Photoinduced Electron-Transfer in Porphyrin-Quinone Cyclophanes, 18[◇]

Porphyrin-Cyclophanes with 7,7,8,8-Tetracyanoquinodimethane as an Especially Strong Electron-Acceptor: Syntheses, Properties, Electron-Transfer Interactions

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Previous work on intramolecular electron-transfer compounds of the quinone-porphyrin cyclophane type with gradually increasing electron-acceptor strength was now extended to acceptor-porphyrin cyclophanes with 7,7,8,8-tetracyanoquinodimethane (TCNQ) as an especially strong electron-acceptor. The vertically stacked TCNQ-porphyrin cyclophane **1** was prepared in a multi-step synthesis. Physical properties related to structure and electron-transfer processes of **1** are reported. To determine the distance dependence of the interaction between the electron-acceptor TCNQ and the porphyrin, first results on the synthesis of the corresponding naphthalene-spacered TCNQ-porphyrin cyclophane **15** are presented.

Donor-acceptor cyclophanes are of increasing interest for investigating charge- and electron-transfer interactions. In contrast to the flexible *inter*molecular interactions of individual donor- and acceptor-molecules, the cyclophane structures provide an *intra*molecular fixation of electron-donating and electron-accepting units which are linked together in well-defined and adjustable orientations and distances. Thus, the structural variability of donor-acceptor cyclophanes is certainly the most suitable way of studying charge-transfer interactions and electron-transfer reactions in their dependence on electronic and steric effects.

In preceding papers[1][2][3][4] we reported the synthesis and properties of porphyrin-quinone cyclophanes of which the photoinduced electron-transfer from porphyrins to the quinones as models for the first step of biological photosynthesis was of special interest. In this context, the reduction potentials of the acceptors and the oxidation potentials of the porphyrins were varied systematically[2], and the porphyrin-acceptor distances were increased step-by-step by porphyrin-acceptor cyclophanes with rigid spacers of different size, keeping porphyrin and acceptors in gradually fixed distances[3]. The rates of intramolecular electron-transfer reactions from donor to acceptor units were measured with 'ultrafast spectroscopy' by the Munich group of Michel-Beyerle, Heitele, Pöllinger, and their coworkers in an exemplary cooperation[4].

So far, as electron-acceptors we used quinones with a variety of electron-withdrawing and electron-donating substituents covering already a wide range of electron affinities. In the present paper, however, this program is extended further by using the quinone-related 7,7,8,8-tetracyanoquinodimethane (TCNQ) as a very strong electron-acceptor in the cyclophane bridge opposite to the porphyrin. Porphyrin-tetracyanoquinodimethane cyclophanes like **1** provide the further advantage that in the longitudinal axis of the electron-acceptor both quinone oxygens in the **2**-family are now replaced by the planar dicyanomethylene groups with the four linear C−C≡N bonds, leading to a considerably longer spatial extension as compared to the quinones. Thus, this elongated structure of the electron-acceptor should prevent the remarkable deviations from a parallel orientation of the quinones to the porphyrin plane as have been observed for the porphyrin-quinone cyclophanes of type **2** by X-ray structure analysis[2] and conformational studies by low-temperature ^{1}H-NMR spectra[5].

Syntheses of Porphyrin-TCNQ Cyclophanes

The 7,7,8,8-tetracyanoquinodimethane (TCNQ) itself can be prepared easily from *p*-benzoquinone by a modified Knoevenagel reaction with dicyanomethane [malononitrile $CH_2(CN)_2$; $TiCl_4$, pyridine][6]. In preliminary experiments, 2,5-dimethyl-1,4-benzoquinone with an analogous alkyl-substitution pattern as in **2** was reacted to 2,5-dimethyl-TCNQ in the presence of tetraphenylporphyrin to prove that the porphyrin under the reaction conditions remains intact. 2,5-Dimethyl-7,7,8,8-tetracyanoquinodimethane was

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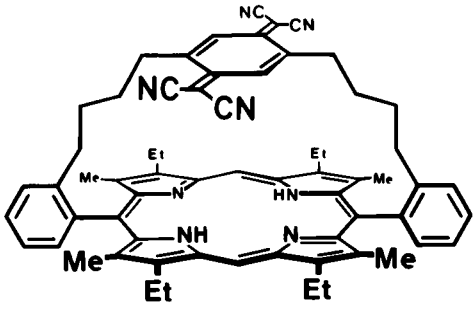

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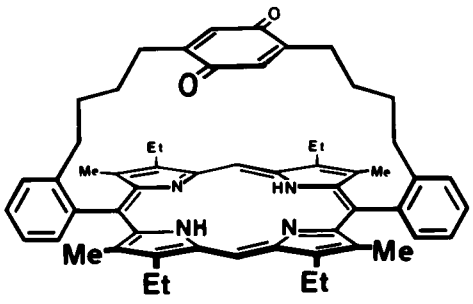

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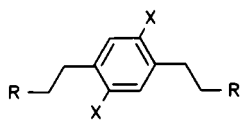
obtained after separation and crystallization in good yield, and the tetraphenylporphyrin was recovered after crystallization to about 90%.

Based on this result the conversion of the quinone unit into the TCNQ was tried directly from the porphyrin-quinone cyclophane **2** by the reaction with dicyanomethane in the presence of titanium tetrachloride in pyridine. In fact, however, only one of the carbonyl groups of the quinone in **2** was converted into a dicyanomethylene group by condensation with dicyanomethane, leading in moderate yield to compound **3**. Further reaction to **1** did not occur, obviously due to steric reasons as a result of the introduction of the dicyanomethylene group in the first reaction step. Apparently, the first substitution of one of the two carbonyl oxygens of the benzoquinone by the spatially more demanding dicyanomethylene groups turns the quinoid ring into a position in which the second carbonyl group is sterically shielded by the porphyrin ring, and therefore it does not react further to the TCNQ. Instead, in addition to the formation of **3**, a series of further side-products was formed of which the 4-(tricyanovinyl)phenol-bridged cyclophane **4** was isolated and its structure was determined. Even from simple 1,4-benzoquinones in the reaction with malononitrile, products corresponding to **3** and **4** had been observed.

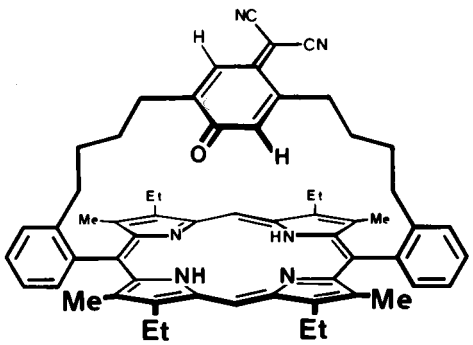
These results show that the porphyrin-TCNQ cyclophane **1** was not available by direct condensation of dicyanomethane with the two carbonyl groups of the porphyrin-quinone cyclophane **2**. Therefore, the consequence for the synthesis of **1** was to prepare the TCNQ or one of its immediate precursors in an independent way with side-chains substituted suitably for later bridging the porphyrin to the porphyrin-TCNQ cyclophane.

Synthesis of 5,15-[7,7,8,8-Tetracyanoquinodimethane-1,4-diylbis(1,4-butanediyl-1,2-benzeno)]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (**1**): The preparation of **1** was achieved in a 12-step synthesis starting from 1,4-dibromobenzene. A Heck reaction of 1,4-dibromobenzene with methyl acrylate, palladium(II) acetate, and tri(*ortho*-tolyl)phosphane yielded (*E*,*E*)-1,4-bis(2-methoxycarbonylethenyl)benzene (86% yield, m.p. 166°C), which was hydrogenated (Pd/C, toluene/methanol, 8:3) to 1,4-bis(2-methoxycarbonylethyl)benzene (**5**; 90% yield, m.p. 113°C). Bromination in the presence of iodine in dichloromethane yielded 1,4-dibromo-2,5-bis(2-methoxycarbonylethyl)benzene (**6**; 70% yield, m.p. 94°C), which was reduced by diisobutylaluminium hydride to the corresponding dialdehyde **7** (88% yield, m.p. 76−78°C).



