Photoinduced Electron-Transfer in Porphyrin-Acceptor Cyclophanes, 19[+]

Pyromellitic Diimide-Porphyrin Cyclophanes: Syntheses, Transannular Interactions, and Structure Analysis

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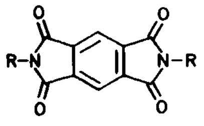
The acceptor-porphyrin cyclophanes **2** and **4** with pyromellitic diimide **(1)** as strong electron-acceptor, and the corresponding porphyrin zinc complexes **3** and **5** were prepared by a route which differs considerably from that in the syntheses of previously prepared electron-acceptor porphyrin cyclophanes. The conformations of these electron-acceptor-porphyrin cyclophanes are discussed based on ^{1}H-NMR and the X-ray structural analysis of **2**. According to the results obtained, the plane of **1** and that of the porphyrin unit (at least in the crystalline state) are neither close nor parallel to each other. An unusual dihedral orientation of the donor and acceptor planes was detected for **2**.

Introduction

Pyromellitic diimides (**1**) have been used as strong electron acceptors in the [*n*,*m*]paracyclophanes by Verhoeven et al.,[2] and in recent years the electron transfer interactions of **1** in combination with porphyrins were studied by Sanders et al.[3] and Osuka et al.[4] In these investigations, however, the **1**-containing acceptor units were mainly linked to the porphyrins by single conformationally flexible chains, or by heterocyclic acceptors complexing the nitrogens to the zinc of the corresponding zinc porphyrins. In the present work the synthesis of pyromellitic diimide-porphyrin cyclophanes with **1** is reported, yielding the cyclophanes **2** and **4** as well as their zinc-porphyrin complexes **3** and **5**. Here the links are from *N* and *N'* via $-(CH_2)_n-$ chains (n = 3 and 4) to the *ortho*-positions of the phenyl rings at the opposite C-5 and C-15 positions of porphyrins.



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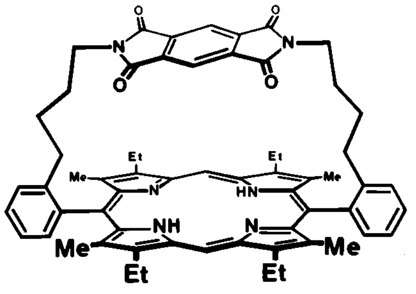

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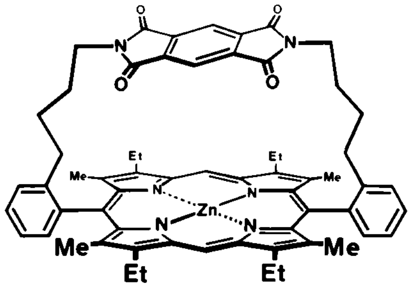

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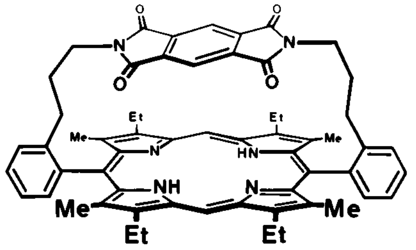

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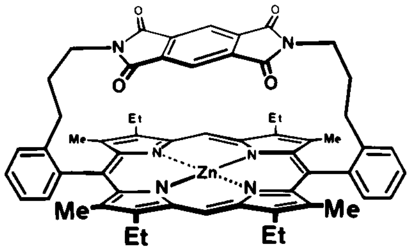

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Since in recent years a great number of structurally different porphyrin-acceptor cyclophanes were synthesized and

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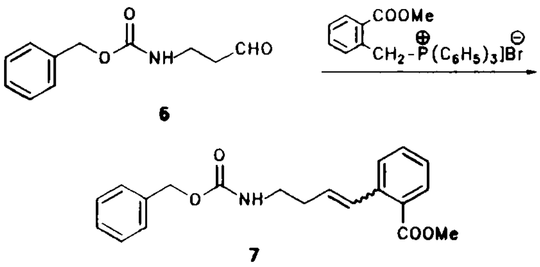
investigated by the authors,[5][6] the pyromellitic diimido-porphyrin cyclophanes, so far missing in the series, were expected to contribute further information on aspects of steric and charge-transfer interactions. For example, due to the rather long planar extension of the **1**-acceptor in the cyclophane bridges across the porphyrin unit, the influence on the transannular interaction, to compare with our previously synthesized porphyrin-quinone cyclophanes, was of interest. Furthermore, with a first reduction potential of $E^1_{\text{red}} = -1.37$ V, **1** is a rather strong electron acceptor, and in the event that an electron transfer from the porphyrin donor occurs, leading to a radical anion of **1**, the charge separation should be indicated by a typical absorption of the **1**-radical anion at $\lambda \approx 715$ nm (see below).

In analogy to the previous preparations of other acceptor-bridged porphyrin cyclophanes, the syntheses of **2** and related porphyrin cyclophanes with pyromellitic diimide as the acceptor unit, were planned by first building up the bridges with the acceptor **1** in the centre, linked by tetramethylene chains into the *ortho*-position of the benzaldehyde groups at the two ends of the prospective bridging unit. The two aldehyde groups should then finally yield the pyromellitic diimide-porphyrin cyclophanes by condensation with the appropriate pyrrole systems and cyclization to porphyrins. In a corresponding reaction sequence the analogue **4**, with chains of only three methylene groups in the bridges instead of the four in **2**, was synthesized with the expectation of shorter transannular distances occurring and, possibly, stronger donor−acceptor interactions. The zinc complexes **3** and **5** of the porphyrin cyclophanes **2** and **4** were also of interest since, due to the long extension of **1**, a direct approach of the functional groups of this electron-acceptor to the porphyrin-complexed metal is sterically hindered, whereas in the case of the zinc porphyrin−quinone cyclophanes the donor−acceptor interaction occurs, at least partly, not through-space but by direct interaction of the quinone-carbonyl groups to the metal complexed in the centre of the porphyrin.[5]

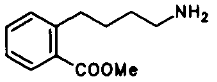
Syntheses of Pyromellitic Diimide-Porphyrin Cyclophanes

Syntheses of [4.4]Pyromellitic Diimide-Porphyrin Cyclophanes 2 and 3

The first synthetic approach to **2** took *N*-(3,3-diethoxypropyl)phthalimide as the starting material which, with water-free hydrazine, was converted into 3-amino-1,1-diethoxypropane,[6][7] the amino group of which was protected by reaction with benzyloxycarbonyl chloride to give 3-(benzyloxycarbonylamino)propionaldehyde diethyl acetal.[7][8] Acetal hydrolysis yielded 3-(benzyloxycarbonylamino)propionaldehyde (**6**)[7][8] (for improvements of these literature steps see Experimental Section). The Wittig reaction of **6** with (2-methoxycarbonylbenzyl)triphenylphosphonium bromide yielded methyl 2-(4-benzyloxycarbonylamino-but-1-enyl)benzoate (**7**, *cis*/*trans* isomers).



Catalytic hydrogenation of the double bond of **7**, and acidic splitting off of the carbamate group, yielded methyl 2-(4-aminobutyl)benzoate (**8**). Reaction of **8** with pyromellitic dianhydride resulted in the formation of *N*,*N'*-bis[4-(2-methoxycarbonylphenyl)butyl]pyromellitic diimide (**9**), which already contains the carbon skeleton for the preparation of the two aldehyde functions required for the condensation reaction to form the porphyrin systems.



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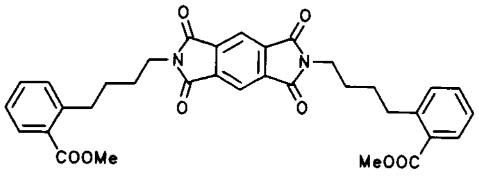

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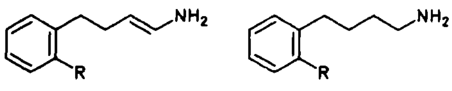
However, the reduction of the two carboxylic ester groups in **9** to the corresponding hydroxymethyl functions, under a variety of conditions, was not successful; instead, the two −CO−NR−CO− units of the pyromellitic diimide were partially reduced, with a preference for one carbonyl group on either side. Consequencely the hydroxymethyl or aldehyde groups on the lateral phenyl rings were introduced at an earlier stage.

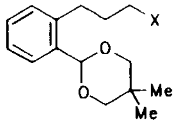
In fact, starting from **7** with excess lithium borohydride (boiling tetrahydrofuran, 23 h), the carbamate was cleaved and the methyl ester group in **10** reduced to the hydroxymethyl substituent in **11**. Catalytic hydrogenation of the olefinic double bond under mild conditions (PtO_2, ethanol, 2 h, 20 °C) resulted in the desired formation of the 2-(4-aminobutyl)benzyl alcohol (**13**); under stronger conditions (Pd/10% on charcoal, 3 bar, 22 h, ethyl acetate/methanol) 2-(4-aminobutyl)toluene (**12**) was obtained as the unwanted major product.



10: R = COOMe **12:** R = CH_3
11: R = CH_2OH **13:** R = CH_2OH

In the reaction of **13** with pyromellitic dianhydride, there is, in principle, a competition between hydroxy and amino groups which was checked by the reaction with 3-amino-1-propanol (which contains the competing groups in the same molecule). As expected, the reaction occurred with the more nucleophilic amino group yielding (with pyromellitic dianhydride) the *N*,*N'*-bis(3-hydroxypropyl)pyromellitic diimide together with unwanted minor products, which were difficult to separate by chromatography and recrystallization.

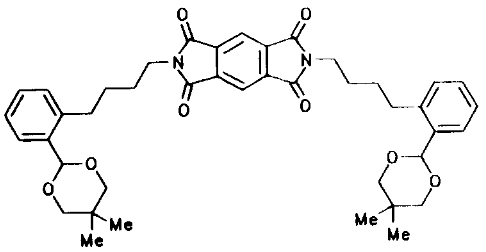
A straightforward preparation of the dialdehyde **18** for the condensation reaction to yield the pyromellitic diimide-porphyrin cyclophane is based on the early introduction of the two aldehyde functions of **18** which should be protected, as bis(acetals), for the precursors **14**−**17**.



14: X=Br.

15: X=CN.

16: X=CH$_2$NH$_2$.



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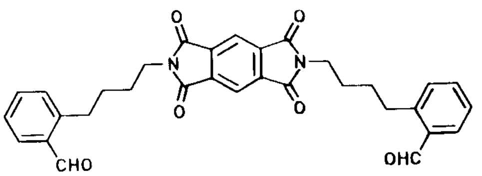

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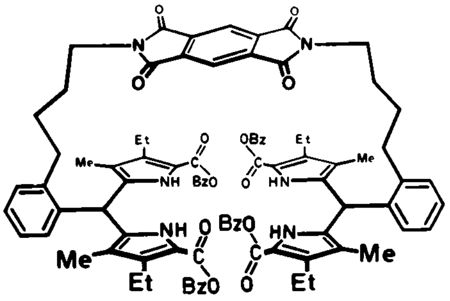
Thus, for the synthesis of **18**, 2-(3-bromopropyl)benzaldehyde was converted into the acetal 2-(3-bromopropylphenyl)-5,5-dimethyl-1,3-dioxane (**14**) by reaction with 2,2-dimethyl-1,3-propanediol. The addition of sodium cyanide in triethylene glycol led to the substitution of the bromo- by the cyano-substituent (**15**). This cyano compound was hydrogenated by lithium aluminium hydride (tetrahydrofuran, 30 min, 0 °C) to yield the corresponding 4-[2-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl]butylamine (**16**) which, in a suspension in *N*,*N*-dimethylformamide and in presence of potassium carbonate, was added dropwise to a solution of pyromellitic dianhydride in dimethylformamide, under argon and in a dry atmosphere. After 4 h at 180 °C the reaction mixture was poured onto ice, the precipitate formed was sucked off, washed with water and dried on a lyophilizer. The *N*,*N'*-bis[2-(5,5-dimethyl-1,3-dioxan-2-yl)phenylbutyl]pyromellitic diimide **17** was obtained (71% yield, m.p. 206−208 °C) by flash chromatography on silica (diethyl ether/*n*-pentane) and subsequent crystallization from diethyl ether/*n*-pentane. The dioxane, as the bis(acetal)-protecting group of **17**, was removed by chloroform in trifluoroacetic acid/5% sulfuric acid (22 h, room temp.); the organic phase was separated, and the aqueous phase extracted with chloroform. After evaporation in vacuo the dialdehyde **18** was obtained from **14** in an excellent overall yield (white solid, m.p. 190 °C, dec.).

