Photoinduced Electron Transfer in Porphyrin-Quinone Cyclophanes, 9[1]

Syntheses and Properties of New Quinone-Bridged Diphenyl- and Tetraphenylporphyrins

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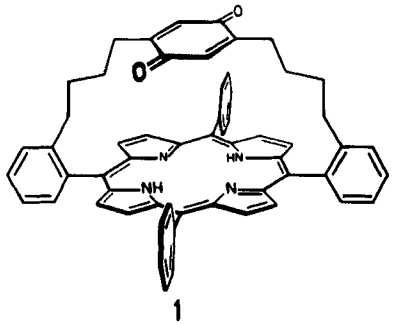
Syntheses and spectroscopic properties of the porphyrin-quinone cyclophanes **1**, **2** and **3** of which structural and/or conformational studies have recently reported[1] are described. Physical properties related to photoinduced electron-transfer reactions like redox potentials, absorption and emission spectra were determined for these compounds.

In preceding publications we reported on the syntheses and characterizations of porphyrin-quinone cyclophanes[2,3], on the determination of their structures and conformations by X-ray structure analyses and temperature-dependent ^{1}H-NMR[1], and on physical properties relating to intramolecular electron transfer[4]. Results of emission and absorption spectroscopy in the picosecond time-scale were recently published for some of these compounds by Michel-Beyerle, Heitele, Staab et al.[5] and by Elsaesser, Staab et al.[6]. The present paper deals with the syntheses and physical properties of the quinone-bridged tetraphenylporphyrin cyclophane **1** which forms a link so far missing between single-bridged quinone-diphenylporphyrin and double-bridged quinone-tetraphenylporphyrin cyclophanes. Whereas the X-ray structure analysis of **1** and ^{1}H-NMR investigations of its conformational mobility were already included in the preceding paper[1], the synthesis and some electron-transfer related properties of **1** are reported here. In addition to **1**, the tetraphenylporphyrin-dibromoquinone cyclophane **2** was prepared as a second member of this group containing a quinone unit with higher electron affinity. The corresponding dibromoquinone-bridged octamethyldiphenylporphyrin **3** complements the previously described series of porphyrin-quinone cyclophanes with varying acceptor strength[3,4]. Furthermore, the syntheses of **2** and **3** prepared the ground for the syntheses of other quinone-porphyrin cyclophanes in which quinone and porphyrin units are kept in an especially rigid orientation with well-defined donor-acceptor distances[7].



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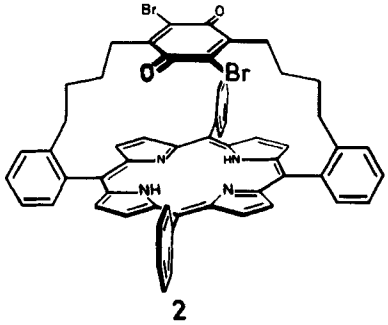

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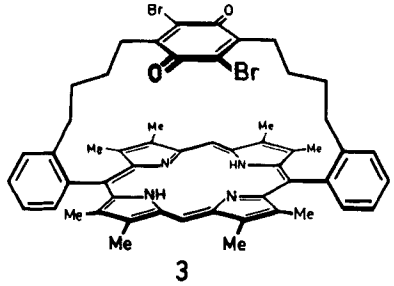

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Synthesis and Properties of 5,15-[*p*-Benzoquinone-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-10,20-diphenylporphyrin (1)

The synthesis of **1** started from the dialdehyde **4** the preparation of which was reported in the context of previous syntheses of single- and double-bridged quinone-porphyrin cyclophanes[2,3]. **4** contains the complete carbon skeleton of the cyclophane bridges including the carbon atoms which eventually become the two porphyrin methine groups by

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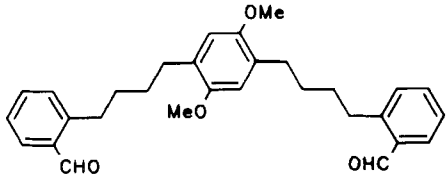
which the cyclophane bridge will be inserted into the porphyrin system; the central aromatic ring of **4** is substituted by two methoxy groups by which the aromatic unit may easily be transformed into the quinoid system wanted.



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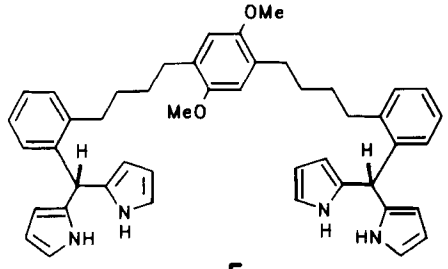

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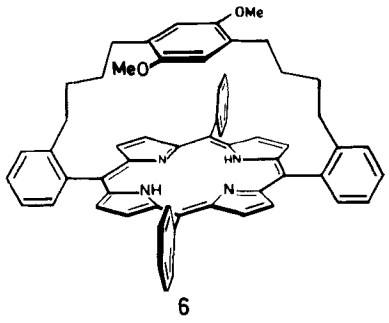
En route to the porphyrin cyclophane **1**, the preparation of the bis(di-2-pyrrolylmethyl) compound **5** from the dialdehyde **4** was first tried via the reaction of **4** with 2-ethoxycarbonylpyrrole making use of the stabilizing effect of the ethoxycarbonyl groups on the pyrrole units. From this reaction, however, three structural isomers were obtained which were separated by chromatography (silica gel, toluene/ethyl acetate) and identified on the basis of their ^{1}H-NMR spectra: In addition to the wanted compound to be expected by the reaction of **4** with all four pyrroles into their free α-positions C-5 (15% yield), the two other isomers (about 10 to 20% yield each) were formed by competing condensations of the aldehyde groups of **4** into the 4-position of one and of two 2-ethoxycarbonylpyrrole units, respectively. From the first mentioned isomer by ether cleavage and decarboxylation (sodium hydroxide, boiling ethylene glycol, under argon) **5** was obtained. Knowing the properties of **5**, an easier access to **5** was the reaction of **4** with unsubstituted pyrrole (10-fold excess of pyrrole, toluene, *p*-toluenesulfonic acid, 48% yield; for details of isolation and for analytical data see Experimental).

Condensation of **5** with benzaldehyde in propionic acid (2 h, 70°C) yielded after chromatography and recrystallization the bridged tetraphenylporphyrin **6** (violet needles, m.p. 288–300°C; 6% yield). The structure of **6** is confirmed by the ^{1}H-NMR spectrum showing the expected shifts of 5,15-bridged porphyrin cyclophanes[3] and by FAB mass spectrometry (LSI-MS) including high-resolution of the molecular ion M^+ and of MH^+.

