argon at 20°C within 3.5 h. Thereafter, the reaction mixture was heated at reflux for 2.5 h and kept for a further 14 h at room temp. with stirring. After the addition of 50 ml of water/tetrahydrofuran (1:4) the precipitate was filtered off and extracted three times with 100 ml of boiling tetrahydrofuran each. The combined filtrates were dried with magnesium sulfate; the solvent was evaporated: 8.25 g of a colourless crystalline product consisting to ^{1}H NMR of a mixture of **29** and **30** (difficult to separate); this product was directly used without further purification and characterization in the following oxidation reaction.

1-Chloro-2,5-bis[4-(2-formylphenyl)butyl]-3,6-dimethoxybenzene (**18**) *and 1,4-dichloro-2,5-bis[4-(2-formylphenyl)butyl]-3,6-dimethoxybenzene* (**19**): A solution of 7.80 g of a mixture of **29** and **30** in 250 ml of dichloromethane after the addition of 10.0 g (46.5 mmol) of pyridinium chlorochromate, 8 g of magnesium sulfate and 8 g of Celite was stirred at 20°C for 3.5 h. During the filtration through a silica gel column (h = 10 cm, d = 9 cm) with dichloromethane as the eluent a beginning separation of **18** ($R_f \approx 0.19$) and **19** ($R_f \approx 0.22$) was observed. Separation on a preparative scale was achieved by medium-pressure chromatography: 7.8 g of a mixture of **18** and **19** was dissolved in 160 ml of cyclohexane/ethyl acetate (15:1) of which 4-ml portions were injected per separation cycle (h = 48 cm, d = 3.7 cm; silica gel 20–45 µ, 410 ml; flow rate 40 ml/min). **19** ($R_f \approx 0.17$): crystallization from cyclohexane yielded 2.55 g (31%, relative to **24**): colourless needles, m.p. 86–88°C. – MS: m/z (%) = 526 (44) [M^+], 491 (12) [M^+ – Cl], 145 (20), 143 (21), 132 (30), 131 (44), 129 (67), 119 (27), 117 (42), 91 (100). – ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.63–1.78 (m, 8H, β- and γ-CH_2), 2.78–2.82 (m, 4H, δ-CH_2), 3.06–3.11 (m, 4H, α-CH_2), 3.79 (s, 6H, OCH_3), 7.28 ("d", $J \approx 7.6$ Hz, 2H, ar-6-H), 7.35 ("t", $J \approx 7.5$ Hz, 2H, ar-4-H), 7.48 ("td", $J \approx 7.5$ and 1.4 Hz, 2H, ar-5-H), 7.82 (dd, J = 7.5 and 1.0 Hz, 2H, ar-3-H), 10.29 (s, 2H, CHO).

$C_{30}H_{32}Cl_2O_4$ (527.5) Calcd. C 68.31 H 6.12 Cl 13.44
Found C 68.28 H 6.30 Cl 13.17

18 ($R_f \approx 0.13$): Recrystallization from cyclohexane yielded 1.50 g (20% relative to **24**), colourless needles, m.p. 87–88°C. – MS: m/z (%) = 492 (100) [M^+], 199 (16), 131 (27), 129 (19), 117 (20), 91 (87). – ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.58–1.72 (m, 8H, β- and γ-CH_2), 2.63–2.67 (m, 2H, δ-CH_2), 2.76–2.80 (m, 2H, δ-CH_2), 3.04–3.09 (m, 4H, α-CH_2), 3.75 and 3.76 (two s, 6H, OCH_3), 6.55 (s, 1H, ar-H, central arom. ring), 7.25–7.30 (m, 2H, ar-6-H), 7.31–7.38 (m, 2H, ar-4-H), 7.46–7.51 (m, 2H, ar-5-H), 7.80–7.84 (m, 2H, ar-3-H), 10.27 (s, 1H, CHO), 10.31 (s, 1H, CHO).

$C_{30}H_{33}ClO_4$ (493.0) Calcd. C 73.08 H 6.75 Cl 7.19
Found C 73.09 H 6.78 Cl 7.22

1,4-Dichloro-2,5-bis[4-(2-hydroxymethylphenyl)butyl]-3,6-dimethoxybenzene (**30**) *and 1,4-Dichloro-2,5-bis[4-(2-formylphenyl)butyl]-3,6-dimethoxybenzene* (**19**): For the selective reduction of the ester groups of **24**, to a solution of 4.50 g (7.60 mmol) of **24** in 150 ml of dry tetrahydrofuran 3.30 g (152 mmol) of lithium borohydride was added under argon and the reaction was kept at reflux for 8 h. While cooling with ice, 10 ml of water and within 1 h 20 ml of 2 N hydrochloric acid were added. After the addition of 150 ml of water the reaction mixture was extracted three times with 150 ml of dichloromethane each. The combined extracts were washed with 150 ml of a saturated sodium hydrogen carbonate solution and 150 ml of water, then dried with magnesium sulfate, and the solvent was distilled off: yield 3.30 g (82%) of **30**, m.p. 106°C (from ethyl acetate). – ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.65–1.71 (m, 10H, β- and γ-CH_2, OH), 2.72 (t, J = 7.5 Hz, 4H, α-CH_2), 2.79 (t, J = 7.5 Hz, 4H, δ-CH_2), 3.78 (s, 6H, OCH_3), 4.71 (s, 4H, ar-2,5-CH_2), 7.18–7.34 (m, 8H, ar-H).

$C_{30}H_{36}Cl_2O_4$ (531.5) Calcd. C 67.79 H 6.83 Cl 13.34
Found C 67.76 H 6.81 Cl 13.14

In analogy to the oxidation of the **29**/**30** mixture, 9.80 g (18.5 mmol) of **30** was oxidized with 12.0 g (55.6 mmol) of pyridinium chlorochromate in 300 ml of dichloromethane in the presence of 9.0 g of Celite and 9.0 g of magnesium sulfate (3 h, 20°C). Chromatography on silica gel (h = 12 cm, d = 7 cm, dichloromethane) yielded 8.30 g (85%) of **19** (m.p. 87°C), which was identical with the product described above.

1,4-Dicyano-3,6-dimethoxy-2,5-bis[4-(2-hydroxymethylphenyl)butyl]benzene (**31**): To a solution of 2.08 g (3.66 mmol) of 1,4-dicyano-2,5-bis[4-(2-methoxycarbonylphenyl)butyl]-3,6-dimethoxybenzene(**25**)[15] in 100 ml of dry tetrahydrofuran 320 mg (14.7 mmol) of lithium borohydride was added, and the reaction mixture was heated under argon at reflux for 24 h. Then again 320 mg (14.7 mmol) of lithium borohydride was added, and heating at reflux was continued for a further 6 h. While cooling with ice, 100 ml of water and 50 ml of 2 N hydrochloric acid were added. Extraction with 200 ml and twice with 100 ml of dichloromethane each, washing of the combined extracts with 200 ml of water, drying with magnesium sulfate and distilling off the solvents resulted in a residue which was crystallized from ethyl acetate: yield 1.44 g (77%) of **31**, m.p. 119–120.5°C. – MS: m/z (%) = 494 (68) [M^+ – H_2O], 479 (37), 132 (20), 131 (66), 129 (39), 117 (42), 116 (41), 105 (100), 91 (67). – ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.68–1.75 (m, 10H, β- and γ-CH_2, OH), 2.74 (t, J = 7.3 Hz, 4H, α-CH_2), 2.82 (t, J = 7.3 Hz, 4H, δ-CH_2), 3.95 (s, 6H, OCH_3), 4.71 (s, 4H, ar-2-CH_2), 7.18–7.26 (m, 6H, ar-4,5,6-H), 7.36 ("dd", $J \approx 7.5$ and 2 Hz, 2H, ar-3-H).

$C_{32}H_{36}N_2O_4$ (512.6) Calcd. C 74.95 H 7.08 N 5.46
Found C 75.11 H 7.19 N 5.36

1,4-Dicyano-2,5-bis[4-(2-formylphenyl)butyl]-3,6-dimethoxybenzene (**20**): 1.40 g (2.73 mmol) of **31**, 1.76 g (8.19 mmol) of pyridinium chlorochromate together with 700 mg of magnesium sulfate and 700 mg of Celite in 30 ml of dichloromethane were stirred under argon at 20°C for 2.5 h. By chromatography on silica gel (h = 10 cm, d = 5 cm, dichloromethane) the fraction with $R_f \approx 0.36$ was isolated and crystallized from ethyl acetate: yield 1.02 g (74%) of **20**, m.p. 131–133°C. – MS: m/z (%) = 508 (32) [M^+], 145 (22), 133 (28), 132 (71), 131 (29), 129 (74), 119 (56), 118 (21), 117 (76), 116 (67), 105 (33), 91 (100). – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.69–1.75 (m, 8H, β- and γ-CH_2), 2.84 (t, J = 7.4 Hz, 4H, δ-CH_2), 3.10 (t, J = 7.2 Hz, 4H, α-CH_2), 3.96 (s, 6H, OCH_3), 7.29 (d, J = 7.6 Hz, 2H, ar-6-H), 7.38 ("td", $J \approx 7$ and 1 Hz, 2H, ar-4-H), 7.51 ("td", $J \approx 7$ and 1 Hz, 2H, ar-5-H), 7.81 ("dd", $J \approx 7.4$ and 1.1 Hz, 2H, ar-3-H), 10.24 (s, 2H, CHO).

$C_{32}H_{32}N_2O_4$ (508.6) Calcd. C 75.57 H 6.34 N 5.51
Found C 75.49 H 6.54 N 5.28

5,15: 10,20-Bis[2,5-dimethoxy-3,6-dimethylbenzene-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]porphyrin (**42**): To 2 l of propionic acid, heated with vigorous stirring to 120°C, 9.73 g (20.0 mmol) of **15** and 2.77 ml (40.0 mmol) of pyrrole were added, and the reaction mixture was heated under reflux for 4 h. The propionic acid then was distilled off in vacuo, the black residue was dissolved in 500 ml of toluene and the resulting solution filtered through silica gel (h = 9 cm, d = 13 cm). The product obtained after evaporation of the toluene was purified by medium-pressure chromatography (h = 48 cm, d = 3.7 cm; silica gel 60, 20–45 µm; n-hexane/ethyl acetate, 16:1; flow rate 40 ml/min). The fraction with $R_f \approx 0.20$, pure according to TLC (silica gel, n-hexane/ethyl acetate, 16:1), was dissolved in a small volume of dichloromethane; after the addition of a threefold volume of methanol, **42** crystallized by cooling the solution to 4°C: yield 94 mg (0.8%), violet crystals m.p. 180–185°C. – MS (LSI-MS): m/z (%) = 1165 (23), 1164 (64), 1163 (100) [MH^+], 1162 (98) [M^+], 1161 (22). – ^{1}H NMR (500 MHz, CD_2Cl_2, 303 K; COSY assignment): δ = –2.72 (s, 2H, NH), 0.28 (m, 16H, γ-CH_2 and δ-CH_2), 0.34 (s, 12H, ar-CH_3), 0.72–0.76 (m, 8H, β-CH_2), 1.99–2.03 (m, 20H, α-CH_2 and ar-OCH_3), 7.51 (d, J = 7.3 Hz, 4H, ar-3′-H), 7.62 ("t", $J \approx 7.5$ Hz, 4H, ar-5′-H), 7.68 ("t", $J \approx 7.5$ Hz, 4H, ar-4′-H), 8.28 (d, J = 7.4 Hz, 4H, ar-6′-H), 8.60 (s, 8H, 2,3,7,8,12,13,17,18-H).

$C_{80}H_{83}N_4O_4$ Calcd. 1163.6414 Found 1163.6356 (MS: MH^+)

5,15: 10,20-Bis[2,3,5,6-tetramethoxybenzene-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]porphyrin (**43**): Under the same conditions as used for the preparation of **42**, 10.4 g (20.0 mmol) of **16** was treated with 2.77 ml (40.0 mmol) of pyrrole in 2 l of boiling propionic acid, and the isolation and purification of the product were performed accordingly: yield 98 mg (0.8%) of **43**: $R_f \approx$ 0.24 (silica gel, n-hexane/ethyl acetate, 16:1); violet crystals m.p. 326–328°C (dichloromethane/methanol, 1:3); for elemental analysis recrystallized from methylcyclohexane. – MS (LSI-MS): m/z (%) = 1229 (25), 1228 (61), 1227 (100) [MH^+], 1226 (80) [M^+], 1225 (13). – ^{1}H NMR (500 MHz, CD_2Cl_2, 303 K; COSY assignment): δ = –2.85 (s, 2H, NH), –0.15 to –0.12 (m, 8H, δ-CH_2), 0.56–0.61 (m, 8H, γ-CH_2), 0.72–0.78 (m, 8H, β-CH_2), 2.02 (s, 24H, ar-OCH_3), 2.06–2.09 (m, 8H, α-CH_2), 7.52 (d, J = 8.0 Hz, 4H, ar-3′-H), 7.61 ("t", $J \approx 7.4$ Hz, 4H, ar-5′-H), 7.69 ("t", $J \approx 7.4$ Hz, 4H, ar-4′-H), 8.30 (d, J = 7.3 Hz, 4H, ar-6′-H), 8.53 (s, 8H, 2,3,7,8,12,13,17,18-H).

$C_{80}H_{82}N_4O_8$ (1227.6) Calcd. C 78.28 H 6.73 N 4.56
Found C 78.02 H 7.02 N 4.39

5,15: 10,20-Bis[2,5-dichloro-3,6-dimethoxybenzene-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]porphyrin (**45**): To 950 ml of propionic acid at 120°C 5.00 g

(9.48 mmol) of **19** and 1.42 ml (20.3 mmol) of pyrrole were added with vigorous stirring. After heating at reflux for 4 h the propionic acid was evaporated, and the residue was filtered from toluene through silica gel (h = 8.5 cm, d = 13 cm). The product was further purified by medium-pressure chromatography (silica gel 60, 20–45 µm; h = 48 cm, d = 3.7 cm, flow rate 40 ml/min; eluent cyclohexane/ethyl acetate, 30:1). The fraction with $R_f \approx 0.43$, after evaporation of the solvent, was crystallized from dichloromethane/methanol (1:1) at 4°C: yield 33 mg (0.56%) of **45**; violet crystals, m.p. 172°C. – MS (LSI-MS): m/z (%) = 1249 (31), 1248 (54), 1247 (76), 1246 (91), 1245 (100) [(MH + 2)$^+$], 1244 (73), 1243 (57) [MH$^+$], 1242 (16) [M$^+$]. – ^{1}H NMR (500 MHz, CD_2Cl_2, 303 K; COSY assignment): δ = –2.72 (s, 2H, NH), 0.23–0.34 (m, 8H, δ-CH_2), 0.41–0.56 (m, 8H, γ-CH_2), 0.73–0.85 (m, 8H, β-CH_2), 2.03 (s, 12H, OCH_3), 2.05–2.10 (m, 8H, α-CH_2), 7.52 (d, J = 7.5 Hz, 4H, ar-3′-H), 7.62 (m, 4H, ar-5′-H), 7.69 (m, 4H, ar-4′-H), 8.30 (d, J = 7.2 Hz, 4H, ar-6′-H), 8.59 (s, 8H, 2,3,7,8,12,13,17,18-H).