As the first step of the porphyrin synthesis, **18** was treated with 2-benzyloxycarbonyl-3-ethyl-4-methylpyrrole to afford **19** (ethanol, under argon, catalytic amount of hydrochloric acid; details in Experimental Section). The benzyl groups were split off by catalytic hydrogenation leaving the corresponding tetracarboxylic acids which were then decarboxylated. The four 3-ethyl-4-methylpyrrole groups underwent ring closure in the conventional way [by condensation with triethyl orthoformate/trichloroacetic acid (dichloromethane, magnesium sulfate)][6] to yield the pyromellitic diimide-porphyrin cyclophane **2** as the final product (for X-ray structural analysis and other analytic data see below).



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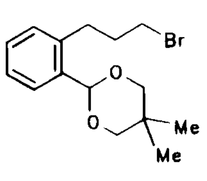
Under argon, and in the presence of excessive zinc(II) acetate in chloroform/methanol (5:1) **2** yielded the zinc complex **3**. For further details of this multistep synthesis of **2** and **3** see the Experimental Section.

Syntheses of [3.3]Pyromellitic Diimide-Porphyrin Cyclophanes 4 and 5

In principle the synthesis of the [3.3]pyromellitic diimide-porphyrin cyclophane **4** followed a route similar to the synthesis of the corresponding [4.4] analogue **2**. In 2-(3-bromopropyl)benzaldehyde the aldehyde group was protected as acetal, yielding 1-[3-bromopropyl-2-(5,5-dimethyl-1,3-dioxan-2-yl)]benzene (**20**). **20** was treated with potassium phthalimide (6 h, 145 °C, sealed tube) to obtain *N*-3-[2-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl]propylphthalimide (**21**), which was then reacted with hydrazine hydrate in methanol (3 h, reflux) to yield 1-(3-aminopropyl)-2-(5,5-dimethyl-1,3-dioxan-2-yl)benzene (**22**). The twofold reaction of pyromellitic dianhydride with the amino groups of **22**, by the addition of the dianhydride within 2.5 h to a suspension of **22** in dimethylformamide in the presence of dry potassium carbonate, led to the protected dialdehyde **23**. After acidic



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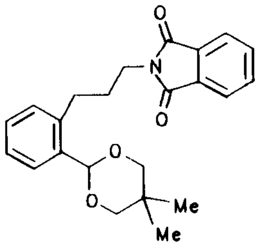

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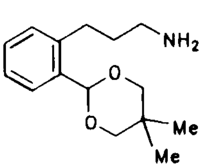

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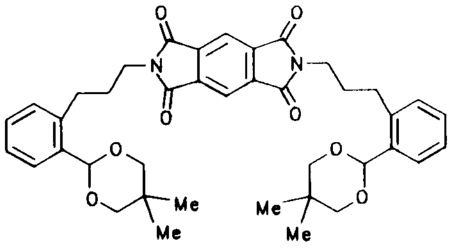

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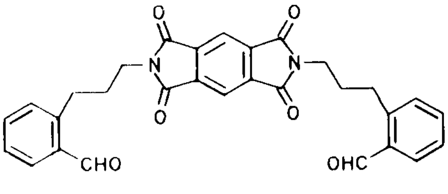

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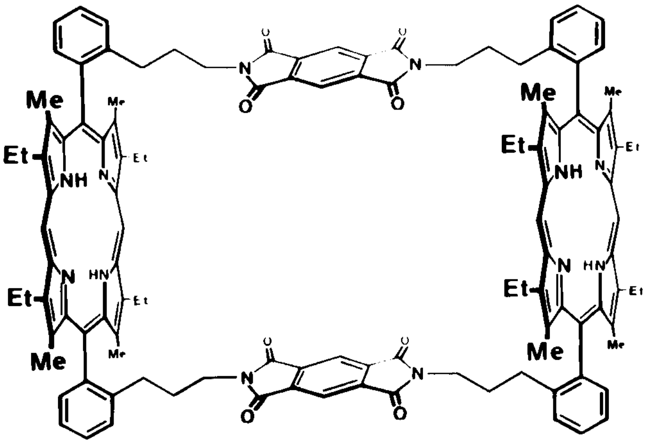
deprotection, by splitting off the two acetal groups, the dialdehyde **24** was obtained, which is the key compound for building up the [3.3]porphyrin cyclophanes **4** and **5**, in a route closely following the synthesis of the [4.4] analogues as discussed above.

As discussed for the corresponding reaction of the [4.4] analogue **18** to **19**, the dialdehyde **24** was treated with 2-benzyloxycarbonyl-3-ethyl-4-methylpyrrole (ethanol, catalytic amount of hydrochloric acid); the benzyl groups were split off by hydrogenation, leaving, after decarboxylation, the 3-ethyl-4-methylpyrrole units. Their reaction with trichloroacetic acid and triethyl orthoformate (dichloromethane, 17 h, room temp.) led to the partially protonated porphyrin system which was dehydrogenated by 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) to yield the [3.3]pyromellitic diimide-porphyrin cyclophane **4**. The zinc complex **5** was obtained from **4** in the same manner that **3** was obtained from **2**.



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The shorter C_3-chains between the acceptor and the porphyrin in the cyclophane **4** compared to the C_4-linked cyclophane **2** did not significantly reduce the porphyrin yields, which for both **2** and **4** are rather poor. The only difference observed in the cyclization to the [3.3]- and the [4.4]-linked porphyrin-acceptor cyclophanes **2** and **4** is the finding that in the reaction to **4** a dimer was isolated as a by-product of **4**. The structure of **25** is suggested for this dimer, on the basis of spectroscopic and analytical data.

Physical Properties of Pyromellitic Diimide-Porphyrin Cyclophanes

X-Ray Structural Analysis of [4.4]Pyromellitic Diimide-Porphyrin Cyclophane (2)

For structural analysis [4.4]pyromellitic diimide-porphyrin cyclophane (**2**) was crystallized from methyl acetate as dark red orthorhombic prisms of space group *Pnam* (N° 62, Internat. Tables); cell parameters a = 2190.6 (8), b = 935.8 (2), c = 2679.0 (8) pm; Z = 4; $C_{62}H_{62}N_6O_4 \cdot C_3H_6O_2$ (1029.30), D_{calc} = 1.245 gcm^{-3}; symmetry of the molecule in the crystal: C_s. For further details of data collection and structure determination of **2** see Experimental Section.

The results of the X-ray structural analysis of **2** differ considerably from all other structures of donor-acceptor cyclophanes determined so far.[5][6] For the intramolecular structures of porphyrin-quinone cyclophanes the porphyrin, as well as the acceptor units, are usually planar or nearly planar, and the centres of the donor and acceptor units are approximately superimposed above each other. For **2**, the porphyrin is planar, whereas the acceptor part of the five-membered rings are bent relative to the planar central ring by about 7°. The two phenyl groups in 5- and 15-positions of the porphyrin, as well as the first methylene groups of the bridges at those phenyl groups, are perpendicular to the porphyrin plane. The intramolecular orientation of the donor and acceptor units, however, is completely different from all other acceptor-porphyrin cyclophanes for which the structures are known: the bridge with the pyromellitic diimide as the acceptor is shifted away from the position parallel to the porphyrin plane, resulting in a dihedral inclination between the acceptor plane and the plane of the porphyrin of about 69° (see Figure 1a). Figure 1a shows that the vertical projection from the acceptor centre to the porphyrin plane meets this plane outside the porphyrin cycle at a distance of 497 pm, leading to a negligible intramolecular interaction between the electron acceptor *N*,*N'*-pyromellitic diimide and the donor porphyrin. Obviously this very specific intramolecular structure of an electron-acceptor-porphyrin cyclophane is the result of the long extension of the acceptor unit **1**, which from *N* to *N'* amounts to 670 pm, thus being close to the diagonal distance of 723 pm between C(5) and C(15) of the porphyrin. Based on these structural conditions it is understandable that the porphyrin cannot be bridged by the extended $-(CH_2)_4-$**1**$-(CH_2)_4-$ chain in the typical sandwich-like structure of normal porphyrin-acceptor cyclophanes.

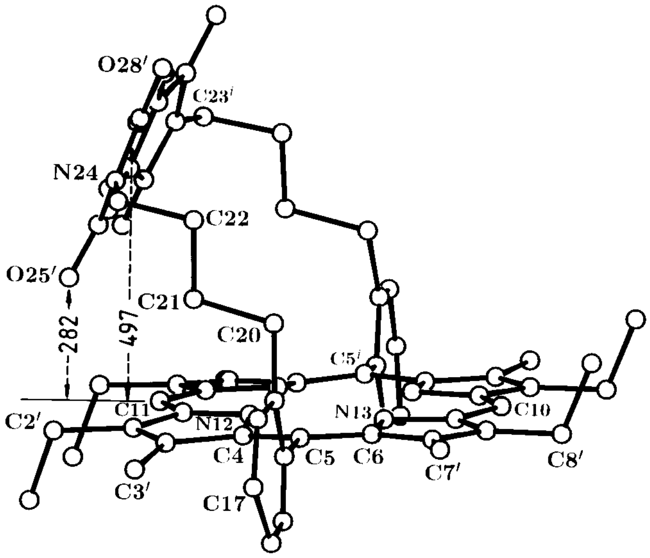

Figure 1a. Molecular structure of the crystal of **2** in a side view

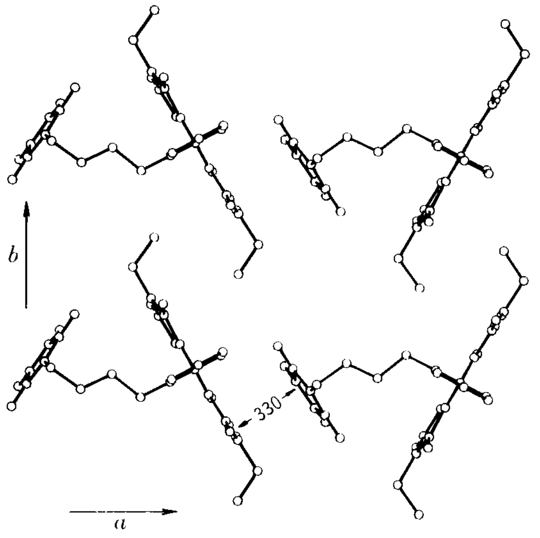

Figure 1b. Packing arrangement of **2** in a projection of (001)-mirror plane

In the unit cell of **2** (Figure 1b) the cyclophane molecules are stacked along the short crystallographic *b* axis. In contrast to the intramolecular π-π interaction of the porphyrin-acceptor cyclophanes, in the crystal of **2** an acceptor unit of one molecule and the porphyrin ring of a second molecule of a neighbouring stack are nearly parallel to each other, and partially overlap with a distance of about 330 pm. Thus, in the solid state an intermolecular photoinduced electron-transfer from porphyrin to the **1**-acceptor would probably be more likely than the intramolecular electron-transfer from donor to acceptor within the same molecule.

Of course, the preceding discussion of the structure of **2** is based on the crystalline state as determined by X-ray analysis. For the solution state, we know from earlier conformational studies on other acceptor-porphyrin cyclophanes, that different donor-acceptor orientations can easily be achieved by swinging of the methylene−acceptor−methylene bridges across the porphyrin plane; most probably this also happens with **2**.