	X	R
5	H	COOMe
6	Br	COOMe
7	Br	CHO

(2-Cyanobenzyl)triphenylphosphonium bromide, prepared from 2-(bromomethyl)benzonitrile and triphenylphosphane (toluene, 5 h reflux; nearly quantitative



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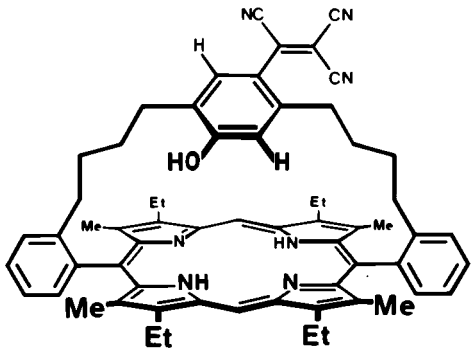

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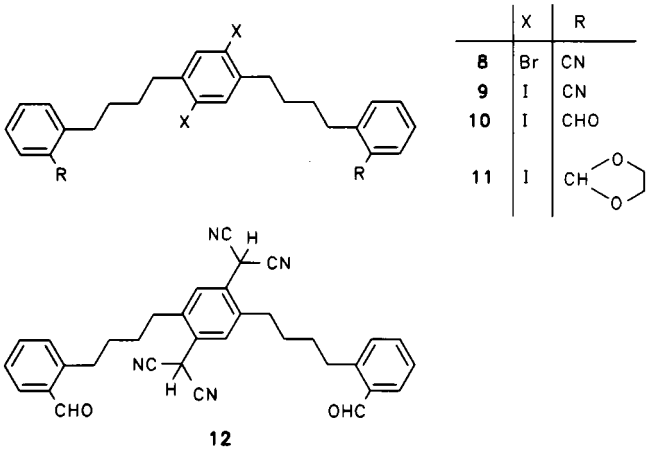
yield, m.p. 258°C), was reacted in a Wittig reaction with **7** to 1,4-dibromo-2,5-bis[4-(2-cyanophenyl)-3-butenyl]benzene [84% yield, (*E/Z*) mixture], which was hydrogenated to 1,4-dibromo-2,5-bis[4-(2-cyanophenyl)butyl]benzene (**8**; 90% yield, m.p. 131−132°C). On **8** the bromo substituents were exchanged to yield the corresponding iodine compound by reaction with copper iodide/potassium iodide in 1,3-dimethyltetrahydro-2(1*H*)-pyrimidinone (16 h, 160°C; yield of **9**: 82%, m.p. 109°C). With diisobutylaluminium hydride (toluene, 30 min at 0°C) 1,4-diiodo-2,5-bis[4-(2-formylphenyl)butyl]benzene (**10**) was obtained (yield 87%, m.p. 108°C).



	X	R
8	Br	CN
9	I	CN
10	I	CHO
11	I	CH(O)O

12

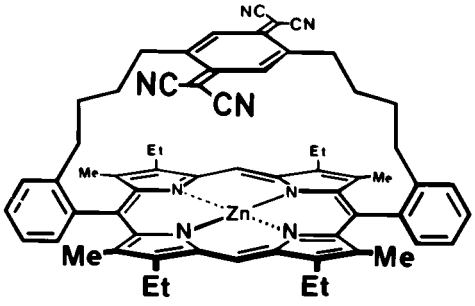
In the diiodo-substituted dialdehyde **10,** after protection of the aldehyde groups as dioxolanes (**11**), the iodine substituents were replaced by reaction with dicyanomethane to 1,4-bis(dicyanomethyl) groups leading to the dihydro-TCNQ system in the central ring. After restoring the aldehyde groups, **12** was obtained which reacts in the usual way with bis(3-ethyl-4-methyl-2-pyrryl)methane to the reduced form of the corresponding porphyrin-cyclophane. The deprotonation by dichlorodicyanoquinone (DDQ) yielded the desired TCNQ-porphyrin-cyclophane **1**. The corresponding zinc complex **13** was obtained with zinc(II) acetate (for details of these syntheses see Experimental Section).

Since the dialdehyde **10**, which was obtained anyway in the synthesis of **1**, in its carbon skeleton is analogous to the intermediates which we had used before for porphyrin-cyclophane syntheses, the corresponding bridged cyclophane was prepared by condensation of **10** with bis(3-ethyl-4-methyl-2-pyrryl)methane and subsequent oxidation to yield the so far unknown porphyrin-cyclophane **14** with the 2,5-diiodobenzene structural unit in the centre of the bridge across the porphyrin (for structural data of **14** see Experimental Section).

Synthetic Route to 5,15-[7,7,8,8-Tetracyanoquinodimethane-1,4-diylbis(1,4-butanediyl-7,1-naphthaleno)]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (**15**): For the quinone-porphyrin cyclophanes the donor-acceptor distances were varied by rigid spacers[1][3]. For the TCNQ-porphyrin cyclophanes the controlled gradation of transannular donor-acceptor distances was of even more interest because of the much stronger electron-acceptor TCNQ. For this reason, the syntheses of the naphthalene-spacered TCNQ-porphyrin cyclophane **15** and of cyclophanes with even longer spacers keeping rigid and well-defined distances between TCNQ and porphyrin were started.

The first steps of the synthesis of **15** made use of the synthesis of 1,4-dibromo-2,5-bis(formylethyl)benzene (**7**) mentioned above. For the introduction of the naphthalene as the second component for the twofold Wittig reaction the (8-methoxycarbonyl-2-naphthyl)methyltriphenylphosphonium bromide[3] was used leading to the (*Z/E*) isomers of 1,4-dibromo-2,5-bis[4-(8-methoxycarbonyl-2-naphthyl)-3-butenyl]benzene (83% yield). After catalytic hydrogenation (89% yield), for the bromo/iodo exchange in the central ring the conditions used for the conversion of **8** to **9** were applied (84% yield). Reduction of the methoxycarbonyl groups by lithium borohydride/dried tetrahydrofuran to the hydroxymethyl groups and oxidation by barium manganate (in methylene chloride) yielded the dialdehyde (81% yield). Protection of the aldehyde groups by reaction with ethylene glycol to the corresponding dioxolanes and substitution of iodine by dicyanomethane followed by deprotection to the aldehyde groups resulted in the formation of the dialdehyde **16** with the substitution in the central aromatic ring suitable for the conversion to TCNQ.

The last step from **16** to **15**, in analogy to the abovementioned conversion of **12** to **1**, however, yielded **15** only in an extremely poor yield (see Experimental Section for details). Although **15** was identified as such, the amount available was too small for further purification and the intended physical studies. Based on the preparative experience



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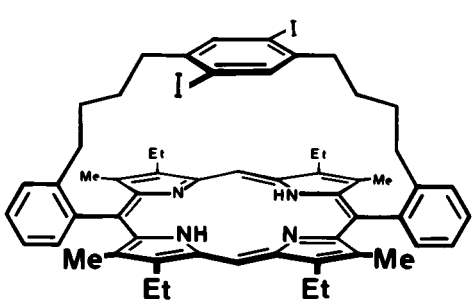

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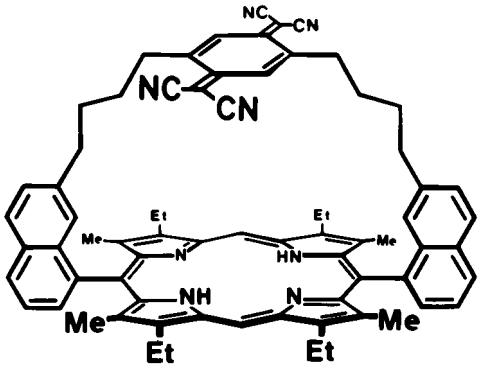

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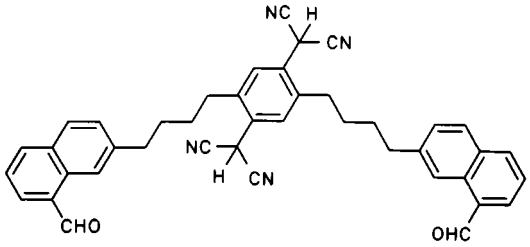

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obtained so far, attempts to improve the synthesis of **15** and the preparation of TCNQ-porphyrin cyclophanes with even longer rigid donor-acceptor spacers will be continued.

Physical Properties of the TCNQ-Bridged Porphyrin Cyclophane 1

^{1}H-NMR-Spectroscopy; Ring-Current Effect of Porphyrins: For the quinone-porphyrin cyclophane **2**, the quinone analogon to the TCNQ cyclophane **1**, the ^{1}H-NMR spectrum (500 MHz, CD_2Cl_2) suggests an apparent C_{2V}-symmetrical structure which results from a fast rotation of the quinone ring around the axis through its bridgehead atoms; this process starts to be frozen-in only at very low temperatures (ca. 190 K). In contrast to these results, for the TCNQ-porphyrin cyclophane **1** a corresponding rotation of the TCNQ cannot occur due to the two spatially extended dicyanomethylene substituents preventing sterically this rotation.

The 'swinging bridge process' discussed in detail for quinone-porphyrin cyclophanes[2], leading to a splitting of the methine protons in 10- and 20-positions of the porphyrin, is not completely suppressed by the larger steric requirement of the TCNQ. For example, for the zinc complex **13** of **1** on cooling-down below 200 K separated ^{1}H-NMR signals appear of the protons in 10- and 20-positions of the porphyrin. Based on these low-temperature measurements the free activation energy for the 'swinging bridge process' of the TCNQ-porphyrin cyclophanes is roughly estimated to about 9.5 kcal/mol. Further studies of the conformational properties of the TCNQ analogues in comparison with the corresponding quinone-porphyrin systems are intended, including molecular dynamics simulations[5] .

