Self-Assembly by Hydrogen Bonding and π−π Interactions in the Crystal of a Porphyrin − Attempts to Mimic Bacteriochlorophyll *c*

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Porphyrins bearing undecyl side chains, which confer solubility, and 4-(methoxycarbonyl)phenyl substituents in the *meso* positions have been prepared. The 4-(methoxycarbonyl) substituent could be transformed into groups tailored for self-assembly. The crystal structure of the dihydroxymethyleneporphyrin, bis[4-(hydroxymethyl)phenyl]porphyrin **7**, shows strong hydrogen bonds between the hydroxy group and pyrrole nitrogen atoms in neighboring molecules, resulting in a two-dimensional network of hydrogen-bonded porphyrins. π–π Interactions are also encountered, bringing porphyrins into laddered stacks with edge-to-edge contacts of 3.5 Å. The isomeric diesters **Zn-3** and **Zn-4** show different tendencies in π–π stacking. Models of bacteriochlorophyll *c* **Zn-8** and **Zn-11**, possessing a formyl group, a hydroxymethyl group, and a central zinc atom, have been synthesized. In contrast to bacteriochlorophyll *c*, which self-assembles both in the natural antenna system of green photosynthetic bacteria and in nonpolar solvents, the self-assembly **Zn-8** and **Zn-11** could not be observed in solution. The results provide information for the design of better mimics of natural light-harvesting arrays formed by self-assembling porphyrins.

Introduction

The determination of the structure of the bacterial photosynthetic reaction center[1] triggered more than a decade of intense research into synthetic mimics.[2] A similar impact on the imagination of chemists is to be expected from the structure of the light-harvesting complex LH2 of *Rhodopseudomonas acidophila*.[3] This fascinating bis(annular) set of bacteriochlorophyll *a* pigments embedded in a polypeptide matrix ensures efficient light collection and energy transfer to a larger LH1 complex and from there to the reaction center, where charge separation allows photosynthesis to proceed. Coupling of an antenna to a reaction center is beneficial as it allows a larger quantity and broader range of photons to be captured.

Covalent linking of pigments in artificial light-harvesting devices has been repeatedly attempted, in spite of the considerable synthetic effort it requires.[4] Recently, dendrimers have been shown to be an elegant way to form covalent assemblies of chromophores.[5,6] The generation of noncovalent supramolecular antenna architectures by means of self-assembly with robust pigments appears synthetically less demanding and presents wider perspectives. In particular, it is possible in self-assembling systems to disassemble and reassemble misplaced components, so that a repair mechanism operates and ensures that only the thermodynamically favored structure is obtained in the end. Self-assembly is also used in nature in the antenna system of green photosynthetic bacteria, in which bacteriochlorophyll *c*, *d*, or *e*, are agglomerated in the chlorosome organelles.[7]

Self-assembling porphyrins may be generated by equipping this ubiquitous macrocycle with groups suitably endowed for supramolecular interactions. Metal ligation,[8] hydrogen bonding, and π−π and hydrophobic interactions may all be put to use, often cooperatively. Here we report the synthesis of porphyrin **7**, containing two hydroxymethyl groups, together with the crystal structure of the assembly it forms. Crystal structures of tetraarylporphyrins which form supramolecular assemblies have been described previously.[9] One may note that interactions involving hydroxy groups have been shown to play an important role in the formation and organization of natural bacteriochlorophyll arrays.[10,11]

Results and Discussion

Synthesis of Porphyrins 1−7

meso-Bonded *para*-methyl benzoate groups appeared well suited for subsequent functionalization, while the introduction of long alkyl chains was envisaged in order to confer solubility. Optimized methods[12] permitted the preparation of a mixture of porphyrins **1−6** in almost gram quantities. When using the mixed aldehyde condensation of pyrrole, or when preforming either of the two required dipyrrylmethanes (Scheme 1), with boron trifluoride−diethyl ether catalysis, scrambling of the porphyrinogens occurred. The alternative standard method for the synthesis of porphyrins under mild conditions, involving trifluoroacetic acid catalysis, did not lead to isolable products. 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) oxidation