Temperature-Dependent ^{1}H-NMR Spectrometry

As mentioned above and in preceding papers,[6][10] for acceptor-containing bridges in quinone-porphyrin cyclophanes in general two conformational processes have to be considered. The first is the complete rotation of the quinones or other electron-acceptors within the bridges in the case where the vertical extensions of the acceptor units are sufficiently small, or the porphyrin-acceptor distances are wide enough, as in the series of porphyrin-quinone cyclophanes with systematically increased porphyrin-quinone distances due to the use of built-in spacers.[6c] The second process is a pendular motion back and forth of the whole acceptor-containing bridges from C-5 to C-15 on the porphyrin leading to two equivalent unsymmetrical conformations.[10] This process is best observed by the broadening, and sometimes even splitting, of the methine protons H-10 and H-20 of the porphyrin. For the ^{1}H-NMR signal of these two *meso*-protons of **2** a broadening is indeed observed in the temperature range of 180−210 K. For the porphyrin cyclophane **4**, where the pyromellitic diimide is linked to the porphyrin on both sides by only three methylene groups, the ^{1}H-NMR signals for the protons on C(10) and C(20) do not show any broadening or splitting. Obviously, the [3.3]pyromellitic diimide-porphyrin cyclophane **4**, due to the shortening of the methylene chains by one methylene group on each side of the electron acceptor in the central bridge, is too strained to swing back and forth as observed for **2**. This indication of the more pronounced molecular rigidity of **4** as compared to **2** is in agreement with molecular dynamics simulations.[10] The different configurations and conformational mobility of the cyclophanes **2** and **4** is also reflected by a comparison of their ^{1}H-NMR spectra (500 MHz, CD_2Cl_2, 303 K). In the non-cyclized precursors of the cyclophanes already containing the pyromellitic diimide and the methylene chains up to the dialdehydes **18** and **24**, the two protons on the central ring of pyromellitic diimide show rather normal and similar chemical shifts (**18**: δ = 8.09, s, 2 H; **24**: δ = 8.22, s, 2 H). As soon, however, as the ring closure to the pyromellitic diimide-porphyrin cyclophanes occurs, the pyromellitic ring protons are exposed to the ring current effect of the cyclic-conjugated π-system of the porphyrin, as discussed before for our series of quinone-porphyrin cyclophanes and related analogues of electron-acceptor porphyrin cyclophanes. Indeed for **4** the signal for the aromatic protons in the pyromellitic part is shifted considerably to δ = 5.01, indicating that these protons are shielded by the ring current of the porphyrin. For the [4.4]pyromellitic diimide-porphyrin cyclophane **2** the corresponding shift appears only at δ = 6.85, indicating that these protons are less affected by the porphyrin ring current. Most probably this difference is caused, not by the slightly longer distance between the two ring systems of the cyclophane, but due to a different sterical configuration of **2** and **4**, possibly corresponding to the result of the X-ray analysis of **2** with non-planar, non-parallel orientation of the porphyrin and the pyromellitic ring planes.

Cyclovoltammetry and Free Reaction Enthalpies ΔG of Electron Transfer

The determination of the redox potentials was of particular interest in order to assess the free reaction enthalpy, ΔG, of the electron transfer in the new donor-acceptor cyclophanes **2** to **5**. These measurements were made in cooperation with J. Daub and C. Stadler with whom the completed results will be published jointly.[11] Due to the importance of the redox potentials for the general topic of the present paper, a short preliminary survey will be given below. For the potentiometric measurements the potentiostat Amel System 5000 was used (platinum disc electrode as working electrode, Ag/AgCl electrode as reference electrode, calibrated against ferrocene); the solvent used was dichloromethane with 0.1 M tetra-*n*-butylammonium hexafluorophosphate as conducting salt (see ref.[11] for further details).

For the pyromellitic-diimide porphyrin cyclophanes **2** and **4** and their zinc complexes **3** and **5**, the first oxidation and reduction potentials $E^1{}_{ox}$ and $E^1{}_{red}$ are listed in Table 1. The first reduction potentials of the **1**-containing compounds **2** and **4** with $E_{red}{}^1$ = −1.52 V and −1.45 V are significantly more negative than those of the pyromellitic diimide itself (**1**: $E_{red}{}^1$ = −1.37 V), and even more so in comparison to **9** ($E_{red}{}^1$ = −1.34 V). The porphyrin zinc complexes (**3** of **2**, and **5** of **4**) do not show a significant influence on $E^1{}_{red}$, whereas $E^1{}_{ox}$-values are considerably reduced in comparison to the corresponding uncomplexed systems.

Table 1. First oxidation potentials $E^1{}_{ox}$ and first reduction potentials $E^1{}_{red}$ in volts (± 0.02 V) of the pyromellitic diimide porphyrin cyclophanes **2** and **4** and their zinc complexes **3** and **5**; $E^1{}_{red}$ of **1** and **9** are included for comparison

Compound	2	3	4	5	1	9
$E^1{}_{ox}$ [V]	+0.35	+0.21	+0.41	+0.21		
$E^1{}_{red}$ [V]	−1.45	−1.44	−1.52	−1.50	−1.37	−1.34

From the first oxidation and reduction potentials listed in Table 1, according to the Rehm−Weller approach,[12] the enthalpy $\Delta G'$ of the electron transfer reactions can roughly be approximated by $\Delta G' = (E^1{}_{ox} - E^1{}_{red}) - E_{00}$, where E_{00} represents the energy of the first excited singlet state derived from the adjacent edges of the absorption and the emission bands of the cyclophanes concerned. For example, the $\Delta G'$ value of **2** (−0.16 ± 0.02 eV) and that of the porphyrin-2,5-dimethyl-*p*-benzoquinone cyclophane (−0.15 ± 0.002 eV) are of the same order of magnitude. This similarity, however, does not apply to **3**, the zinc complex of **2**, in comparison to the zinc-porphyrin-benzoquinone cyclophane, since in the latter there are specific interactions between the quinone carbonyl groups and the zinc in the centre of the porphyrins. In contrast, for the zinc complexes **3** and **5** a similar intramolecular complexation of the zinc in the centre of the porphyrins by **1** is impossible. Due to the extended structure of *N*,*N'*-disubstituted pyromellitic diimide (**1**), its heteroatoms cannot get into close contact with the zinc for sterical reasons (see above). This specific sterical situation of the electron-acceptor prevents the direct approach to the zinc in the porphyrin centre and, consequently, leads to a reduction of the driving-force for an electron-transfer.

Absorption- and Fluorescence Spectra

The absorption spectra of **2** to **5** are dominated by the porphyrin chromophore, and, consequently, show the Soret band in the area of 380−420 nm and the less intense Q-bands between 500−650 nm; as expected, for symmetry reasons, there are four Q-bands for **2** and **4**, and only two Q-bands for the zinc-porphyrin compounds **3** and **5**. Just as the quinones in porphyrin-quinone cyclophanes do not significantly influence the predominating porphyrin chromophore, in **2** and **4** the pyromellitic diimides as electron-acceptors do not exert a perceptible transannular effect on the absorption of the porphyrin chromophore. As is the case for the quinone-porphyrin cyclophanes, for the new intramolecular donor−acceptor systems **2**−**5** no specific transannular charge-transfer absorptions are observable; a possible explanation may be the dominating long wavelength absorptions of the porphyrin parts of these compounds. The absorption spectrum of the "dimer" **24,** which has no close and parallel donor−acceptor structure, is very similar to the spectra of **2** and **4**, based on a comparison made in four different solvents.

Preliminary fluorescence measurements on **2** and **4** and their zinc complexes **3** and **5** were made in toluene, methyl acetate, dichloromethane, and *N*,*N*-dimethylformamide. On excitation at the maxima of the Soret bands, the relative quantum yields of fluorescence increased with increasing polarities of the solvents. It seems likely that this effect is due to a stabilization of the charge-separated state. For the *N*,*N′*-pyromellitic diimide-porphyrin cyclophanes with $-(CH_2)_3-$ bridges **4** and **5**, the relative quantum yield was found to be significantly smaller than for the corresponding $-(CH_2)_4-$bridged compounds **2** and **3**.

Time-resolved absorption measurement at the donor−acceptor cyclophanes **2**, **3**, **4**, and **5** were carried out in collaboration with the Munich group (M. E. Michel-Beyerle, H. Heitele, F. Pöllinger, and co-workers[13]). As a first result of the time-resolved investigations of these cyclophanes, an intramolecular charge-separation in the case of **2** (excitation at 390 nm, Soret band) led to the observation of a deep-red absorption band at $\lambda = 720$ nm for the pyromellitic diimide radical anion, the rate of formation of which depends on the polarity of the solvents (within about 10 ps in toluene and 2−4 ps in dimethylformamide). The charge-recombination to the ground state of **2** again depends on solvent polarity (approximate lifetime in dimethylsulfoxide 26 ps, in methyl acetate 100 ps, in toluene 600 ps). For **4** the charge-transfer rates are similar, whereas for the pyromellitic diimide-zinc porphyrin cyclophane **5** the charge-separation is in the order of 1 ps for all three solvents mentioned above; the charge recombinations occur from 4 ps in dimethylformamide to 170 ps in toluene. These results are tentative and need further verification.

Experimental Section

General: M.p.′s: Büchi 512; m.p. > 250 °C, Bock monoscope (m.p.′s uncorrected). − IR: Perkin−Elmer FT-IR 1760X. − UV/Vis: Varian Cary 2300. − Fluorescence: SPEX Fluorolog F 112 XE. − MS: Jeol JMS SX 102 A; Finnigan MAT 212 (only the most prominent peaks are listed, usually with $I_{rel} > 15\%$); FAB spectra (LSIMS, positive): VG Analytical ZAB 2E/70 SE ($I_{rel} > 15\%$). − ^{1}H NMR: Bruker Physik HX 360 and AM 500 (internal standards: solvent signals; $CHDCl_2$: $\delta = 5.32$, $CHCl_3$: $\delta = 7.26$, D_5HMSO: $\delta = 2.50$). − Microanalyses: Elemental Analyzer 1106, Carlo Erba. − Analytical TLC: DC Microcards Polygram SIL G/UV$_{254}$ and Polygram Alox N/UV, Macherey−Nagel. − CC: Silica gel Sili Tech 63−200 µm, Merck. − Flash CC: silica (35−70 µm, 60 Å), Amicon. − GC-MS: GC HP 6890 Series II, mass-selective detector HP 5972; capillary column OPIMA-5 DF −0.25 (94% methyl silicon, 5% phenyl silicon, 1% vinyl silicon), Macherey−Nagel.

***N*-(3,3-Diethoxypropyl)phthalimide:** To improve the preparation described in ref.[7] (26.0 g, 140 mmol) potassium phthalimide was added [in a sealed tube (d = 5 cm, h = 45 cm) under argon] to 3-chloro-1,1-diethoxypropane (20.1 mL, 120 mmol) dissolved in anhydrous *N*,*N*-dimethylformamide while stirring vigorously. After 5 h at 145 °C the reaction mixture was cooled to room temp., and water (300 mL) and dichloromethane (200 mL) were added. The organic phase was separated and the aqueous phase was extracted with dichloromethane (4× 200 mL). After drying the combined organic solutions with magnesium sulfate, the solvent was distilled off in vacuo. The remaining dark brown oil was flash-chromatographed (silica, diethyl ether/*n*-pentane, 1:1, $R_f \approx 0.40$), and the product obtained crystallized from diethyl ether (400 mL) to yield colourless crystals of the imide: 30.3 g (91%) (ref.[7]: 83%), m.p. 176 °C.

3-(Benzlyoxycarbonylamino)propionaldehyde (6): Subsequent synthetic steps from *N*-(3,3-diethoxypropyl)phthalimide as the starting material, via 3-amino-1,1-diethoxypropane,[7] 3-(benzyloxycarbonylamino)propionaldehyde diethyl acetal (**6**),[8] and 3-(benzyloxycarbonylamino)propionaldehyde,[8] followed the literature methods with minor improvements (slightly higher melting points, higher yields).