$C_{76}H_{70}Cl_4N_4O_4$ Calcd. 1242.4151 Found 1242.4102 (MS: M$^+$)

5,15: 10,20-Bis[3,6-dimethyl-p-benzoquinone-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]porphyrin (**1**): To a solution of 58 mg (50 µmol) of **42** in 50 ml of dichloromethane 2.0 ml of a 1 M boron tribromide solution in dichloromethane was added under argon and the mixture was stirred at 20°C for 2 h. After cooling to 0°C, 50 ml of a saturated sodium carbonate solution was added, the dichloromethane phase was separated, washed with 50 ml saturated sodium carbonate solution and twice with 50 ml of water each and then dried with magnesium sulfate. Then 100 mg (0.44 mmol) of DDQ was added and the solution kept with stirring at 20°C for 3 h. The solution was washed twice with 50 ml of a saturated sodium carbonate solution each and twice with 50 ml of water each. After drying with magnesium sulfate and evaporation of the solvent the crude product was purified by medium-pressure chromatography (h = 48 cm, d = 3.7 cm; silica gel 60, 20–45 µm, cyclohexane/ethyl acetate, 30:1; flow rate 40 ml/min). The isolated violet substance ($R_f \approx 0.24$, silica gel, cyclohexane/ethyl acetate, 16:1) was dissolved in a small volume of dichloromethane and, after a threefold volume of methanol has been added, brought to crystallization by cooling to 4°C: yield 40 mg (73%) **1**, m.p. 308–312°C. – MS (LSI-MS): m/z (%) = 1107 (19), 1106 (37), 1105 (79), 1104 (100) [MH$^+$], 1103 (66) [M$^+$], 1102 (15). – ^{1}H NMR (500 MHz, CD_2Cl_2, 303 K; COSY assignment): δ = –2.87 (s, 2H, NH), 0.06–0.11 (m, 8H, γ-CH_2), 0.17–0.20 (m, 8H, δ-CH_2), 0.29 (s, 12H, ar-CH_3), 0.68–0.71 (m, 8H, β-CH_2), 2.17–2.20 (m, 8H, α-CH_2), 7.52 (d, J = 7.2 Hz, 4H, 3′-H), 7.62 ("t", $J \approx$ 7.3 Hz, 4H, 5′-H), 7.69 ("t", $J \approx$ 7.2 Hz, 4H, 4′-H), 8.40 (d, J = 7.4 Hz, 4H, 6′-H), 8.62 (s, 8H, 2,3,7,8,12,13,17,18-H).

$C_{76}H_{71}N_4O_4$ Calcd. 1103.5475 Found 1103.5443 (MS: MH$^+$)

5,15: 10,20-Bis[3,6-dimethoxy-p-benzoquinone-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]porphyrin (**2**): 37 mg (30 µmol) of **43** in 30 ml of dichloromethane together with 4.5 g (≈ 1.6 mmol) of cerium(IV) ammonium nitrate (20% on silica gel) were stirred at 20°C for 5 h. Gaseous ammonia was passed through the reaction mixture for 15 h. Then the mixture was filtered through a glass frit (D3); the separated silica gel was washed with 50 ml of dichloromethane. The combined filtrates were concentrated by evaporation of the solvent, and the residue was purified by medium-pressure chromatography (h = 48 cm, d = 3.7 cm; silica gel 60, 20–45 µm, eluent: cyclohexane/ethyl acetate, 30:1; flow rate 40 ml/min). The fraction with $R_f \approx 0.26$ (silica gel, cyclohexane/ethyl acetate, 16:1) was dissolved in a small volume of dichloromethane; after the addition of the threefold volume of methanol the solution was cooled to 4°C to crystallize the product: yield 22 mg (63%) of **2**, violet crystals, m.p. 290–295°C. – MS (LSI-MS): m/z (%) = 1170 (35), 1169 (73), 1168 (100) [MH$^+$], 1167 (64) [M$^+$], 1166 (11). – ^{1}H NMR (500 MHz, CD_2Cl_2, 303 K; assignment by COSY): δ = –2.79 (s, 2H, NH), –0.39 to –0.36 (m, 8H, δ-CH_2), 0.35–0.38 (m, 8H, γ-CH_2), 0.79–0.82 (m, 8H, β-CH_2), 1.96 (s, 12H, ar-OCH_3), 2.17–2.20 (m, 8H, α-CH_2), 7.55 (d, J = 7.8 Hz, 4H, ar-3′-H), 7.64 ("t", $J \approx$ 8.1 Hz, 4H, ar-5′-H), 7.72 ("t", $J \approx$ 7.8 Hz, 4H, ar-4′-H), 8.26 (d, J = 8.1 Hz, 4H, ar-6′-H), 8.62 (s, 8H, 2,3,7,8,12,13,17,18-H).

$C_{76}H_{71}N_4O_8$ Calcd. 1167.5272 Found 1167.5242 (MS: MH$^+$)

5,15: 10,20-Bis[3,6-dichloro-p-benzoquinone-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]porphyrin (**4**): To a solution of 18.0 mg (14.5 µmol) of **45** in 30 ml of dichloromethane 2.9 ml of a 1 M solution of boron tribromide in dichloromethane was added under argon. The reaction mixture was stirred for 1 h at 20°C; then 40 ml of a saturated sodium carbonate solution was added, and the aqueous phase was separated and washed three times with 25 ml of dichloromethane each. The combined dichloromethane solutions were extracted twice with 40 ml of a saturated sodium chloride solution each and three times with 40 ml of water each. After drying with sodium sulfate the organic solution was concentrated in a rotary evaporator to 60 ml of its volume. Then 16.4 mg (72.7 µmol) of DDQ in 5 ml of dichloromethane was added, and the reaction mixture was stirred at 20°C for 2 h. After the addition of 40 ml of a saturated sodium carbonate solution and 50 ml of water, the organic phase was separated, washed three times with 40 ml of water each, dried with sodium sulfate, and the solvent was evaporated. The residue was purified like **2** by medium-pressure chromatography (eluent: cyclohexane/ethyl acetate, 20:1). The fraction with R_f = 0.25 was crystallized from dichloromethane/methanol (1:1): yield 12.3 mg (72%) of **4**, deep-violet needles, m.p. 181°C. – MS (LSI-MS): m/z (%) = 1191 (43), 1190 (67), 1188 (100), 1187 (94), 1185 (44) [(MH + 2)$^+$], 1183 (10) [MH$^+$]. – ^{1}H NMR (500 MHz, CD_2Cl_2, 303 K; COSY assignment): δ = –2.92 (s, 2H, NH), 0.16–0.26 (m, 8H, γ-CH_2), 0.40 (t, J = 7.1, 8H, δ-CH_2), 0.71–0.82 (m, 8H, β-CH_2), 2.22 (t, J = 7.9 Hz, 8H, α-CH_2), 7.52 (d, J = 7.5 Hz, 4H, ar-3′-H), 7.61 ("t", $J \approx$ 7.1 Hz, 4H, ar-5′-H), 7.69 ("t", $J \approx$ 7.4 Hz, 4H, ar-4′-H), 8.52 (d, J = 7.1 Hz, 4H, ar-6′-H), 8.62 (s, 8H, 2,3,7,8,12,13,17,18-H).

$C_{72}H_{58}Cl_4N_4O_4$ Calcd. 1182.3212 Found 1182.3217 (MS: M$^+$)

1,4-Bis{4-[2-(bis⟨5-benzyloxycarbonyl-3,4-dimethyl-2-pyrrolyl⟩methyl)-phenyl]butyl}-2,5-dimethoxy-3,6-dimethylbenzene (**46**): A suspension of 3.90 g (8.02 mmol) of **15** and 9.16 g (40 mmol) of 2-benzyloxycarbonyl-3,4-dimethylpyrrole in 100 ml of ethanol, after the addition of 1.30 ml of concentrated hydrochloric acid, was heated at reflux for 4 h. The reaction mixture was cooled to room temp. and diluted with 100 ml of dichloromethane. The products adsorbed on Florisil were chromatographed on silica gel (h = 9 cm, d = 13 cm): with toluene/ethyl acetate (100:1) excess pyrrole ($R_f \approx 0.23$) was removed, and with toluene/ethyl acetate (8:1) **46** ($R_f \approx 0.55$) was eluted. After evaporation of the solvents 10.9 g (99%) of **46** was obtained, m.p. 80–88°C. – MS (LSI-MS): m/z (%) = 1367 (36) [MH$^+$], 1366 (34) [M$^+$], 1365 (34), 1276 (91) [(MH – 91)$^+$], 1275 (100) [(M – 91)$^+$]. – ^{1}H NMR (360 MHz, CD_2Cl_2; assignment by COSY and NOE): δ = 1.45–1.54 (m, 8H, β- and γ-CH_2), 1.75 (s, 12h, pyr-3-CH_3), 2.10 (s, 6H, ar-CH_3), 2.25 (s, 12H, pyr-4-CH_3), 2.50–2.58 (m, 8H, α- and δ-CH_2), 3.56 (s, 6H, ar-OCH_3), 5.22 (s, 8H, ar-CH_2), 5.68 [s, 2H, ar-CH(pyr)$_2$], 6.83 (d, J = 6.4 Hz, 2H, ar-3′-H), 7.14–7.36 (m, 26H, all other ar-H), 8.15 (s, 4H, NH).

$C_{88}H_{94}N_4O_{10}$ (1367.7) Calcd. C 77.28 H 6.93 N 4.10
Found C 77.55 H 7.16 N 3.82

1,4-Bis{4-[2-(bis⟨5-benzyloxycarbonyl-3,4-dimethyl-2-pyrrolyl⟩methyl)-phenyl]butyl}-2,3,5,6-tetramethoxybenzene (**47**): The reaction of 3.11 g (6.00 mmol) of **16** with 6.87 g (30.0 mmol) of 2-benzyloxycarbonyl-3,4-dimethylpyrrole in 80 ml of ethanol in the presence of 1.0 ml of concentrated hydrochloric acid and the separation and purification of the product were carried out in close analogy to the preparation of **46**: yield 8.33 g (99%) of **47**, m.p. 83–90°C, $R_f \approx$ 0.52 (silica gel; toluene/ethyl acetate, 8:1). – MS (LSI-MS): m/z (%) = 1399 (39) [MH$^+$], 1398 (42) [M$^+$], 1397 (41), 1308 (95) [(MH – 91)$^+$], 1307 (100) [(M – 91)$^+$]. – ^{1}H NMR (360 MHz, CD_2Cl_2): δ = 1.52–1.58 (m, 8H, β- and γ-CH_2), 1.75 (s, 12H, pyr-3-CH_3), 2.25 (s, 12H, pyr-4-CH_3), 2.52–2.58 (m, 8H, α- and δ-CH_2), 3.70 (s, 12H, ar-OCH_3), 5.22 (s, 8H, ar-CH_2), 5.69 [s, 2H, ar-CH(pyr)$_2$], 6.83 (d, J = 6.4 Hz, 2H, 3′-H), 7.14–7.36 (m, 26H, all other arom. H), 8.15 (s, 4H, NH).

$C_{88}H_{94}N_4O_{12}$ (1399.7) Calcd. C 75.51 H 6.77 N 4.00
Found C 75.64 H 6.87 N 3.71

1,4-Bis{4-[2-(bis⟨5-ethoxycarbonyl-3,4-dimethyl-2-pyrrolyl⟩methyl)phenyl]butyl}-2,5-dimethoxybenzene and 1,4-Bis{4-[2-(bis⟨5-benzyloxycarbonyl-3,4-dimethyl-2-pyrrolyl⟩methyl)phenyl]butyl}-2,5-dimethoxybenzene (**48**): 2.29 g (5.00 mmol) of **17** and 3.34 g (20 mmol) of 2-ethoxycarbonyl-3,4-dimethylpyrrole in 25 ml of ethanol, after addition of 0.5 ml of concentrated hydrochloric acid were heated at reflux for 1 h. Chromatography on silica gel (eluent: toluene/ethyl acetate, 10:1: $R_f \approx$ 0.15), afforded 4.58 g (84%) of analytically pure product which was used in the following reaction furnishing **48**. 1.09 g (1 mmol) of the above-mentioned product was heated to 100°C for 4 h in benzyl alcohol in the presence of sodium benzyl alcoholate prepared from 138 mg (6 mmol) of sodium. Benzyl alcohol was distilled off in vacuo, and the residue was dissolved in 50 ml of diethyl ether, the solution was washed with water, saturated ammonium chloride and sodium chloride solutions, dried with magnesium sulfate, and concentrated in a rotary evaporator. Chromatography on silica gel (eluent: toluene/ethyl acetate, 15:1: $R_f \approx$

0.41) afforded of 1.1 g (82%) **48**, waxy product deliquescent at 50–70°C. – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 1.40–1.70 (m, 8H, β- and γ-CH_2), 1.75 (s, 12H, pyr-3-CH_3), 2.28 (s, 12H, pyr-4-CH_3), 2.52–2.65 (m, 8H, α- and δ-CH_2), 3.72 (s, 6H, ar-OCH_3), 5.18 (s, 8H, ar-CH_2), 5.69 [s, 2H, ar-CH(pyr)$_2$], 6.58 (s, 2H, ar-H, central ring), 6.85–7.45 (m, 28H, all other ar-H), 8.15 (s, 4H, NH).

$C_{86}H_{90}N_4O_{10}$ (1339.7) Calcd. C 77.10 H 6.77 N 4.18
Found C 77.16 H 6.81 N 4.06

1,4-Bis{4-[2-(bis⟨5-benzyloxycarbonyl-3,4-dimethyl-2-pyrrolyl⟩methyl)-phenyl]butyl}-2-chloro-3,6-dimethoxybenzene (**49**): 1.20 g (2.43 mmol) of **18** and 2.45 g (10.7 mmol) of 2-benzyloxycarbonyl-3,4-dimethylpyrrole in 12.5 ml of ethanol, after the addition of 0.25 ml of concentrated hydrochloric acid, were heated at reflux for 1.5 h. By chromatography on silica gel (h = 15 cm, d = 4.5 cm) with toluene/ethyl acetate (50:1) excess pyrrole ($R_f \approx$ 0.35) was removed, then with toluene/ethyl acetate (100:4) **49** with $R_f \approx$ 0.22 was eluted. Evaporation of the solvents yielded 3.02 g (90% yield) of **49** as a voluminous, waxy product deliquescing at 80–92°C. – MS (LSI-MS): m/z (%) = 1374 (23), 1373 (33) [MH$^+$], 1372 (22) [M$^+$], 1371 (23), 1284 (40), 1283 (71), 1282 (88), 1281 (100) [(M – 91)$^+$]. – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.48–1.60 (m, 8H, β- and γ-CH_2), 1.73/1.75 (two "s", 12H, pyr-4-CH_3), 2.25/2.26 (two "s", 12H, pyr-3-CH_3), 2.51–2.57 (m, 6H, ar-CH_2), 2.67–2.71 (m, 2H, ar-CH_2), 3.69/3.70 (two "s", 6H, ar-OCH_3), 5.24/5.25 (two "s", 8H, ar-CH_2), 5.62 [s, 1H, ar-CH(pyr)$_2$], 5.65 [s, 1H, ar-CH(pyr)$_2$], 6.47 (s, 1H, ar-H, central ring), 6.81 ("d", $J \approx$ 7.8 Hz, 2H, ar-3-H), 7.13–7.36 (m, 26H, all other ar-H), 8.14/8.15 (two "s", 4H, NH).