A specific feature of the ^{1}H-NMR spectra of porphyrin cyclophanes is the strong shielding of all hydrogens (of quinones, arenes, etc.) located above the porphyrin ring inside the ring-current of the cyclic conjugated π-system of the porphyrins. This effect was already discussed for the quinone protons of quinone-porphyrin cyclophanes[2][3]; it is the result of the 'annulene'-character of porphyrins which in the cyclic conjugation of alternating σ- and π-bonds corresponds to the [18]annulene structure. For the two aromatic protons on the central benzene ring of the open-chained intermediate **10** a singlet at δ = 7.58 (2 H; 360 MHz, $CDCl_3$) is observed; when **10**, however, was ring-closed to the porphyrin cyclophane **14**, these protons in spite of their preserved chemical surroundings, were shifted to δ = 4.74 (s, 2 H; 500 MHz, $CDCl_3$), because they were now exposed to the ring-current of the cyclic conjugated porphyrin. For the TCNQ-porphyrin cyclophanes a corresponding shielding is being observed: for **1** and its zinc complex **13** the chemical shifts of the two ring-hydrogens on the TCNQ units are at δ = 4.15 ([D_8]toluene, 500 MHz) and δ = 3.78 ($CHCl_3$; 500 MHz), respectively, whereas normally the δ-values of hydrogens bound to the six-membered rings of TCNQs are in the order of about δ = 7 to 8, depending on the substitution; for example, in 2,5-dialkyl-TCNQ the 3- and 6-protons on the ring absorb at δ ≈ 7.65.

Cyclovoltammetry; Absorption and Fluorescence Spectra; Preliminary Electron-Transfer-Related Data: To assess the feasibility of an electron-transfer in our donor-acceptor cyclophanes, the free reaction enthalpy of the electron-transfer has been determined (see below). In this connection the oxidation and reduction potentials were measured by cyclovoltammetry against an Ag/AgCl-electrode (3.5 M KCl, water) and converted into the E_{ox}^1 using the ferrocene/ferrocenium system (+0.46 ±0.02 V, in dichloromethane) as reference standard. The first oxidation potentials E_{ox}^1 of the porphyrin unit in quinone-porphyrin cyclophanes are nearly constant in the whole series with $E_{ox}^1 \approx +0.35 \pm 0.02$ V, independent of a broad range of electron-donating and electron-withdrawing substituents on the quinones. Obviously the porphyrin parts of these cyclophanes are not significantly affected through space by the electronically different substituents on the adjacent quinone units. So far, the only exception is the TCNQ-porphyrin cyclophane **1**, for which the first oxidation potential of the porphyrin part is significantly increased to $E_{ox}^1 = +0.42 \pm 0.02$ V, evidently due to the transannular influence of the very strong electron-acceptor TCNQ. For the zinc porphyrin-quinone cyclophane $E_{ox}^1 \approx +0.14 \pm 0.02$ V and for the corresponding TCNQ-system **13** $E_{ox}^1 = +0.19$ V were observed.

In contrast to the rather constant E_{ox}^1 values of the porphyrins in quinone-porphyrin cyclophanes, the first reduction potentials E_{red}^1 within this series are strongly dependent upon different substituents in the 2,5-positions of the quinone units in **2**, which range from alkyl- < alkoxy- < chloro- < bromo- to trifluoromethyl substituents. Accordingly, in this series E_{red}^1 changes considerably from $E_{red}^1 = -1.45$ V of the 2,5-dimethyl derivative of **2** to $E_{red}^1 = -0.86$ V for the cyclophane with the two trifluoro-

methyl substituents in the 2- and 5-positions of **2**. In the context of this paper, the most interesting question is the comparison of **1** and **2**, which differ in the replacement of the quinone in **2** by TCNQ in **1**. For **2**, the parent quinone-porphyrin cyclophane, the first reduction potential is $E_{red}^1 = -1.25$ V. For the TCNQ-porphyrin cyclophane **1**, in which the quinone is replaced by the TCNQ in an otherwise constant structure, the E_{red}^1-value was measured to -0.46 V, indicating the strongest electron-acceptor so far in our series of acceptor-porphyrin cyclophanes.

Another difference between the quinone- and the TCNQ-porphyrin cyclophanes is evident in porphyrin cyclophanes containing the zinc complexation in the porphyrin centres of the two different acceptor-porphyrin cyclophane series. For the zinc-complexed porphyrin-benzoquinone cyclophane the reduction is made considerably easier than for the uncomplexed porphyrin system, most probably due to the direct interactions of quinone oxygens and the zinc, leading to a stabilization of the quinone anions. For the TCNQ in a porphyrin cyclophane, however, any specific interactions with the zinc in the centre of the porphyrin are impossible due to the longitudinal extension of TCNQ with the cyano groups far away from the centre of the porphyrins.

The determinations of the first reduction and oxidation potentials E_{ox}^1 and E_{red}^1 are of interest with regard to charge-separation and charge-recombination processes between electron-donors and electron-acceptors. In a first approximation, the free reaction enthalpy $\Delta G°$ of electron-transfer in a porphyrin-acceptor cyclophane can be described as $\Delta G° = (E_{ox}^1 - E_{red}^1) - E_{00}$, where E_{00} is the energy of the first excited singlet state of the respective porphyrin which is available from the absorption and fluorescence spectra (see below). E_{00} of the porphyrins in the cyclophanes is practically independent of the specific porphyrin, amounting to 1.96 eV for the porphyrin cyclophanes, and to 2.14 eV for their zinc complexes. Thus, for each of the two series, the $\Delta G°$-values are almost exclusively dependent upon $(E_{ox}^1 - E_{red}^1)$ which were discussed above. For the TCNQ-porphyrin cyclophane **1**, $(E_{ox}^1 - E_{red}^1)$ amounts to 0.88 V as compared to the corresponding quinone-porphyrin cyclophane **2** with $(E_{ox}^1 - E_{red}^1) = 1.61$ V. The respective values for the zinc complexes of **2** and the TCNQ-analogue **1** are 1.07 and 0.58 V. The comparison of these values for **1** and **2** again demonstrates the strong increase of the electron-acceptor property of TCNQ in relation to the quinone analogues exceeding even those with strongly electron-withdrawing substituents on the quinones like, for example, CF_3 substituents.

The absorption spectra of the porphyrin-quinone cyclophanes like **2** are dominated by the porphyrin chromophore present in **2**: the typical porphyrin absorptions of **2** are the Soret band at $\lambda_{max} = 411$ nm ($\varepsilon = 21.5 \cdot 10^4$ M^{-1}cm^{-1}) and the Q-bands at 508 (1.6; Q_y, 1/0), 539 (0.5; Q_y, 0/0), 578 (0.7; Q_x, 1/0), 631 (0.3; Q_x, 0/0) (in toluene). The corresponding data for **1** are 409 (12.5), 507 (1.1), 540 (0.3), 575 (0.5), 624 (0.2), showing that also for the TCNQ-porphyrin cyclophane the dominating chromophore is the porphyrin; the only difference is that for **1** at shorter wavelength there is a shoulder on the Soret band at about 380 nm. For the zinc complexes, due to the increased molecular symmetry of D_{4h} there are in addition to the Soret band only two Q bands. Again the absorption spectra of the zinc complexes of **1** and **2** are rather similar [**13**: $\lambda = 413$ (16.5, Soret band), 540 (1.1), 574 (0.7); **2**-zinc complex: $\lambda = 417$ (39.6), 544 (2.1), 578 (0.9), in toluene]. For **13**, like for **1**, at shorter wavelength a shoulder at 390 nm on the Soret band is observed.

In the fluorescence spectra of porphyrins generally two emission bands are observed. However, for porphyrin-acceptor systems the quantum yield of fluorescence is reduced, due to the quenching of the excited state by the competition of intramolecular electron-transfer. This can be shown by the comparison of fluorescence quantum yields of porphyrin-quinone cyclophanes with those of corresponding porphyrin-TCNQ cyclophanes. Relative fluorescence quantum yields were obtained from the division of the fluorescence integrals of porphyrin-quinone cyclophanes by those of porphyrin-TCNQ cyclophanes. First results for electron-transfer rates as well as for fluorescence quenching have been obtained. Based on $\Delta G°$ values of charge-separation and recombination, preliminary data for the rate of charge-separation were estimated for **1** to about 250 femtoseconds (in toluene) and for charge-recombination to about 990 femtoseconds. These results need further experiments and interpretations on their physical properties according to the previous investigations on the 'ultra-fast' photoinduced electron-transfer in our porphyrin-acceptor cyclophanes in cooperation with Michel-Beyerle, Heitele, Pöllinger, and coauthors[4]. Nevertheless, the present data already show the trend by comparing the electron-transfer in TCNQ-porphyrin cyclophanes with the previously investigated quinone-porphyrin cyclophanes.