Methyl 2-(4-Benzyloxycarbonylamino-2-but-1-enyl)benzoate (*cis*/*trans*-Isomers) (7): In a Wittig reaction (2-methoxycarbonylbenzyl)triphenylphosphonium bromide[6a] (100 g, 204 mmol) was added to sodium (4.70 g, 204 mmol) in absolute methanol (350 mL) under argon, and the solution was stirred for 60 min. A solution of **6** (14.1 g, 68.1 mmol) in dry tetrahydrofuran (260 mL) was added to this mixture within 30 min at room temp. Hydrolysis was achieved by adding water (600 mL) and stirring the solution for 24 h. Extraction with dichloromethane (5× 400 mL), and drying of the combined extracts with magnesium sulfate yielded an orange oil (after removal of the solvent) which was adsorbed on aluminium oxide (400 g) and chromatographed using diethyl ether as an eluent. The solvent was distilled off in vacuo from the fraction of $R_f \approx 0.39$ to yield the *cis*/*trans* isomers of **7** as a yellow oil. The following analytical data refer to the stereoisomer mixture **7**: yield 10.2 g (72%). − MS (FAB positive, *m*-nitrobenzyl alcohol, 1% trifluoroacetic acid); *m*/*z* (%): 342 (26) $[MH_2]^+$, 340 (100) $[MH]^+$, 339 $[M]^+$. − ^{1}H NMR (500 MHz, $CDCl_3$): all signals in agreement with *cis*/*trans* mixture. − $C_{20}H_{21}N_1O_4$ (339.4): calc. C 70.78, H 6.24, N 4.13; found C 70.61, H 6.48, N 4.28.

Methyl 2-(4-Aminobutyl)benzoate (8): After the addition of Pd/C (290 mg, 10%) and hydrochloric acid (6.7 mL 1 M) in distilled water (40 mL) to a solution of the *cis*/*trans* isomer mixture of **7** (5.0 g, 14.7 mmol) in toluene/methanol/methyl acetate (400 mL, 1:2:1) the mixture was hydrogenated under normal pressure until no further hydrogen was taken up. The catalyst was separated by filtration through a fibreglass filter, and the filtrate removed from the solvent and dried in vacuo. Further purification of the viscous product by flash chromatography on silica with ethanol/triethylamine (10:1) yielded **8** as light yellow oil, $R_f \approx 0.30$: 3.03 g (99%). − MS; *m*/*z* (%): 207 (35) $[M]^+$, 164 (100), 148 (24), 147 (56), 146 (32), 132 (37), 118 (82), 91 (94), a.o. − ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 1.40−1.54 (m, 2 H, ar-$CH_2-CH_2-CH_2$), 1.54−1.64 (m, 2 H, ar-$CH_2-CH_2-CH_2$), 1.67 (s, 2 H, NH_2), 2.67 (t, ^3J = 6.9 Hz, 2 H, CH_2-NH_2), 2.91 ("t", $^3J \approx 7.8$ Hz, 2 H, ar-CH_2), 3.84 (s, 3 H, OCH_3), 7.22 ("t", $^3J \approx 8.2$ Hz, 1 H, 5-H), 7.24 (d, ^3J = 8.3 Hz, 1 H, 3-H), 7.39 (d"t", $^3J \approx 7.2$ Hz, $^4J \approx 1.3$ Hz, 1 H, 4-H), 7.80 (dd, ^3J = 7.1 Hz, $^4J \approx 1.1$ Hz, 1 H, 6-H). − $C_{12}H_{17}N_1O_2$ (207.27): calc. C 69.54, H 8.27, N 6.76; found C 69.28, H 8.28, N 6.93.

***N*,*N′*-Bis[4-(2-methoxycarbonylphenyl)-*n*-butyl]pyromellitic Diimide (9):** A solution of **8** (1.00 g, 4.82 mmol) in anhydrous *N*,*N*-dimethylformamide (10 mL) was dropped, under argon, into a solution of pyromellitic dianhydride (516 mg, 2.36 mmol) in *N*,*N*-dimethylformamide within 2 h. The yellow solution was heated under reflux for 4 h and then, after cooling, poured onto ice water (100 mL). The colourless precipitate was filtered off and washed with water (2× 10 mL). By repeated crystallization from water/*N*,*N*-dimethylformamide (10:1) and drying in vacuo at 60 °C 1.21 g (86%) of **9** were obtained (analytically pure) as white solid of m.p. 181−183 °C. − MS (FAB positive, *m*-nitrobenzyl alcohol/1% trifluoroacetic acid): *m*/*z* (%): 597 (46) $[MH]^+$, 596 (6) $[M]^+$, 566 (41), 565 (100) $[M - OMe]^+$, a.o. − ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 1.60−1.66 (m, 4 H, ar-$CH_2-CH_2-CH_2-CH_2$), 1.72−1.78 (m, 4

H, ar-CH$_2$−CH$_2$−CH_2−CH$_2$), 2.97 (“t”, ^3J = 7.8 Hz, 4 H, ar-CH_2−CH$_2$−CH$_2$−CH$_2$), 3.74 (t, ^3J = 7.2 Hz, 4 H, ar-CH$_2$−CH$_2$−CH$_2$−CH_2), 3.82 (s, 6 H, ar-COOCH_3), 7.22 (“t”, $^3J \approx$ 8.1 Hz, 2 H, 5-H), 7.24 (d, ^3J = 7.5 Hz, 2 H, 3-H), 7.40 d“t”, ^3J = 8.1 Hz, ^4J = 1.5 Hz, 2 H, 4-H), 7.81 (dd, ^3J = 7.7 Hz, ^4J = 1.4 Hz, 2 H, 6-H), 8.19 (s, 2 H, H$_{\mathrm{pyrom.}}$). − $C_{34}H_{32}N_2O_8$ (596.64): calc. C 68.45, H 5.41, N 4.70; found C 68.38, H 5.60, N 4.93.

2-(4-Aminobut-1-enyl)benzyl Alcohol (11): A solution of **7** (1.0 g, 2.95 mmol) in tetrahydrofuran (10 mL) was added within 30 min to a suspension of lithium borohydride (1.28 g, 59 mmol) in anhydrous tetrahydrofuran (100 mL), under argon and with the exclusion of moisture. The reaction mixture was heated under reflux for 23 h, and after cooling to room temp., water (75 mL) was added to the suspension to enable hydrolysis. The sediment formed was dissolved by dropping 5 mL of concentrated hydrochloric acid into the reaction mixture. The tetrahydrofuran was distilled off, and the remaining aqueous solution extracted with chloroform (3× 100 mL). Drying with magnesium sulfate, removal of the solvent, and chromatography (aluminium oxide, methanol/ethyl acetate, 1:10) yielded the *cis*/*trans* isomer mixture as white solid after crystallization from methanol, m.p. 40−43°C; ca. 450 mg (86%). − ^{1}H NMR (500 MHz, DMSO) agrees with the *cis*/*trans* mixture. − $C_{11}H_{15}NO$ (177.25): calc. C 74.54, H 8.53, N 7.90; found C 74.41, H 8.65, N 7.62.

2-(4-Aminobutyl)toluene (12): In order to achieve hydrogenation of the double bond, **11** (230 mg, 1.3 mmol) was dissolved in ethyl acetate (30 mL) and methanol (20 mL). After addition of the Pd/C catalyst (47 mg) the suspension was hydrogenated (3 bar, 22.5 h). The catalyst was separated by filtering the reaction mixture through a celite-filled glass frit and washed with ethyl acetate (700 mL). The solvent was distilled off in vacuo, and the residue purified by preparative TLC with ethyl acetate/methanol (15:1, yielding 210 mg (98%) of **12** as light yellow oil. − MS; *m*/*z* (%): 163 (10) [M$^+$], 146 (29), 105 (100), a.o. − ^{1}H NMR (360 MHz, [D$_6$]DMSO): δ = 1.42−1.55 (m, 4 H, CH$_2$−CH_2−CH_2−CH$_2$), 2.25 (s, 3 H, ar-CH_3), 2.55 (“t”, $^3J \approx$ 7.4 Hz, 2 H, ar-CH_2), 3.11 (m, 2 H, CH_2−NH$_2$), 7.04−7.13 (m, 4 H, ar-H), 7.99 (s, 2 H, NH_2). − $C_{11}H_{17}N$ (163.26): calc. C 80.93, H 10.50, N 8.58; found C 80.68, H 10.70, N 8.44.

2-(4-Aminobutyl)benzyl Alcohol (13): At room temp. hydrogen was passed through a suspension of platinum(II) oxide (270 mg), sodium nitrite (27.0 mg), and water (1 mL) in ethanol (200 mL). Alcohol **11** (3.0 g, 16.9 mmol) was then added, and the hydrogenation continued under normal pressure for 24.5 h. The catalyst was separated by filtration through a fibreglass filter, and from the filtrate the solvent was distilled off in vacuo. Chromatography on aluminium oxide with ethyl acetate/methanol (12:1; $R_f \approx$ 0.46) yielded **13** as light-yellow oil after distilling off the solvents: 2.94 g (97% yield). − MS; *m*/*z* (%): 161 (2) [M − H$_2$O], 160 (2) [M − OH], 144 (46), 129 (84), 91 (100), a.o. − ^{1}H NMR (360 MHz, [D$_6$]DMSO): δ = 1.44−1.60 (m, 4 H, ar-CH$_2$−CH_2−CH_2−CH$_2$−NH$_2$), 2.58 (“t”, $^3J \approx$ 7.5 Hz, 2 H, ar-CH_2), 3.08−3.13 (m, 2 H, CH_2−NH$_2$), 4.52 (d, ^3J = 5.2 Hz, CH_2−OH), 5.05 (t, ^3J = 5.2 Hz, CH$_2$−OH), 7.12−7.17 (m, 3 H, ar-H), 7.33−7.37 (m, 1 H, ar-H), 7.99 (s, 2 H, NH_2). − $C_{11}H_{17}NO$ (179.26): calc. 73.70, H 9.56, N 7.81; found C 73.87, H 9.70, N 7.71.

1-(3-Bromopropyl)-2-(1,3-dioxolanyl-2)benzene: *p*-Toluenesulfonic acid (2.2 mg) was added, under argon, to a solution of 2-(3-bromopropyl)benzaldehyde (5.0 g, 22 mmol) and ethylene glycol (1.5 mL) in anhydrous toluene (60 mL), and the reaction mixture heated for 9.5 h under reflux using a water separator. After cooling to room temp. the solution was washed with a sodium carbonate solution (20 mL, 2 M) and water (3× 20 mL). The organic phase was dried with magnesium sulfate and the solvent distilled off in vacuo leaving the acetal as red-orange oil: 5.57 g (93% yield) of the acetal. Chromatography on aluminium oxide with diethyl ether/*n*-pentane ($R_f \approx$ 0.07) yielded an analytically pure product. − MS; *m*/*z* (%): 272 (23) [M$^+$, ^{81}Br], 271 (38), 270 (24), 270 (24) [M$^+$, ^{79}Br], 269 (38), 149 (100), a.o. − ^{1}H NMR (500 MHz, CD$_2$Cl$_2$): δ = 2.13−2.19 (m, 2 H, ar-CH$_2$−CH_2−CH$_2$Br), 2.85−2.88 (m, 2 H, ar-CH_2), 3.44 (t, ^3J = 6.6 Hz, 2 H, ar-CH$_2$−CH$_2$−CH_2−Br), 3.96−4.14 (m, 4 H, CH_2−CH$_2$−O), 5.93 (s, 1 H, ar-CH), 7.20 (d, ^3J = 7.4 Hz, 1 H, 3-H), 7.22 (“t”, $^3J \approx$ 8.4 Hz, 1 H, 5-H), 7.29 (“t”, $^3J \approx$ 7.5 Hz, 1 H, 4-H), 7.52 (d, ^3J = 7.3 Hz, 1 H, 6-H). − $C_{12}H_{15}BrO_2$ (271.15): calc. C 53.16, H 5.58, Br 29.47; found C 52.92, H 5.59, Br 29.29.