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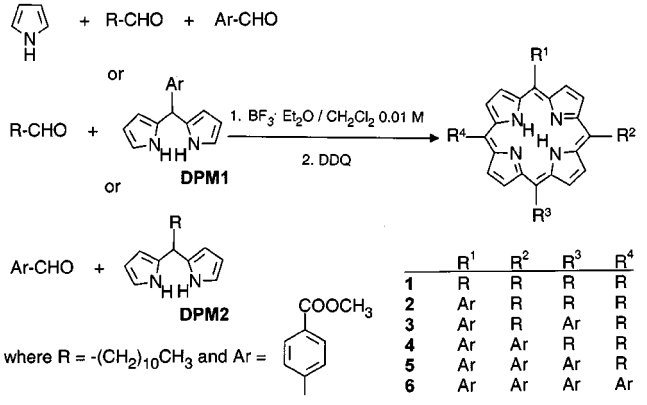
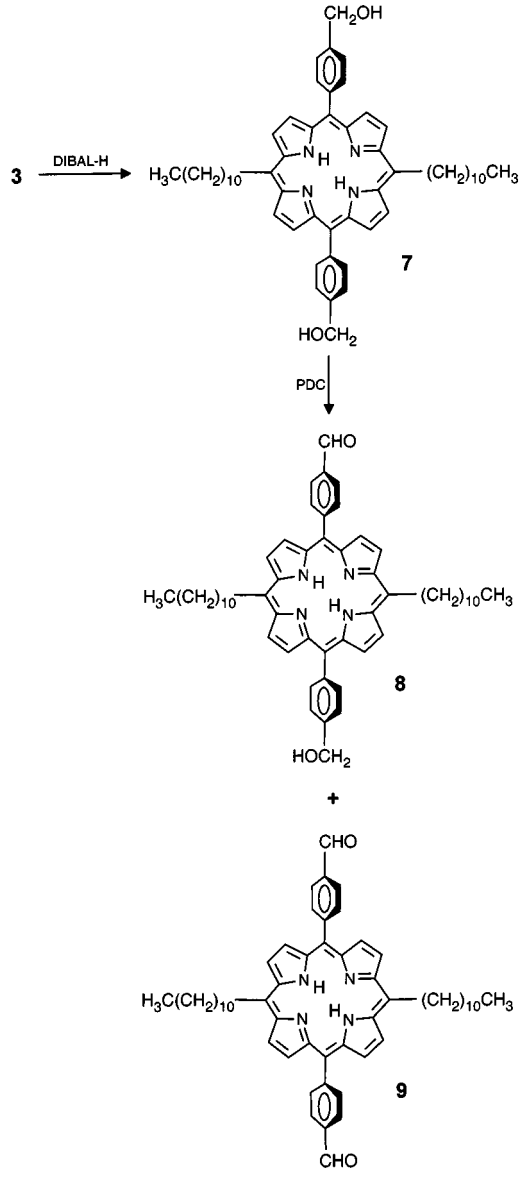
gave an almost statistical mixture of porphyrins. Best yields (about 40%) of porphyrins, over several runs, were achieved by the condensation of dodecanal with [4-(methoxycarbonyl)phenyl]dipyrrylmethane (**DPM1**), which is also more easily available in pure form than the (undecyl)dipyrrylmethane (**DPM2**). See the Experimental Section for detailed yields of porphyrins **1**−**6**. Separation of this mixture (or minilibrary!) of porphyrins was achieved by column chromatography on silica gel. Usually, two columns were needed after an initial filtration through a plug of silica gel. A first column eluted with dichloromethane did not always allow a clean separation of the dialkyl-substituted porphyrins **3** and **4** (the numbering of the porphyrins corresponds to their elution order). These could, however, be neatly separated on a second column eluted with a 1:1 (v/v) mixture of cyclohexane and dichloromethane.



	R^1	R^2	R^3	R^4
1	R	R	R	R
2	Ar	R	R	R
3	Ar	R	Ar	R
4	Ar	Ar	R	R
5	Ar	Ar	Ar	R
6	Ar	Ar	Ar	Ar

Scheme 1

Reduction of the diester **3** with diisobutylaluminum hydride (DIBAL-H) in toluene resulted in the bis(benzylic alcohol) **7**, which was obtained in 78% yield after chromatography (Scheme 2). Slow diffusion of *n*-hexane into a chloroform solution of **7** contained in a 5-mm NMR tube provided microcrystals. It was possible to obtain a single crystal suitable for X-ray diffraction by very slow crystallization over about 20 months.