Demethylation by boron tribromide (dichloromethane, 20 min, 20°C) and oxidation with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (dichloromethane, 20 min, 20°C) yielded **1**, purified by medium pressure chromatography (silica gel, n-hexane/ethyl acetate, 100:7.5) and crystallization from



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dichloromethane/methanol/water (10:10:1): dark-red platelets, deliquescing > 180°C; 75% yield. ^{1}H-NMR and mass spectra (LSI-MS, high-resolution) are in accordance with structure **1**. Based on X-ray structure analysis and low-temperature ^{1}H-NMR, details of the crystal structure and of the residual conformational mobility of **1** in solution were reported previously[1].

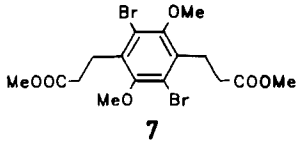
The cyclovoltammetric determination of redox potentials of **1** (vs. Ag/AgCl; dichloromethane, 0.2 M TBAP, 20°C; for further details see ref.[4]) resulted in $E^1_{ox} = 0.54$ and $E^1_{red} = -1.22 \pm 0.01$ V [referred to ferrocene $E(Fc/Fc^+) = 0$]. As compared to the corresponding single-bridged porphyrin-quinone cyclophane with an octamethyldiphenyl-substituted porphyrin as donor[4], the first oxidation potential of the porphyrin part in **1** is about 200 mV more positive, whereas the first reduction potential of the quinone unit, as expected, is only slightly different (40 mV less negative). As for the previously described systems the driving force for the charge separation by electron transfer is roughly approximated by $\Delta G'_{cs} = (E^1_{ox} - E^1_{red}) - E_{00}$ where E_{00} is the energy of excitation to the first excited singlet state of the porphyrin chromophore. With $E_{00} = 1.91$ V for the tetraphenylporphyrin unit, for **1** $\Delta G'_{cs} = -0.15$ V is obtained which is considerably less negative than for the reference compound mentioned (−0.37 V)[4], indicating a correspondingly smaller driving force for the electron transfer in **1**.

Concerning the Soret band and the Q bands the absorption spectra of **1** and **6** (10^{-5} M solution in dichloromethane) nearly coincide with the spectrum of simple 5,10,15,20-tetraphenylporphyrin (TPP)[4] [**6**: λ_{max} ($\varepsilon \cdot 10^4$ M^{-1} cm^{-1}) = 418 nm (39.6), 514 (1.7), 549 (0.6), 590 (0.5), 647 (0.3); **1**: λ_{max} ($\varepsilon \cdot 10^4 \cdot M^{-1}$ cm^{-1}) = 418 nm (38.7), 515 (1.6), 549 (0.6), 591 (0.5), 647 (0.3)]. This agreement and especially the close similarity of the quinone-bridged porphyrin **1** to its non-quinoid precursor **6** demonstrate that the bridging of the porphyrin and even the introduction of the quinone as an electron-acceptor leave the porphyrin chromophore essentially undisturbed. The more significant are the differences observed for the emission spectra for which the respective fluorescence intensities can be approximated by simple integration of the fluorescence spectra since TPP, **1** and **6** each show two emission bands at the same wavelengths (TPP: 650 and 716 nm; **1**: 650 and 717 nm; **6**: 650 and 717 nm). With reference to 1.0 for TPP the relative fluorescence intensity of **6** is 0.9 whereas that of

1 amounts to only about $0.7 \cdot 10^{-3}$ (excitation at Soret bands; 10^{-7} M solutions in dichloromethane). In fact, fluorescence life-time measurements[8] on **1** in dichloromethane show a life-time in the picosecond range [3 ps (70%), 9 ps (30%)]; in unpolar solvents like n-hexane, however, the electron-transfer is considerably slowed down resulting in fluorescence life-times in the normal order of nanoseconds. This solvent dependence is in agreement with earlier results on porphyrin-quinone cyclophanes consisting of relatively weak donor and acceptor units[4,5]. If the donorstrength of the porphyrin unit in **1** is increased by conversion into the zinc porphyrin the electron transfer competes much more efficiently with the fluorescence leading to fluorescence life-times of less than 2 ps independent of solvent polarities. These results will be further discussed in connection with other zinc porphyrin-quinone cyclophanes for which a specific electron-transfer mechanism different from a through-space transfer has to be considered[9].

5,15-[3,6-Dibromo-p-benzoquinone-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-10,20-diphenylporphyrin (2) and 5,15-[3,6-Dibromo-p-benzoquinone-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-2,3,7,8,12,13,17,18-octamethylporphyrin (3)

The syntheses of the porphyrin-dibromoquinone cyclophanes **2** and **3** follow the general strategy used for the syntheses of previously described porphyrin-quinone cyclophanes with various substituents in the 3,6-positions of the quinone systems[3]. 1,4-Bis(2-methoxycarbonylethyl)-2,5-dimethoxybenzene, prepared by twofold Heck reaction of 1,4-dibromo-2,5-dimethoxybenzene with acrylic methylester and following catalytic hydrogenation of the two carbon-carbon double-bonds, was brominated to 1,4-dibromo-2,5-dimethoxy-3,6-bis(2-methoxycarbonylethyl)benzene (**7**). From **7** the corresponding dialdehyde **8** was obtained either by sodium borohydride reduction and subsequent pyridinium chlorochromate oxidation, or in one step by reduction with diisobutyl aluminium hydride (toluene, −78°C, ≈70% yield)[10]. Wittig reaction of **8** with (2-methoxycarbonylbenzyl)triphenyl-phosphonium bromide[2] yielded 1,4-dibromo-3,6-dimethoxy-2,5-bis[4-(2-methoxycarbonylphenyl)-3-butenyl]benzene[10] from which by catalytic hydrogenation (Pd/charcoal, toluene/methanol; 90% yield) 1,4-dibromo-3,6-dimethoxy-2,5-bis[4-(2-methoxycarbonylphenyl)butyl]benzene (**9**) was obtained.