1-(3-Bromopropyl)-2-(5,5-dimethyl-1,3-dioxanyl-2)benzene (14): 2-(3-bromopropyl)benzaldehyde[9] (4.68 g, 20.6 mmol) and 2,2-dimethyl-1,3-propanediol (4.29 g, 41.2 mmol) in dry toluene (150 mL) in the presence of *p*-toluenesulfonic acid (627 mg, 3.3 mmol) were heated under argon for 3.5 h in an apparatus equipped with a water separator. After cooling the reaction mixture was washed with a sodium carbonate solution (50 mL of 2 M) and water (3× 150 mL). After drying with magnesium sulfate, the solvent was distilled off in vacuo leaving **14** as an orange oil: 6.46 g (almost quantitative yield) of **14**, chromatographed on aluminium oxide from diethyl ether/*n*-pentane (1:1) with $R_f \approx$ 0.77. − MS; *m*/*z* (%): 315 (16), 314 (92) [M$^+$, ^{81}Br], 313 (60), 312 (94) [M$^+$, ^{79}Br], 311 (42), 229 (64), 228 (42), 227 (86), 191 (63), 147 (68), 129 (87), 91 (100), a.o. − ^{1}H NMR (500 MHz, CD$_2$Cl$_2$): δ = 0.78 (s, 3 H, CH_3), 1.27 (s, 3 H, CH_3), 2.10−2.16 (m, 2 H, ar-CH$_2$−CH_2−CH$_2$Br), 2.84−2.87 (m, 2 H, ar-CH_2), 3.44 (t, ^3J = 6.5 Hz, 2 H, CH_2−Br), 3.65 (d, ^2J = 10.7 Hz, 2 H, O−CH_2), 3.72 (d, ^2J = 11.1 Hz, 2 H, O−CH_2), 5.53 (s, 1 H, ar-CH), 7.17 (dd, ^3J = 7.4 Hz,^4J = 1.4 Hz, 1 H, 3-H), 7.21 (d “t”, ^3J = 7.5 Hz, ^4J = 1.5 Hz,1 H, 5-H), 7.26 (d “t”, ^3J = 7.3 Hz, ^4J = 1.6 Hz, 1 H, 4-H), 7.60 (dd, ^3J = 7.6 Hz, ^4J = 1.5 Hz, 1 H, 6-H). − $C_{15}H_{21}BrO_2$ (313.23): calc. C 57.52, H 6.76, Br 25.51; found C 57.70, H 6.93, Br 25.72.

1-(3-Cyanopropyl)-2-(5,5-dimethyl-1,3-dioxanyl-2)benzene (15): Compound **14** (13.4 g, 42.8 mmol) was added under argon to a suspension of sodium cyanide (2.73 g, 55.7 mmol) in dry triethylene glycol (130 mL). After 75 min of stirring at room temp. and then heating for 60 min to 14°C, the reaction mixture was cooled to room temp. while stirring; water (600 mL) was added, and the product extracted with chloroform (4 × 200 mL). The combined organic phase was washed with sodium chloride solution (200 mL, 4 M), dried with magnesium sulfate, and the solvent distilled off in vacuo. Chromatography of the product on aluminium oxide with cyclohexane/ethyl acetate (10:1) yielded **15** ($R_f \approx$ 0.20); after removal of the solvents 8.88 g (ca. 80%) of **15** as a yellow viscous oil. − MS; *m*/*z* (%): 259 (92) [M$^+$], 258 (58), 174 (100), 145 (54), 133 (50), 115 (32), 91 (49), a.o. − ^{1}H NMR (500 MHz, CD$_2$Cl$_2$): δ = 0.78 (s, 3 H, CH$_3$), 1.27 (s, 3 H, CH$_3$), 1.91−1.97 (m, 2 H, ar-CH$_2$−CH_2−CH$_2$−CN), 2.33 (t, ^3J = 6.9 Hz, 2 H, CH_2−CN), 2.85 (m, 2 H, ar-CH_2), 3.65 (d, ^2J = 11.5 Hz, 2 H, O−CH_2), 3.73 (d, ^2J = 11.4 Hz, 2 H, O−CH_2), 5.50 (s, 1 H, ar-CH), 7.15 (dd, ^3J = 7.4 Hz, ^4J = 1.3 Hz, 1 H, 6-H), 7.23 (d“t”, ^3J = 7.5 Hz, ^4J = 1.4 Hz, 1 H, 4-H), 7.28 (d“t”, ^3J = 7.5 Hz, ^4J = 1.6 Hz, 1 H, 5-H), 7.59 (dd, ^3J = 7.7 Hz, ^4J = 1.4 Hz, 1 H, 3-H). − $C_{16}H_{21}NO_2$ (259.35): calc. C 74.10, H 8.16, N 5.40; found C 74.33, H 8.35, N 5.69.

1-(3-Amino-*n*-butyl)-2-(5,5-dimethyl-1,3-dioxanyl-2)benzene (16): Compound **15** (200 mg, 0.77 mmol) dissolved in anhydrous tetrahydrofuran (5 mL) was dropped onto a suspension of lithium aluminium hydride (16.1 mg, 0.42 mmol) in dry tetrahydrofuran (20 mL) within 30 min at 0°C, under argon and with the exclusion of moisture. After stirring for further 4 h at 0°C, 50 mL of water were added and the reaction mixture heated for 1.5 h under reflux in order to achieve hydrolysis. Distilling off the solvents in vacuo left a product which was extracted by chloroform in a Soxhlet apparatus within 2 h. The chloroform extract was adsorbed on 2 g florisil (magnesium silicate gel), and the product purified by flash chromatography on silica (d = 2 cm, l = 17 cm) with ethanol/triethylamine (10:1) as eluent ($R_f \approx 0.38$): 185 mg of **16** (91%). − MS; m/z (%): 263 (11) [M^+], 220 (19), 205 (71), 177 (23), 176 (100), 159 (38), 91 (53), a.o. − ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 0.77 (s, 3 H, CH_3), 1.27 (s, 3 H, CH_3), 1.34 (br.m, NH_2), 1.44−1.50 (m, 2 H, ar-$CH_2-CH_2-C\mathit{H}_2-CH_2-NH_2$), 1.56−1.63 (m, 2 H, ar-$CH_2-CH_2-CH_2-C\mathit{H}_2-NH_2$), 2.66 (t, ^2J = 7.0 Hz, 2 H, ar-$CH_2-CH_2-CH_2-C\mathit{H}_2-NH_2$), 2.68 ("t", ^3J = 7.9 Hz, 2 H, ar-$C\mathit{H}_2-CH_2-CH_2-CH_2-NH_2$), 3.62 (d, ^2J = 10.8 Hz, 2 H, $O-C\mathit{H}_2$), 3.72 (d, ^2J = 10.1 Hz, 2 H, $O-C\mathit{H}_2$), 5.51 (s, 1 H, ar-$C\mathit{H}$), 7.15 (d, ^3J = 8.6 Hz, 1 H, 6-H), 7.18 (d "t", ^3J = 7.5 Hz, ^4J = 1.4 Hz, 1 H, 4-H), 7.24 (d "t", ^3J = 7.5 Hz, ^4J = 1.4 Hz, 1 H, 5-H), 7.58 (dd, ^3J = 7.6 Hz, ^4J = 1.1 Hz, 1 H, 3-H). − $C_{16}H_{25}NO_2$ (263.38): calc. C 72.97, H 9.57, N 3.32; found C 73.07, H 9.56, N 5.60.

***N,N′*-Bis[2-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl-1-*n*-butyl]pyromellitic Diimide (17):** In a dry atmosphere and under argon, **16** (2.0 g, 7.6 mmol) and anhydrous potassium carbonate (500 mg) were dissolved in anhydrous dimethylformamide (5 mL) and stirred at room temp. for 30 min. A solution of pyromellitic acid dianhydride (812 mg, 3.7 mmol) in anhydrous dimethylformamide (10 mL) was slowly added to this reaction mixture within 1 h, and the reaction mixture heated to 180°C for 4 h. After cooling, ice water (150 mL) was added and stirring continued at room temp. for 12 h. The precipitate was sucked off, washed with water (250 mL) and dried by lyophilization. The product obtained was further purified by flash chromatography on silica (d = 10 cm, h = 12 cm) with diethyl ether/pentane (1:1) as eluent (**17**: $R_f \approx 0.33$): 1.87 g (71%) of **17** as white solid of m.p. 206−208°C. − MS (FAB positive, *m*-nitrobenzyl alcohol/1% trifluoroacetic acid, 2% PEG 1000); m/z (%): 711 (12) [MH_3^+], 710 (41) [MH_2^+], 709 (88) [MH^+], 709 (24) [M^+], 537 (31), 536 (100) [M − 172]. − ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 0.76 (s, 6 H, $C\mathit{H}_3$), 1.25 (s, 6 H, $C\mathit{H}_3$), 1.61−1.66 (m, 4 H, ar-$CH_2-C\mathit{H}_2-CH_2-CH_2-N$), 1.73−1.77 (m, 4 H, ar-$CH_2-CH_2-C\mathit{H}_2-CH_2-N$), 2.74 ("t", ^3J = 7.8 Hz, 4 H, ar-$C\mathit{H}_2$), 3.62 (d, ^2J = 10.8 Hz, 4 H, $O-C\mathit{H}_2$), 3.69 (d, ^2J = 11.0 Hz, 4 H, $O-C\mathit{H}_2$), 3.74 (t, J = 7.1 Hz, 4 H, ar-$CH_2-CH_2-CH_2-C\mathit{H}_2-N$), 5.49 (s, 2 H, ar-$C\mathit{H}$), 7.14 (d, ^3J = 7.5 Hz, 2 H, 6-H), 7.19 (d"t", ^3J = 7.5 Hz, ^4J = 1.1 Hz, 2 H, 4-H), 7.23 (d"t", $^3J \approx$ 7.5 Hz, ^4J = 1.4 Hz, 2 H, 5-H), 7.55 (dd, ^3J = 7.5 Hz, ^4J = 1.0 Hz, 2 H, 3-H), 8.19 (s, 2 H, H_{pyrom}.). − $C_{42}H_{48}N_2O_8$: calc. 708.3411 [M^+]; found 708.3379; $C_{42}H_{49}N_2O_8$: calc. 709.3489 [MH^+]; found 709.3493.

***N,N′*-Bis(2-formylphenyl-1-butyl)pyromellitic Diimide (18):** Trifluoroacetic acid (24.6 mL) and 5% sulfuric acid (18.5 mL) were added, under argon, to the diacetal **17** (1.92 g, 2.71 mmol) in chloroform (60 mL). After stirring for 22 h at room temp. water (140 mL) was added, and the stirring continued for a further 30 min. The organic phase was then separated and the aqueous phase extracted with chloroform (3× 60 mL). The combined organic phases were washed with sodium hydrogen carbonate solution (2 M, 2× 40 mL) and water (3× 10 mL). After drying with magnesium sulfate, the solvent was removed in vacuo at room temp. leaving the dialdehyde **18** as a white solid: 1.45 g of **18** (almost quant.), m.p. 190°C (dec.). − MS (FAB positive, *m*-nitrobenzyl alcohol/1% trifluoroacetic acid); m/z (%): 538 (37) [$(MH+H)^+$], 537 (100) [MH^+], 536 (11) [M^+]. − ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 1.61−1.68 (m, 4 H, ar-$CH_2-C\mathit{H}_2-CH_2-CH_2-N$), 1.75−1.81 (m, 4 H, ar-$CH_2-CH_2-C\mathit{H}_2-CH_2-N$), 3.07 ("t", $^3J \approx$ 7.8 Hz, 4 H, ar-$C\mathit{H}_2-CH_2-CH_2-CH_2-N$), 3.74 (t, ^3J = 7.0 Hz, 4 H, ar-$CH_2-CH_2-CH_2-C\mathit{H}_2-N$), 7.28 (d, ^3J = 7.5 Hz, 2 H, 3-H), 7.36 ("t", $^3J \approx$ 7.3 Hz, 2 H, 5-H), 7.49 (dt, $^3J \approx$ 7.1 Hz, ^4J = 1.5 Hz, 2 H, 4-H), 7.67 (dd, ^3J = 7.3 Hz, ^4J = 1.4 Hz, 2 H, 6-H), 8.09 (s, 2 H, H_{pyrom}), 10.06 (s, 2 H, ar-$C\mathit{H}O$). − HR-MS: $C_{32}H_{28}N_2O_6$: calc. 536.1947 [M^+]; found 536.1974; $C_{32}H_{29}N_2O_6$: calc. 537.2026 [MH^+]; found 537.2034.