Scheme 2

Crystal Structure of Porphyrin 7

The molecular structure of **7** (Figure 1) possesses inversion ($\bar{1}$) symmetry. All hydrogen atoms were located directly, and the thermal ellipsoids indicate a relatively rigid core structure with somewhat dangling side chains. A 65° orientation of the phenyl rings with respect to the porphyrin plane is found, in addition to a peculiar kink in the undecyl side chain, due to a *gauche* conformation of the bond between C18 and C19. All the other carbon−carbon single bonds are *s-trans*. This kink allows the undecyl chains to diverge above and below the porphyrin plane. The interdigitating undecyl chains segregate the crystal into distinct planes of porphyrins, which form a hydrogen-bonded network within such a plane. Each molecule of **7** is linked by four strong hydrogen bonds between the hydroxy moieties and the pyrrole nitrogen atoms to the four adjacent molecules, as shown in Figure 2. The two hydroxy groups in a molecule point in opposite directions and the hydrogen bonds have a length of 2.116 Å and an O−H···N angle of 167.4°. Thus, the central molecule represented in Figure 2, which acts as a hydrogen bond acceptor with the two pyrrole nitrogen atoms is, in turn, a double hydrogen bond donor (through the hydroxy groups) to the other two molecules. The two pyrrole nitrogen atoms are hydrogen-bonded: one from above and one from below the porphyrin plane. Two alternating orientations of the porphyrins are encountered, as seen from the different perspectives of the undecyl side chains and the tetrapyrrole cores. Hydrogen bonding is thus the stronger self-assembling interaction sequestering each porphyrin macrocycle in this two-dimensional network.

π−π Interactions are the second crystal assembly element and involve an edge-to-edge overlap, as shown in Figure 3.

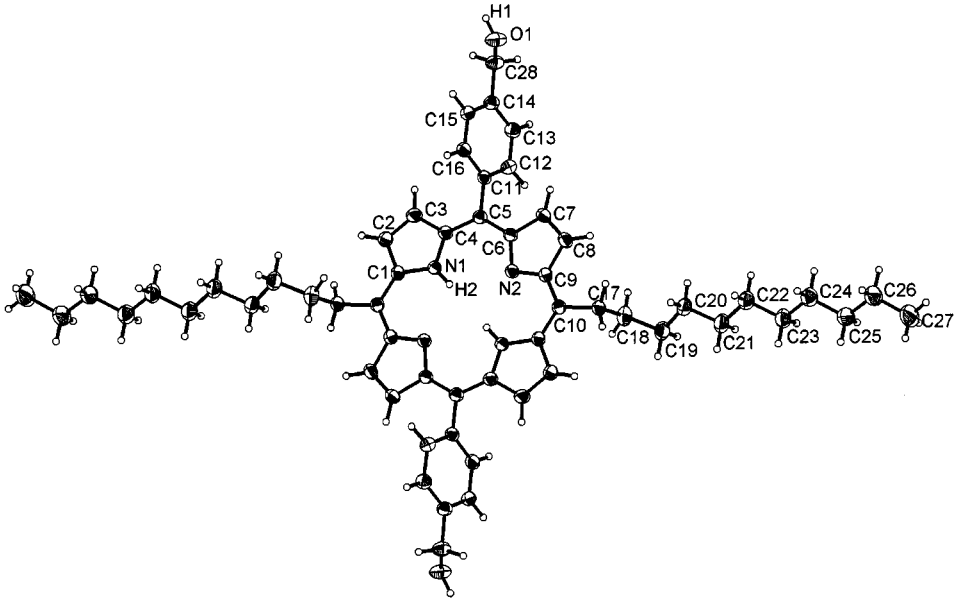


Figure 1. Molecular structure of **7** and atom numbering; thermal ellipsoids are drawn at the 50% probability level