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Experimental Section

Melting points: Büchi SMP 512; for m.p. > 240°C Bock Monoskop. − Elemental Analysis: Elemental Analyzer 1106 and 1108 Carlo Erba. − IR: Perkin-Elmer FT-IR 1760 X (KBr). − UV/VIS: Varian Cary 2300. − Fluorescence spectra: Fluorolog F 112 XE, Spex. − NMR: Bruker HX-360 and AM-500, internal reference TMS or the solvent signals C*H*DCl$_2$, $\delta = 5.52$; C*H*Cl$_3$, $\delta = 7.26$; [D$_5$*H*]DMSO, $\delta = 2.50$. − MS: CEC 21-492 (DuPont) and MAT (Finnigan); FAB: ZAB 2E/SE (VG Analytical), JMS SX-102A (JEOL); only signals with intensities > 10% are quoted. − Analytical TLC: DC-Micro Cards SIL G/UV$_{254}$, Macherey-Nagel. − CC: Silica gel SiliTech 63-200 μ, ICN Biochemicals. − MPLC: Labomatic and Abimed, Silica gel 60 Å (Kronwald). − Gas chromatography: HP 5890 II plus, detector HP 5972 (Hewlett Packard). − Cyclovoltammetry: Potentiostat 263 A (EG&G Princeton Applied Research), 'Glassy carbon electrode', reference electrode Ag/AgCl (3.5 M KCl/water), tetrabutylammonium hexafluorophosphate (Fluka) as conducting salt; solvent dichloromethane (99.8%, waterfree; Aldrich).

Attempted Synthesis of **1** *from 5,15-[p-Benzoquinone-1,4-diylbis(4,1-butanediyl-2,1-benzeno)]-2,8,12,18-tetraethyl-3,7,13,17-tetrameth-*

ylporphyrin (**2**)[2]: *a) 5,15-[4-Dicyanomethylene-1-oxo-2,5-cyclohexadiene-2,5-diylbis(4,1-butanediyl-2,1-benzeno)]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin* (**3**): To 21.4 mg (25.0 μmol) of **2**, dissolved under argon in 4 ml of dichloromethane, at −15°C within 3 min succesively solutions of 0.75 ml (0.75 mmol) of 1 M titanium tetrachloride in dichloromethane, and of 11.7 mg (117 μmol) of malononitrile and 0.03 ml (354 μmol) of pyridine in 2 ml of dichloromethane were added. After 30 min 1 ml of 2 M sulfuric acid was added, and the organic phase was washed with 10 ml of water; the aqueous phase was extracted with 10 ml of dichloromethane, and the solvents of the united organic phases after drying with magnesium sulfate were distilled off in vacuo below 30°C. Medium-pressure chromatography (silica; cyclohexane/ethyl acetate, 30:1) yielded in the first fraction ($R_f \approx 0.11$) **3**, after crystallization from dichloromethane/methanol (1:1): 8.5 mg (38% yield) of a violet powder, m.p. 298°C. − MS (FAB positive, *m*-nitrobenzyl alcohol/1% trifluoroacetic acid): *m/z* (%) = 895 (14) [MH^+], 897 (100) [$MH + 2]^+$. − ^{1}H NMR (500 MHz, CD_2Cl_2, 303 K): δ = −2.60 (s, 1 H, NH), −2.55 (s, 1 H, NH), −0.81 (t, ^3J = 7.2 Hz, 2 H, δ-CH_2), −0.22 to −0.20 (m, 2 H, γ-CH_2), 0.65−0.72 (m, 2 H, γ′-CH_2), 0.95−1.00 (m, 4 H, β-CH_2, δ′-CH_2), 1.10 (m, 2 H, β′-CH_2), 1.84 (t, ^3J = 7.6 Hz, 12 H, CH_2-CH_3), 2.25−2.35 (m, 4 H, α-CH_2, α′-CH_2), 2.46 (s, 6 H, CH_3), 2.50 (s, 6 H, CH_3), 3.10 (s, 1 H, 6-H, centr.ring), 3.95−4.10 (m, 8 H, CH_2-CH_3), 5.14 (s, 1 H, 3-H, centr.ring), 7.60−7.75 (m, 6 H, ar-H), 8.00 (d, ^3J = 7.0 Hz, 1 H, ar-H), 8.25 (d, ^3J = 7.0 Hz, 1 H, ar-H), 10.20 (s, 2 H, 10,20-H). − HR-MS $(MH + 2)^+$: $C_{61}H_{65}N_6O$: calc. 897.5220, found 897.5201.

b) *5,5-[4-Tricyanovinylphenol-2,5-diylbis(4.1-butanediyl-2,1-benzeno)]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin* (**4**): To 84.6 mg (100 μmol) of porphyrin-quinone cyclophane **2** in 20 ml of dichloromethane under argon alternately 0.5 ml of solutions of 2.80 ml (2.80 mmol) of titanium tetrachloride (1 M in dichloromethane) and of 0.5 ml of 52.0 mg (0.18 mmol) of malononitrile, 0.20 ml (2.36 mmol) of pyridine in 3 ml of dichloromethane were added at 10−15°C. After 30 min of stirring at 40°C 0.5 ml of 2 N sulfuric acid were added. After washing the organic phase with 15 ml of water and extracting the aqueous phase with 5 ml of dichloromethane, the organic phase was dried with magnesium sulfate, concentrated at 30°C and chromatographed (silica; cyclohexane/ethyl acetate 30:1). With $R_f \approx 0.19$ **4** was obtained and crystallized from methanol/dichloromethane (10:1) as red-violet needles, m.p. 305°C; yield 79 mg (84%). − MS (FAB positive, *m*-nitrobenzyl alcohol (1% trifluoroacetic acid): *m/z* (%) = 934 (47) [M^+], 935 (100) [MH^+], 936 (98) a.o. − ^{1}H NMR (500 MHz, CD_2Cl_2, 303 K): δ = −1.70 (s, 2 H, NH), −0.48 (s, 1 H, phenol-H), −0.20 (m, 2 H, γ-CH_2), 0.07 (t, ^3J = 7.4 Hz, 2 H, δ-CH_2), 0.57 (m, 2 H, β′-CH_2), 0.72 (m, 2 H, γ′-CH_2), 1.07 (t, ^3J = 6.2 Hz, 2 H, δ′-CH_2), 1.12 (m, 2 H, β-CH_2), 1.65 (t, ^3J = 7.5 Hz, 6 H, CH_2-CH_3), 1.68 (t, ^3J = 7.2 Hz, 2 H, α-CH_2), 1.80 (t, J = 7.5 Hz, 6 H, CH_2-CH_3), 2.38 (t, ^3J = 7.4 Hz, 2 H, α′-CH_2), 2.50 (s, 6 H, CH_3), 2.55 (s, 6 H, CH_3), 3.95 (q, ^3J = 7.5 Hz, 2 H, CH_2-CH_3), 4.02−4.10 (m, 6 H, CH_2-CH_3), 5.95 (s, 1 H, phenol-H), 7.55 (d, ^3J = 7.1 Hz, 1 H, ar-H), 7.65 (m, 2 H, ar-H), 7.70 (m, 1 H, ar-H), 7.80 ('t', 2 H, ar-H), 8.15 (d, ^3J = 7.1 Hz, 1 H, ar-H), 8.35 (d, ^3J = 7.1 Hz, 1 H, ar-H), 10.30 (s, 2 H, methine-H). − HR-MS (LSIMS positive, *m*-nitrobenzylalcohole/1% trifluoroacetic acid, 2% PEG 1000): $C_{63}H_{64}N_7O$: calc. 934.5172, found 934.5180 [MH^+].

1,4-Dibromo-2,5-bis(2-methoxycarbonylethyl)benzene (**6**): For the synthesis of **6**, 1,4-bis(2-methoxycarbonylethyl)benzene (**5**) had already been prepared starting from 1,4-dibromobenzene by double Heck reaction and the following hydrogenation to **5** (see preceding papers of this series). To a solution of 26.8 g (0.11 mol) of **5** in 200 ml of dichloromethane 3.3 g (10 mmol) of iodine were added and the mixture was heated under reflux. Within 3 h 16.0 ml (0.31 mol) of bromine in 50 ml of dichloromethane were added dropwise. After heating for further 36 h the hot reaction mixture was poured on 600 g of ice, and saturated sodium thiosulfate solution was added until decoloration. The phases were separated; the aqueous phase was extracted three times with 100 ml of trichloromethane each. The combined organic phases were washed twice with 100 ml of water each, and dried with magnesium sulfate. The solvents were distilled off leaving a colourless solid which was crystallized from methanol: 31.6 g (70%) of **6**, m.p. 94°C. − MS: *m/z* (%) = 327 (100) [M − Br]$^+$, 329 (98), 330 (10), 406 (0.3), 408 (0.6) [M^+], a.o. − ^{1}H NMR (360 MHz, $CDCl_3$, 303 K): δ = 2.62 (t, ^3J = 7.8 Hz, 4 H, CH_2COOR), 2.99 (t, ^3J = 7.8 Hz, 4 H, CH_2-ar), 3.69 (s, 6 H, OCH_3), 7.42 (s, 2 H, ar*H*). − $C_{14}H_{16}O_4Br_2$ (408.09): calc. C 41.21, H 3.95, Br 39.16; found C 41.33, H 4.01, Br 39.01.