***N,N′*-Bis[4-{2-[bis(5-benzyloxycarbonyl-4-ethyl-3-methyl-2-pyrrolyl)methyl]phenyl}butyl]pyromellitic Diimide (19):** The dialdehyde **18** (976 mg, 1.82 mmol) and 2-benzyloxycarbonyl-3-ethyl-4-methylpyrrole (2.21 g, 9.10 mmol) were suspended in absolute ethanol (37 mL), under argon; 37% hydrochloric acid (0.3 mL) was added, and the reaction mixture heated to boiling for 5 h. After cooling to room temp. the gel-like sediment formed was dissolved in dichloromethane (100 mL), adsorbed on magnesium silicate gel (5 g), and purified by flash chromatography on silica [d = 5 cm, h = 35 cm; toluene/ethyl acetate (10:1)] with $R_f \approx 0.20$. After evaporation of the solvent under reduced pressure 2.20 g (82%) of **19** was obtained as an orange oil which, after further drying in vacuo, solidified to a foam-like solid (decomposition at ca. 90°C). − MS (FAB positive, *m*-nitrobenzyl alcohol/1% trifluoroacetic acid); m/z (%): 1475 (43) [$(MH+H)^+$], 1474 (55) [MH^+], 1473 (54) [M^+], 1383 (95) [$(MH-91)^+$], 1392 (100) [$(M-91)^+$], a.o. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.04 (t, ^3J = 7.5 Hz, 12 H, $CH_2-C\mathit{H}_3$), 1.41−1.48 (m, 4 H, ar-$CH_2-C\mathit{H}_2-CH_2-CH_2-N$), 1.59−1.69 (m, 4 H, ar-$CH_2-CH_2-C\mathit{H}_2-CH_2-N$), 1.72 (s, 12 H, pyr-$CH_3$), 2.54 (m, 4 H, ar-$C\mathit{H}_2-CH_2-CH_2-CH_2-N-$), 2.71 (q, ^3J = 7.4 Hz, 8 H, $C\mathit{H}_2-CH_3$), 3.61 (t, ^3J = 7.2 Hz, 4 H, $CH_2-CH_2-C\mathit{H}_2-CH_2-N$), 5.21 (d, ^3J = 2.4 Hz, 8 H, $COOC\mathit{H}_2$-ar), 5.63 (s, 2 H, ar-$C\mathit{H}(pyr)_2$), 6.79 (d, ^3J = 7.6 Hz, 2 H, 3-H), 7.09−7.33 (m, 26 H, 4-, 5-, 6-H, $COOH-CH_2C_6H_5$), 8.14 (s, 4 H, $N\mathit{H}$), 8.21 (s, 2 H, H_{pyrom}). − $C_{92}H_{92}N_6O_{12}$ (1473.77): calc. C 74.98, H 6.29, N 5.70; found C 74.83, H 6.42, N 5.49.

***N,N′*-Bis[4-{2-[bis(5-carboxy-4-ethyl-3-methyl-2-pyrrolyl)methyl]-phenyl}butyl]pyromellitic Diimide (20):** To carry out the reductive splitting-off of the benzyl group, palladium catalyst [3.4 g, Pd/C (10%), oxidized form] suspended in tetrahydrofuran (20 mL) was added to **19** (2.48 g, 1.68 mmol) in tetrahydrofuran (220 mL) at room temp. and normal pressure for 6 h in order to achieve hydrogenation. To separate the catalyst the reaction mixture was filtered through silica (celite, d = 10 cm, h = 10 cm), washed with tetrahydrofuran (1000 mL), and the solvent removed in vacuo at room temp.: 1.88 g of **20**, m.p. ≈ 100−106°C, dec. − MS (FAB negative, *m*-nitrobenzyl alcohol/1% trifluoroacetic acid); m/z (%): 1113 (66), 1112 (100) [M^-], 1111 (39) [$(M-H)^-$], 1098 (36), 1097 (49), a.o. − ^{1}H NMR (500 MHz, DMSO): $\delta \approx$ 0.99 (t, 7.4 Hz, 12 H, pyr-$CH_2-C\mathit{H}_3$), 1.23−1.31 (m, 4 H, ar-$CH_2-C\mathit{H}_2-CH_2-CH_2-N$), 1.53−1.56 (m, 4 H, ar-$CH_2-CH_2-C\mathit{H}_2-CH_2-N$), 1.79 (s, 12 H, pyr-$C\mathit{H}_3$), 2.44−2.46 (m, 4 H, ar-$C\mathit{H}_2-CH_2-CH_2-CH_2-N$), 2.59−2.64 (m, 8 H, pyr-$C\mathit{H}_2-CH_3$), 3.53−3.60 (m, 4 H, ar-$CH_2-CH_2-CH_2-C\mathit{H}_2-N$), 5.72 [s, 2 H, ar-$C\mathit{H}(pyr)_2$], 7.02 (d, ^3J = 7.7 Hz, 2 H, 3-H), 7.10−7.19 (m, 6 H, 4-, 5-, 6-ar-H), 8.15 (s, 2 H, H_{pyrom}), 10.49 (s, 4 H, NH), 11.95 (s, 4 H, $COO\mathit{H}$). − HR-MS: $C_{64}H_{68}N_6O_{12}$: calc. 1112.4895 [M^+]; found 1112.4867.

[4.4]-*N,N′*-Pyromellitic-Diimide-Porphyrin Cyclophane (2): 20 (1.55 g, 1.39 mmol), trichloroacetic acid (14.5 g), and triethyl orthoformate (2.3 mL, 13.8 mmol) were added to 730 mL of dichloromethane within a few seconds; the mixture was then stirred for 1 h under argon with magnesium sulfate (14.5 g). Under exclusion of light the reaction mixture was stirred for 23 h during which the colour of the solution changed from a light violet to dark red. To this solution anhydrous sodium acetate (1.45 g) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (0.98 g, 4.3 mmol) were added. The solution was stirred for a further 3 h, then, after the addition of satd. sodium hydrogen carbonate (300 mL) the organic phase was separated and washed with satd. sodium hydrogen carbonate solution (2× 300 mL) and water (2× 300 mL). After drying with magnesium sulfate the solvent was distilled off, and the dark viscous oil was filtered with toluene/ethyl acetate (10:1) as eluent through an aluminium oxide column (activity II and III; d = 5 cm, h = 6 cm). The fraction containing the porphyrin ($R_f \approx 0.64$) was further purified by flash chromatography on silica (d = 4 cm, h = 16 cm, cyclohexane/ethyl acetate, 20:1); subsequent chromatography on a silica column (d = 5 cm, h = 20 cm; solvents: cyclohexane/ethyl acetate 8:1; $R_f \approx 0.19$) yielded **2** as violet crystals which after recrystallization from cyclohexane/ethyl acetate (8:1) were suitable for the X-ray structure analysis discussed above; yield 17.4 mg (1.3%), m.p. 202°C (dec.). − MS (FAB positive, *m*-nitrobenzyl alcohol (1% trifluoroacetic acid); m/z (%): = 956 (68) [MH_2^+], 955 (100) [MH^+], 954 (23) [M^+], a.o. − ^1H NMR (500 MHz, CD_2Cl_2): δ = −2.71 (s, 2 H, internal porph-N−H), 1.25 (m, 8 H, centre of β- and γ-CH_2), 1.82 (t, ^3J = 7.7 Hz, 12 H, pyr-CH_3), 2.41 (m, 4 H, centre of α-CH_2), 2.46 (s, 12 H, porph-CH_3), 3.32 (m, 4 H, centre of δ-CH_2), 3.99−4.06 (m, 4 H, porph-CH_3−$\mathrm{C}H_2$), 4.22−4.29 (m, 4 H, porph-CH_3−$\mathrm{C}H_2$), 6.85 (s, 2 H, pyrom.-H), 7.52 (d “t”, 2 H, ^3J = 7.5 Hz, ^4J = 1.3 Hz, phen-4-H), 7.66 (dd, 2 H, ^3J = 7.5 Hz, $^4J \approx$ 1.0 Hz, phen-3-H), 7.67 (dd, 2 H, ^3J = 7.2 Hz, ^4J = 1.3 Hz, phen-6-H), 7.73 (d “t”, 2 H, ^3J = 7.7 Hz, ^4J = 1.3 Hz, phen-5-H), 10.28 (s, 2 H, porph-methin-H). − HR-MS: $C_{62}H_{62}O_4N_6$: calc. 954.4832, found 956.4858 [M^+]; calc. 955.4911, found 955.4918 [MH^+]. − X-Ray analysis of **2**: crystal size: 0.3 × 0.2 × 0.1 mm, Enraf-Nonius CAD4 four-circle diffractometer, graphite-monochromatized Mo-K_α radiation (λ = 0.071073 nm), θ/2θ-scan; measured: 3448 symmetry-independent reflexes up to sinδ/λ = 5.5 nm^{-1} of which 1895 with $I \geq 2\sigma(I)$ were graded as observed. Structure solution according to direct method (SIR); refinement convergent to R = 0.059 (R_w = 0.066), all non-hydrogen atoms anisotropically refined whereas hydrogen atoms were included in a ′riding model′ with fixed temperature factors. The resulting molecular structure and the packing in the crystal are shown in Figure 1a. For further data of the crystal structure see ref.[14]

[4.4]-*N,N′*-Pyromellitic-Diimide-Porphyrin Cyclophane Zinc (3): For the zinc complexation of **2**, the metal-free parent compound **2** (12.3 mg, 13 µmol) was dissolved in chloroform/methanol (80 mL, 5:1). Zinc(II) acetate dihydrate (240 mg, 1.1 mmol) was added to this solution under argon. After heating at reflux for 1.5 h, the solvents were distilled off in vacuo, and the residue dissolved in chloroform (50 mL). This solution was stirred with a satd. aqueous sodium hydrogen carbonate solution (2× 10 mL) and water (2× 10 mL). The organic phase was dried with sodium sulfate. After distilling off the solvent, the remaining solid was dissolved in ethyl acetate (10 mL) and covered with a layer of cyclohexane (5 mL). After 2 d at 4°C the zinc complex **3** was obtained as pink-coloured powder which by crystallization from ethyl acetate formed needle-shaped crystals: 10.6 mg (81% yield), m.p. 190°C (dec.). − MS (FAB positive, *m*-nitrobenzyl alcohol/1% trifluoroacetic acid); m/z (%): 1020 (76) [$(MH_4)^+$], 1019 (95) [$(MH_3)^+$], 1018 (98) [$(MH_2)^+$], 1017 (100) [$(MH)^+$], 1016 (33) [M^+], a.o. − ^1H NMR (500 MHz, CD_2Cl_2): δ = 1.18−1.25 (m, 4 H, ar-CH_2−$\mathrm{C}H_2$−CH_2−CH_2−N), 1.30−1.35 (m, 4 H, ar-CH_2−CH_2−$\mathrm{C}H_2$−CH_2−N), 1.80 (t, ^3J = 7.7 Hz, 12 H, pyr-CH_3), 2.42−2.46 (m, 4 H, ar-$\mathrm{C}H_2CH_2CH_2CH_2$−N), 3.33 (“t”, ^3J = 5.4 Hz, 4 H, ar-CH_2−CH_2CH_2−$\mathrm{C}H_2$−N), 3.97−4.04 (m, 4 H, $\mathrm{C}H_2$−CH_3), 4.18−4.26 (m, 4 H, CH_2−CH_3), 6.83 (s, 2 H, pyrom.-H), 7.51 (d “t”, ^3J = 7.4 Hz, ^4J = 1.2 Hz, 2 H, phen-4-H), 7.64 (dd, ^3J = 7.3 Hz, $4J$ = 1.1 Hz, 2 H, phen-3-H), 7.65 (d, ^3J = 7.1 Hz, 2 H, phen-6-H), 7.73 (d “t”, ^3J = 7.3 Hz, ^4J = 1.3 Hz, 2 H, phen-5-H), 10.22 (s, 2 H, porph-methin-H). − MS-HR: $C_{62}H_{60}N_6O_4Zn$: calc. 1016.3968, found 1016.4012 [M^+]. − $C_{62}H_{61}N_6O_4Zn$: calc. 1017.4046, found 1017.4031.