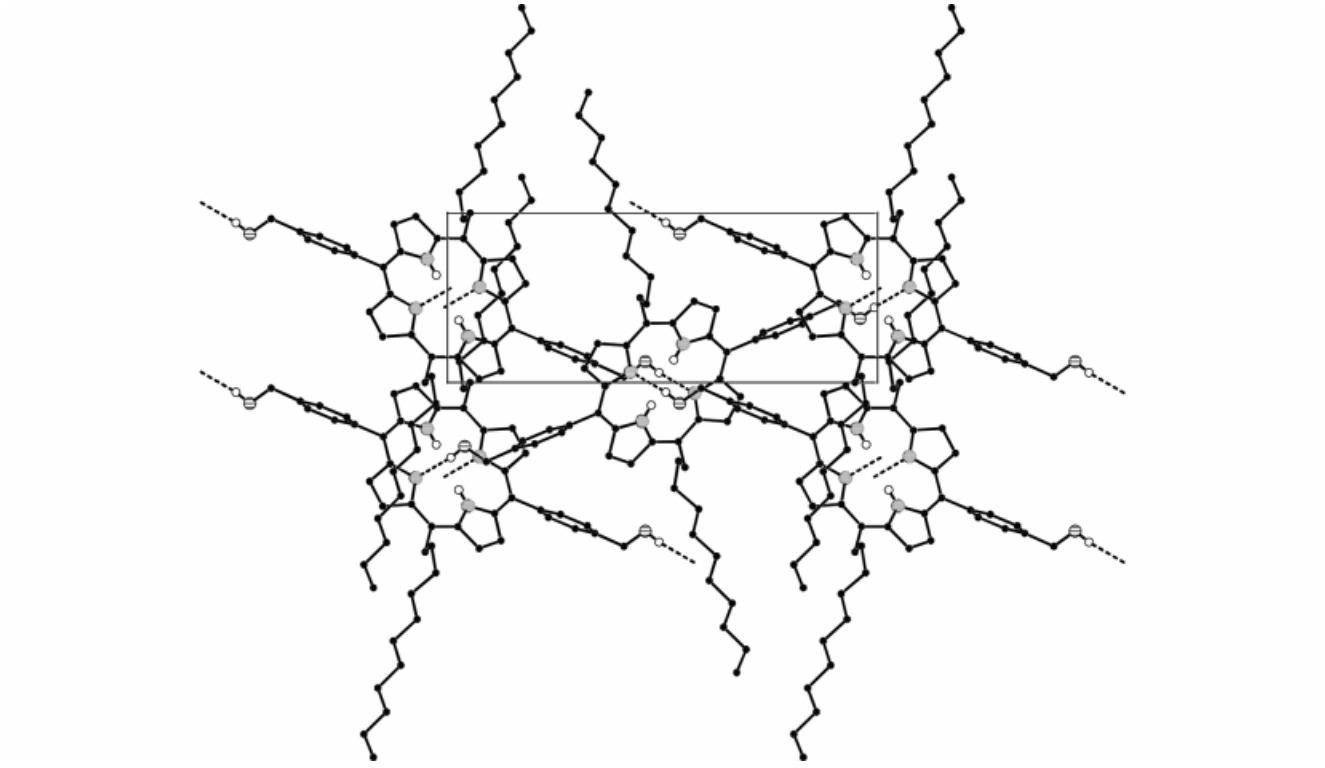


Figure 2. Hydrogen-bonded network in the crystal packing of **7**, viewed along the *a* axis; hydrogen bonds are indicated by the dashed lines; hydrogen atoms bonded to carbon atoms have been omitted for clarity; nitrogen atoms are represented by grey circles and oxygen atoms by hatched circles

These laddered stacks, which bring porphyrin rings into close contact, are quite remarkable in the structure. The edge-to-edge distance between two adjacent porphyrins is about 3.5 Å, the distances between almost overlapping atoms C2 and C1, C3 and C10, and C17 and C4 being 3.564, 3.520 and 3.536 Å, respectively. There is practically no contact between the alkyl chains, their interaction being probably the third and weakest supramolecular force determining the crystal packing. To the best of our knowledge, this is the first porphyrin with such long alkyl side chains to be crystallized. Crystallization of compounds possessing long chains, such as chlorophylls or bacteriochlorophylls,