$C_{86}H_{89}ClN_4O_{10}$ (1374.13) Calcd. C 75.17 H 6.53 Cl 2.58 N 4.08
Found C 75.02 H 6.58 Cl 2.66 N 3.81

1,4-Bis{4-[2-(bis⟨5-benzyloxycarbonyl-3,4-dimethyl-2-pyrrolyl⟩methyl)-phenyl]butyl}-2,5-dichloro-3,6-dimethoxybenzene (**50**): The reaction of 2.80 g (5.30 mmol) of **19** with 6.10 g (26.6 mmol) of 2-benzyloxycarbonyl-3,4-dimethylpyrrole in 50 ml of ethanol in the presence of 0.8 ml of concentrated hydrochloric acid as well as the product isolation and purification were carried out in close analogy to the synthesis of **49**. By chromatography on silica gel (h = 15 cm, d = 7 cm, eluent: toluene/ethyl acetate, 100:1) excess pyrrole ($R_f \approx$ 0.31) was separated, and subsequently with toluene/ethyl acetate (100:4) **50** with $R_f \approx$ 0.25 was obtained; after evaporation of the solvents and drying in vacuo: yield 7.30 g (98%) of **50**, waxy product, slowly deliquescing at 50–70°C (after precipitation from dichloromethane/methanol: 83–96°C); R_f (silica gel, toluene/ethyl acetate, 8:1) ≈ 0.51. – MS (LSI-MS): m/z (%) = 1409 (33), 1408 (42), 1407 (51) [MH$^+$], 1406 (38) [M$^+$], 1320 (38), 1319 (69), 1318 (100), 1316 (97) [(M – 91)$^+$]. – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.51–1.57 (m, 8H, β- and γ-CH_2), 1.75 (s, 12H, pyr-4-CH_3), 2.26 (s, 12H, pyr-3-CH_3), 2.52–2.56 (m, 4H, α-CH_2), 2.66–2.70 (m, 4H, δ-CH_2), 3.73 (s, 6H, ar-OCH_3), 5.25 (s, 8H, ar-CH_2-O), 5.64 [s, 2H, ar-CH(pyr)$_2$], 6.81 (d, J = 7.6 Hz, 2H, ar-3′-H), 7.11–7.37 (m, 26H, all other ar-H), 8.14 (s, 4H, NH).

$C_{86}H_{88}Cl_2N_4O_{10}$ (1408.6) Calcd. C 73.33 H 6.30 Cl 5.03 N 3.88
Found C 73.55 H 6.48 Cl 5.17 N 3.93

1,4-Bis{4-[2-(bis⟨5-benzyloxycarbonyl-3,4-dimethyl-2-pyrrolyl⟩methyl)-phenyl]butyl}-2,5-dicyano-3,6-dimethoxybenzene (**51**): The reaction of 0.89 g (1.75 mmol) of **20** with 2.00 g (8.73 mmol) of 2-benzyloxycarbonyl-3,4-dimethylpyrrole in 10 ml of ethanol in the presence of 0.2 ml of concentrated hydrochloric acid (2 h at reflux temp.) and product isolation as in the case of **49** resulted in the formation of 2.42 g (99%) of **51**, R_f (toluene/ethyl acetate, 9:1) ≈ 0.45, foamy, waxy product, deliquescent at 80–90°C. – MS (LSI-MS): m/z (%) = 1390 (54), 1388 (37) [M$^+$], 1299 (91), 1298 (100) [(MH – 91)$^+$]. – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.54–1.58 (m, 8H, β- and γ-CH_2), 1.75 (s, 12H, pyr-4-CH_3), 2.25 (s, 12H, pyr-3-CH_3), 2.54–2.58 (m, 4H, δ-CH_2), 2.68–2.72 (m, 4H, α-CH_2), 3.88 (s, 6H, ar-OCH_3), 5.25 (s, 8H, ar-CH_2-O), 5.63 [s, 2H, ar-CH(pyr)$_2$], 6.82 (d, J = 7.7 Hz, 2H, ar-3′-H), 7.14–7.36 (m, 26H, all other ar-H), 8.13 (s, 4H, NH).

$C_{88}H_{88}N_6O_{10}$ (1389.7) Calcd. C 76.06 H 6.38 N 6.05
Found C 76.27 H 6.51 N 5.78

1,4-Bis{4-[2-(bis⟨5-carboxy-3,4-dimethyl-2-pyrrolyl⟩methyl)phenyl]butyl}-2,5-dimethoxy-3,6-dimethylbenzene (**52**): 6.10 g (4.46 mmol) of **46** was hydrogenated with 6.00 g of palladium catalyst (5% on charcoal) in 200 ml of tetrahydrofuran at 20°C within 30 min. Isolation of **52** by sucking off the catalyst, washing with tetrahydrofuran, distilling off the solvent and drying the product at 40°C in vacuo afforded 4.45 g (99%) of **52**, m.p. 133–137°C (dec.). – MS (LSI-MS negative): m/z (%) = 1007 (19), 1006 (55) [M$^-$], 1005 (100) [(M – H)$^-$], 1004 (13). – ^{1}H NMR (360 MHz, [D$_6$]DMSO): δ = 1.32–1.42 (m, 8H, β- and γ-CH_2), 1.75 (s, 12H, pyr-3-CH_3), 2.08 (s, 6H, ar-CH_3), 2.15 (s, 12H, pyr-4-CH_3), 2.41–2.50 (m, 8H, α- and δ-CH_2), 3.53 (s, 6H, ar-OCH_3), 5.73 [s, 2H, ar-CH(pyr)$_2$], 7.03 (d, J = 7.5 Hz, 2H, ar-3′-H), 7.10–7.25 (m, 6H, ar-4′,5′,6′-H), 10.45 (s, 4H, NH), 12.00 (s, 4H, COOH).

1,4-Bis{4-[2-(bis⟨5-carboxy-3,4-dimethyl-2-pyrrolyl⟩methyl)phenyl]butyl}-2,3,5,6-tetramethoxybenzene (**53**): Hydrogenation as in the case of **52** with 8.30 g (5.93 mmol) of **47**, 8.3 g palladium catalyst (5% on charcoal) in 200 ml of tetrahydrofuran (30 min, 20°C) yielded 6.10 g (99%) of **53**, m.p. 124–128°C (dec.). – MS (LSI-MS negative): m/z (%) = 1038 (69) [M$^-$], 1037 (100) [(M – H)$^-$]. – ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 1.35–1.48 (m, 8H, β- and γ-CH_2), 1.78 (s, 12H, pyr-3-CH_3), 2.15 (s, 12H, pyr-4-CH_3), 2.45–2.50 (m, 8H, α- and δ-CH_2), 3.67 (s, 12H, ar-OCH_3), 5.72 [s, 2H, ar-CH(pyr)$_2$], 7.05 (d, J = 7.7 Hz, 2H, ar-3′-H), 7.11–7.18 (m, 6H, ar-4′,5′,6′-H), 10.48 (s, 4H, NH), 12.03 (br. s, 4H, COOH).

1,4-Bis{4-[2-(bis⟨5-carboxy-3,4-dimethyl-2-pyrrolyl⟩methyl)phenyl]butyl}-2,5-dimethoxybenzene (**54**): Hydrogenation of 1.15 g (1.12 mmol) of **48** with 750 mg of Pd (10% on charcoal) in 250 ml of tetrahydrofuran (30 min, 20°C) resulted in the formation of 1.1 g (91%) of **54**, (dec. >104°C). – MS: m/z = 803 (85), 802 (100) [(M – 4 CO_2)$^-$].

$C_{58}H_{66}N_4O_4$ (979.2) Calcd. C 71.14 H 6.79 N 5.72
Found C 71.16 H 6.81 N 5.61

1,4-Bis{4-[2-(bis⟨5-carboxy-3,4-dimethyl-2-pyrrolyl⟩methyl)phenyl]butyl}-2-chloro-3,6-dimethoxybenzene (**55**): Hydrogenation of 3.00 g (2.18 mmol) of **49** (1.5 g of Pd/5% on charcoal, 180 ml of tetrahydrofuran, 20 min at 20°C) yielded 2.20 g (99%) of **55** (dec. > 130°C), $R_f \approx$ 0.36 (toluene/acetic acid, 9:1). – MS (LSI-MS negative): m/z (%) = 1013 (13), 1012 (48) [M$^-$], 1011 (100) [(M – H)$^-$]. – ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 1.26–1.55 (m, 8H, β- and γ-CH_2), 1.76 and 1.77 (two s, 12H, pyr-4-CH_3), 2.16 (s, 12H, pyr-3-CH_3), 2.43–2.54 (m, 6H, ar-CH_2), 2.60–2.63 (m, 2H, ar-CH_2), 3.63 (s, 3H, ar-OCH_3), 3.73 (s, 3H, ar-OCH_3), 5.70 and 5.71 [two s, 2H, ar-CH(pyr)$_2$], 6.70 (s, 1H, ar-H, central ring), 7.02–7.26 (m, 8H, ar-H), 10.48 (br. s, 4H, NH), 12.01 (br. s, 4H, COOH).

1,4-Bis{4-[2-bis⟨5-carboxy-3,4-dimethyl-2-pyrrolyl⟩methyl)phenyl]butyl}-2,5-dichloro-3,6-dimethoxybenzene (**56**): 7.30 g (5.18 mmol) of **50** in the presence of 7.3 g of palladium catalyst (5% on charcoal) was hydrogenated (180 ml of tetrahydrofuran, 30 min, 20°C) to yield 5.4 g (99%) of **56** (dec. >138°C), $R_f \approx$ 0.39 (silica gel, toluene/acetic acid, 9:1). – MS (LSI-MS negative): m/z (%) = 1044 (15), 1045 (100) [(M – H)$^-$], 1046 [M$^-$], 1047 (79), 1048 (44), 1049 (21). – ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 1.34 to 1.52 (m, 8H, β- and γ-CH_2), 1.76 (s, 12H, pyr-4-CH_3), 2.15 (s, 12H, pyr-3-CH_3), 2.44–2.66 (m, 8H, α- and δ-CH_2), 3.70 (s, 6H, ar-OCH_3), 5.71 [s, 2H, ar-CH(pyr)$_2$], 7.04 (d, J = 7.5 Hz, 2H, ar-3′-H), 7.10–7.19 (m, 6H, ar-4′,5′,6′-H), 10.48 (br. s, 4H, NH), 12.02 (br. s, 4H, COOH).

1,4-Bis{4-[2-(bis⟨5-carboxy-3,4-dimethyl-2-pyrrolyl⟩methyl)phenyl]butyl}-2,5-dicyano-3,6-dimethoxybenzene (**57**): The hydrogenation was carried out with 2.40 g (1.73 mmol) of **51** and 1.2 g of palladium catalyst (5% on charcoal) in 180 ml tetrahydrofuran at 20°C for 3.5 h to furnish 1.75 g (98%) of **57**, (dec. >129°C), $R_f \approx$ 0.32 (silica gel, toluene/acetic acid, 9:1. – MS (LSI-MS negative): m/z (%) = 1028 (65) [M$^-$], 1027 (100) [(M – H)$^-$]. – ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 1.35–1.52 (m, 8H, β- and γ-CH_2), 1.76 (s, 12H, pyr-4-CH_3), 2.15 (s, 12H, pyr-3-CH_3), 2.45–2.50 (m, 4H, α-CH_2), 2.67–2.70 (m, 4H, δ-CH_2), 3.87 (s, 6H, ar-OCH_3), 5.70 [s, 2H, ar-CH(pyr)$_2$], 7.04 (d, J = 7.7 Hz, 2H, ar-3′-H), 7.11–7.18 (m, 6H, ar-4′,5′,6′-H), 10.48 (br. s, 4H, NH), 12.00 (br. s, 4H, COOH).

5,15-[2,5-Dimethoxy-3,6-dimethylbenzene-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-2,3,7,8,12,13,17,18-octamethylporphyrin (**58**): 1 l of dichloromethane and 20 g of magnesium sulfate were stirred under argon for 15 min. Then within a few seconds 2.10 g (2.09 mmol) of **52**, 20 g trichloroacetic acid, and 3.30 ml (19.8 mmol) of triethyl orthoformate were added in this order, and the mixture was stirred at 20°C under argon and with the exclusion of light for 16 h. After the addition of 2 g of sodium acetate and 1.42 g (6.21 mmol) of DDQ stirring was continued for a further 3 h. The black solution was shaken with 500 ml of a saturated sodium carbonate solution for 15 min. The separated organic phase was washed with 500 ml of a saturated sodium carbonate solution and three times with 500 ml of water each. After drying with magnesium sulfate and distilling off the dichloromethane,

the residue was chromatographed on silica gel (h = 16 cm, d = 6.5 cm) with toluene/ethyl acetate (16:1) as the eluent. The porphyrin-containing fraction ($R_f \approx 0.63$) was concentrated to a volume of about 2 ml, the residue diluted with 10 ml of cyclohexane/ethyl acetate (30:1) and subjected to medium-pressure chromatography (h = 48 cm, d = 3.7 cm; silica gel 60, 20–45 μm; cyclohexane/ethyl acetate, 30:1; flow rate 40 ml/min). The product ($R_f \approx 0.13$) was crystallized from dichloromethane/methanol (1:3): yield 375 mg (21%) of **58**, violet crystals, m.p. >330°C. – MS (LSI-MS): m/z (%) = 851 (24), 850 (70), 849 (100) [MH^+], 848 (17) [M^+]. – ^{1}H NMR (360 MHz, CD_2Cl_2, 303 K; assignment by NOE and COSY): δ = –2.40 (br. s, 2H, NH), 0.14–0.26 (m, 8H, γ- and δ-CH_2), 0.47 (s, 6H, ar-CH_3), 0.73–0.77 (m, 4H, β-CH_2), 1.77 (s, 6H, ar-OCH_3), 1.88–1.93 (m, 4H, α-CH_2), 2.44 (s, 12H, 3,7,13,17-CH_3), 3.50 (s, 12H, 2,8,12,18-CH_3), 7.54 (dd, J = 7.4 and 1.0 Hz, 2H, ar-3′-H), 7.63 ("td", $J \approx$ 7.3 and 1.2 Hz, 2H, ar-5′-H), 7.71 ("td", $J \approx$ 7.4 and 1.2 Hz, 2H, ar-4′-H), 8.23 (dd, J = 7.3 and 1.2 Hz, 2H, ar-6′-H), 10.12 (s, 2H, 10,20-H).