1,4-Dibromo-2,5-bis(2-formylethyl)benzene (**7**): 6.55 g (18.8 mmol) of **6** were dissolved under argon in 130 ml of toluene and cooled to −70°C. At this temperature within 15 min 30.2 ml (45.1 mmol) of diisobutylaluminium hydride as 1.5 M solution in toluene were added. After further 90 min 150 ml of aqueous 2 M hydrochloric acid were added for hydrolysis. The phases formed were separated and the aqueous phase was extracted three times with 100 ml of toluene. The combined organic phases were washed with 100 ml each of water and of saturated sodium chloride solution, and then dried with magnesium sulfate. By distilling off the solvents in vacuo a yellowish oil was obtained which from dichloromethane was filtered through silica, yielding a colourless solid which was crystallized from *n*-hexane/diethyl ether: 5.76 (88%) of **7**, m.p. 76−78°C. − MS: *m/z* (%) = 348 (20) [M^+], 346 (10) [M^+], 275 (32), 269 (95), 267 (100) [M − Br], a.o. − ^{1}H NMR (360 MHz, $CDCl_3$, 303 K): δ = 2.79 (t, ^3J = 7.5 Hz, 4 H, CH_2CHO), 2.99 (t, ^3J = 7.5 Hz, 4 H, ar-CH_2), 7.42 (s, 2 H, ar*H*), 9.82 (s, 2 H, C*H*O). − $C_{12}H_{12}O_2Br_2$ (348.04): calc. C 41.41, H 3.48, Br 45.95; found C 41.70, H 3.65, Br 45.79.

(2-Cyanobenzyl)triphenylphosphonium Bromide: 50.0 g (256 mmol) of 2-(bromomethyl)benzonitrile and 200.8 g (766 mmol) of triphenylphosphane in 1 l of toluene were heated under reflux for 2.5 h. After additional stirring at room temperature for 16 h, the white precipitate was sucked off, washed twice with 60 ml of acetone each and dried at 50°C/50 mbar; 116.5 g (ca. 99% yield), m.p. 258°C. − $C_{26}H_{21}BrNP$ (458.34): calc. C 68.13, H 4.62, N 3.06, Br 17.43; found C 67.84, H 4.55, N 3.09, Br 17.28.

1,4-Dibromo-2,5-bis[4-(2-cyanophenyl)-3-butenyl]benzene (E/Z isomer mixture): For the Wittig reaction, 35.6 g (77.7 mmol) of the precedingly described phosphonium salt was suspended in 250 ml of tetrahydrofuran to which under argon sodium bis(trimethylsilyl)-amide (14.5 g, 79.0 mmol) was added. After stirring for 30 min at 60°C the suspension formed a solution of 7.9 g (22.7 mmol) of **7** in 400 ml of tetrahydrofuran was added over 10 h. After stirring at 60°C for further 10 h, 250 ml of 2 M hydrochloric acid was added. The organic solvents were removed in vacuo, and the remaining aqueous suspension was extracted three times with 200 ml each of dichloromethane. The united organic phases were washed twice with 100 ml of water each, dried with magnesium sulfate, and filtered through silica with cyclohexane/ethyl acetate (10:1): 10.3 g (84% yield) of the (*E/Z*)-isomer mixture (m.p. 155°C) of which for elemental analysis a test sample was crystallized. − $C_{28}H_{22}N_2Br_2$ (546.31): calc. C 61.56, H 4.06, N 5.13, Br 29.25; found C 61.48, H 4.18, N 4.90, Br 29.03.

1,4-Dibromo-2,5-bis[4-(2-cyanophenyl)butyl]benzene (**8**): Through a solution of 5.60 (10.3 mmol) of the precedingly de-

scribed isomer mixture in 50 ml of tetrahydrofuran in a 100-ml autoclave, argon was passed for 10 min. Then 410 mg (0.44 mmol) of chlorotris(triphenylphosphane)rhodium catalyst were added. The hydrogenation was carried out under stirring for 14 h at 80−90°C and 25 bar hydrogen pressure. The solvents then were distilled off in vacuo, and the residue was extracted three times with 50 ml of diethyl ether each. The united extracts were filtered with diethylether as elution agent on a column of 15 cm of aluminium oxide. The resulting colourless solid was crystallized from methanol: 5.1 g (90% yield); m.p. 131−132°C. − $C_{28}H_{26}N_2Br_2$ (550.34): calc. C 61.11, H 4.76, N 5.09, Br 29.09; found C 61.05, H 4.84, N 5.07, Br 29.04.

1,4-Diiodo-2,5-bis[4-(2-cyanophenyl)butyl]benzene (**9**): 550 mg (1.0 mmol) of **8**, 1.90 g (10.0 mmol) of copper(I) iodide, and 4.98 g (30.0 mmol) of potassium iodide were thoroughly mixed and under argon in 5 ml of 1,3-dimethyltetrahydro-2(1*H*)-pyrimidinone (DMPU) suspended and stirred for 16 h at 160°C. After hydrolysis by 30 ml of 2 M hydrochloric acid and 10 min of stirring with 50 ml of diethylether, the reaction mixture was filtered off from insoluble salts, and the residue was washed with diethylether. The phases of the united filtrate were separated, and the aqueous phase was extracted twice with 50 ml of diethylether each. The combined organic phases were washed with saturated sodium thiosulfate solution and twice with saturated sodium chloride solution, then dried with magnesium sulfate, and the solvents were removed in vacuo. Recrystallization from 40 ml of methanol yielded colourless, fine needles: 527 mg (82% yield), m.p. 109°C. − MS: *m/z* (%) = 644 (9) [M^+], 517 (38) [$M - I]^+$, 390 (74), 274 (45), 131 (42), 130 (36), 129 (33), 117 (28), 116 (100) [C_8H_6N], a.o. − $C_{28}H_{26}N_2I_2$ (644.33): calc. C 52.19, H 4.07, N 4.35, I 39.39; found C 51.97, H 4.25, N 4.05, I 39.54.

1,4-Diiodo-2,5-bis[4-(2-formylphenyl)butyl]benzene (**10**): 600 mg (0.93 mmol) of **9** under argon were dissolved in 80 ml of toluene and cooled to 0°C. At this temperature within 10 min 2.0 ml (3.0 mmol) of a 1.5 M solution of diisobutyl aluminium hydride in toluene were added. After stirring for further 30 min, 80 ml of 2 M hydrochloric acid were added. The organic and aqueous phases were separated, the latter was extracted three times by 100 ml each of diethylether. The combined organic phases were washed with 100 ml each of water and saturated sodium chloride solution, dried with magnesium sulfate, and the solvents were distilled off in vacuo yielding a colourless solid which could be used for the following synthesis step without further purification: 520 mg (87% yield), m.p. 108°C. − MS: *m/z* = 650 (6) [M^+], 380 (23), 378 (56), 132 (65), 131 (44), 129 (98), 128 (25), 119 (35), 117 (72), 116 (86), 115 (33), 105 (30), 91 (100), a.o. − ^{1}H NMR (360 MHz, $CDCl_3$, 303 K): δ = 1.63−1.73 (m, 8 H, $CH_2CH_2CH_2CH_2$), 2.64 [t, ^3J = 7.4 Hz, 4 H, ar(I_2)-CH_2], 3.09 [t, ^3J = 7.3 Hz, 4 H, ar(CHO)-CH_2], 7.28−7.30 (m, 2 H, ar*H*), 7.35−7.40 (m, 2 H, ar*H*), 7.49−7.53 (m, 2 H, ar*H*), 7.58 [s, 2 H, ar(I_2)*H*], 7.82−7.84 (m, 2 H, ar*H*), 10.28 (s, 2 H, C*H*O). − HR-MS (LSI-MS positive, 3-nitrobenzyl alcohol, 1% trifluoro acetic acid): $C_{28}H_{28}O_2I_2$: calc. 650.0179, found 650.0192 [M^+]; calc. 651.0257, found 651.0252 [MH^+].