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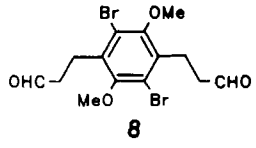

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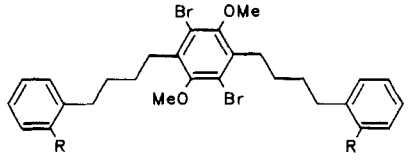


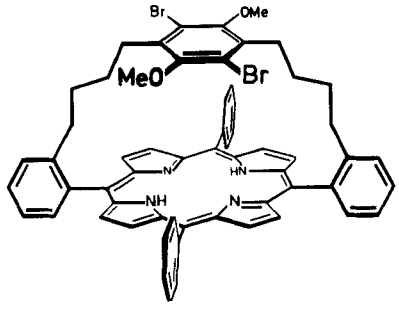
9 : R = COOMe
10 : R = CH_2OH
11 : R = CHO

Reduction of the dicarboxylic ester **9** by lithium tetrahydroborate (tetrahydrofuran, 24 h reflux; 93% yield) to the bis(hydroxymethyl) compound **10** and subsequent oxidation with barium manganate (dichloromethane, 1 h reflux; 84% yield) resulted in the formation of the dialdehyde **11** which, in analogy to the syntheses of all single- and double-bridged porphyrin cyclophanes, is the key intermediate for building up the porphyrin units of the porphyrin-dibromoquinone cyclophanes **2** and **3**. In analogy to the preparation of **1** from **4**, the dialdehyde **11** was reacted with excess pyrrole in toluene in the presence of p-toluenesulfonic acid (5 h, reflux) to the bis(di-2-pyrrolyl) derivative which was isolated by chromatography (silica gel, toluene/ethyl acetate). Reaction with benzaldehyde in propionic acid (2 h, 90 → 140°C) yielded the porphyrin cyclophane **12** (2.3%, m.p. 274°C; for details and spectroscopic data see Experimental).

Cleavage of the methoxy groups of **12** by boron tribromide in dichloromethane and oxidation of the hydroquinone formed by 2,3-dichloro-5,6-dicyano-p-benzoquinone yielded after chromatographic purification the porphyrin-quinone cyclophane **2** (41%, m.p. 237°C), fully characterized by ^{1}H-NMR, high resolution mass spectrum and other spectroscopic data (see Experimental). The Vis-absorption spectra of **2** and its non-quinoid precursor **12** again are very similar [**12**: λ_{max} = 420 nm, 516, 550, 591, 648; **2**: λ_{max} = 419 nm, 514, 548, 591, 647 nm, in dichloromethane]. On excitation at the Soret band (420 nm) the fluorescence bands appear for **12** at 653 and 721 nm and for **2** at 652 and 719 nm (in toluene). The relative fluorescence intensity of **2** as referred to **12**, however, is only about $7 \cdot 10^{-4}$ (in toluene) indicating for **2** an effective competition of the electron-transfer reaction with the fluorescence emission. Fluorescence life-time measurements by time-resolved emission spectroscopy are not yet available for **2**.

For the preparation of porphyrin cyclophane **13** the dialdehyde **11** was treated with 2-benzoxycarbonyl-3,4-dimethylpyrrole (hydrochloric acid, ethanol, 4 h reflux) to give the bis(dipyrrolylmethyl) derivative **14** (98% yield) which by catalytic hydrogenation (Pd/C, tetrahydrofuran, 1 h, 20°C) yielded **15** (97% yield). The cyclization to **13** was achieved in analogy to ref.[3] by condensation with triethyl orthoformate in the presence of trichloroacetic acid (dichloromethane, 13.5 h, 20°C) and subsequent dehydrogenation with 2,3-dichloro-5,6-dicyano-p-benzoquinone (dichloromethane, 2 h, 20°C). After chromatography (silica gel, toluene/ethyl acetate, 10:1) and recrystallization from dichloromethane/methanol the porphyrin cyclophane **13** was obtained in the remarkably good yield of 22%; the yield is strongly dependent on details of reaction and isolation conditions as mentioned below. Analytical data (elemental analysis, mass spectra, Vis-spectra) are fully in accordance with the suggested structure, as is especially the ^{1}H-NMR spectrum which shows the very typical shifts due to the ring-current effect of porphyrin (see Experimental).

Ether cleavage of the methoxy groups by boron tribromide (dichloromethane, 1 h, 20°C) and oxidation of the hydroquinone formed, followed by chromatographic separ-



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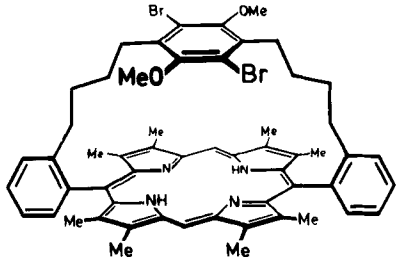

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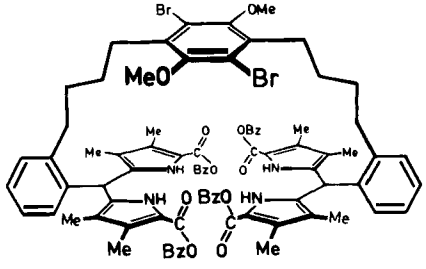

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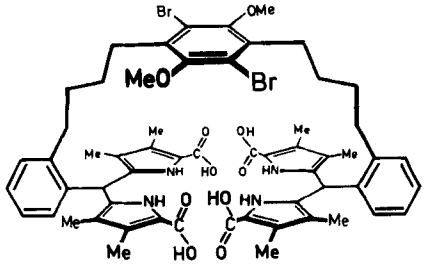

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ation and recrystallization from dichloromethane/methanol led in 53% yield to the porphyrin-quinone cyclophane **3** (darkred-violet crystals, dec. >260°C). The structure of **3** is clearly proven by analytical data like mass spectra (LSI-MS) and ^{1}H-NMR (500 MHz, assignment by COSY). Whereas the absorption spectrum of **3** corresponds very closely to that of **13**, the extremely strong fluorescence quenching of **3** indicates a high electron-transfer rate. Fluorescence life-time measurements by time-resolved emission spectroscopy are in progress[8].

Experimental

Melting points: Büchi SMP 512, Bock Monoskop (m.p. >240°C). – IR: Beckmann IR-4240 (KBr) and Perkin-Elmer FT-IR 1760X. – UV/Vis: Varian Cary 2300. – Fluorescence: Fluorolog F112, Spex. – MS: DuPont CEC 21-492, Finigan MAT 212 (70 eV), FAB spectra (LSI-MS positive, 3-nitrobenzylic alcohol/1% trifluoroacetic acid): VG ZAB 2E/70SE. – ^{1}H-NMR: Bruker HX 360 and AM 500. – Microanalysis: Elemental Analyzer EA 1106 and 1108, Carlo Erba. – Analytical TLC: DC Micro Cards Polygram SIL G/UV$_{254}$ Macherey-Nagel. – CC: Silica gel 63–200 μ, ICN Biomedicals. – MPLC: Abimed (h = 48 cm, d = 3.7 cm), Silica gel 60 (20–45 μm), flow rate 40 ml/min. – HPLC: Abimed, HPLC-column 20 × 2 cm, Macherey-Nagel, flow rate 15 ml/min.