***N*-{3-[2-(5,5-Dimethyl-1,3-dioxanyl-2)phenyl]propyl}phthalimide (19):** The bromo-substituted compound **14** (270 g, 8.62 mmol) and *N*-potassium phthalimide (1.92 g, 10.3 mmol) in dry *N,N*-dimethylformamide (10 mL) were heated in a sealed tube, under argon, for 6 h at 145°C. After cooling, water (200 mL) was added and the solution extracted with dichloromethane (4× 100 mL). The combined organic phases were dried with magnesium sulfate, the solvents distilled off in vacuo, and the residual brown oil purified by flash chromatography on silica (d = 3 cm, h = 40 cm; diethyl ether/*n*-pentane, 1:1; $R_f \approx 0.48$). Crystallization from methanol yielded 2.71 g (83%) of **19**, m.p. 75−77°C. − MS; m/z (%): 380 (11) [MH^+], 379 (42) [M^+], 191 (100), 161 (56), 147 (61), a.o. − ^1H NMR (500 MHz, CD_2Cl_2): δ = 0.72 (s, 3 H, $\mathrm{C}H_3$), 1.24 (s, 3 H, $\mathrm{C}H_3$), 1.92−1.99 (m, 2 H, ar-CH_2−$\mathrm{C}H_2$−CH_2−N), 2.71−2.74 (m, 2 H, ar-$\mathrm{C}H_2$−CH_2−CH_2−N), 3.53 (d, ^3J = 10.5 Hz, 2 H, O−$\mathrm{C}H_2$), 3.67 (d, ^3J = 11.2 Hz, 2 H, O−$\mathrm{C}H_2$), 3.73 (t, ^3J = 7.1 Hz, 2 H, phen-CH_2−CH_2−CH_2−N), 5.43 (s, 1 H, ar-$\mathrm{C}H$), 7.17−7.20 (m, 2 H, 3-H, 5-H), 7.24 (d “t”, ^3J = 7.4 Hz, ^4J = 1.6 Hz, 1 H, 4-H), 7.55 (d, ^3J = 7.6 Hz, 1 H, 6-H), 7.69−7.83 (m, 4 H, ar-H of phthalimide). − $C_{23}H_{25}NO_4$ (379.45): calc. C 72.70, H 6.64, N 3.69; found C 72.81, H 6.83, N 3.66.

3-[2-(5,5-Dimethyl-1,3-dioxan-yl-2)phenyl]propylamin (22): In order to split the phthalimide **19** to yield the amino compound **22**, hydrazine hydrate (8.60 mL, 177 mmol) was added to **19** (22.3 g 58.8 mmol) in methanol (500 mL) and the reaction mixture heated to b.p. for 3 h under stirring. After cooling to room temp. the precipitate was filtered off, and the solvent distilled off from the filtrate. The precipitated solid was washed with dichloromethane (60 mL), and further purified by flash chromatography on silica (d = 10 cm, h = 15 cm) with ethanol/triethylamin (10:1) as eluent. The amine **22** was obtained as yellow, viscous oil: 14.2 g (97%) yield. − MS; m/z (%): 249 (11) [M^+], 219 (14), 206 (15), 146 (39), 145 (61), 144 (30), 134 (39), 133 (100), 130 (93), 120 (58), a.o. − ^1H NMR (500 MHz, CD_2Cl_2): δ = 0.77 (s, 3 H, $\mathrm{C}H_3$), 1.13 (m, 2 H, $\mathrm{N}H_2$), 1.28 (s, 3 H, $\mathrm{C}H_3$), 1.67−1.70 (m, 2 H, ar-CH_2−$\mathrm{C}H_2$−CH_2−N), 2.69 (t, ^3J = 6.9 Hz, 2 H, ar-CH_2−CH_2−$\mathrm{C}H_2$−N), 2.72 (“t”, $^3J \approx$ 7.9 Hz, 2 H, ar-$\mathrm{C}H_2$−CH_2−CH_2−N), 3.63 (d, ^3J = 10.7 Hz, 2 H, O−$\mathrm{C}H_2$), 3.72 (d, ^3J = 11.2 Hz, 2 H, O−CH_2), 5.53 (s, 1 H, ar-$\mathrm{C}H$), 7.16 (dd, ^3J = 7.4 Hz, ^4J = 1.0 Hz, 1 H, 6-H), 7.18 (d“t”, ^3J = 7.4 Hz, ^4J = 1.4 Hz, 1 H, 4-H), 7.24 (d “t”, ^3J = 7.4 Hz, ^4J = 1.5 Hz, 1 H, 5-H), 7.58 (dd, ^3J = 7.7 Hz, ^4J = 1.3 Hz, 1 H, 3-H). − $C_{15}H_{23}NO_2$ (249.35): calc. C 72.25, H 9.30, N 5.62; found C 72.16, H 9.49, N 5.85.

***N,N′*-Bis[2-(5,5-dimethyl-1,3-dioxan-2-yl)phenylpropyl]pyromellitic Diimide (23):** Under argon and with exclusion of moisture the amino compound **22** (7.56 g, 30.0 mmol) was dissolved in dry *N,N*-dimethylformamide (10 mL) and potassium carbonate (100 mg) added to the mixture. Within 2.5 h a solution of pyromellitic dianhydride (3.24 g, 14.9 mmol) in *N,N*-dimethylformamide (20 mL) was added dropwise. After the reaction mixture was stirred for 4 h while boiling, the orange coloured product was hydrolysed by the addition of ice water (560 mL), stirred for 12 h and a white sediment filtered off which was then washed with 500 mL of water and dried on a lyophilizer. Crystallization from diethyl ether/*n*-pentane (1:1) yielded 9.52 g (94%) of **23** as white powder of m.p. 142−149°C. − MS (FAB positive, *m*-nitrobenzyl alcohol/1% trifluoroacetic acid); *m*/*z* (%): 682 (92) [MH_2], 681 (100) [MH], 680 (25) [M], 679 (23), 510 (71), [MH − 172] a.o. − ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 0.75 (s, 6 H, $C\mathit{H}_3$), 1.25 (s, 6 H, CH_3), 1.97−2.03 (m, 4 H, ar-$CH_2{-}C\mathit{H}_2{-}CH_2{-}N$), 2.77 ("t", ^3J ≈ 8.1 Hz, 4 H, ar-$C\mathit{H}_2{-}CH_2{-}CH_2{-}N$), 3.60 (d, ^3J = 10.6 Hz, 4 H, $O{-}C\mathit{H}_2$), 3.70 (d, ^3J = 11.2 Hz, 4 H, $O{-}C\mathit{H}_2$), 3.78 (t, ^3J = 7.3 Hz, 4 H, ar-$CH_2{-}CH_2{-}C\mathit{H}_2{-}N$), 5.46 (s, 2 H, ar-$C\mathit{H}$), 7.16−7.20 (m, 4 H, 6-H, 4-H), 7.24 (d "t", ^3J ≈ 7.5 Hz, ^2J ≈ 1.7 Hz, 2 H, 5-H), 7.55 (dd, ^3J = 7.6 Hz, ^4J = 1.3 Hz, 2 H, 3-H), 8.21 (s, 2 H, H_{pyrom}). − $C_{40}H_{44}N_2O_8$ (680.80): calc. C 70.57, H 6. 51, N 4.11; found C 70.42, H 6.75, N 4.12.

***N*,*N'*-Bis(2-formylphenyl-1-propyl)pyromellitic Diimide (24):** In order to achieve the synthesis of the dialdehyde **24** by cleavage of the two acetal groups of **23**, trifluoroacetic acid (4.64 mL) and sulfuric acid (3.50 mL, 5%) were added to **23** (348 mg, 511 µmol) in chloroform (12 mL) under argon. The mixture was stirred at room temp. for 11 h. Then the reaction was stopped by the addition of 55 mL of water. The combined organic phases were washed with sodium hydrogen carbonate (2 M, 2× 20 mL) and water (2× 10 mL). The organic solution was dried with magnesium, the solvent distilled off in vacuo, and the remaining solid crystallized from diethyl ether/*n*-pentane (1:1) as white powder: 246 mg (95% yield), m.p. 195°C (dec). − MS (FAB positive, *m*-nitrobenzyl alcohol/1% trifluoroacetic acid); *m*/*z* (%): 511 (10) [MH_3], 510 (37) [MH_2], 509 (100) [MH], a.o. − ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 1.96−2.02 (m, 4 H, ar-$CH_2{-}C\mathit{H}_2{-}CH_2{-}N$), 3.06−3.09 (m, 4 H, ar-$C\mathit{H}_2{-}CH_2{-}CH_2{-}N$), 3.81 (t, *J* = 6.9 Hz, 4 H, ar-$CH_2{-}CH_2{-}C\mathit{H}_2{-}N$), 7.31 (d, ^3J = 7.1 Hz, 2 H, 3-H), 7.37 (d "t", ^3J ≈ 7.5 Hz, ^4J = 1.2 Hz, 2 H, 4-H), 7.48 (d "t", ^3J ≈ 7.9 Hz, ^4J ≈ 1.6 Hz, 2 H, 5-H), 7.75 (d, ^3J = 8.2 Hz, 2 H, 6-H), 8.22 (s, 2 H, H_{pyrom}), 10.10 (s, 2 H, $-C\mathit{H}O$). − $C_{30}H_{24}N_2O_6$ (508.53): calc. C 70.86, H 4.76, N 5.51; found C 70.63, H 4.96, N 5.47.

***N*,*N'*-Bis[2-di(2-benzyloxy-3-ethyl-4-methylpyrrolyl)methylphenyl-1-propyl]pyromellitic Diimide:** The dialdehyde **24** (1.85 g, 3.36 mmol) and 2-benzyloxycarbonyl-3-ethyl-4-methylpyrrole (4.42 g, 18.2 mmol) were suspended in dry ethanol (80 mL) under argon and, after addition of hydrochloric acid (0.6 mL, 37%), heated to b.p. for 5 h. On cooling to room temp. a gel-like red precipitate was obtained which was dissolved in dichloromethane (25 mL) and chromatographed on silica (*d* = 10 cm, *h* = 30 cm) from toluene/ethyl acetate (10:1) as eluent. After separation of the excess of the pyrrole fraction (R_f ≈ 0.56) the product was obtained with R_f ≈ 0.17. After removal of the solvent by distillation, an orange oil was isolated which in vacuo solidified to a foam-like product: 4.29 g (82% yield), m.p. 101−104°C (from toluene/ethyl acetate, 10:1). − MS; *m*/*z* (%): 1446 (34) [MH^+], 1445 (44) [M^+], 1444 (32) 1355 (46) [MH − 91], 1354 (89) [M − 91], 1352 (100), a.o. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.06 (t, ^3J = 7.5 Hz, 12 H, $CH_2{-}C\mathit{H}_3$), 1.74 (s, 12 H, pyr-$C\mathit{H}_3$), 1.86−1.90 (m, 4 H, ar-$CH_2{-}C\mathit{H}_2{-}CH_2{-}N$), 2.58 ("t", ^3J ≈ 7.7 Hz, 4 H, ar-$C\mathit{H}_2{-}CH_2{-}CH_2{-}N$), 2.72 (q, ^3J = 7.4 Hz, 8 H, $C\mathit{H}_2{-}CH_3$), 3.71 (t, ^3J = 1.0 Hz, 4 H, ar-$CH_2{-}CH_2{-}C\mathit{H}_2{-}N$), 5.25 (s, 8 H, $CO{-}OC\mathit{H}_2{-}C_6H_5$), 5.63 (s, 2 H, ar-$C\mathit{H}{-}pyr_2$), 6.78 (d, ^3J = 7.6 Hz, 2 H, 3-H), 7.07−7.36 (m, 26 H, 4-, 5-, 6-H and $COOCH_2C_6H_5$), 8.16 (s, 2 H, H_{pyrom}), 8.19 (s, 4 H, $N\mathit{H}$). − $C_{98}H_{88}N_6O_{12}$ (1445.72): calc. C 74.77, H 6.14, N 5.81; found C 74.92, H 6.32, N 5.89.