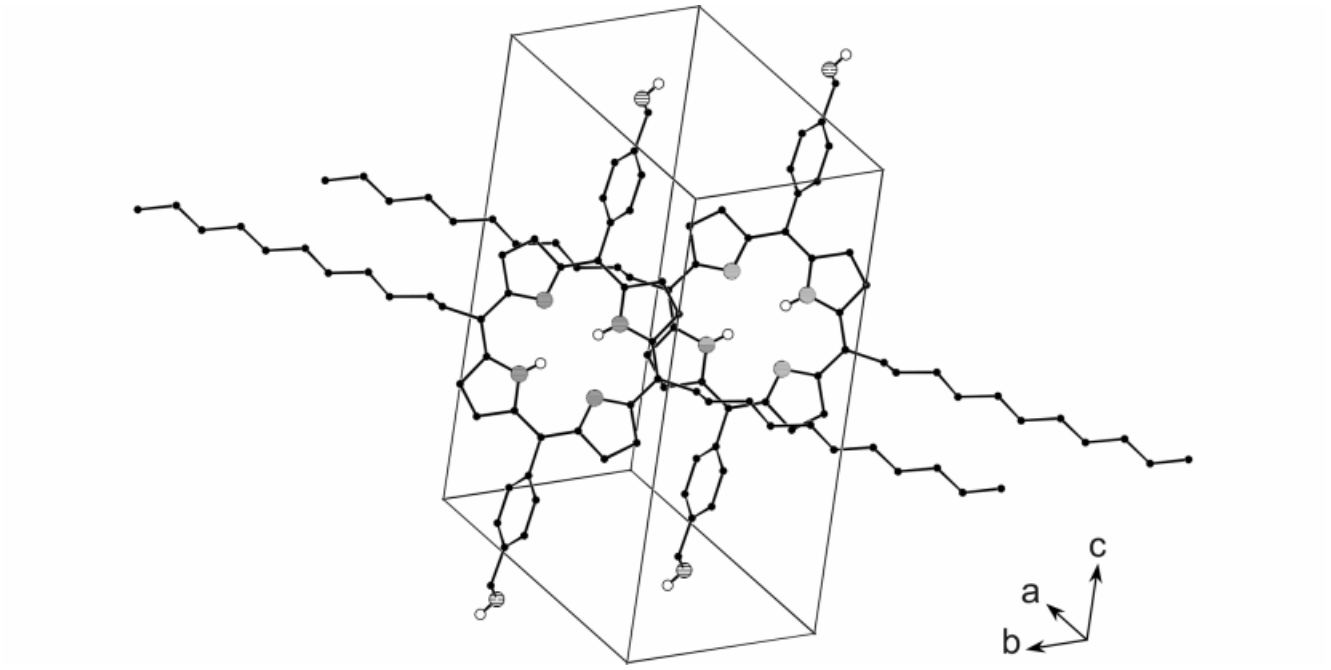


Figure 3. Another view of the crystal packing of **7**; the viewing direction is perpendicular to the porphyrin planes; hydrogen atoms bonded to carbon atoms have been omitted for clarity

has not yet been achieved despite numerous attempts; the known structures are transesterification analogs with the long chains amputated.[13] However, similar π−π interactions to those in **7** are encountered in these systems, involving a marginal overlap of the chlorophylls.

Solution Studies on Porphyrins 3, 4, and 7 and their Zinc Complexes

In solution, neither at the low concentrations used for UV/Vis spectroscopy (in dichloromethane), nor at the millimolar concentrations used for NMR spectroscopy (in deuteriochloroform), were signs of associations of **7** − such as broadening or splitting of the Soret band or shifts of proton signals − encountered. However, the self-assembly of **7** in the solid state produces characteristic effects. Indeed, a UV/Vis spectrum of microcrystals in a nujol mull shows strong excitonic interactions, with a splitting ($\Delta\tilde{\nu}$ = 1960 cm^{-1}) and broadening of the Soret band, together with bathochromic shifts in the Q bands (Figure 4).