$C_{58}H_{64}N_4O_2$ (849.2) Calcd. C 82.04 H 7.60 N 6.60
Found C 82.10 H 7.81 N 6.43

5,15-[2,3,5,6-Tetramethoxybenzene-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-2,3,7,8,12,13,17,18-octamethylporphyrin (**59**): According to the procedure described for the synthesis of **58**, 2.05 g (1.97 mmol) of **53**, 20 g of trichloroacetic acid, and 3.20 ml (19.3 mmol) of triethyl orthoformate were allowed to react in 1 l of dichloromethane at 20°C for 16 h. Dehydrogenation with DDQ, separation and purification as with **58** yielded 184 mg (11%) of **59**; $R_f \approx 0.13$ (silica gel, cyclohexane/ethyl acetate, 30:1); violet crystals, m.p. >330°C. – MS (LSI-MS): m/z (%) = 883 (21), 882 (61), 881 (100) [MH^+], 880 (44) [M^+], 879 (10). – ^{1}H NMR (500 MHz, CD_2Cl_2, 303 K; assignment by COSY): δ = –2.41 (br. s, 2H, NH), –0.10 to –0.07 (m, 4H, δ-CH_2), 0.47–0.52 (m, 4H, γ-CH_2), 0.71–0.77 (m, 4H, β-CH_2), 1.87–1.90 (m, 4H, α-CH_2), 1.92 (s, 12H, ar-OCH_3), 2.43 (s, 12H, 3,7,13,17-CH_3), 3.47 (s, 12H, 2,8,12,18-CH_3), 7.55 (d, J = 7.6 Hz, 2H, 3′-H), 7.63 ("t", $J \approx$ 7.1 Hz, 2H, 5′-H), 7.71 ("t", $J \approx$ 7.4 Hz, 2H, 4′-H), 8.24 (d, J = 7.6 Hz, 2H, 6′-H), 10.08 (s, 2H, 10,20-H). For an X-ray structure analysis of **59** see ref.[3].

$C_{58}H_{64}N_4O_4$ (881.2) Calcd. C 79.06 H 7.32 N 6.36
Found C 78.98 H 7.06 N 6.24

5,15-[2,5-Dimethoxybenzene-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-2,3,7,8,12,13,17,18-octamethylporphyrin (**60**): In analogy to the preparation of **58**, 979 mg (1.00 mmol) of **54**, 10 g of trichloroacetic acid, and 1.48 g (10.0 mmol) of triethyl orthoformate were allowed to react in 500 ml of dichloromethane (14 h, 20°C); dehydrogenation with 0.68 g (3.0 mmol) of DDQ, separation and purification yielded 191 mg (23%) of **60**; $R_f \approx 0.70$ (silica gel, toluene/ethyl acetate, 10:1); violet needles, m.p. 311–320°C (from methylcyclohexane). – MS: m/z (%) = 820 (100) [M^+], 806 (47), 410 (60) [M^{++}]. – ^{1}H NMR (360 MHz, CD_2Cl_2, 303 K): δ = –2.45 (s, 2H, NH), –0.10–0.0 (m, 4H, δ-CH_2), 0.29–0.33 (m, 4H, γ-CH_2), 0.79–0.88 (m, 4H, β-CH_2), 1.98–1.94 (m, 4H, α-CH_2), 2.05 (s, 6H, ar-OCH_3), 2.46 (s, 12H, 3,7,13,17-CH_3), 3.52 (s, 12H, 2,8,12,18-CH_3), 4.15 (s, 2H, ar-H, central ring), 7.56 ("d", $J \approx$ 7.5 Hz, 2H, 3′-H), 7.63 ("t", $J \approx$ 7.5 Hz, 2H, ar-5′-H), 7.71 ("t", $J \approx$ 7.5 Hz, 2H, ar-4′-H), 8.21 ("d", $J \approx$ 7.5 Hz, 2H, ar-6′-H), 10.13 (s, 2H, 10,20-H).

$C_{56}H_{60}N_4O_2$ (821.1) Calcd. C 81.91 H 7.37 N 6.82
Found C 81.93 H 7.28 N 6.86

5,15-[2-Chloro-3,6-dimethoxybenzene-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-2,3,7,8,12,13,17,18-octamethylporphyrin (**61**): The reaction of 1.01 g (1.00 mmol) of **55**, with 1.66 ml (10.0 mmol) of triethyl orthoformate, and 10 g of trichloroacetic acid in 500 ml of dichloromethane was accomplished in analogy to **58**. After dehydrogenation with 0.68 g (3.0 mmol) of DDQ and working up as before 11.7 mg (1.6%) of **61** was obtained: $R_f \approx 0.29$ (silica gel, cyclohexane/ethyl acetate, 9:1); violet crystals (from dichloromethane/methanol, 1:1), m.p. >300°C. – MS (LSI-MS): m/z (%) = 859 (21), 858 (71), 857 (99), 856 (100), 855 (100) [MH^+], 854 (49) [M^+], 853 (18). – ^{1}H NMR (500 MHz, CD_2Cl_2, 303 K; assignment by COSY): δ = –2.50 (br. s, 2H, NH), –0.42 to –0.40 (m, 2H, δ-CH_2), 0.17–0.21 (m, 2H, δ-CH_2), 0.25–0.30 (m, 2H, γ-CH_2), 0.46–0.52 (m, 2H, γ-CH_2), 0.75–0.81 (m, 2H, β-CH_2), 0.87–0.93 (m, 2H, β-CH_2), 1.19 (s, 3H, ar-3-OCH_3), 1.84–1.87 (m, 2H, α-CH_2), 2.08–2.12 (m, 2H, α-CH_2), 2.27 (s, 3H, ar-6-OCH_3), 2.41 and 2.47 (two s, 6H each, 3,7,13,17-CH_3), 3.48 and 3.52 (two s, 6H each, 2,8,12,18-CH_3), 3.78 (s, 1H, ar-5-H), 7.55 ("dd", $J \approx$ 7.8 and 0.8 Hz, 1H, ar-3′-H), 7.57 ("dd", $J \approx$ 7.5 and 0.9 Hz, 1H, ar-3′-H), 7.61 and 7.63 (two "td", $J \approx$ 7.4 and 1.3 Hz, 2H, ar-5′-H), 7.69–7.72 (m, 2H, ar-4′-H), 8.09 ("dd", $J \approx$ 7.2 and 1.2 Hz, 1H, ar-6′-H), 8.26 ("dd", $J \approx$ 7.3 and 1.2 Hz, 1H, ar-6′-H), 10.21 (s, 2H, 10,20-H).

$C_{56}H_{60}ClN_4O_2$ Calcd. 855.4405 Found 855.4426 (MS: MH^+)

5,15-[2,5-Dichloro-3,6-dimethoxybenzene-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-2,3,7,8,12,13,17,18-octamethylporphyrin (**62**): In analogy to the preparation of **58**, 2.00 g (1.91 mmol) of **56**, 3.16 ml (19.0 mmol) of triethyl orthoformate and 20 g of trichloroacetic acid were allowed to react in 1 l of dichloromethane under argon at 20°C for 16 h. Thereafter, 2 g of sodium acetate and 1.31 g (5.79 mmol) of DDQ were added, and the reaction was kept at 20°C for 3 h. Product isolation as with **58** by a first chromatography (silica gel, h = 16 cm, d = 6.5 cm, toluene/ethyl acetate, 16:1; fraction $R_f \approx$ 0.63) and subsequent medium-pressure chromatography (silica gel 60, 20–45 μm; h = 51 cm, d = 3.7 cm; cyclohexane/ethyl acetate, 30:1; flow rate 40 ml/min) yielded **62** with $R_f \approx 0.20$; crystallization from dichloromethane/methanol (1:3) afforded 351 mg (21%), violet crystals, m.p. >330°C. – MS (LSI-MS): m/z (%) = 893 (23), 892 (44), 891 (82), 890 (71), 889 (100) [MH^+], 888 (17) [M^+]. – ^{1}H NMR (500 MHz, CD_2Cl_2): δ = –2.40 (s, 2H, NH), 0.13–0.17 (m, 4H, δ-CH_2), 0.37–0.43 (m, 4H, γ-CH_2), 0.76–0.83 (m, 4H, β-CH_2), 1.72 (s, 6H, ar-OCH_3), 1.93–1.98 (m, 4H, α-CH_2), 2.45 (s, 12H, 3,7,13,17-CH_3), 3.51 (s, 12H, 2,8,12,18-CH_3), 7.56 ("dd", $J \approx$ 7.7 and 1.0 Hz, 2H, ar-3′-H), 7.65 ("td", $J \approx$ 7.6 and 1.4 Hz, 2H, ar-5′-H), 7.72 ("td", $J \approx$ 7.7 and 1.4 Hz, 2H, ar-4′-H), 8.23 ("dd", $J \approx$ 7.3 and 1.3 Hz, 2H, ar-6′-H), 10.14 (s, 2H, 10,20-H).

$C_{56}H_{58}Cl_2N_4O_2$ (890.0) Calcd. C 75.57 H 6.57 Cl 7.97 N 6.30
Found C 75.74 H 6.84 Cl 7.91 N 6.30

5,15-[2,5-Dicyano-3,6-dimethoxybenzene-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-2,3,7,8,12,13,17,18-octamethylporphyrin (**63**): As in the preceding preparations, 1.03 g (1.00 mmol) of **57**, 1.66 ml (10.0 mmol) of triethyl orthoformate and 10 g trichloroacetic acid were allowed to react in 500 ml of dichloromethane at 20°C for 18 h. After dehydrogenation with 0.68 g (3.0 mmol) of DDQ, separation and isolation by filtration through silica gel (toluene/ethyl acetate, 9:1) followed by medium-pressure chromatography (silica gel 60, 20–45 μm; h = 51 cm, d = 3.7 cm; cyclohexane/ethyl acetate, 30:1, flow rate 41 ml/min) yielded **63** ($R_f \approx 0.07$); after crystallization from dichloromethane/methanol (1:1) 22.6 mg (2.6%) of violet crystals was obtained, m.p. >300°C. – MS (LSI-MS): m/z (%) = 873 (33), 872 (92), 871 (100) [MH^+], 870 (36) [M^+]. – ^{1}H NMR (500 MHz, CD_2Cl_2, 303 K): δ = –2.48 (s, 2H, NH), –0.47 to –0.37 (m, 2H, CH_2), 0.16–0.27 (m, 2H, CH_2), 0.46–0.63 (m, 4H, CH_2), 0.63–0.76 (m, 2H, CH_2), 0.86–0.95 (m, 2H, CH_2), 1.56 (s, 6H, ar-OCH_3), 1.77–1.85 (m, 2H, CH_2), 2.14–2.23 (m, 2H, CH_2), 2.39 and 2.48 (br. s, 6H each, 3,7,13,17-CH_3), 3.52 (s, 12H, 2,8,12,18-CH_3), 7.56 ("d", $J \approx$ 7.5 Hz, 2H, ar-3′-H), 7.63 ("td", $J \approx$ 7.3 and 1 Hz, 2H, ar-5′-H), 7.72 ("td", $J \approx$ 7.2 and 1.3 Hz, 2H, ar-4′-H), 8.16 ("dd", $J \approx$ 6.8 and 1 Hz, 2H, ar-6′-H), 10.20 (s, 2H, 10,20-H).

$C_{58}H_{58}N_6O_2$ Calcd. 870.4621 Found 870.4631 (MS: M^+)

5,15-[3,6-Dimethyl-p-benzoquinone-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-2,3,7,8,12,13,17,18-octamethylporphyrin (**5**): To 50 mg (59 μmol) of **58** in 50 ml of dichloromethane 5.0 ml (5.0 mmol) of a 1 M solution of boron tribromide in dichloromethane was added under argon. The reaction mixture was stirred at 20°C for 2 h, cooled to 0°C and hydrolyzed by the addition of 50 ml of a saturated sodium carbonate solution. The separated dichloromethane solution was washed with 50 ml of a saturated sodium carbonate solution and twice with 50 ml of water each and dried with magnesium sulfate. After the addition of 27 mg (0.12 mmol) of DDQ the reaction mixture was kept at 20°C for further 3 h and then washed twice with 50 ml each of a saturated sodium hydrogen carbonate solution and twice with 50 ml each of water, dried with magnesium sulfate, and then the solvent was evaporated. To the residue 10 ml of cyclohexane/ethyl acetate (16:1) was added and a medium-pressure chromatography with this solvent mixture (h = 48 cm, d = 3.7 cm; silica gel 60, 20–45 μm; flow rate 40 ml/min) afforded 32 mg (67%) of **5** with $R_f \approx 0.28$, violet crystals, m.p. >330°C (dichloromethane/methanol, 1:3); for elemental analysis, **5** was recrystallized from methylcyclohexane. – MS (LSI-MS): m/z (%) = 821 (34), 820 (68), 819 (100) [MH^+], 818 (17) [M^+]. – ^{1}H NMR (500 MHz, CD_2Cl_2, 303 K; assignment by COSY): δ = –2.43 (br. s, 2H, NH), –0.05 to 0.05 (m, 8H, δ- and γ-CH_2), 0.24 (s, 6H, quin-CH_3), 0.75–0.81 (m, 4H, β-CH_2), 2.03–2.06 (m, 4H, α-CH_2), 2.47 (s, 12H, 3,7,13,17-CH_3), 3.55 (s, 12H, 2,8,12,18-CH_3), 7.57 (dd, J = 7.2 and 1.0 Hz, 2H, ar-3′-H), 7.66 ("td", $J \approx$ 7.3 and 1.4 Hz, 2H, ar-5′-H), 7.73 ("td", $J \approx$ 7.3 and

1.4 Hz, 2H, ar-4′-H), 8.19 (dd, J = 7.4 and 1.3 Hz, 2H, ar-6′-H), 10.19 (s, 2H, 10,20-H).

$C_{56}H_{58}N_4O_2$ (819.1) Calcd. C 82.12 H 7.14 N 6.84
Found C 81.83 H 7.01 N 6.64

5,15-[3,6-Dimethoxy-p-benzoquinone-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-2,3,7,8,12,13,17,18-octamethylporphyrin (6): 75 mg (85 μmol) of **59** and 5.0 g (≈ 2 mmol) of cerium(IV) ammonium nitrate (20% on silica gel) in 50 ml of dichloromethane were stirred at 20°C for 16 h. Then ammonia gas was passed through the reaction mixture for 15 min (colour change from green to dark-red); the silica gel was filtered off and washed with 50 ml of dichloromethane. The united organic solutions were stirred with 50 ml of 2 N hydrochloric acid at room temp. for 2 h, afterwards washed twice with 50 ml each of a saturated sodium carbonate solution and twice with 50 ml of water each and dried with magnesium sulfate. The solvent was distilled off in vacuo and the violet product was purified by medium-pressure chromatography (h = 48 cm, d = 3.7 cm; silica gel 60, 20–45 μm; cyclohexane/ethyl acetate, 16:1; flow rate 40 ml/min) to afford 37 mg (50%) of **6**, R_f ≈ 0.28, m.p. >330°C (dichloromethane/methanol, 1:3). – MS (LSI-MS): m/z (%) = 854 (29), 853 (59), 852 (74), 851 (100) [MH^+], 850 (13) [M^+]. – ^{1}H NMR (500 MHz, CD_2Cl_2, 303 K; assignment by COSY): δ = −2.42 (br. s, 2H, NH), −0.51 to −0.48 (m, 4H, δ-CH_2), 0.26–0.28 (m, 4H, γ-CH_2), 0.78–0.82 (m, 4H, β-CH_2), 1.91 (s, 6H, quin-OCH_3), 2.00–2.03 (m, 4H, α-CH_2), 2.45 (s, 12H, 3,7,13,17-CH_3), 3.49 (s, 12H, 2,8,12,18-CH_3), 7.56 (d, J = 7.5 Hz, 2H, ar-3′-H), 7.63 ("t", J ≈ 7.5 Hz, 2H, ar-5′-H), 7.72 ("t", J ≈ 7.2 Hz, 2H, ar-4′-H), 8.17 (d, J = 7.5 Hz, 2H, ar-6′-H), 10.13 (s, 2H, 10,20-H).