***N*,*N'*-Bis[2-di(2-carboxyl-3-ethyl-4-methylpyrrolyl)methylphenyl-1-propyl]pyromellitic Diimide:** The preceding tetrabenzyl ester (523 mg, 364 µmol) was dissolved in tetrahydrofuran (100 mL) and, together with 860 mg of palladium catalyst (10% on charcoal) in tetrahydrofuran (20 mL), was hydrogenated for 1 h at normal pressure and room temp. By filtration through celite (silica of different particle size; *d* = 10 cm, *h* = 3 cm) the catalyst was separated, and the product obtained by chromatography (R_f ≈ 0.14; toluene/acetic acid, 15:1) as red-orange oil: 392 mg (ca. quant.), m.p. 144°C (dec., from tetrahydrofuran). − MS (FAB negative, *m*-nitrobenzyl alcohol/1% trifluoroacetic acid); *m*/*z* (%): 1087 (27), 1085 (65), 1084 (100) [M], 1083 (35) [M − H]. − ^{1}H NMR (500 MHz, [D_6]DMSO): δ = 0.99 (t, 7.4 Hz, 12 H, pyr-$CH_2{-}C\mathit{H}_3$), 1.62−1.71 (m, 4 H, ar-$CH_2{-}C\mathit{H}_2{-}CH_2{-}N$), 1.78 (s, 12 H, pyr-$C\mathit{H}_3$), 2.42−2.45 (m, 4 H, ar-$C\mathit{H}_2{-}CH_2{-}CH_2{-}N$), 2.56−2.69 (m, 8 H, pyr-$C\mathit{H}_2{-}CH_3$), 3.50−3.53 (m, 4 H, ar-$CH_2{-}CH_2{-}C\mathit{H}_2{-}N$), 5.71 (s, 2 H, ar-$(pyr)_2{-}CH$), 7.00 (d, ^3J = 7.6 Hz, 2 H, 3-H), 7.07−7.28 (m, 6 H, 4-, 5-, 6-H), 8.14 (s, 2 H, H_{pyrom}), 10.42 (s, 4 H, NH), 12.00 (s, 4 H, COOH). − HR-MS (negative, *m*-nitrobenzyl alcohol/1% trifluoroacetic acid, 2% PEG 1000): $C_{62}H_{64}N_6O_{12}$ [M]: calc. 1084.4582, found 1084.4615; $C_{62}H_{63}N_6O_{12}$ [M − H]: calc. 1083.4504, found 1083.4490.

[3.3]Pyromellitic Diimide-Porphyrin Cyclophane (4) and Its Dimer 25: For the cyclization to the electron-acceptor porphyrin cyclophane **4** the procedure closely followed that of the corresponding reaction leading to **2** (see above). As solvent dichloromethane (1000 mL) was stirred together with magnesium sulfate (20 g) for 45 min, and oxygen removed by an argon stream. Within 15 s, 2.17 g (2.0 mmol) of the preceding compound, trifluoroacetic acid (20.2 g), and triethyl orthoformate (3.33 mL, 20.0 mmol) were added in this sequence. This reaction mixture was stirred at room temp. and under exclusion of light for 17 h, during which time the colour of the solution changed from pink to dark violet. Then dry sodium acetate (2.1 g) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (1.36 g, 6.0 mmol) were added to the mixture which was stirred for further 3 h. After thev addition of satd. sodium hydrogen carbonate solution (430 mL) the organic phase was separated and washed with sodium hydrogen carbonate solution (2× 300 mL) and water (2× 300 mL). After drying with magnesium sulfate the solvent dichloromethane was distilled off, and the remaining dark viscous oil was chromatographed on aluminium oxide (*d* = 4 cm, *h* = 12 cm) with toluene/ethyl acetate (10:1) as eluent. The fraction of R_f ≈ 0.20 was further purified by flash-chromatography on silica (*d* = 5 cm, *h* = 30 cm) with cyclohexane/ethyl acetate (8:1) as eluent. The product **4** wanted was eluted at R_f ≈ 0.19, the solvents distilled off, the residue dissolved in ethyl acetate (3 mL), and the solution was covered with a layer of cyclohexane (10 mL). After 2 d at 4°C the porphyrin cyclophane **4** was isolated as blue/violet powder: 16.5 mg (0.9%) of **4**. By flash chromatography after distilling off of the solvents and crystallization from ethyl acetate/cyclohexane as a second product a pink-coloured substance was isolated which unexpectedly was proved to be **25**, a dimer of **4** (see below).

4: R_f ≈ 0.19 (cyclohexane/ethyl acetate, 8:1), m.p. > 300°C (dec.). − MS (FAB positive, *m*-nitrobenzyl alcohol/1% trifluoroacetic acid); *m*/*z* (%): 929 (65) [MH_3], 928 (100) [MH_2], 927 (43) [MH], 926 (22) [M]. − ^{1}H NMR (500 MHz, CD_2Cl_2): δ = −2.91 (s, 2 H, $N\mathit{H}$), 1.86 (t, ^3J = 7.6 Hz, 12 H, $CH_2{-}C\mathit{H}_3$), 2.07−2.15 (m, 4 H, ar-$CH_2{-}C\mathit{H}_2{-}CH_2{-}N$), 2.39 (s, 12 H, $C\mathit{H}_3$), 3.03−3.05 (m, 4 H, ar-$CH_2{-}CH_2{-}C\mathit{H}_2{-}N$), 3.14−3.17 (m, 4 H, ar-$C\mathit{H}_2{-}CH_2{-}CH_2{-}N$), 3.98−4.09 (m, 8 H, $C\mathit{H}_2{-}CH_3$), 5.01 (s, 2 H, pyromell.H), 7.24 (d, ^3J = 7.2 Hz, 2 H, 6-H), 7.41 ("t", ^3J ≈ 7.2 Hz, 2 H, 5-H), 7.71 ("t", ^3J ≈ 7.6 Hz, 2 H, 4-H), 7.78 (d, ^3J = 7.7 Hz, 2 H, 3-H), 10.15 (s, 2 H, methine-H). − HR-MS (FAB positive, *m*-nitrobenzyl alcohol/1% trifluoroacetic acid, 1% PEG 1000): $C_{60}H_{58}N_6O_4$ [M]: calc. 926.4519, found 926.4537.

25: (= dimer of **4**); $R_f \approx 0.09$ (cyclohexane/ethyl acetate, 8:1), yield 24.5 mg (1.3%), m.p. > 300°C (cyclohexane/ethyl acetate). − MS (FAB positive, *m*-nitrobenzyl alcohol/1% trifluoroacetic acid); *m*/*z* (%): 1856 (56) [MH_4], 1855.5 (59) [MH_3], 1854.5 (42) [MH_2], 929.8 (81), 928.3 (100), 927.8 (96), a.o. − ^1H NMR (500 MHz, CD_2Cl_2): δ = −2.60 (s, 4 H, N*H*), 1.78 (t, ^3J = 7.6 Hz, 24 H,CH_2-CH_3), 2.05−2.13 (m, 8 H, ar-$CH_2-CH_2-CH_2-N$), 2.40 (s, 24 H, CH_3), 3.04−3.07 (m, 8 H, ar-$CH_2-CH_2-CH_2-N$), 3.31−3.34 (m, 8 H, ar-$CH_2-CH_2-CH_2-N$), 3.90−3.95 (m, 8 H, CH_2-CH_3), CH_2-CH_3), 4.04−4.08 (m, 12 H, CH_2-CH_3), 5.20 (s, 4 H, pyromell H), 7.25 (d, ^3J = 7.1 Hz, 4 H, 3-H), 7.44 ("t", $^3J \approx$ 7.5 Hz, 4 H, 5-H), 7.78 ("t", $^3J \approx$ 7.6 Hz, 4 H, 4-H), 7.86 (d, ^3J = 8.21 Hz, 4 H, 6-H), 9.96 (s, 4 H, methine-H). − HR-MS (FAB positive, *m*-nitrobenzyl alcohol/1% trifluoroacetic acid, 2% PEG 1500): $C_{120}H_{117}N_{12}O_8$ [MH]: calc. 1853.9117, found 1853.9178.

[3.3]Pyromellitic Diimide-Porphyrin Cyclophane Zinc (5): Zinc(II) acetate dihydrate (3.31 mg, 1.51 mmol) was added, under argon, to **4** (16.6 mg, 17.9 µmol) dissolved in chloroform/methanol (5:1). After 1.5 h of heating to boiling the reaction mixture was cooled to room temp., the excess of zinc acetate was removed by washing with satd. sodium hydrogen carbonate solution (2× 10 mL) and water (2× 10 mL). After drying with sodium sulfate the solvent was distilled off in vacuo, and the residue dissolved in ethyl acetate (5 mL) and covered with a layer of cyclohexane (2 mL). After 2 d at 4°C the zinc porphyrin cyclophane **5** was obtained as violet microcrystals: 8.9 mg (50% yield), m.p. > 300°C (dec.), $R_f \approx 0.17$ (cyclohexane/ethyl acetate, 8:1). − MS (FAB positive, *m*-nitrobenzyl alcohol/1% trifluoroacetic acid); *m*/*z* (%): 991 (64) [MH_3], 990 (88) [MH_2], 989 (85) [MH], 988 (110) [M], 987 (18), 928 (13), [MH_2 − Zn], 927 (21) [MH − Zn], 926 (17) [M − Zn], a.o. − ^1H NMR (500 MHz, CD_2Cl_2): δ = 185 (t, ^3J = 7.5 Hz, 12 H, CH_2-CH_3), 2.14−2.17 (m, 4 H, ar-$CH_2-CH_2-CH_2-N$), 2.17 (s, 12 H, CH_3), 3.07−3.12 (m, 8 H, ar-$CH_2-CH_2-CH_2-N$), 3.97−4.08 (m, 8 H, CH_2-CH_3), 5.04 (s, 2 H, H_{pyrom}), 7.21 (d, ^3J = 7.3 Hz, 2 H, 6-H), 7.39 ("t", ^3J = 7.3 Hz, 2 H, 5-H), 7.71 ("t", $^3J \approx$ 7.9 Hz, 2 H, 4-H), 7.79 (d, ^3J = 8.2 Hz, 2 H, 3-H), 10.10 (s, 2 H, methine-H). − HR-MS (FAB positive, *m*-nitrobenzyl alcohol (1% trifluoroacetic acid, 2% PEG 1000): $C_{60}H_{57}N_6O_4Zn$ [MH]: calc. 989.3733, found 989.3735.

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[14] Crystallographic data (excluding structure factors) for the structure of **2** reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-112275. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code +44 (1223) 336-033; E-mail: deposit@ccdc.cam.ac.uk].

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