1,4-Bis{4-[2-(bis⟨2-pyrrolyl⟩methyl)phenyl]butyl}-2,5-dimethoxybenzene (**5**): Under argon 2.5 g (5.5 mmol) of dialdehyde **4**[2,3] and 3.66 g (54.6 mmol) of pyrrole in 120 ml of toluene were heated in the presence of 0.5 g of *p*-toluenesulfonic acid monohydrate to reflux for 4 h. After cooling the solvent was distilled off and the product was purified by flash-chromatography on silica gel (d = 5 cm, h = 5 cm) with toluene/ethyl acetate (15:1). By evaporation of the solvents from the product fraction, dissolving the residue in dichloromethane and distilling off the solvent in vacuo, 1.8 g (48%) of **5** were obtained as glassy foam deliquescing above 95°C; (in solution **5** decomposes rapidly at room temperature). – ^{1}H-NMR (360 MHz, CD_2Cl_2): δ = 1.50–1.70 (m, 8H, β- and γ-CH_2), 2.55–2.70 m, 8H, α- and γ-CH_2), 3.69 (s, 6H, OCH_3), 5.63 (s, 2H, methine-H), 5.75–5.80 (m, 4H, pyr-4-H), 6.07 ('dd', $J \approx$ 5.6 and 2.6 Hz, 4H, pyr-5-H), 6.61 (s, 2H, ar-2,5-H), 6.68–6.75 (m, 4H, pyr-3-H), 6.98 ('d', $J \approx$ 7.5 Hz, 2H, phen-6-H), 7.10–7.25 (m, 6H, phen-H), 7.91 (br. s, 4H, NH). – MS: *m/z* (%) = 690 (100) [M$^+$], 623 (58), 168 (69) a.o. – $C_{46}H_{50}N_4O_2$: calcd. 690.3934, found 690.4039 (MS: M$^+$).

5,15-[2,5-Dimethoxybenzene-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-10,20-diphenylporphyrin (**6**): 300 mg (0.43 mmol) of **5** and 184 mg (1.74 mmol) of benzaldehyde in 30 ml of propionic acid in analogy to ref.[11] were slowly heated to 70°C and kept at this temperature under stirring for 2 h. After addition of 300 ml of dichloromethane the reaction mixture was washed twice with 300 ml of water each and then with 300 ml of a saturated aqueous solution of sodium hydrogen carbonate. The organic phase was dried with magnesium sulfate, the solvent was evaporated, and the residue was chromatographed on silica gel (d = 6 cm, h = 18.5 cm) from toluene/ethyl acetate (10:1). From the first fraction (ca. 150 ml) the solvents were evaporated, and the product was further purified by medium pressure chromatography (MPLC conditions see above; *n*-hexane/ethyl acetate, 100:7.5). The first fraction ($R_f \approx$ 0.45) after evaporation of the solvents was crystallized from dichloromethane/methanol/water (10:10:1): 21 mg (6%) violet crystals of m.p. 288–300°C. – ^{1}H-NMR (500 MHz, CD_2Cl_2): δ = –2.87 (s, 2H, NH), 0.02–0.05 (m, 4H, δ-CH_2), 0.39–0.42 (m, 4H, γ-CH_2), 0.77–0.83 (m, 4H, β-CH_2), 1.94 (s, 6H, OCH_3), 2.06–2.09 (m, 4H, α-CH_2), 4.24 (s, 2H, ar-2,5-H), 7.53 ('d', $J \approx$ 7.9, 2H, phen-3′-H), 7.57–7.59 (m, 2H, phen-5′-H), 7.67–7.72 (m, 8H, phen-4′,3″,4″,5″-H), 8.02 ('d', $J \approx$ 7.0 Hz, 2H, phen-6′-H), 8.06 ('d', $J \approx$ 7.1 Hz, 2H, phen-2″- or 6″-H), 8.27 ('d', $J \approx$ 6.6 Hz, 2H, phen-2″ or 6″-H), 8.64 (d, J = 4.7 Hz, 4H, pyr-H), 8.74 (d, $J \approx$ 4.6 Hz, 4H, pyr-H). – MS (LSI-MS): *m/z* (%) = 860 (85) [M$^+$], 862 (52). – $C_{60}H_{52}N_4O_2$: calcd. 860.4090, found 860.404 (LSI-MS: M$^+$); calcd. 861.4168, found 861.4135 (LSI-MS: MH$^+$).

5,15-[p-Benzoquinone-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-10,20-diphenylporphyrin (**1**): To 50 mg (58 μmol) of **6** in 20 ml of dichloromethane a solution of 0.2 ml boron tribromide in 5 ml of

dichloromethane was added, and the reaction mixture was stirred at 20°C for 20 min. After addition of 300 ml of dichloromethane the organic phase was twice extracted with 150 ml each of saturated aqueous sodium hydrogen carbonate solution. The organic phase was dried over magnesium sulfate and the solvent was evaporated. The residue was dissolved in 10 ml of dichloromethane and stirred for 20 min at 20°C with 100 mg of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ). The reaction mixture was again diluted by addition of 300 ml dichloromethane, and this solution was extracted twice with 300 ml of water each with 200 ml of saturated aqueous sodium hydrogen carbonate solution. After drying the organic phase over magnesium sulfate and evaporation of the solvent the violet residue was further purified by MPLC (conditions see above); n-hexane/ethyl acetate (100:7.5). The violet residue obtained was crystallized from dichloromethane/methanol/water (10:10:1): 36.2 mg (75%) as slowly deliquescent dark-red platelets (dec. > 180°C) which were suited for an X-rax analysis. For fluorescence measurements **1** was further purified by high-pressure chromatography (silica gel 100 A/7 μm; n-hexane/ethylacetate, 100:7.5). – ^{1}H-NMR (500 MHz, CD_2Cl_2): δ = −2.84 (s, 2H, NH), 0.07−0.11 (m, 4H, δ-CH_2), 0.22−0.25 (m, 4H, γ-CH_2), 0.80−0.86 (m, 4H, β-CH_2), 2.31−2.34 (m, 4H, α-CH_2), 3.97 (s, 2H, quin-2,5-H), 7.54−7.59 (m, 4H, ar-3′,5′-H), 7.65−7.80 (m, 8H, ar-4′-H, phen-3″,4″,5″-H), 8.10−8.12 (m, 4H, ar-6′-H, phen-2″-H), 8.52 ('d', $J \approx 6.8$ Hz, 2H), phen-6″-H), 8.67 (d, $J = 4.7$ Hz, 4H, pyr-H), 8.80 (d, $J = 4.7$ Hz, 4H, pyr-H). – MS (LSI-MS): *m/z* (%) = 833 (93) [(MH + 2)$^+$], 832 (94) [(MH + 1)$^+$], 831 (100) [MH$^+$], 830 (53) [M$^+$]. – For the X-ray structure analysis of **1** see lit.[1]. – $C_{58}H_{46}N_4O_2$: calcd. 830.3621, found 830.3582 (LSI-MS: M$^+$); calcd. 831.3699, found 831.3643 (LSI-MS: MH$^+$).