1,4-Diiodo-2,5-bis{4-[2-(1,3-dioxolan-2-yl)phenyl]butyl}benzene (**11**): 2.65 g (4.08 mmol) of the dialdehyde **10** and 6.0 ml (106 mmol) of ethylene glycol as well as 300 mg (1.58 mmol) of p-toluenesulfonic acid in 250 ml of benzene were heated for 12 h on a water separator. After cooling and adding 500 mg of potassium hydroxide the solution was washed four times with 200 ml of water each. After drying with magnesium sulfate and evaporation of the solvent in vacuo, the product obtained was crystallized from methanol/acetone (3:1): 2.77 g (94% yield) of a colourless solid of m.p. 125°C. − MS: *m/z* = 738 (48) [M^+], 694 (32), 611 (61), 204 (40), 149 (100), 129 (50), 117 (47), 116 (44), a.o. − ^{1}H NMR (360 MHz, $CDCl_3$, 303 K): δ = 1.55−1.75 (m, 8 H, methylene chain), 2.65 (t, ^3J = 7.6 Hz, 4 H, CH_2 neighbouring the central benzene ring), 2.79 (t, ^3J = 7.6 Hz, 4 H, CH_2 neighbouring the lateral benzene rings), 4.03−4.18 (m, 8 H, CH_2-CH_2 of oxolane group), 6.00 (s, 2 H, −C*H*< of dioxolane), 7.19−7.31 (m, 6 H, ar-*H*), 7.55−7.59 (m, 2 H, ar-*H*), 7.61 (s, 2 H, central benzene ring). − $C_{32}H_{36}O_4I_2$ (738.45): calc. C 52.05, H 4.91, I 34.37; found C 51.80, H 5.16, I 34.54.

1,4-Bis(dicyanomethyl)-2,5-bis[4-(2-formylphenyl)butyl]benzene (**12**): In 10 ml of dimethylformamide (dried with calcium hydride, distilled under argon) the catalyst from 222 mg (0.40 mmol) of 1,1′-bis(diphenylphosphanyl)ferrocene and 45 mg (0.20 mmol) of palladium(II) acetate was prepared by stirring for 90 min. 500 mg (0.68 mmol) of **11** were added. Separately under argon 119 mg (4.26 mmol) of sodium hydride (95%) in 10 ml of dry *N,N*-dimethylformamide were suspended to which 197 mg (2.98 mmol) of malononitrile were added; after the termination of gas evolution this suspension was transferred by a syringe into the educt-catalyst solution. The reaction mixture then was heated to 80°C for 1 h, and after cooling to 0°C was hydrolyzed by 150 ml of 2 M hydrochloric acid. The precipitated brown solid was sucked off and dried in vacuo at room temperature. Flash chromatography on silica with cyclohexane/ethyl acetate (1:1) as eluant yielded, after evaporation of the solvent in vacuo, **12** as yellowish solid: 293 mg (82% yield), m.p. 181°C. − MS: *m/z* (%) = 526 (29) [M^+], 146 (20), 132 (39), 131 (33), 129 (76), 117 (58), 105 (27), 91 (100), a.o. − ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ = 1.71−1.77 (m, 4 H, $CH_2CH_2CH_2CH_2$), 1.80−1.86 (m, 4 H, $CH_2CH_2CH_2CH_2$), 2.80 (t, ^3J = 7.7 Hz, 4 H, centr.ar-CH_2), 3.12 (t, ^3J = 7.7 Hz, 4 H, lateral ar-CH_2), 5.22 [s, 2 H, -C*H*$(CN)_2$], 7.30 (d, ^3J = 7.4 Hz, 2 H, lateral ar-*H*), 7.39−7.43 (m, 2 H, lateral ar-*H*), 7.51−7.53 (m, 2 H, lateral ar-*H*), 7.56 (s, 2 H, central ar-*H*), 7.81 (d, ^3J = 7.4 Hz, 2 H, lateral ar-*H*), 10.28 (s, 2 H, C*H*O). − HR-MS (LSI-MS positive, 3-nitrobenzyl alcohol, 1% trifluoroacetic acid): $C_{34}H_{30}N_4O_2$: calc. 527.2447, found 527.2455 (MH^+).

5,15-[7,7,8,8-Tetracyanoquinodimethane-1,4-diylbis(1,4-butanediyl-1,2-benzeno)]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (**1**): Under argon, to 270 mg (0.51 mmol) of **12** in 50 ml of acetonitrile (filtered through aluminium oxide) 236 mg (1.02 mmol) of bis(3-ethyl-4-methylpyrrolyl-2)methane and 442 mg (2.71 mmol) of trichloroacetic acid were simultaneously added. After stirring for 20 min under exclusion of light, during further stirring for 40 min 600 mg (2.64 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in 40 ml of tetrahydrofuran were added. After addition of 100 ml of saturated sodium hydrogencarbonate solution, the reaction mixture was extracted twice by 100 ml each of dichloromethane, and the combined organic phases were separated, washed with water and dried with sodium sulfate. The solvent was distilled off in vacuo, and the residue was filtered on silica from cyclohexane/ethyl acetate (1:1). Flash-chromatography on silica (cyclohexane/ethylacetate, 5:1) yielded porphyrin-containing fractions of which the solvents were removed by distillation, and the product was dried in high vacuum, dissolved in about 1 ml of dichloromethane and covered with a layer of 20 ml of methanol; at 4−8°C within 15 h a red-brown solid precipitated: 48 mg (10% yield), m.p. > 335°C. − MS: *m/z* (%) = 946 (92), 945 (100) [$M + 2]^+$, 944 (99), 943 (38), 942 (34), a.o. − ^{1}H NMR (500 MHz, [D_8]toluene, 303 K; all signals are broadened, and only the maxima are listed): δ = −2.35 (NH), 0.40 (CH_2), 0.93 (CH_2), 1.35 (CH_2), 1.84 (CH_2CH_3), 2.47 (CH_2), 2.61 (CH_3), 3.99 (CH_2CH_3), 4.15 (TCNQ-*H*), 7.33 (ar-*H*), 7.41 (ar-*H*), 7.67 (ar-*H*), 7.99 (ar-*H*), 10.38 (meso-C*H*). −

$C_{64}H_{62}N_8$ (942.52): calc. 943.5176, found 943.5138 $[MH]^+$; calc. 942.5097, found 942.5020 $[M]^+$.

5,15-[7,7,8,8-Tetracyanoquinodimethane-1,4-diylbis(1,4-butanediyl-1,2-benzeno)]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrinatozinc(II) (**13**): For zinc complexation, to 20 mg (21μmol) of **1** in 50 ml of trichloromethane/methanol (4:1) under argon 500 mg (2.3 mmol) of zinc(II)acetate dihydrate were added, and under exclusion of light the reaction mixture was stirred for 15 h at room temperature. The reaction mixture was washed successively with 50 ml of water, 50 ml of saturated ammonium chloride solution, and again with 50 ml each of water. After drying with sodium sulfate the solvent was removed in vacuo; the remaining red product was purified by preparative thin-layer chromatography (silica 60, toluene). The product fraction (R_f = 0.40−0.55) was precipitated from cyclohexane/ethyl acetate (50:1) as violet powder: 12 mg (57% yield), m.p. > 335°C. − MS(LSI positive, 3-nitrobenzyl alcohol): *m/z* (%) = 1008 (75), 1007 (94), 1006 (92), 1005 (100) $[MH]^+$, 1004 (65), 1003 (51), a.o. − ^{1}H NMR (500 MHz, $CDCl_3$, 330 K): δ = 0.26 (m, 4 H, δ-CH_2), 0.54 (m, 4 H, γ-CH_2), 1.54 (m, 4 H, β-CH_2), 1.85 (t, ^3J = 7.6 Hz, 12 H, CH_2CH_3), 2.43 (s, 12 H, CH_3), 2.66 (m, 4 H, α-CH_2), 3.78 (s, 2 H, TCNQ-*H*), 3.94 (m, 4 H, CH_2CH_3), 4.16 (m, 4 H, CH_2CH_3), 7.56 (t, ^3J = 7.3 Hz, 2 H, ar-H), 7.68 (d, ^3J = 7.4 Hz, 2 H, ar-H), 7.77 (d, ^3J = 7.6 Hz, 2 H, ar-H), 7.82 (t, ^3J = 7.5, 2 H, ArH), 10.19 (s, 2 H, 10,20-H). − HR-MS: $C_{64}H_{60}N_8Zn$: calc. 1005.4311 $[MH]^+$, found 1005.4257.