$C_{56}H_{59}N_4O_4$ Calcd. 851.4536 Found 851.4532 (MS: MH^+)

5,15-[p-Benzoquinone-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-2,3,7,8,12,13,17,18-octamethylporphyrin (7): 100 mg (0.12 mmol) of **60** and 1.2 g (4.8 mmol) of boron tribromide in 90 ml of dichloromethane were stirred at −40°C for 3 h and at 20°C for further 2 h. The solution was then extracted twice with 50 ml each of a saturated sodium hydrogen carbonate solution and with 50 ml of a saturated sodium chloride solution, dried with magnesium sulfate and, after the addition of 54.5 mg (0.24 mmol) of DDQ, the reaction mixture was stirred at room temp. for 14 h, then washed twice with 50 ml each of a saturated sodium hydrogen carbonate solution and with 50 ml of a saturated sodium chloride solution. After drying with magnesium sulfate and evaporation of the solvent the residue was filtered with toluene/ethyl acetate (10:1) through alumina; the fraction of the first violet zone (R_f ≈ 0.64, silica gel, toluene/ethyl acetate, 10:1) was concentrated and crystallized from dichloromethane/methanol to yield 71.5 mg (74%) of **7**, violet needles, m.p. >350°C (from methylcyclohexane). – MS (T_Q > 400°C): m/z (%) = 792 (100) [(M + 2)$^+$], 790 (28) [M^+], 777 (40), 572 (18), 396 (90). – ^{1}H NMR (360 MHz, CD_2Cl_2, 303 K): δ = −2.41 (s, 2H, NH), 0.00–0.09 (m, 4H, γ-CH_2), 0.17 to 0.20 (m, 4H, δ-CH_2), 0.86–0.96 (m, 4H, β-CH_2), 1.96–2.01 (m, 4H, α-CH_2), 2.47 (s, 12H, 3,7,13,17-CH_3), 3.56 (s, 12H, 2,8,12,18-CH_3), 4.06 (s, 2H, quinone-H), 7.56 ("d", J ≈ 7.5 Hz, 2H, ar-3′-H), 7.63 ("t", J ≈ 7.5 Hz, 2H, ar-5′-H), 7.72 ("t", J ≈ 7.5 Hz, 2H, ar-4′-H), 8.17 ("d", J ≈ 7.5 Hz, 2H, ar-6′H), 10.21 (s, 2H, 10,20-H).

$C_{54}H_{54}N_4O_2$ (791.1) Calcd. C 81.99 H 6.88 N 7.08
Found C 81.99 H 6.93 N 7.04

5,15-[3-Chloro-p-benzoquinone-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-2,3,7,8,12,13,17,18-octamethylporphyrin (8): To 5,6 mg (6.5 μmol) of **61** in 10 ml of dichloromethane 0.65 ml (0.65 mmol) of a 1 M solution of boron tribromide in dichloromethane was added, and the reaction was kept at room temp. with stirring for 2 h. Then 30 ml of dichloromethane and 40 ml of a saturated sodium hydrogen carbonate solution were added, the organic phase was separated, washed with 40 ml each of a saturated sodium hydrogen carbonate and a sodium chloride solution, dried with magnesium sulfate and concentrated in vacuo to a volume of 5 ml. After the addition of 6.1 mg (27 μmol) of DDQ the mixture was stirred at room temp. under argon and with the exclusion of light for 3 h, then diluted with 50 ml of dichloromethane and washed twice with 50 ml each of a saturated sodium hydrogen carbonate solution and with a sodium chloride solution. After drying with magnesium sulfate and evaporation of the solvent the residue was chromatographed (eluent: cyclohexane/ethyl acetate, 30:1) on a medium-pressure column (silica gel 60, 12–21 μm; h = 51 cm, d = 3.7 cm; flow rate 21 ml/min) to afford 3.4 mg (63%) of **8**, R_f ≈ 0.13, after crystallization from dichloromethane/methanol (1:1) violet crystals, m.p. >300°C. – MS (LSI-MS): m/z (%) = 830 (23); 829 (50), 828 (66), 827 (100) [(MH + 2H)$^+$], 826 (24), 825 (12) [MH^+]. – ^{1}H NMR (500 MHz, CD_2Cl_2, 303 K; assignment by COSY): δ = −2.41 (br. s, 2H, NH), −0.36 to −0.31 (m, 4H, γ- and δ-CH_2), 0.40–0.47 (m, 2H, γ′-CH_2), 0.73–0.80 (m, 2H, β′-CH_2), 0.89–0.95 (m, 4H, β- and δ′-CH_2), 1.84–1.88 (m, 2H, α-CH_2), 2.09–2.13 (m, 2H, α′-CH_2), 2.45 and 2.48 (two s, 6H each, 3,7,13,17-CH_3), 3.12 (s, 1H, quinone-H), 3.55 and 3.56 (two s, 6H each, 2,8,12,18-CH_3), 7.55 ("dd", J ≈ 7.6 and 1.3 Hz, 1H, ar-3′-H), 7.57 ("dd", J ≈ 7.8 and 1.5 Hz, 1H, ar-3′-H), 7.61 and 7.65 (two "td", J ≈ 7.5 and 1.5 Hz, 2H, ar-5′-H), 7.69–7.74 (m, 2H, ar-4′-H), 8.08 (dd, J = 7.5 and 1.1 Hz, 1H, ar-6′-H), 8.26 (dd, J = 7.1 and 1.1 Hz, 1H, ar-6′-H), 10.21 (s, 2H, 10,20-H).

$C_{54}H_{54}ClN_4O_2$ Calcd. 825.3935 Found 825.3914 (MS: MH^+)

5,15-[3,6-Dichloro-p-benzoquinone-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-2,3,7,8,12,13,17,18-octamethylporphyrin (9): 50 mg (56 μmol) of **62** in 50 ml of dichloromethane was, after the addition of 5.0 ml (5.0 mmol) of a 1 M solution of boron tribromide in dichloromethane, stirred under argon at 20°C for 2 h. As described for the preparation of **5** the reaction mixture was hydrolyzed with 50 ml of a saturated sodium hydrogen carbonate solution and oxidized with 26 mg (0.11 mmol) of DDQ. Separation and isolation as with **5** yielded 17 mg (35%) of **9**, R_f ≈ 0.38 (silica gel, cyclohexane/ethyl acetate, 16:1), violet crystals, m.p. >330°C. – MS (LSI-MS): m/z (%) = 865 (23), 864 (44), 863 (80), 862 (70), 861 (100) [(MH + 2H)$^+$], 860 (23), 859 (15) [MH^+]. – ^{1}H NMR (500 MHz, CD_2Cl_2, 303 K; assignment by COSY): δ = −2.42 (br. s, 2H, NH), 0.13–0.18 (m, 8H, δ- and γ-CH_2), 0.82–0.87 (m, 4H, β-CH_2), 2.01–2.05 (m, 4H, α-CH_2), 2.45 (s, 12H, 3,7,13,17-CH_3), 3.53 (s, 12H, 2,8,12,18-CH_3), 7.55 (dd, J = 7.7 and 1.2 Hz, 2H, ar-3′-H), 7.63 ("td", J ≈ 7.4 and 1.4 Hz, 2H, ar-5′-H), 7.71 ("td", J ≈ 7.6 and 1.5 Hz, 2H, ar-4′-H), 8.16 (dd, J = 7.3 and 1.4 Hz, 2H, ar-6′-H), 10.18 (s, 2H, 10,20-H).

$C_{54}H_{53}Cl_2N_4O_2$ Calcd. 859.3545 Found 859.3528 (MS: MH^+)

1,4-Bis{4-[2-(bis⟨5-benzyloxycarbonyl-4-ethyl-3-methyl-2-pyrrolyl⟩methyl)-phenyl]butyl}-2,5-dimethoxy-3,6-dimethylbenzene (**64**). 1.94 g (4.00 mmol) of dialdehyde **15** and 4.86 g (20.0 mmol) of 2-benzyloxycarbonyl-3-ethyl-4-methylpyrrole (prepared by transesterification of the corresponding 2-ethoxycarbonyl-3-ethyl-4-methylpyrrole[27] with sodium benzylalcoholate in benzyl alcohol) in 50 ml of ethanol were, after the addition of 0.65 ml of concentrated hydrochloric acid, heated at reflux for 4 h. Then the reaction mixture was cooled to room temp. and 100 ml of dichloromethane was added. By chromatography on silica gel (h = 9 cm, d = 13 cm) with toluene/ethyl acetate (100:1) as the eluent excess pyrrole (R_f ≈ 0.23) was separated, and with toluene/ethyl acetate (8:1) **64** (R_f ≈ 0.60) was isolated; after drying in vacuo at 40°C 5.35 g (94%) of analytically pure **64** was obtained, m.p. 84–90°C. – MS (LSI-MS): m/z (%) = 1424 (22), 1423 (42) [MH^+], 1422 (49) [M^+], 1421 (43), 1333 (43), 1332 (92) [(MH − 91)$^+$], 1331 (100) [(M − 91)$^+$]. – ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.07 (t, J = 7.4 Hz, 12H, pyr-4-CH_2CH_3), 1.49–1.58 (m, 8H, β- and γ-CH_2), 1.76 (s, 12H, pyr-3-CH_3), 2.12 (s, 6H, ar-CH_3), 2.51–2.58 (m, 8H, α- and δ-CH_2), 2.73 (q, J = 7.3 Hz, 8H, pyr-4-CH_2CH_3), 3.59 (s, 6H, ar-OCH_3), 5.24 (s, 8H, ar-CH_2-O), 5.65 [s, 2H, ar-CH(pyr)$_2$], 6.82 (d, J = 7.5 Hz, 2H, ar-3′-H), 7.11–7.34 (m, 26H, all other ar-H), 8.13 (s, 4H, NH).

$C_{92}H_{102}N_4O_{10}$ (1423.8) Calcd. C 77.61 H 7.22 N 3.93
Found C 77.52 H 7.50 N 3.66

1,4-Bis{4-[2-(bis⟨5-benzyloxycarbonyl-4-ethyl-3-methyl-2-pyrrolyl⟩methyl)-phenyl]butyl-2,3,5,6-tetramethoxybenzene (**65**): The reaction of 2.00 g (3.86 mmol) of **16** with 4.69 g (19.3 mmol) of 2-benzyloxycarbonyl-3-ethyl-4-methylpyrrole in 50 ml of ethanol, to which 0.65 ml concentrated hydrochloric acid was added, and the product isolation were carried out as in the preparation of **64**. By chromatography with toluene/ethyl acetate (8:1) as the eluent on silica gel 5.03 g (90%) of **65** (R_f ≈ 0.60) was obtained, m.p. 72–80°C. – MS (LSI-MS): m/z (%) = 1455 (44) [MH^+], 1454 (44) [M^+], 1453 (62), 1365 (44), 1364 (91) [(MH − 91)$^+$], 1363 (100) [(M − 91)$^+$]. – ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.07 (t, J = 7.4 Hz, 12H, pyr-4-CH_2CH_3), 1.51–1.61 (m, 8H, β- and γ-CH_2), 1.76 (s, 12H, pyr-3-CH_3), 2.50–2.60 (m, 8H, α- and δ-CH_2), 2.73 (q, J = 7.3 Hz, 8H, pyr-4-CH_2CH_3), 3.73 (s, 12H, ar-OCH_3), 5.24 (s, 8H, ar-CH_2–O), 5.65 [s, 2H, ar-CH(pyr)$_2$], 6.81 (d, J = 7.5 Hz, 2H, ar-3′-H), 7.11–7.35 (m, 26H, all other ar-H), 8.12 (s, 4H, NH).

$C_{92}H_{102}N_4O_{12}$ (1455.8) Calcd. C 75.90 H 7.06 N 3.85
Found C 75.85 H 7.22 N 3.66

1,4-Bis{4-[2-(bis⟨5-benzyloxycarbonyl-4-ethyl-3-methyl-2-pyrrolyl⟩methyl)-phenyl]butyl}-2,5-dimethoxybenzene (**66**): 1.37 g (3.00 mmol) of **17**, and 3.65 g (15.0 mmol) 2-benzyloxycarbonyl-3-ethyl-4-methylpyrrole in 25 ml of ethanol were, after the addition of 0.3 ml of concentrated hydrochloric acid, heated at reflux for 4 h. Product isolation was performed as described for **64**. Chromatography (silica gel, toluene/ethyl acetate, 50:1, $R_f \approx 0.15$) yielded 4.17 g (99%) of **66**, m.p. 78°C. – MS (LSI-MS): *m/z* (%) = 1394 (100) [M^+], 1304 (93), 1303 (96) [$(M - 91)^+$]. – ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.10 (t, J = 7.4 Hz, 12H, pyr-4-CH_2CH_3), 1.40–1.60 (m, 8H, β- and γ-CH_2), 1.75 (s, 12H, pyr-3-CH_3), 2.50–2.58 (m, 8H, α- and δ-CH_2), 2.70 (q, J = 7.4 Hz, 8H, pyr-4-CH_2CH_3), 3.70 (s, 6H, ar-OCH_3), 5.23 (s, 8H, ar-CH_2-O), 5.63 [s, 2H, ar-CH(pyr)$_2$], 6.55 (s, 2H, ar-H, central arom. ring), 6.82 (d, J = 8.2 Hz, 2H, ar-H), 7.09–7.40 (m, 26H, all other ar-H), 8.11 (s, 4H, NH).

$C_{90}H_{98}N_4O_{10}$ (1394.7) Calcd. C 77.45 H 7.08 N 4.01
Found C 77.59 H 7.32 N 3.81

1,4-Bis{4-[2(bis⟨5-benzyloxycarbonyl-4-ethyl-3-methyl-2-pyrrolyl⟩methyl)-phenyl]butyl}-2,5-dichloro-3,6-dimethoxybenzene (**67**): 1.38 g (2.62 mmol) of **19** was allowed to react with 3.18 g (13.1 mmol) 2-benzyloxycarbonyl-3-ethyl-4-methylpyrrole in 60 ml of ethanol in the presence of 0.40 ml concentrated hydrochloric acid as in the preceding reactions. Separation and product isolation performed as described before: chromatography (silica gel, toluene/ethyl acetate, 100:1) yielded 3.50 g (91%) of **67**, $R_f \approx 0.14$, m.p. 69–70°C. – MS (LSI-MS): *m/z* (%) = 1465 (27), 1464 (37), 1463 (46) [MH^+], 1462 (36) [M^+], 1375 (36), 1374 (70), 1373 (100), 1371 (95) [$(M - 91)^+$], 1370 (20). – ^{1}H-NMR (500 MHz, CD_2Cl_2): δ = 1.05 (t, J = 7.4 Hz, 12H, pyr-4-CH_2CH_3), 1.45–1.57 (m, 8H, β- and γ-CH_2), 1.75 (s, 12H, pyr-3-CH_3), 2.53–2.59 (m, 4H, α-CH_2), 2.66–2.70 (m, 4H, δ-CH_2), 2.70–2.75 (m, 8H, pyr-CH_2-CH_3), 3.69 (s, 6H, ar-OCH_3), 5.19 (s, 8H, ar-CH_2-O), 5.66 [s, 2H, ar-CH(pyr)$_2$], 6.81 (d, J = 7.6 Hz, 2H, ar-3-H), 7.09–7.37 (m, 26H, all other arom. H), 8.11 (s, 4H, NH).