1,4-Dibromo-2,5-dimethoxy-3,6-bis(2-methoxycarbonylethyl)benzene (**7**)[10]: To 20.0 g (64.5 mmol) of 1,4-dimethoxy-2,5-bis(2-methoxycarbonylethyl)benzene in 120 ml of dichloromethane in the presence of 1.0 g of iodine a solution of 10 ml (195 mmol) of bromine in 80 ml of dichloromethane were added within 3 min. The reaction mixture was heated for 30 min to reflux and then was given into 300 ml of water under stirring. After separation of the aqueous phase 150 ml of a saturated sodium sulfite solution was added to the organic solution. The organic phase was washed with 200 ml of water, 200 ml of saturated aqueous sodium hydrogen carbonate solution and then again with 200 ml of water. After drying over magnesium sulfate the solvent was evaporated, and the crystalline residue was recrystallized from 600 ml of methanol: 19.9 g (66%) **7**, white needles of m.p. 141−142°C. – ^{1}H-NMR (360 MHz, $CDCl_3$): δ = 2.54−2.60 (mc, 4H), 3.13−3.19 (mc, 4H), 3.72 (s, 6H), 3.82 (s, 6H). – MS: *m/z* (%) = 466 (21) [M$^+$], 387 (100) [(M−Br)$^+$]. – $C_{16}H_{20}Br_2O_6$ (468.14): calcd. C 41.05, H 4.31, Br 34.14; found C 40.92, H 4.33, Br 34.28.

1,4-Dibromo-2,5-bis(3-hydroxypropyl)-3,6-dimethoxybenzene: To 25.0 g (53.4 mmol) of **7** in 250 ml of tetrahydrofuran 10.1 g (267 mmol) of sodium borohydride were added, and at 80−90°C under argon within 3 h 70 ml of methanol were dropped to this suspension. After 30 min stirring at this temperature the reaction mixture was cooled to room temperature, and 150 ml of water were added. Tetrahydrofuran was distilled off in vacuo; the resulting suspension was poured into 500 ml of water. The white precipitate formed was filtered off and dried in a desiccator. By recrystallization from 300 ml of ethanol 19.1 g (87%) of the bis(hydroxypropyl) compound of m.p. 132−133°C was obtained. $R_f \approx 0.30$ (silica gel, dichloromethane/methanol, 95:5). – ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.86 (mc, 4H), 1.95 (t, $J = 6.5$ Hz, 2H), 2.95 ('t', $J \approx 7.5$ Hz, 4H), 3.60−3.63 (m, 4H), 3.83 (s, 6H). – MS: *m/z* (%) = 410 (100) [M$^+$]. – $C_{14}H_{20}Br_2O_4$ (412.12): calcd. C 40.87, H 4.89, Br 38.78; found C 40.72, H 5.04, Br 38.57.

1,4-Dibromo-2,5-bis(2-formylethyl)-3,6-dimethoxybenzene (**8**): To a solution of 15.0 g (36.4 mmol) of the aforementioned bis(hydroxypropyl) compound in 550 ml of dichloromethane 20 g each of celite and magnesium sulfate as well as 23.5 g (109 mmol) of pyridinium chlorochromate were added. The reaction mixture was stirred at 20°C for 3 h and then filtered on silica gel ($h = 17$ cm, $d = 9.5$ cm; dichloromethane/diethylether, 1:1; $R_f \approx 0.75$). Evaporation of the solvents from the eluate yielded 12.7 g (85%), m.p. 158−159°C (from acetone). – $C_{14}H_{16}Br_2O_4$ (408.09): calcd. C 41.21, H 3.95, Br 39.16; found C 41.41, H 3.91, Br 39.04.

1,4-Dibromo-3,6-dimethoxy-2,5-bis[4-(2-methoxycarbonylphenyl)3-butenyl]-benzene: 33.5 g (68.2 mmol) of (2-methoxycarbonylbenzyl)triphenyl-phosphonium bromide[2] was under argon added to a solution of 1.57 g (68.3 mmol) of sodium in 200 ml of methanol. After 30 min stirring at 20°C, 6.96 g (17.1 mmol) of **8** in 170 ml of tetrahydrofuran were dropped to the solution in 90 min. The reaction mixture was stirred for 12 h, then poured into 600 ml of water and extracted five times with 150 ml of trichloromethane. The organic phase was dried over magnesium sulfate, and the solvent was distilled off in vacuo. The residue was chromatographed from n-hexane/ethyl acetate (5:1) on silica gel ($h = 24$ cm, $d = 9$ cm): 10.7 g (93%) of an oily cis-trans mixture which crystallized from n-hexane/ethyl acetate (4:1). Recrystallization from methanol yielded the pure cis-isomer, m.p. 106°C. – ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.31−2.36 (m, 4H), 2.84−2.88 (m, 4H), 3.66 (s, 6H, OCH_3), 3.88 (s, 6H, $COOCH_3$), 5.78−5.83 (m, 2H, −C*H*=CH-ar), 6.89 (d, $J \approx 11.5$ Hz, 2H, −CH=C*H*-ar), 7.23 ('d', $J \approx 7.6$ Hz, 2H, ar-6-H),7.29 ('t', $J \approx 7.6$ Hz, 2H, ar-4-H), 7.43 ('t', $J \approx 7.6$ Hz, 2H, ar-5-H), 7.89 ('d', $J \approx 7.6$ Hz, 2H, ar-3′-H). – $C_{32}H_{32}Br_2O_6$ (672.41): calcd. C 57.16, H 4.80, Br 23.77; found C 57.05, H 4.81, Br 23.57.