5,15-[2,5-Diiodobenzene-1,4-diylbis(1,4-butanediyl-1,2-benzeno)]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (**14**): Under argon 150 mg (0.23 mmol) of the diiodo-substituted dialdehyde **10** was dissolved in 50 ml of acetonitrile (filtered through aluminium oxide) and 10 ml of dichloromethane. To this solution 106 mg (0.46 mmol) of bis(3-ethyl-4-methylpyrrolyl-2)methane and 215 mg (1.32 mmol) of trichloroacetic acid were added simultaneously, and this mixture was stirred for 15 min under exclusion of light. Afterwards 300 mg (1.32 mmol) of dichlorodicyanoquinone (DDQ) in 40 ml of tetrahydrofuran were added under stirring for further 40 min. After addition of 100 ml of saturated sodium hydrogen carbonate solution the reaction mixture was extracted twice with 100 ml each of dichloromethane, and the combined organic phase was washed with water until the aqueous extract was colourless. The organic phase was dried with sodium sulfate, the solvent was distilled off in vacuo, and the residue was chromatographed on silica from cyclohexane/ethyl acetate (5:1). The solvents were distilled off, and the product was dissolved in about 1 ml of dichloromethane and covered with a layer of 20 ml of methanol. At 10°C within 15 h deep-violet crystals were obtained: 32 mg (13% yield), m.p. 233−234°C. − MS (LST-positive, 3-nitrobenzyl alcohol, 1% trifluoroacetic acid): *m/z* (%) = 1070 (65), 1069 (100), 1068 a.o. − ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ = −2.54 (s, 2 H, NH), −0.51 (m, 4 H, δ-CH_2), 0.38 (m, 4 H, γ-CH_2), 1.35 (m, 4 H, β-CH_2), 1.83 (t, ^3J = 7.0 Hz, 12 H, CH_2CH_3), 2.01−2.06 (m, 4 H, α-CH_2), 2.61 (s, 12 H, CH_3), 4.01−4.08 (m, 8 H, CH_2CH_3), 4.74 (s, 2 H, central benzene ring), 7.55 (d, ^3J = 7.2 Hz, 2 H, 3-ar-H), 7.59−7.64 (m, 2 H, 5-ar-H), 7.68−7.73 (m, 2 H, 4-ar-H), 8.21 (d, ^3J = 7.3 Hz, 2 H, 6-ar-H), 10.20 (s, 2 H, 10,20-H). − HR-MS: $C_{58}H_{62}N_4I_2$ (1068.98): calc. 1069.3142 $[MH]^+$, found 1069.3124; calc. 1068.3016 $[M]^+$, found 1068.3040.

1,4-Dibromo-2,5-bis[4-(8-methoxycarbonyl-2-naphthyl)-3-butene-1-yl]benzene (Z/E isomer mixture): Under argon 13.65 g (25.2 mmol) of (8-methoxycarbonyl-2-naphthyl)methyltriphenylphosphonium bromide[3] in 200 ml of tetrahydrofuran were suspended, and 4.70 g (25.61 mmol) of sodium bis(trimethylsilyl)amide were added, yielding a red suspension which was stirred at 60°C for 30 min. Then, 2.56 g (7.36 mmol) of 1,4-dibromo-2,5-bis(formylethyl)benzene (**7**), dissolved in 200 ml of tetrahydrofuran, was added within 10 h. After further 10 h of stirring at 60°C, 150 ml of 2 M hydrogen chloride was slowly added. The organic solvent was removed in vacuo, leaving a brownish suspension which was extracted three times with 150 ml of dichloromethane. The combined organic phases were washed with 150 ml of saturated sodium hydrogen carbonate solution and then washed with water. The organic phase was dried with magnesium sulfate yielding a yellow solid which, dissolved in dichloromethane, was filtered through silica. From the yellow oil in a small amount of dichloromethane the reaction product was precipitated by addition of ethanol and crystallized from methylcyclohexane/methanol (50:1): 4.3 g (83% yield) of the (*Z/E*) mixture. − $C_{38}H_{32}Br_2O_4$ (710.07): calc. C 64.06, H 4.53, Br 22.43; found C 64.02, H 4.82, Br 22.71.

1,4-Dibromo-2,5-bis[4-(8-methoxycarbonyl-2-naphthyl)but-1-yl]-benzene: 5.1 g (7.2 mmol) of the preceding (*Z/E*)-isomer mixture in 250 ml of tetrahydrofuran in the presence of 1.5 g of palladium (10% on charcoal; Merck) was hydrogenated at room temperature and under normal pressure (ca. 4 h). The catalyst was filtered off, and the solvent was removed in vacuo. The solid residue was crystallized from ethyl acetate: 4.57 g (89% yield; m.p. 120°C). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.62−1.68 ('quint', ^3J = 7.1 Hz, 4 H, γ-H), 1.75−1.81 ('quint', ^3J = 7.7 Hz, 4 H, β-H), 2.70 (t, ^3J = 7.8 Hz, 4 H, δ-H), 2.84 (t, ^3J = 7.8 Hz, 4 H, α-H), 3.95 (s, 6 H, CO-OCH_3), 7.35 (s, 2 H, phen-H), 7.40 (dd, ^3J = 8.4 Hz, ^4J = 1.7 Hz, 2 H, 3-H), 7.43 ('t', ^3J = 7.5 Hz, 2 H, 6-H), 7.81 (d, ^3J = 8.4 Hz, 2 H, 4-H), 7.97 (d, ^3J = 8.1 Hz, 2 H, 5-H), 8.11 (dd, ^3J = 7.3 Hz, ^4J = 1.2 Hz, 2 H, 7-H), 8.67 (s, 2 H, 1-H). − $C_{38}H_{36}Br_2O_4$ (714.10): calc. C 63.70, H 5.06, Br 22.30; found C 63.95, H 5.20, Br 22.50.

1,4-Diiodo-2,5-bis[4-(8-methoxycarbonyl-2-naphthyl)but-1-yl]benzene: In 1.43 g (2.0 mmol) of the preceding dibromo compound the bromo/iodo exchange was performed with 3.8 g (20 mmol) of copper(I) iodide and 9.96 g (60 mmol) of potassium iodide in 10 ml of dimethyltetrahydro-2(*1H*)-pyrimidinone suspension under stirring at 160°C for 20 h. After cooling to 60°C, 50 ml of 2 M hydrochloric acid was added, and afterwards 50 ml of dichloromethane. The phases were separated, and the aqueous phase was extracted three times with 100 ml of dichloromethane each. To the combined organic phases 100 ml of an aqueous saturated solution of sodium sulfite was added, and the mixture was stirred for 5 min. The copper salts precipitated and were sucked off on a glass frit; the filtrate was washed twice with 100 ml of water each. The organic phase then was dried with magnesium sulfate, the solvent was removed in vacuo leading to a yellow oil which on addition of ethanol yielded 1.35 g (84%; m.p. 146°C) of the product as colourless powder which was directly used for the next reaction step. − HR-MS (FAB^+, *m*-nitrobenzylic alcohol): calc. 810.0703; found 810.0735 (M^+; $C_{38}H_{36}O_4I_2$). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.53−1.68 (m, 4 H, γ-H), 1.79−1.85 (m, 4 H, β-H), 2.64−2.70 (t, ^3J = 8.2 Hz, 4 H, δ-H), 2.86−2.90 (t, ^3J = 7.6 Hz, 4 H, α-H), 4.00 (s, 6 H, $COOCH_3$), 7.39 (dd, ^3J = 8.3 Hz, ^4J = 1.7 Hz, 2 H, 3-H), 7.43 ('t', ^3J = 7.6 Hz, 2 H, 6-H), 7.58 (s, 2 H, phen-H), 7.81 (d, ^3J = 8.5 Hz, 2 H, 4-H), 7.98 (d, ^3J = 8.2 Hz, 2 H, 5-H), 8.16 (dd, ^3J = 8.2 Hz, ^{4}J = 1.2 Hz, 2 H, 7-H), 8.74 (s, 2 H, 1-H).

1,4-Diiodo-2,5-bis[4-(8-hydroxymethyl-2-naphthyl)but-1-yl]-benzene: To 400 mg (0.55 mmol) of the precedingly prepared compound, dissolved in 25 ml of water-free tetrahydrofuran, 330 mg (15 mmol) of lithium borohydride were added and the reaction was kept under reflux for 3.5 h. Then the reaction mixture was cooled down to 0°C and hydrolyzed by adding 20 ml of water. The precipitate formed was dissolved again by dropwise addition of 2 M hydro-

chloric acid. After separation of the organic phase by addition of 100 ml of dichloromethane and threefold extraction of the aqueous phase by 100 ml each of dichloromethane, the combined organic phases were washed with 50 ml of saturated sodium hydrogen carbonate solution and 100 ml of water. After drying on magnesium sulfate the solvent was distilled off in vacuo leaving an analytically pure solid: 390 mg (94%), m.p. 132°C. − MS: *m/z* (%): 754 (5) [M^+], 736 (95) [$M^+ - H_2O$], 181 (85), 171 (49), 155 (100), a.o. − ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 1.54−1.60 ('quint', ^3J = 7.1 Hz, 4 H, γ-H), 1.69−1.75 ('quint', ^3J = 7.3 Hz, 4 H, β-H), 2.65 (t, ^3J = 7.7 Hz, 4 H, δ-H), 2.80 (t, ^3J = 7.5 Hz, 4 H, α-H), 4.95 (d, ^3J = 5.1 Hz, 4 H, CH_2OH), 5.22 (t, ^3J = 5.1 Hz, 2 H, CH$_2$O*H*), 7.38 (dd, ^3J = 6.6 Hz, ^4J = 1.3 Hz, 2 H, 3-H), 7.39 ('t', ^3J = 7.1 Hz, 2 H, 6-H), 7.51 (d, ^3J = 8.4 Hz, 2 H, 7-H), 7.69 (s, 2 H, phen-H), 7.76 (d, ^3J = 8.1 Hz, 2 H, 5-H), 7.83 (d, ^3J = 8.4 Hz, 2 H, 4-H), 7.85 (s, 2 H, 1-H). − $C_{36}H_{36}I_2O_2$ (754.07): calc. C 57.31, H 4.81, I 33.64; found C 57.20, H 4.52, I 33.85.