$C_{90}H_{96}Cl_2N_4O_{10}$ (1464.7) Calcd. C 73.73 H 6.61 Cl 4.84 N 3.82
Found C 73.48 H 6.69 Cl 4.71 N 3.69

1,4-Bis{4-[2-(bis⟨5-carboxy-4-ethyl-3-methyl-2-pyrrolyl⟩methyl)phenyl]-butyl}-2,5-dimethoxy-3,6-dimethylbenzene (**68**): 5.23 g (3.67 mmol) of **64** in 200 ml of tetrahydrofuran was hydrogenated (30 min, 20°C, normal pressure) in the presence of 5.2 g of palladium catalyst (5% on charcoal). After filtering off the catalyst, the solvent was evaporated from the filtrate, and the residue dried in vacuo at 40°C to afford 3.89 g (99%) of **68**, m.p. 146–148°C (dec.); the unstable product, for which a correct elemental analysis was not obtained, was directly used for the porphyrin synthesis as in the case of **69**, **70** and **71**. – MS (LSI-MS negative): *m/z* (%) = 1064 (14), 1063 (38), 1062 (92) [M^-], 1061 (100) [$(M - H)^-$], 1060 (43), 1059 (11). – ^{1}H NMR (360 MHz, [D$_6$]DMSO): δ = 1.01 (t, J = 7.4 Hz, 12H, pyr-4-CH_2CH_3), 1.33–1.45 (m, 8H, β- and γ-CH_2), 1.78 (s, 12H, pyr-3-CH_3), 2.08 (s, 6H, ar-CH_3), 2.42–2.52 (m, 8H, α- and δ-CH_2), 2.60–2.69 (m, 8H, pyr-4-CH_2CH_3), 3.53 (s, 6H, ar-OCH_3), 5.74 [s, 2H, ar-CH(pyr)$_2$], 7.05 (d, J = 7.4 Hz, 2H, ar-3′-H), 7.13–7.18 (m, 6H, ar-4′,5′,6′-H), 10.48 (s, 4H, NH), 11.98 (s, 4H, COOH).

1,4-Bis{4-[2-(bis⟨5-carboxy-4-ethyl-3-methyl-2-pyrrolyl⟩methyl)phenyl]-butyl}-2,3,5,6-tetramethoxybenzene (**69**): Hydrogenation of 4.90 g (3.37 mmol) of **65** in 200 ml of tetrahydrofuran in the presence of 4.9 g of palladium catalyst (5% on charcoal) and product isolation carried out as described for **68** yielded 3.66 (99%) of **69**, m.p. 130–135°C (dec.). – MS (LSI-MS negative): *m/z* (%) = 1096 (34), 1095 (54), 1094 (84) [M^-], 1093 (100) [$(M - H)^-$], 1092 (43), 1091 (15). – ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 1.01 (t, J = 7.4 Hz, 12H, pyr-4-CH_2CH_3), 1.35–1.38 (m, 4H, β- or γ-CH_2), 1.43–1.46 (m, 4H, β- or γ-H), 1.82 (s, 12H, pyr-3-CH_3), 2.40–2.55 (m, 8H, α- and δ-CH_2), 2.61–2.69 (m, 8H, pyr-4-CH_2CH_3), 3.67 (s, 12H, ar-OCH_3), 5.73 [s, 2H, ar-CH(pyr)$_2$], 7.08 (d, J = 7.6 Hz, 2H, ar-3′-H), 7.11–7.26 (m, 6H, ar-4′,5′,6′-H), 10.57 (s, 4H, NH), 12.03 (s, 4H, COOH).

1,4-Bis{4-[2-(bis⟨5-carboxy-4-ethyl-3-methyl-2-pyrrolyl⟩methyl)phenyl]-butyl}-2,5-dimethoxybenzene (**70**): Hydrogenation of 2.00 g (1.43 mmol) of **66** in 200 ml of tetrahydrofuran (3.00 g of palladium catalyst, 5% on charcoal, 25 min, 20°C) and isolation of the product in analogy to the preceding reaction yielded 1.89 g (99%) of **70**, (dec. > 150°C). – MS (LSI-MS negative): *m/z* (%) = 1035 (28), 1034 (72) [M^-], 1033 (100) [$(M - H)^-$], 1032 (13). – ^{1}H NMR (360 MHz, [D$_6$]DMSO): δ = 1.00 (t, J = 7.6 Hz, 12H, pyr-4-CH_2CH_3), 1.22 (m, 4H, γ-CH_2), 1.48–1.52 (m, 4H, β-CH_2), 1.81 (s, 12H, pyr-3-CH_3), 2.41–2.49 (m, 8H, α- and δ-CH_2), 2.65 (q, J = 7.6 Hz, 8H, pyr-4-CH_2CH_3), 3.68 (s, 6H, ar-OCH_3), 5.71 [s, 2H, ar-CH(pyr)$_2$], 6.64 (s, 2H, ar-H, central ring), 6.90 (d, J = 8.3 Hz, 2H, ar-3′-H), 7.08–7.25 (m, 6H, ar-4′,5′,6′-H), 10.58 (s, 4H, NH), 12.00 (s, 4H, COOH).

1,4-Bis{4-[2-(bis⟨5-carboxy-4-ethyl-3-methyl-2-pyrrolyl⟩methyl)phenyl]-butyl}-2,5-dichloro-3,6-dimethoxybenzene (**71**): Hydrogenation of 3.50 g (2.4 mmol) of **67** in 150 ml of tetrahydrofuran in the presence of 1.25 g of palladium catalyst (10% on charcoal) at 20°C for 15 min, and isolation of the product in analogy to the preceding reaction afforded 2.60 g (99%) of **71** (dec. >137°C). – MS (LSI-MS negative): *m/z* (%) = 1105 (24), 1104 (47), 1103 (88), 1102 (79) [M^-], 1101 (100) [$(M - H)^-$], 1100 (17). – ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 1.00 (t, 12H, J = 7.4 Hz, pyr-4-CH_2CH_3), 1.35–1.42 (m, 4H, β- or γ-CH_2), 1.43–1.53 (m, 4H, β- or γ-CH_2), 1.78 (s, 12H, pyr-3-CH_3), 2.40–2.48 (m, 4H, α-CH_2), 2.57–2.70 (m, 12H, pyr-4-CH_2CH_3 and δ-CH_2), 3.70 (s, 6H, ar-OCH_3), 5.71 [s, 2H, ar-CH(pyr)$_2$], 7.04 (d, J = 7.0 Hz, 2H, ar-3′-H), 7.11–7.22 (m, 6H, ar-4′,5′,6′-H), 10.51 (s, 4H, NH), 12.00 (s, 4H, COOH).

5,15-[2,5-Dimethoxy-3,6-dimethylbenzene-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (**72**): In analogy to the procedure used for the syntheses of **58**–**63**, 2.20 g (2.07 mmol) of **68** was allowed to react with 3.30 ml (19.8 mmol) triethyl orthoformate and 20 g of trichloroacetic acid in 1 l of dichloromethane under argon at 20°C for 16 h. Dehydrogenation with 1.41 g (6.21 mmol) of DDQ (3 h, 20°C) and isolation by a first chromatography on silica (h = 16 cm, d = 6.5 cm, toluene/ethyl acetate, 16:1, fraction with $R_f \approx 0.63$) followed by medium-pressure chromatography (silica gel 60, 20–45 μm, 40 ml/min; cyclohexane/ethyl acetate, 30:1, $R_f \approx 0.19$) yielded 317 mg (17%) of **72**, violet crystals, m.p. 277–278°C (dichloromethane/methanol, 1:3), recrystallized for analysis from methylcyclohexane. – MS (LSI-MS): *m/z* (%) = 907 (25), 906 (69), 905 (100) [MH^+], 904 (25) [M^+]. – ^{1}H NMR (500 MHz, CD_2Cl_2, 303 K; assignment by COSY): δ = −2.45 (br. s, 2H, NH), −0.04–0.00 (m, 4H, δ-CH_2), 0.24–0.30 (m, 4H, γ-CH_2), 0.36 (s, 6H, ar-CH_3), 0.74–0.80 (m, 4H, β-CH_2), 1.67 (s, 6H, ar-OCH_3), 1.79 (t, J = 7.6 Hz, 12H, 2,8,12,18-CH_2CH_3), 1.89–1.93 (m, 4H, α-CH_2), 2.46 (s, 12H, 3,7,13,17-CH_3), 4.00 (q, J = 7.7 Hz, 8H, 2,8,12,18-CH_2CH_3), 7.55 (d, J = 7.6 Hz, 2H, ar-3′-H), 7.65 ("t", $J \approx$ 7.5 Hz, 2H, ar-5′-H), 7.71 ("t", $J \approx$ 7.3 Hz, 2H, ar-4′-H), 8.25 (d, J = 7.5 Hz, 2H, ar-6′-H), 10.13 (s, 2H, 10,20-H).

$C_{62}H_{72}N_4O_2$ (905.3) Calcd. C 82.26 H 8.02 N 6.19
Found C 81.97 H 8.31 N 5.91

5,15-[2,3,5,6-Tetramethoxybenzene-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (**73**): The reaction of 2.10 g (1.92 mmol) of **69**, with 3.16 ml (19.0 mmol) of triethyl orthoformate and 20 g of trichloroacetic acid in 1 l dichloromethane (16 h, 20°C), followed by dehydrogenation with 1.31 g (5.77 mmol) of DDQ (3 h, 20°C) and chromatographic separation of the product in analogy to the preparation of **72** (preceding) yielded 148 mg (8.3%) of **73**, $R_f \approx 0.19$ (silica gel, cyclohexane/ethyl acetate, 30:1), m.p. 262–264°C (dichloromethane/methanol, 1:3), recrystallized for analysis from methylcyclohexane. – MS (LSI-MS): *m/z* (%) = 939 (27), 938 (70), 937 (100) [MH^+], 936 (22) [M^+]. – ^{1}H NMR (360 MHz, CD_2Cl_2, 303 K; assignment by COSY): δ = −2.42 (br. s, 2H, NH), −0.15 to −0.11 (m, 4H, δ-CH_2), 0.49–0.54 (m, 4H, γ-CH_2), 0.73–0.81 (m, 4H, β-CH_2), 1.79 (t, J = 7.6 Hz, 12H, 2,8,12,18-CH_2CH_3), 1.88–1.91 (m, 4H, α-CH_2), 1.93 (s, 12H, ar-OCH_3), 2.46 (s, 12H, 3,7,13,17-CH_3), 3.91–4.04 (m, 8H, 2,8,12,18-CH_2CH_3), 7.56 (dd, J = 7.6 and 1.1 Hz, 2H, ar-3′-H), 7.65 ("td", $J \approx$ 7.5 and 1.4 Hz, 2H, ar-5′-H), 7.72 ("td", $J \approx$ 7.5 and 1.4 Hz, 2H, ar-4′-H), 8.28 (dd, J = 7.4 and 1.4 Hz, 2H, ar-6′-H), 10.11 (s, 2H, 10,20-H).

$C_{62}H_{72}N_4O_4$ (937.3) Calcd. C 79.45 H 7.74 N 5.98
Found C 79.48 H 7.94 N 5.81

5,15-[2,5-Dimethoxybenzene-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (**74**): 2.18 g (2.11 mmol) of **70** was allowed to react with 22 g of trichloroacetic acid and 3.49 ml (21.0 mmol) of triethyl orthoformate in 1.1 l of dichloromethane in analogy to the preceding preparations. Dehydrogenation with 1.49 g (6.57 mmol) of DDQ, isolation of the product by silica gel chromatography (eluent: toluene/ethyl acetate, 16:1) and further purification with the fraction with $R_f \approx 0.64$ by medium-pressure chromatography (silica gel 60, 20–45 μm; h = 48 cm, d = 3.7 cm; flow rate 40 ml/min; cyclohexane/ethyl acetate, 30:1; $R_f \approx 0.23$) followed by crystallization from dichloromethane/methanol (1:1) yielded 222 mg (12%) of **74**, violet needles, m.p. 315°C (methylcyclohexane). – MS

(LSI-MS): *m/z* (%) = 880 (12), 879 (48), 878 (94), 877 (100) [MH^+], 876 (36) [M^+], 875 (12). – ^{1}H-NMR (500 MHz, CD_2Cl_2, 303 K; assignment by COSY): δ = −2.49 (s, 2H, NH), −0.04–0.00 (m, 4H, δ-CH_2), 0.29–0.32 (m, 4H, γ-CH_2), 0.80–0.88 (m, 4H, β-CH_2), 1.74 (t, *J* = 7.6 Hz, 12H, 2,8,12,18-CH_2CH_3), 1.81 (s, 6H, ar-OCH_3), 1.90–1.98 (m, 4H, α-CH_2), 2.47 (s, 12H, 3,7,13,17-CH_3), 4.02 (q, *J* = 7.6 Hz, 8H, 2,8,12,18-CH_2CH_3), 4.15 (s, 2H, ar-H, central ring), 7.54 (d, *J* = 7.9 Hz, 2H, ar-3′-H), 7.60–7.65 (m, 2H, ar-5′-H), 7.69–7.75 (m, 2H, ar-4′-H), 8.26 (d, *J* = 7.7 Hz, 2H, ar-6′-H), 10.12 (s, 2H, 10,20-H).