1,4-Dibromo-3,6-dimethoxy-2,5-bis[4-(2-methoxy-carbonylphenyl)butyl]benzene (**9**): In analogy to previously synthesized 1,4-disubstituted 3,6-dimethoxy-2,5-bis[4-(2-methoxycarbonylphenyl)butyl]benzenes[4] **9** was obtained from 1,4-dibromo-3,6-dimethoxy-2,5-bis[4-(2-methoxycarbonylphenyl)-3-butenyl]benzene by catalytic hydrogenation on palladium catalyst (10% on charcoal) in methanol/toluene/ethyl acetate (2:1:1) in 90% yield. Recrystallization from ethanol yielded colourless needles of m.p. 188−120°C. – ^{1}H-NMR (360 MHz, $CDCl_3$; COSY assignment): δ = 1.58−1.75 (m, 8H, γ- and β-CH_2), 2.84 ('t', $J \approx 7.8$ Hz, 4H, α-CH_2), 3.01 ('t', $J \approx 7.6$ Hz, 4H, δ-CH_2), 3.79 (s, 6H. OCH_3), 3.89 (s, 6H, $COOCH_3$), 7.21−7.28 (m, 4H-, ar-4- and 6-H), 7.40 ('dt', $J \approx 1.3$ and 7.5 Hz, 2H, ar-5-H), 7.85 (dd, $J = 1.3$ and 7.8 Hz, 2H, ar-3-H). – $C_{32}H_{36}Br_2O_6$ (676.42): calcd. C 56.82, H 5.36, Br 23.62, found C 56.82, H 5.49, Br 23.59.

1,4-Dibromo-3,6-dimethoxy-2,5-bis[4-(2-hydroxymethylphenyl)butyl]benzene (**10**): Under argon to a solution of 4.7 g (6.95 mmol) of **9** in 200 ml of tetrahydrofuran 870 mg (40 mmol) of lithium tetrahydroborate were added. After 6 h reflux boiling further 870 mg (40 mmol) of lithium tetrahydroborate were added, and the boiling was continued for 18 h. To the reaction mixture cooled to room temperature 5 ml of water were added, and the solvent was distilled off in vacuo. The solution of the residue in 300 ml of dichloromethane was washed twice with 300 ml of diluted hydrochloric acid each and then with 300 ml of water. From the organic phase, after drying over magnesium sulfate, the solvent was evaporated, and the remaining colourless oil was dissolved in warm toluene from which on cooling 4.0 g (93%) of **10** were obtained as white needles; m.p. 113−115°C (recrystallized from ethyl acetate).

– ^{1}H-NMR (360 MHz, $CDCl_3$): δ = 1.54 ('t', H/D exchange, 2H, OH), 1.65–1.75 (m, 8H, β- and γ-CH_2), 2.74 ('t', $J \approx 7.5$ Hz, 4H, α-CH_2), 2.84 ('t', $J \approx 7.6$ Hz, 4H, δ-CH_2), 3.78 (s, 6H, OCH_3), 4.73 ('d', $J \approx 5.3$ Hz, 4H, $-CH_2OH$), 7.19–7.25 (m, 6H, ar-4,5,6-H), 7.36 ('d', $J \approx 6.7$ Hz, 2H, ar-3-H). – $C_{30}H_{36}Br_2O_4$ (620.42): calcd. C 58.08, H 5.85, Br 25.76; found C 58.18, H 5.89, Br 25.85.

1,4-Dibromo-3,6-dimethoxy-2,5-bis[4-(2-formylphenyl)butyl]-benzene (**11**): 3.1 g (5 mmol) of **10** and 12.83 g (50 mmol) of barium manganate in 250 ml of dichloromethane were heated under reflux. The oxidation was complete after 1 h (TLC-control); barium manganate was filtered off, and the filtrate was concentrated by evaporating the solvent. The yellow oil obtained was crystallized by adding a small amount of ether and then a layer of *n*-hexane: 2.6 g (84%) of **11**, colourless needles of m.p. 86–88°C. – ^{1}H-NMR (360 MHz, $CDCl_3$): δ = 1.64–1.77 (m, 8H, β- and γ-CH_2), 2.84 ('t', $J \approx 7.7$ Hz, 4H, α-CH_2), 3.09 ('t', $J \approx 7.5$ Hz, 4H, δ-CH_2), 3.79 (s, 6H, OCH_3), 7.28–7.38 (m, 4H, ar-4-H), 7.50 ('dt', $J \approx 1.4$ and 7.4 Hz, 2H, ar-H), 7.83 ('dd', $J \approx 1$ and 8 Hz, 2H, ar-H), 10.29 (s, 2H, CHO). – $C_{30}H_{32}Br_2O_4$ (616.39): calcd. C 58.46, H 5.23, Br 25.93; found C 58.57, H 5.18, Br 26.05.

1,4-Dibromo-3,6-dimethoxy-2,5-bis{4-[2-(bis⟨5-benzyloxy-carbonyl-3,4-dimethyl-2-pyrrolyl⟩methyl)phenyl]butyl}benzene (**14**): 1.85 g (3 mmol) of **11** and 3.44 g (15 mmol) of 2-benzyloxycarbonyl-3,4-dimethylpyrrole in 50 ml ethanol after addition of 0.5 ml of concentrated hydrochloric acid were refluxed for 4 h. To the reaction mixture at room temperature 100 ml of dichloromethane and florisil (magnesium silicate gel) were added, and the solvents were distilled off in a rotary evaporator. By chromatography on silica gel first the excess of 2-benzyloxycarbonyl-3,4-dimethylpyrrole was separated with toluene/ethyl acetate (100:1), and then with toluene/ethyl acetate (10:1) **14** ($R_f \approx 0.47$) was isolated. Evaporation of the solvents yielded 4.4 g (98%) of **14** as foamy solid (m.p. 86–98°C) which gave correct elemental analyses and were used without further purification for the preparation of **15**. – $C_{86}H_{88}Br_2N_4O_{10}$ (1497.48): calcd. C 68.98, H 5.92, N 3.74, Br 10.67; found C 69.24, H 5.93, N 3.77, Br 10.46.