1,4-Diiodo-2,5-bis[4-(8-formyl-2-naphthyl)but-1-yl]benzene: To 0.3 g (0.4 mmol) of the precedingly mentioned hydroxymethyl compound in 250 ml of dichloromethane 0.68 g (2.64 mmol) of barium manganate were added and kept under reflux for 20 h. The hot reaction mixture was filtered through celite (d = 4 cm, h = 3 cm), and then the solvent was distilled off in vacuo yielding a colourless solid which was recrystallized from methanol/ethyl acetate (1:1): 0.24 g (81%, m.p. 128°C). − MS: *m/z* (%): 750 (100) [M^+], 732 (22), 478 (45), 169 (85), 141 (57), 44 (99), 18 (47), a.o. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.63−1.69 (m, 4 H, γ-H), 1.80−1.86 (m, 4 H, β-H), 2.66 (t, 4 H, ^3J = 8.0 Hz, δ-H), 2.90 (t, ^3J = 7.7. Hz, 4 H, α-H), 7.46 (dd, ^3J = 8.4 Hz, ^4J = 1.7 Hz, 2 H, 3-H), 7.57 ('dd', ^3J = 8.1 Hz, 2 H, 6-H), 7.58 (s, 2 H, phen-H), 7.85 (d, ^3J = 8.4 Hz, 2 H, 4-H), 7.97 (dd, ^3J = 7.0 Hz, ^4J = 1.3 Hz, 2 H, 7-H), 8.01 (d, ^3J = 8.1 Hz, 2 H, 5-H), 9.08 (s, 2 H, 1-H), 10.40 (s, 2 H, CHO). − HR-MS (FAB positive, *m*-nitrobenzylalcohol): $C_{36}H_{33}O_2I_2$ (MH^+): calc. 751.0570, found 751.0609.

1,4-Diiodo-2,5-bis{4-[8-(1,3-dioxolan-2-ylmethyl)-2-naphthyl]but-1-yl}benzene: To 0.6 g (0.8 mmol) of the preceding dialdehyde, dissolved in 100 ml of benzene, 60 mg of *p*-toluene sulfonic acid and 2 ml of ethylene glycol were added, and the reaction mixture was heated for 12 h under reflux on a water separator. After cooling, the acidic solution was neutralized by addition of 0.5 g of potassium hydroxide. Four times washing with 200 ml of water each, drying with magnesium sulfate and distilling off the solvent in vacuo yielded a colourless solid which was crystallized from ethyl acetate: 610 mg (91%, m.p. 141°C). − MS (FAB positive, *m*-nitrobenzylalcohol): *m/z* (%): 840 (44) [$MH + 1]^+$, 839 (100) [MH^+], 838 (30) [M^+]. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.63−1.69 (m, 4 H, γ-H), 1.78−1.85 (m, 4 H, β-H), 2.67 (t, ^3J = 7.9 Hz, 4 H, δ-H), 2.86 (t, ^3J = 7.8 Hz, 4 H, α-H), 4.14−4.22 [m, 8 H, CH(OCH_2)$_2$], 6.50 [s, 2 H, CH(OCH$_2$)$_2$], 7.35 (dd, ^3J = 8.8 Hz, ^4J = 1.4 Hz, 2 H, 3-H), 7.40 ('t', ^3J = 7.7 Hz, 2 H, 6-H), 7.59 (s, 2 H, phen-H), 7.73 (d, ^3J = 7.1 Hz, 2 H, 7-H), 7.79 ('t', ^3J = 8.2 Hz, 2 H, 4-H), 7.80 (d, ^3J = 8.0 Hz, 2 H, 5-H), 7.84 (s, 2 H, 1-H). − $C_{40}H_{40}I_2O_4$ (838.09): calc. C 57.29, H 4.81, I 30.27; found C 57.31, H 4.94, I 30.11.

1,4-Bis(dicyanomethyl)-2,5-bis[4-(8-formyl-2-naphthyl)but-1-yl]benzene (**16**): The catalyst was prepared from 44 mg (0.14 mmol) of 1,1′-bis(diphenylphosphanyl)ferrocene and 9 mg (0.04 mmol) of palladium(II) acetate by 30 min stirring in 8 ml of absolute dimethylformamide. 120 mg (0.14 mmol) of the precedingly described compound were added and the stirring was continued for 5 min. Separately, under argon 24 mg (0.88 mmol) of sodium hydride (95%) was suspended in 8 ml of dry dimethylformamide to which 41 mg (0.61 mmol) of malononitrile was added in portions. This suspension after the termination of gas-development was added to the educt-catalyst solution. The reaction mixture was stirred for 2 h at 70°C, after cooling down to 0°C 50 ml of 2 M hydrochloric acid were added. The separated solid was filtered off, dissolved in ethyl acetate, and adsorbed on silica gel. Chromatography on silica with cyclohexane/ethyl acetate (1:1) yielded 60 mg (68%) of the wanted product, m.p. 180°C (decomposition). − MS (FAB positive, *m*-nitrobenzyl alcohol/1% trifluoroacetic acid): *m/z* (%): 628 (44) [$MH + 1]^+$, 627 (100) [MH^+], 626 (38) [M^+]. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.67−1.73 (m, 4 H, γ-H), 1.80−1.86 (m, 4 H, β-H), 2.78 (t, ^3J = 7.5 Hz, 4 H, δ-H), 2.95 (t, ^3J = 6.8 Hz, 4 H, α-H), 5.10 [s, 2 H, CH(CN)$_2$], 7.46 (d, ^3J = 8.9 Hz, 2 H, 3-H), 7.50 (s, 2 H, phen-H), 7.60 ('t', ^3J = 7.4 Hz, 2 H, 6-H), 7.87 (d, ^3J = 8.1 Hz, 2 H, 4-H), 7.98 (d, ^3J = 7.0 Hz, 2 H, 7-H), 8.08 (d, ^3J = 8.3 Hz, 2 H, 5-H), 9.12 (s, 2 H, 1-H), 10.38 (s, 2 H, C*H*O). − HR-MS: $C_{42}H_{34}O_2N_4$: calc. 627.2760 $[MH]^+$, found 627.2799.

5,15-[7,7,8,8-Tetracyanodimethane-1,4-diylbis(1,4-butanediyl-1,7-naphthaleno)]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (**15**, *preliminary results*): Under argon a suspension of 64 mg (0.102 mmol) of **16** in 2 ml of pure tetrahydrofuran and 5 ml of absolute acetonitrile was stirred for 10 min; then 47.2 mg (0.204 mmol) of bis(3-ethyl-4-methylpyrrolyl-2)methane were added, and the reaction mixture was stirred for further 5 min. After addition of 10 mg of trichloroacetic acid the suspension was stirred for 2.5 h under exclusion of light. For the oxidation of the porphyrinogene formed, a solution of 120 mg (0.53 mmol) DDQ in 80 ml of tetrahydrofuran were added, and the solution was further stirred for 1 h. After addition of 50 ml of saturated sodium hydrogencarbonate solution and extraction with 50 ml of chloroform, the combined organic phases were washed twice with 100 ml each of saturated sodium hydrogencarbonate solution and 100 ml of water. After drying with sodium sulfate, the solvent was removed in vacuo. By chromatography on silica (d = 2 cm, h = 10 cm; elution by cyclohexane/ethyl acetate, 5:1), followed by elution with methanol, impurities were removed, and eventually the product wanted was eluted by chloroform. Further purification was not possible due to the very small amount of the product: 6 mg of **15**; R_f = 0.82 (silica, chloroform/ethyl acetate, 10:1). − MS (FAB positive, *m*-nitrobenzyl alcohol/1% trifluoro acetic acid): *m/z* (%) = 1042 (21) [M^+], 1043 (51) [MH^+], 1044 (64) [M + 2 H], 1045 (100) [M + 3 H]. − HR-MS (FAB positive): calc. 1043.5488 (MH^+), found 1043.5396. − Absorption spectrum: λ (nm) = 409 (Soret), 505, 545, 573, 630 (methylene chloride).

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