$C_{60}H_{68}N_4O_2$ (876.5) Calcd. C 82.15 H 7.81 N 6.40
Found C 82.33 H 7.61 N 6.70

5,15-[2,5-Dichloro-3,6-dimethoxybenzene-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (**75**): The reaction of 2.02 g (1.83 mmol) of **71**, 18.4 g of trichloroacetic acid and 2.92 ml (17.6 mmol) of triethyl orthoformate in 950 ml of dichloromethane under argon at 20°C for 14 h, and subsequent dehydrogenation with 1.25 g (5.53 mmol) of DDQ were carried out as in the preceding syntheses. Separation by filtration through a silica gel column (*h* = 15 cm, *d* = 6.5 cm; toluene/ethyl acetate, 9:1) and further purification of the porphyrin fraction by medium-pressure chromatography (silica gel 60, 20–45 μm; *h* = 48 cm, *d* = 3.7 cm, flow rate 40 ml/min; cyclohexane/ethyl acetate, 20:1; $R_f \approx 0.37$) followed by crystallization from dichloromethane/methanol (1:1) yielded 228 mg (13%) **75**, violet needles, m.p. >300°C. – MS (LSI-MS): *m/z* (%) = 949 (25), 948 (48), 946 (77), 945 (100) [MH^+], 944 (27) [M^+]. – ^{1}H-NMR (500 MHz, CD_2Cl_2, 303 K; assignment by COSY): δ = −2.45 (s, 2H, NH), −0.10–0.00 (m, 4H, δ-CH_2), 0.38–0.52 (m, 4H, γ-CH_2), 0.74–0.83 (m, 4H, β-CH_2), 1.64 (s, 6H, ar-OCH_3), 1.77 (t, *J* = 7.5 Hz, 12H, 2,8,12,18-CH_2CH_3), 1.90–1.98 (m, 4H, α-CH_2), 2.46 (s, 12H, 3,7,13,17-CH_3), 3.93–4.05 (m, 8H, 2,8,12,18-CH_2CH_3), 7.56 (d, *J* = 8.0 Hz, 2H, ar-3′-H), 7.64 ("t", *J* ≈ 7.8 Hz, 2H, ar-5′-H), 7.71 ("t", *J* ≈ 7.5 Hz, 2H, ar-4′-H), 8.23 (d, *J* = 7.0 Hz, 2H, ar-6′-H), 10.15 (s, 2H, 10,20-H).

$C_{60}H_{67}Cl_2N_4O_2$ Calcd. 945.4641 Found 945.4703 (MS: MH^+)

5,15-[3,6-Dimethyl-p-benzoquinone-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (**11**): To 50 mg (55 μmol) of **72** in 50 ml dichloromethane 5.0 ml (5.0 mmol) of a 1 M solution of boron tribromide in dichloromethane was added. After stirring at 20°C for 2 h the reaction mixture was cooled down to 0°C, and 50 ml of a saturated sodium carbonate solution was added; the organic phase was separated, washed with 50 ml of a saturated sodium carbonate solution and twice with 50 ml of water each, dried with magnesium sulfate and oxidized by 25 mg (0.11 mmol) DDQ (stirring at 20°C for 3 h). After washing again twice with 50 ml each of a saturated sodium carbonate solution and twice with 50 ml water each and drying with magnesium sulfate, the solvent was evaporated, and the residue was purified by medium-pressure chromatography (silica gel 60, 20–45 μm; *h* = 48 cm, *d* = 3.7 cm; cyclohexan/ethyl acetate, 16:1; flow rate 40 ml/min). The isolated violet fraction ($R_f \approx 0.39$) was crystallized from dichloromethane/methanol (1:3): 36 mg (74%) **11**, m.p. 285–287°C, for elemental analysis recrystallized from methylcyclohexane. – MS (LSI-MS): *m/z* (%) = 878 (57), 877 (92), 876 (99), 875 (100) [MH^+], 874 (81) [M^+], 873 (35). – ^{1}H NMR (500 MHz, $CDCl_3$, 303 K; assignment by COSY): δ = −2.40 (s, 2H, NH), −0.03–0.00 (m, 4H, δ-CH_2), 0.07–0.12 (m, 4H, γ-CH_2), 0.20 (s, 6H, ar-CH_3), 0.77–0.81 (m, 4H, β-CH_2), 1.79 (t, *J* = 7.6 Hz, 12H, 2,8,12,18-CH_2CH_3), 2.03–2.07 (m, 4H, α-CH_2), 2.48 (s, 12H, 3,7,13,17-CH_3), 3.97–4.08 (m, 8H, 2,8,12,18-CH_2CH_3), 7.54 (d, *J* = 7.5 Hz, 2H, ar-3′-H), 7.64 ("t", *J* ≈ 7.5 Hz, 2H, ar-5′-H), 7.71 ("t", *J* ≈ 7.5 Hz, 2H, ar-4′-H), 8.23 (d, *J* = 7.6 Hz, 2H, ar-6′-H), 10.17 (s, 2H, 10,20-H).

$C_{60}H_{66}N_4O_2$ (875.2) Calcd. C 82.34 H 7.60 N 6.40
Found C 82.37 H 7.80 N 6.30

5,15-[3,6-Dimethoxy-p-benzoquinone-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (**12**): 75 mg (80 μmol) of **73** in 50 ml of dichloromethane was stirred with 5.0 g (≈ 2 mmol) of cerium(IV) ammonium nitrate (20% on silica gel) at 20°C for 16 h. Then ammonia gas was passed through the mixture for 15 min and the separation and product isolation were carried out as in the synthesis of **6** (see above): yield 44 mg (60%) of **12**, $R_f \approx 0.40$ (silica gel, cyclohexane/ethyl acetate, 16:1), violet crystals, m.p. 295–298°C (from dichloromethane/methanol, 1:3), for elemental analysis recrystallized from methylcyclohexane. – MS (LSI-MS): *m/z* (%) = 911 (19), 910 (55), 909 (98), 908 (84), 907 (100) [MH^+], 906 (17) [M^+]. – ^{1}H NMR (500 MHz, CD_2Cl_2, 303 K; assignment by COSY): δ = −2.44 (s, 2H, NH), −0.52 to −0.49 (m, 4H, δ-CH_2), 0.27–0.31 (m, 4H, γ-CH_2), 0.79–0.85 (m, 4H, β-CH_2), 1.77 (t, *J* = 7.8 Hz, 12H, 2,8,12,18-CH_2CH_3), 1.80 (s, 6H, quin-OCH_3), 1.97–2.01 (m, 4H, α-CH_2), 2.47 (s, 12H, 3,7,13,17-CH_3), 3.93–4.04 (m, 8H, 2,8,12,18-CH_2CH_3), 7.56 (d, *J* = 7.4 Hz, 2H, ar-3′-H), 7.64 ("t", *J* ≈ 7.4 Hz, 2H, ar-5′-H), 7.72 ("t", *J* ≈ 7.4 Hz, 2H, ar-4′-H), 8.21 (d, *J* = 7.5 Hz, 2H, ar-6′-H), 10.14 (s, 2H, 10,20-H). – For an X-ray structure analysis of **12** see ref.[3].

$C_{60}H_{66}N_4O_4$ (907.2) Calcd. C 79.44 H 7.33 N 6.18
Found C 79.45 H 7.45 N 5.96

5,15-[p-Benzoquinone-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (**13**): 52.6 mg (60 μmol) of **74** in 50 ml of dichloromethane was stirred with 5.0 ml (5.0 mmol) of a 1 M solution of boron tribromide in dichloromethane at 20°C for 1.5 h; then 50 ml of a saturated sodium hydrogen carbonate solution was added to the mixture, the aqueous phase was extracted with dichloromethane, the united organic solutions were washed with 100 ml of water, dried with magnesium sulfate, and the solvent was distilled off in vacuo. The residue was dissolved in 50 ml of dichloromethane, and 27.3 g (0.12 mmol) of DDQ and 15 ml of methanol were added. Isolation and purification were performed as in the case of **11** (see above) to afford 43.7 mg (86%) of **13**, $R_f \approx 0.50$ (silica gel, cyclohexane/ethyl acetate, 16:1), violet needles (from methylcyclohexane), m.p. >350°C. – MS (LSI-MS): *m/z* (%) = 850 (43), 849 (82) [$(MH + 2)^+$], 848 (94), 847 (100) [MH^+], 846 (26) [M^+]. – ^{1}H NMR (500 MHz, CD_2Cl_2, 303 K; assignment by COSY): δ = −2.50 (s, 2H, NH), −0.05–0.04 (m, 4H, γ-CH_2), 0.25–0.30 (m, 4H, δ-CH_2), 0.85–0.95 (m, 4H, β-CH_2), 1.80 (t, *J* = 7.6 Hz, 12H, 2,8,12,18-CH_2CH_3), 1.95–2.01 (m, 4H, α-CH_2), 2.45 (s, 12H, 3,7,13,17-CH_3), 4.00–4.10 (m, 8H, 2,8,12,18-CH_2CH_3), 4.15 (s, 2H, quin-H), 7.56 (d, *J* = 7.6 Hz, 2H, ar-3′-H), 7.61–7.64 (m, 2H, ar-5′-H), 7.70–7.75 (m, 2H, ar-4′-H), 8.21 (d, *J* = 7.1 Hz, 2H, ar-6′-H), 10.21 (s, 2H, 10,20-H).

$C_{58}H_{62}N_4O_2$ (847.2) Calcd. C 82.23 H 7.38 N 6.61
Found C 82.41 H 7.46 N 6.79

5,15-[2,5-Dichloro-p-benzoquinone-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (**14**): Ether cleavage of 30.0 mg (31.6 μmol) of **75** in 30 ml of dichloromethane with 3.2 ml (3.2 mmol) of a 1 M solution of boron tribromide in dichloromethane (1 h, 20°C, under argon), subsequent oxidation with 21.5 mg (94.8 μmol) DDQ (3 h, 20°C), and product isolation in analogy to the preparation of **11** furnished 19 mg (66%) of **14**; $R_f \approx 0.40$ (silica gel, cyclohexane/ethyl acetate, 20:1); crystallization from dichloromethane/methanol (1:1) afforded violet crystals, m.p. >300°C. – MS (LSI-MS): *m/z* (%) = 921 (17), 920 (35), 919 (67), 918 (68), 917 (100) [$(MH + 2)^+$], 916 (41) [$(MH + 1)^+$], 915 (37) [MH^+], 914 (10) [M^+]. – ^{1}H NMR (500 MHz, CD_2Cl_2, 303 K; assignment by COSY): δ = −2.50 (s, 2H, NH), −0.03 to 0.01 (m, 4H, δ-CH_2), 0.16–0.25 (m, 4H, γ-CH_2), 0.80 to 0.89 (m, 4H, β-CH_2), 1.78 (t, *J* = 7.7 Hz, 12H, 2,8,12,18-CH_2CH_3), 2.02–2.06 (m, 4H, α-CH_2), 2.42 (s, 12H, 3,7,13,17-CH_3), 3.97–4.07 (m, 8H, 2,8,12,18-CH_2CH_3), 7.55 (d, *J* = 7.6 Hz, 2H, ar-3′-H), 7.63 ("t", *J* ≈ 7.4 Hz, 2H, ar-5′-H), 7.71 ("t", *J* ≈ 7.4 Hz, 2H, ar-4′-H), 8.18 (d, *J* = 7.3 Hz, 2H, ar-6′-H), 10.18 (s, 2H, 10,20-H).

$C_{58}H_{60}Cl_2N_4O_2$ Calcd. 914.4093 Found 914.4077 (MS: M^+)

5,15-[2,5-Dimethoxybenzene-1,4-diylbis[4,1-butanediyl-2,1-benzeno)]-2,3,7,8,12,13,17,18-octamethylporphyrin Zinc (**76**): 15 mg (18 μmol) of **60** and 200 mg (1.1 mmol) of zinc acetate in trichloromethane/methanol (1:1) were heated at reflux for 3 h. The solvents were distilled off in vacuo, to the residue 50 ml toluene was added, and the suspension was washed three times with 40 ml of water each, then with 40 ml of a saturated ammonium chloride solution. The organic phase was dried over magnesium sulfate, and the solvent was removed in a rotary evaporator. Crystallization of the residue from dichloromethane/acetonitrile (1:2) afforded 15 mg (96%) of **76**, m.p. 334 to 335°C, R_f (silica gel, toluene) ≈ 0.86; for elemental analysis recrystallized from dichloromethane/methanol. – MS (T_Q > 400°C): *m/z* (%) = 882 (100) [M^+, Zn isotopic pattern], 441 (10) [M^{++}]. – ^{1}H NMR (360 MHz, CD_2Cl_2 + [D_5]pyridine): δ = −0.04–0.03 (m, 4H, δ-CH_2), 0.37–0.46 (m, 4H, γ-CH_2), 0.93–1.04 (m, 4H, β-CH_2), 1.92 (s, 6H, ar-OCH_3), 1.95–2.00 (m, 4H, α-CH_2), 2.46 (s, 12H, 3,7,13,17-CH_3), 3.47 (s, 12H, 2,8,12,18-CH_3), 4.20 (s, 2H, ar-H, central ring), 7.64–7.56 (m, >4H, ar-3′,5′-H + pyridine-

H), 7.71 ("t", $J \approx 7$ Hz, 2H, ar-4′-H), 8.24 (d, $J = 7$ Hz, 2H, ar-6′-H), 10.01 (s, 2H, 10,20-H).

$C_{56}H_{58}N_4O_2Zn \cdot 2\,CH_3OH$ Calcd. C 73.44 H 7.01 N 5.91
Found C 73.39 H 7.13 N 6.02

$C_{56}H_{58}N_4O_2Zn$ Calcd. 882.3851 Found 882.3889 (MS: M^+)

5,12-[2,5-Dimethoxybenzene-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-2,3,7,8,12,13,17,18-octamethylporphyrin Magnesium (**79**): To methylmagnesium iodide prepared from 1.2 g of magnesium and 7.81 g (55 mmol) of iodomethane in 25 ml of dry ether, a solution of 15 mg (18 μmol) of **60** in 25 ml of dioxane was added within 15 min. After stirring the mixture at room temp. for 30 min, 50 ml of an aqueous ammonium chloride solution (10%) was added, and the ether phase was washed with 50 ml of water and 50 ml of a saturated ammonium chloride solution. After evaporation of the solvent the residue was crystallized from dichloromethane/methanol to yield 14 mg (94%) of **79**; R_f (silica gel, toluene/ethyl acetate, 10:1) ≈ 0.89, for elemental analysis recrystallized from dichloromethane/acetonitrile (1:1): thin, violet needles, m.p. >350°C. – MS (T_Q > 400°C): *m/z* (%) = 842 (100) [M^+] *and 421 (13)* [M^{++}] (Mg isotopic pattern). – ^{1}H NMR (360 MHz, CD_2Cl_2 + [D_5]pyridine): δ = −0.09 to −0.02 (m, 4H, δ-CH_2), 0.32–0.41 (m, 4H, γ-CH_2), 0.91–1.00 (m, 4H, β-CH_2), 1.78 (s, 6H, ar-OCH_3), 1.92–1.99 (m, 4H, α-CH_2), 2.47 (s, 12H, 3,7,13,17-CH_3), 3.49 (s, 12H, 3,8,12,18-CH_3), 4.13 (s, 2H, ar-H, central ring), 7.56 (d, $J = 7$ Hz, 2H, ar-3′-H), 7.60–7.68 (m, >2H, ar-5′-H, pyridine-H), 7.71 ("t", $J \approx 7$ Hz, 2H, ar-4′-H), 8.22 (d, $J = 7$ Hz, 2H, ar-6′-H), 10.02 (s, 2H, 10,20-H).