1,4-Dibromo-3,6-dimethoxy-2,5-bis{4-[2-(bis⟨5-carboxy-3,4-dimethyl-2-pyrrolyl⟩methyl)phenyl]butyl}benzene (**15**): 4.2 g (2.8 mmol) of **14** in 150 ml of tetrahydrofuran were hydrogenated in the presence of 1.5 g palladium catalyst (10% on charcoal). After 1 h the catalyst was filtered off, and from the filtrate the solvent was evaporated: 3.1 g (97%) of **15**, m.p. 148–150°C. – ^{1}H-NMR (500 MHz, [D$_6$]DMSO): δ = 1.36–1.40 (m, 4H), 1.47–1.50 (m, 4H), 1.75 (s, 12H), 2.16 (s, 12H), 2.46–2.50 (m, 4H), 2.69 ('t', $J \approx 7.5$ Hz, 4H), 3.69 (s, 6H), 5.72 (s, 2H), 7.02–7.17 (m, 8H), 10.44 (s, 4H), 11.99 (s, 4H) [the last two signals show H/D exchange and, thus, are assigned to NH- and COOH-protons, respectively]. – MS (LSI-MS): *m/z* (%) = 1137 (33), 1136 (60), 1135 (63) [MH^+, ^{79}Br], 1134 (100) [M^+, ^{79}Br].

5,15-[2,5-Dibromo-3,6-dimethoxybenzene-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-2,3,7,8,12,13,17,18-octamethylporphyrin (**13**): In analogy to the syntheses of bridged porphyrins described in lit.[3] 40 g of magnesium sulfate in 2 l of dichloromethane were stirred at room temperature under argon for 10 min. Then 2.27 g (2 mmol) of **14**, 40 g of trichloroacetic acid and 3.32 ml (20 mmol) of triethyl orthoformate were added within 15 s. After 13.5 h stirring at room temp. 4 g of sodium acetate and 1.36 g (6 mmol) of DDQ were added. The reaction mixture was stirred for further 2 h at room temp., then 1 l of a 10% aqueous solution of sodium carbonate was added, and after stirring for 15 min the organic phase was separated, washed with 10% aqueous sodium carbonate solution, with saturated sodium chloride solution and twice with water, and dried over magnesium sulfate. After filtration 50 ml of toluene were added and the reaction mixture was concentrated to a volume of 100 ml by evaporation in vacuo. For the separation of oligomers and polymers the solution was rapidly chromatographed on silica gel (h = 20 cm, d = 6.5 cm) from toluene/ethyl acetate (10:1). The porphyrin-containing fractions were concentrated and purified further by flash-chromatography on silica gel from toluene/ethyl acetate (40:1). The fraction with $R_f \approx 0.40$ was recrystallized from dichloromethane/methanol: 430 mg (22%) of **13**, violet crystals, dec. >200°C. – ^{1}H-NMR (500 MHz, CD_2Cl_2, COSY assignment): δ = –2.41 (s, 2H, NH), 0.17 (mc, 4H, δ-CH_2), 0.41 ('t', $J \approx 7.1$ Hz, 4H, γ-CH_2), 0.78 ('t', $J \approx 8.2$ Hz, 4H, β-CH_2), 1.64 (s, 6H, OCH_3), 1.92–1.95 (m, 4H, α-CH_2), 2.43 (s, 12H, 3,7,13,17-pyr-CH_3), 3.50 (s, 12H, 2,8,12,18-pyr-CH_3), 7.55 ('d', $J \approx 7.2$ Hz, 2H, ar-3'-H), 7.64 ('dt', $J \approx 1.3$ and 7.5 Hz, 2H, ar-5'-H), 7.71 ('dt', $J \approx 1.4$ and 7.7 Hz, 2H, ar-4'-H), 8.21 (dd, J = 1.1 and 7.3 Hz, 2H, ar-6'-H), 10.13 (s, 2H, 10, 20-H). – MS (LSI-MS): *m/z* (%) = 982 (31), 981 (62), 980 (67), 979 (100), 978 (48), 977 (50) [MH^+, ^{79}Br], 976 (10) [M^+, ^{79}Br]. – $C_{56}H_{58}Br_2N_4O_2$ (978.9): calcd. C 68.71, H 5.97, N 5.72, Br 16.33; found C 68.87, H 6.05, N 5.48, Br 16.17.

5,15-[3,6-Dibromo-p-benzoquinone-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-2,3,7,8,12,13,17,18-octamethylporphyrin (**3**): To 38 mg (39 μmol) of **13** in 50 ml of dry dichloromethane 3.9 ml (3.9 mmol) of a 1 M solution of borontribromide in dichloromethane were added at room temp., and the reaction mixture was stirred at 0°C for about 5 min until no starting material was present anymore (TLC: silica gel, toluene/ethyl acetate, 30:1). Then 100 ml of dichloromethane were added, the solution was washed with saturated aqueous sodium hydrogen carbonate solution and three times with water. After drying over magnesium sulfate and concentration to a volume of 50 ml, 100 mg (0.44 mmol) of DDQ were added, the reaction mixture was stirred for 20 min at room temp., then diluted with dichloromethane to a volume of about 200 ml, and washed with 100 ml saturated sodium hydrogen carbonate solution, with 100 ml saturated sodium chloride solution and twice with 100 ml each of water. After drying over magnesium sulfate and filtration the filtrate was concentrated on a rotary evaporator and chromatographed on silica gel from toluene/ethyl acetate (40:1). The porphyrin fraction ($R_f \approx 0.5$) was crystallized from dichloromethane/methanol; 19.4 mg (53%) of **3** as red-violet microcrystals, dec. >260°C. – ^{1}H-NMR (500 MHz, CD_2Cl_2, COSY assignment): δ = –2.45 (s, 2H, NH), –0.11 (t, J = 7.2 Hz, 4H, δ-CH_2), 0.22–0.28 (m, 4H, γ-CH_2), 0.83–0.89 (m, 4H, β-CH_2), 2.08–2.11 (m, 4H, α-CH_2), 2.44 (s, 12H, 3,7,13,17-pyr-CH_3), 3.52 (s, 12H, 2,8,12,18-pyr-CH_3), 7.55 ('d', $J \approx 7.1$ Hz, 2H, ar-3'-H), 7.62 ('t', $J \approx 7.5$ Hz, 2H, ar-5'-H), 7.71 ('dt', $J \approx 1.6$ and 7.5 Hz, 2H, ar-4'-H), 8.13 (dd, J = 1.6 and 7.2 Hz, 2H, ar-6'-H), 10.15 (s, 2H, 10,20-H). – MS (LSI-MS): *m/z* (%) = 952 (63), 951 (100), 949 (69), 948 (18) [MH^+, ^{79}Br], 947 (14) [M^+, ^{79}Br]; calcd. for $C_{54}H_{52}Br_2N_4O_2$: 948.84.