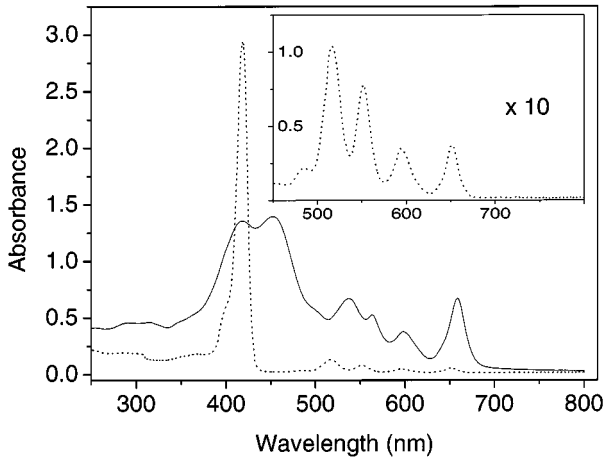


Figure 4. UV/Vis absorption spectra of **7**; full line: nujol mull of microcrystals; dotted line: the same sample after dissolution in dichloromethane, 0.1 cm path length; the inset was recorded with a 1 cm path length

Zinc metallation of the porphyrin might in principle introduce another, even stronger self-assembly interaction: metal ligation of the central zinc atom by a pendant hydroxy group of another molecule. Upon increasing the concentration fivefold, only a slight broadening of the NMR signals and small upfield shifts were encountered in the proton NMR spectrum of **Zn-7**, again indicating that, in solution in deuteriochloroform at millimolar concentrations, there is hardly any association. Evidence for a slight association was encountered in **Zn-3** (Figure 5, A), whereas the isomeric **Zn-4** displayed much stronger effects (Figure 5, B). These included large upfield shifts, splittings, and signal broadenings, followed eventually by the appearance of sharper single resonances, as the concentration in deuteriochloroform increased. This implies a slow − on the NMR timescale − exchange between monomeric and associated species at intermediate concentrations. Pronounced upfield shifts and severe line broadening were also encountered upon cooling (Figure 6). Only the porphyrin protons remote from the phenyl rings showed these effects indicating that π−π stacking takes place only in one portion of the molecule, as shown by the model of a dimer in Figure 7. At low temperatures, extensive aggregation into stacks probably occurs; this fact might also account for the NMR line broadening. Between **Zn-3** and **Zn-4**, the difference in the degrees of association can be explained by the larger area available for stacking in the latter compound. The *meso*-aryl substituents prevent this interaction, due to their al-