$C_{56}H_{58}N_4O_2Mg \cdot 2\,CH_3CN$ Calcd. C 77.86 H 6.97 N 9.08
Found C 78.14 H 6.69 N 9.28

$C_{56}H_{58}N_4O_2Mg$ Calcd. 842.4410 Found 842.4455 (MS: M^+)

5,15-[p-Benzoquinone-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-2,3,7,8,12,13,17,18-octamethylporphyrin Zinc (**77**): 15 mg (19 μmol) of **7** in 20 ml of pyridine was heated at reflux with 200 mg (1.1 mmol) of zinc acetate. After distilling off the solvent in vacuo in a rotary evaporator, the residue was suspended in toluene, washed three times with 40 ml of water each, 40 ml of a saturated ammonium chloride solution and 40 ml of saturated sodium chloride solution and then dried with magnesium sulfate. The residue, obtained by evaporation of the solvent, was crystallized from dichloromethane/methanol to afford 15.5 mg (96%) of **77**; R_f (silica, toluene) ≈ 0.50; recrystallization from *n*-hexane furnished violet needles, m.p. >350°C. – MS (T_Q > 400°C): *m/z* (%) = 854 (100) [$(M + 2)^+$], 852 (35) [M^+] (Zn isotopic pattern). – ^{1}H NMR (360 MHz, CD_2Cl_2): δ = 0.20–0.28 (m, 4H, γ-CH_2), 0.51–0.56 (m, 4H, δ-CH_2), 1.00–1.10 (m, 4H, β-CH_2), 2.13–2.18 (m, 4H, α-CH_2), 2.45 (s, 12H, 3,7,13,17-CH_3), 3.50 (s, 12H, 2,8,12,18-CH_3), 3.64 (s, 2H, quinoid H), 7.58 (dd, $J = 7.5$ and 1.2 Hz, 2H, ar-3′-H), 7.64 ("td", $J \approx 7.5$ and 1.2 Hz, 2H, ar-5′-H), 7.74 ("td", $J \approx 7.5$ and 1.2 Hz, 2H, ar-4′-H), 8.18 (dd, $J = 7.5$ and 1.2 Hz, 2H, ar-6′-H), 10.10 (s, 2H, 10,20-H).

$C_{54}H_{52}N_4O_2Zn$ Calcd. 852.3381 Found 852.3412 (MS: M^+)

5,15-[3,6-Dimethyl-p-benzoquinone-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-2,3,7,8,12,13,17,18-octamethylporphyrin Zinc (**78**): 31 mg (38 μmol) of **5** in 60 ml of trichloromethane/methanol (5:1) was heated with 500 mg (2.28 mmol) of zinc acetate dihydrate under reflux for 1.5 h. The solution was washed with 50 ml of a saturated sodium hydrogen carbonate solution and twice with 50 ml of water each, dried over magnesium sulfate, and then concentrated in a rotary evaporator. Medium-pressure chromatography of the residue [silica gel 60, 20–45 μm, $h = 48$ cm, $d = 3.7$ cm; flow rate 40 ml/min; cyclohexane/ethyl acetate (30:1)] and crystallization from trichloromethane/methanol (1:3) yielded 26 mg (78%) of **78**, R_f (silica gel, cyclohexane/ethyl acetate, 16:1) ≈ 0.29; m.p. >330°C, for analysis recrystallized from toluene/*n*-hexane (1:1). – MS (LSI-MS): *m/z* (%) = 884 (11), 883 (12), 882 (10), 881 (11) [MH^+], 880 (18) [M^+] (Zn isotopic pattern), 822 (10), 821 (32), 820 (71), 819 (100) [$(MH_3 - Zn)^+$], 818 (22) [$(MH_2 - Zn)^+$]. – ^{1}H NMR (500 MHz, $CDCl_3$, 303 K; assignment by COSY): δ = 0.08–0.15 (m, 4H, γ-CH_2), 0.24–0.27 (m, 10H, δ-CH_2 and quin-CH_3), 0.82–0.88 (m, 4H, β-CH_2), 1.92–1.95 (m, 4H, α-CH_2), 2.44 (s, 12H, 3,7,13,17-CH_3), 3.52 (s, 12H, 2,8,12,18-CH_3), 7.53 (d, $J = 7.1$ Hz, 2H, ar-3′-H), 7.62 ("t", $J \approx 7.4$ Hz, 2H, ar-5′-H), 7.72 ("t", $J \approx 7.3$ Hz, 2H, ar-4′-H), 8.23 (d, $J = 7.0$ Hz, 2H, ar-6′-H), 10.12 (s, 2H, 10,20-H).

$C_{56}H_{56}N_4O_2Zn$ (882.5) Calcd. C 76.22 H 6.40 N 6.35
Found C 76.24 H 6.60 N 6.41

5,15-[p-Benzoquinone-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-2,3,7,8,12,13,17,18-octamethylporphyrin Magnesium (**80**): From 96 mg (2.8 m equiv.) of magnesium and 561 mg (3.95 mmol) of iodomethane in 25 ml dry ether a methylmagnesium iodide solution was prepared (30 min, reflux) to which 780 mg (3.54 mmol) of 3,5-di-*tert*-butyl-4-hydroxytoluene in 20 ml of ether was added at 10°C. After 10 min 15 mg (19 μmol) of **7** in 20 ml of ether was added at 10°C, the reaction mixture was stirred for 30 min, then 50 ml of a saturated sodium dihydrogen phosphate solution was added, the ether phase was washed twice with 50 ml each of a saturated sodium dihydrogen phosphate solution, 50 ml of water and 50 ml of a saturated sodium chloride solution. After drying with magnesium sulfate and distilling off the solvent the residue was filtrated over alumina from dichloromethane/methanol (9:1) and then crystallized from dichloromethane/methanol to afford 11.7 mg (76%) of **80**, $R_f \approx 0.10$ (silica gel, toluene), violet crystals, m.p. >350°C. – MS (T_Q > 400°C): *m/z* (%) = 814 (100) [$(M + 2)^+$], 812 (50) [M^+] (Mg isotopic pattern). – ^{1}H NMR (360 MHz, CD_2Cl_2): δ = 0.03–0.12 (m, 4H, γ-CH_2), 0.54–0.58 (m, 4H, δ-CH_2), 0.95–1.04 (m, 4H, β-CH_2), 2.37–2.42 (m, 4H, α-CH_2), 2.46 (s, 12H, 3,7,13,17-CH_3), 3.51 (s, 12H, 2,8,12,18-CH_3), 3.57 (s, 2H, quin-H), 7.58–7.66 (m, 4H, ar-3′,5′-H), 7.73 ("t", $J \approx 7.5$ Hz, 2H, ar-4′-H), 8.14 (d, $J = 7.5$ Hz, 2H, ar-6′-H), 10.12 (s, 2H, 10,20-H).

$C_{54}H_{52}N_4O_2Mg$ Calcd. 812.3941 Found 812.3904 (MS: M^+)

2,3,7,8,12,13,17,18-Octamethyl-5,15-diphenylporphyrin (**81**): To 2.02 g (10 mmol) of bis(3,4-dimethyl-2-pyrrolyl)methane[26] and 1.06 g (10 mmol) of benzaldehyde in 100 ml of methanol 0.56 g (2.95 mmol) of *p*-toluenesulfonic acid was added. After stirring at room temp. for 1 h the reaction mixture was cooled in an ice-bath for 3 h. The precipitate was filtered off, washed with cold methanol and dissolved in 80 ml of tetrahydrofuran. After dehydrogenation with 2.27 g (10 mmol) of DDQ (1 h, 20°C) the solvent was evaporated, the residue extracted with boiling dichloromethane/methanol (1:1), and the insoluble porphyrin dissolved as diprotonated species by the addition of trifluoroacetic acid in dichloromethane/methanol (1:1). Regeneration of the porphyrin by the addition of triethylamine and crystallization from warm tetrachloroethane by addition of methanol yielded 2.15 g (91%) of **81** (violet microcrystals, m.p. >350°C). – MS (T_Q > 400°C): *m/z* (%) = 574 (100) [M^+], 287 (16) [M^{++}]. – ^{1}H NMR (360 MHz, CD_2Cl_2 + [D]trifluoroacetic acid): δ = −3.31 (s, >2H, NH), 2.28 (s, 12H, 3,7,13,17-CH_3), 3.27 (s, 12H, 2,8,12,18-H), 7.90–8.05 (m, 6H, 3′,4′,5′-H), 8.25 (d, $J = 7$ Hz, 4H, 2′,6′-H), 10.41 (s, 2H, 10,20-H).

$C_{40}H_{38}N_4$ (574.8) Calcd. C 83.59 H 6.66 N 9.75
Found C 83.31 H 6.48 N 9.87

2,3,7,8,12,13,17,18-Octamethyl-5,15-diphenylporphyrin Zinc (**82**): 200 mg (0.35 mmol) of **81** and 500 mg (2.73 mmol) of zinc acetate in 30 ml of pyridine were heated at reflux for 1 h, then the pyridine was distilled off, the residue was suspended in 70 ml of toluene and washed three times with 50 ml each of water, 50 ml of a saturated ammonium chloride solution and 50 ml of a saturated sodium chloride solution. The organic phase was dried with magnesium sulfate, and the solvent was evaporated in vacuo. Crystallization from dichloromethane/methanol afforded 204.5 mg (92%) of **82** (m.p. 349–352°C). – MS (T_Q > 400°C): *m/z* (%) = 636 (100) [M^+], 318 (14) [M^{++}], (Zn isotopic pattern). – ^{1}H NMR (360 MHz, CD_2Cl_2): δ = 2.44 (s, 12H, 3,7,13,17-CH_3), 3.49 (s, 12H, 2,8,12,18-CH_3), [6.88–6.98 (m, 2H, pyridine-H), 7.36 to 7.44 (m, 1H, pyridine-H), 7.45–7.57 (m, 2H, pyridine-H)], 7.68–7.82 (m, 6H, 3′,4′,5′-H), 8.05 (d, $J = 7$ Hz, 4H, 2′,6′-H), 10.12 (s, 2H, 10,20-H).

$C_{40}H_{36}N_4Zn \cdot C_5H_5N$ (717.2) Calcd. C 75.35 H 5.76 N 9.76
Found C 75.31 H 5.57 N 9.80

2,3,7,8,12,13,17,18-Octamethyl-5,15-diphenylporphyrin Magnesium (**83**): 200 mg (0.35 mmol) of **81** and 500 mg (2.15 mmol) of magnesium perchlorate were heated in 30 ml of pyridine at reflux for 1 h. Separation and isolation were performed as for the preparation of **82** to furnish 196 mg (94%) of **83**, violet needles, m.p. >350°C. – MS (T_Q > 400°C): *m/z* (%) = 596 (100) [M^+], 298 (17) [M^{++}], (Mg isotopic pattern). – ^{1}H NMR (360 MHz, CD_2Cl_2): δ = 2.44 (s, 12H, 3,7,13,17-CH_3), 3.52 (s, 12H, 2,8,12,18-CH_3), 7.70–7.85 (m, 6H, 3′,4′,5′-H), 8.05 (d, $J = 7$ Hz, 4H, 2′,6′-H), 10.18 (s, 2H, 10,20-H).

$C_{40}H_{36}N_4Mg$ (597.1) Calcd. C 80.47 H 6.08 N 9.38
Found C 80.20 H 6.31 N 9.55

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1: 142294-23-3 / **2**: 142294-24-4 / **4**: 142294-25-5 / **5**: 140188-24-5 / **6**: 140188-25-6 / **7**: 103548-74-9 / **8**: 140188-26-7 / **9**: 140208-85-1 / **11**: 142294-26-6 / **12**: 142294-27-7 / **13**: 142294-28-8 / **14**: 142294-29-9 / **15**: 142397-71-5 / **16**: 142397-72-6 / **17**: 91295-90-8 / **18**: 142397-73-7 / **19**: 142397-74-8 / **20**: 142397-75-9 / **21**: 142397-76-0 / **22**: 142397-77-1 / **24**: 142397-79-3 / **25**: 142397-80-6 / **26**: 142397-81-7 / **27**: 142397-82-8 / **29**: 142397-84-0 / **30**: 142397-85-1 / **31**: 142397-86-2 / **32**: 142397-87-3 / **33**: 142397-88-4 / **34**: 142397-89-5 / **35** (isomer 1): 142397-78-2 / **35** (isomer 2): 142436-36-0 / **35** (isomer 3): 142398-14-9 / **36**: 142397-90-8 / **37**: 142397-91-9 / **38**: 142397-92-0 / **39** (isomer 1): 142397-83-9 / **39** (isomer 2): 142436-37-1 / **39** (isomer 3): 142398-15-0 / **40**: 142397-93-1 / **41** (isomer 1): 142397-94-2 / **41** (isomer 2): 142436-38-2 / **41** (isomer 3): 142398-16-1 / **42**: 142294-30-2 / **43**: 142294-31-3 / **45**: 142294-32-4 / **46**: 142397-95-3 / **47**: 142397-96-4 / **48**: 103548-72-7 / **49**: 142397-97-5 / **50**: 142397-98-6 / **51**: 142397-99-7 / **52**: 142398-00-3 / **53**: 142398-01-4 / **54**: 103577-14-6 / **55**: 142398-02-5 / **56**: 142398-03-6 / **57**: 142398-04-7 / **58**: 142319-21-9 / **59**: 142294-33-5 / **60**: 103548-73-8 / **61**: 142294-34-6 / **62**: 142294-35-7 / **63**: 142397-70-4 / **64**: 142398-05-8 / **65**: 142398-06-9 / **66**: 142398-07-0 / **67**: 142398-08-1 / **68**: 142398-09-2 / **69**: 142398-10-5 / **70**: 142398-11-6 / **71**: 142398-12-7 / **72**: 142294-36-8 / **73**: 142319-22-0 / **74**: 142294-37-9 / **75**: 142294-38-0 / **76**: 142398-17-2 / **77**: 142398-18-3 / **78**: 142421-14-5 / **79**: 142398-19-4 / **80**: 142398-20-7 / **81**: 82542-56-1 / **82**: 142398-21-8 / **83**: 142398-22-9 / 1,4-dibromo-2,5-dimethoxy-3,6-dimethylbenzene: 52954-54-8 / methyl acrylate: [96-33-3] / 1,4-diiodo-2,3,5,6-tetramethoxybenzene: 54812-45-2 / 1,2,4,5-tetramethoxybenzene: 2441-46-5 / 1,4-dichloro-2,5-diformyl-3,6-dimethoxybenzene: 142398-13-8 / 2,5-dimethoxyterephthalaldehyde: 7310-97-6 / (1,3-dioxolan-2-ylmethyl)-triphenylphosphonium bromide: 52509-14-5 / pyrrole: [109-97-7] / 2-benzyloxycarbonyl-3,4-dimethoxypyrrole: 954-92-7 / 1,4-bis{4-[2-(bis⟨5-ethoxycarbonyl-3,4-dimethyl-2-pyrrolyl⟩methyl)phenyl]-butyl}-2,5-dimethoxybenzene: 103548-71-6 / 2-ethoxycarbonyl-3,4-dimethylpyrrole: 938-75-0 / 2-benzyloxycarbonyl-3-ethyl-4-methylpyrrole: 5866-56-8 / bis(3,4-dimethyl-2-pyrrolyl)methane: 5109-25-1 / benzaldehyde: 100-52-7 / (2-methoxycarbonylbenzyl)triphenylphosphoniumbromide: 60494-73-7