5,15-[2,5-Dibromo-3,6-dimethoxybenzene-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-10,20-diphenylporphyrin (**12**): In analogy to the synthesis of **5** and **6**, 0.62 g (1 mmol) of the dialdehyde **11** and 1.00 g (14.9 mmol) of pyrrole in 60 ml of toluene in the presence of 380 mg (2.22 mmol) of p-toluenesulfonic acid monohydrate were heated under reflux for 5 h. After addition of florisil and distilling off the solvent chromatography (silica gel, toluene/ethyl acetate, 20:1, $R_f \approx 0.34$) 650 mg of the double bis(2-pyrrolylmethyl) derivative were obtained which, without further characterization, were reacted with 560 mg (5.82 mmol) of benzaldehyde in the presence of 40 ml of propionic acid by stirring 30 min at room temperature, 1 h at 90°C and then 1 h at 140–150°C. After cooling and addition

of 400 ml of dichloromethane the solution was washed twice with 200 ml of water, 200 ml of saturated aqueous sodium hydrogen carbonate solution and then again with 200 ml of water. The organic phase was dried over magnesium sulfate, and the solvent was removed in a rotary evaporator. For the separation from polymers flash column chromatography (silica gel, toluene/ethylacetate, 20:1, $R_f \approx 0.42$) was used. Further purification was achieved by HPLC (see above) from cyclohexane/ethyl acetate (25:1, $R_f \approx 0.20$) and crystallization from dichloromethane/methanol: 23.9 mg (2.3%) of **12**, violet cubes, m.p. 274°C. – ^{1}H-NMR (500 MHz, CD_2Cl_2, COSY assignment): δ = −2.82 (s, 2H, NH), 0.16 (m, 4H, δ-CH_2), 0.47−0.51 (m, 4H, γ-CH_2), 0.74−0.80 (m, 4H, β-CH_2), 2.08 (s, 6H, OCH_3), 2.15 (t, J = 8.1 Hz, 4H, α-CH_2), 7.56 ('d', $J \approx 8.1$ Hz, 2H, ar-3′-H), 7.62 ('t', $J \approx 7.4$ Hz, 2H, ar-5′-H), 7.70−7.73 (m, 4H, ar-4′-H and phen-3″-H or phen-4″-H or phen-5″-H), 7.77−7.85 (m, 4H, phen-3″-H or phen-4′-H or phen-5″-H), 7.99 ('d' broad, $J \approx 6.8$ Hz, 2H, phen-2″-H or phen-6″-H), 8.25 ('d', $J \approx 7.2$ Hz, 2H, ar-6′-H), 8.47 ('d' broad, $J \approx 7.0$ Hz, 2H, phen-2″-H or phen-6″-H), 8.69 (d, J = 4.6 Hz, 4H, pyr-H), 8.79 (d, J = 4.6 Hz, 4H, pyr-H). – MS (LSI-MS): *m/z* (%) = 1021 (59), 1020 (83), 1019 (100), 1018 (91), 1017 (52) [MH^+, ^{79}Br], 1016 (35) [M^+, ^{79}Br]; isotopic pattern of simulated MS agrees very well with experimental MS. – $C_{60}H_{50}Br_2N_4O_2$: calcd. 1016.2300, found 1016.2358 (MS: M^+, ^{79}Br).

5,15-[2,5-Dibromo-p-benzoquinone-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-10,20-diphenylporphyrin (**2**): Under argon to a solution of 23.9 mg (23.5 μmol) of **12** in 100 ml of dichloromethane 2.40 ml (2.40 mmol) of a 1 M boron tribromide solution in dichloromethane were added under ice-cooling. The reaction mixture was stirred for 1 h during which the temperature was raised to 20°C. After addition of 200 ml of dichloromethane the solution was washed with 200 ml of saturated aqueous sodium hydrogen carbonate solution and with 200 ml of water. The organic phase was dried over magnesium sulfate and concentrated in a rotary evaporator to a volume of about 100 ml. To this solution 80.0 mg (352 μmol) of DDQ were added, the reaction mixture stirred for 30 min at room temperature, then diluted by addition of 200 ml dichloromethane and washed with 200 ml each of saturated aqueous sodium hydrogen carbonate solution, saturated sodium chloride solution and water. After drying over magnesium sulfate 5 ml toluene were added, and the solvent was distilled off. Polymeric products were separated by filtration through a silica gel frit (h = 8 cm, d = 5 cm) with toluene/ethyl acetate (40:1). From the filtrate the solvents were evaporated in vacuo, and the product obtained was subjected to MPLC (see above) from cyclohexane/ethyl acetate (40:1). The porphyrin fraction ($R_f \approx 0.12$) was crystallized from dichloromethane/methanol (1:3), 1 drop of water, 4°C: 9.5 mg (41%) of **2**, m.p. 237°C. – ^{1}H-NMR (500 MHz, CD_2Cl_2): δ = −2.92 (s, 2H, NH), −0.05 (mc, 4H, δ-CH_2), 0.33 ('t', $J \approx 7.0$ Hz, 4H, γ-CH_2), 0.77−0.80 (m, 4H, β-CH_2), 2.28 ('t', $J \approx 8.0$ Hz, 4H, α-CH_2), 7.55 ('d', $J \approx 7.6$ Hz, 2H, ar-3′-H), 7.59 ("dt", $J \approx 1.3$ and 7.3 Hz, 2H, ar-5′-H), 7.70−7.79 (m, 8H, ar-4′, 3″, 4″, 5″-H), 8.13−8.15 (m, 4H, ar-6′, 2″ or 6″-H), 8.46−8.47 (m, 2H, ar-2″ or 6″-H), 8.67 (d, J = 4.6 Hz, 4H, pyr-H), 8.79 (d, J = 4.6 Hz, 4H, pyr-H). – MS (LSI-MS): *m/z* (%) = 992 (46), 991 (81), 990 (97), 989 (100), 988 (84), 987 (42) [MH^+, ^{79}Br], 986 (27) [M^+, ^{79}Br]. – $C_{58}H_{44}Br_2N_4O_2$: calcd. 986.1831, found 986.1863 (MS: M^+).

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