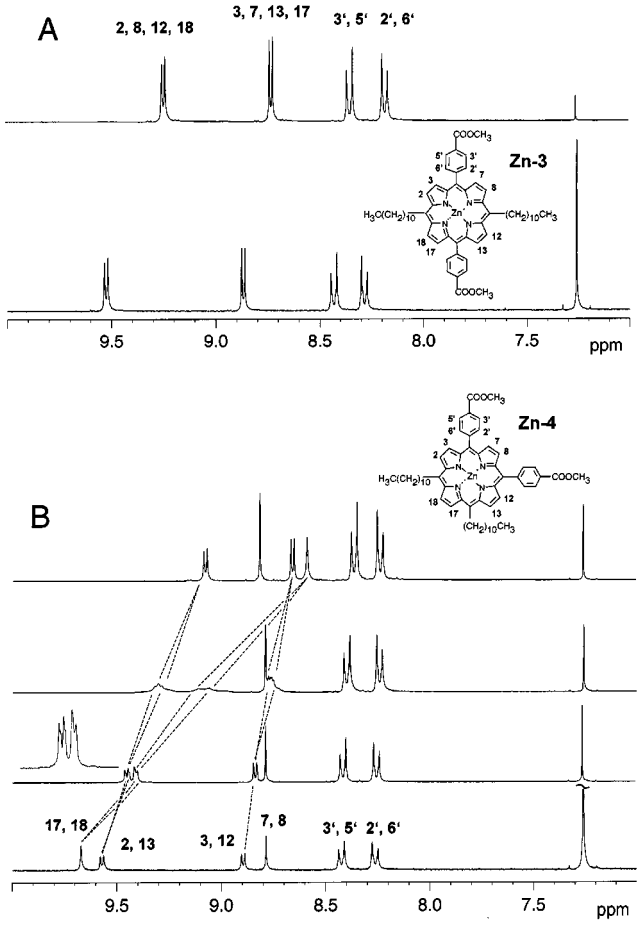


Figure 5. A: Aromatic region of the 300-MHz ^{1}H NMR spectrum of the diester **Zn-3** in $CDCl_3$; in the upper trace the concentration is 53.5 mM while in the lower trace the concentration is 2.4 mM; the first CH_2 triplet is at $\delta = 4.59$ in the concentrated solution and at $\delta = 5.00$ in the dilute solution; B: aromatic region of the 300-MHz ^{1}H NMR spectrum of the diester **Zn-4** in $CDCl_3$; the concentration is 117.6 mM in the upper trace, 58.8 mM in the second trace, 14.0 mM in the third trace and 2.6 mM in the lower trace; note that, upon increasing the concentration, shifts to higher field occur only for the signals indicated by the dotted lines; the inset in the third trace shows an enlargement of the lowest field signals which appear split; the first CH_2 triplet is at $\delta = 4.19$ in the most concentrated solution and at $\delta = 5.03$ in the most dilute solution; the residual $CHCl_3$ peak is at $\delta = 7.26$

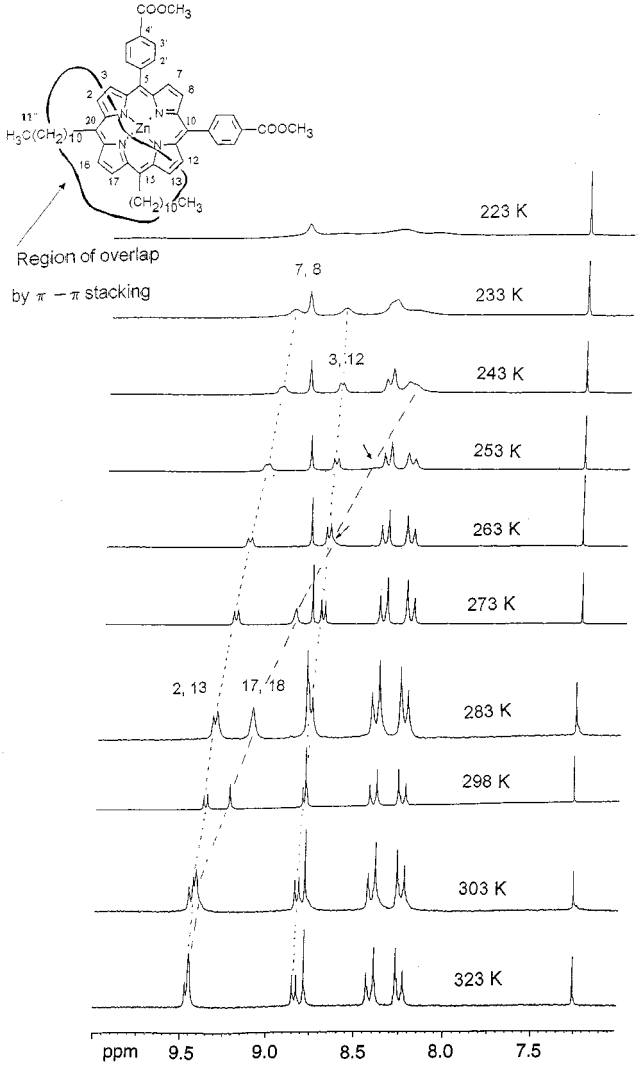


Figure 6. Aromatic region of the 200-MHz ^{1}H NMR spectrum in $CDCl_3$ (about 10 mM) of the diester **Zn-4** at different temperatures; note that upon cooling shifts to higher field are encountered only for some protons, indicated by the dotted and dashed lines; the 1''-CH_2 triplet shifts from $\delta = 4.87$ at 323 K to $\delta = 3.95$ at 243 K (with severe broadening) while the methoxy signal at $\delta \approx 4.10$ is hardly affected

most orthogonal orientation relative to the porphyrin plane. Attempts to crystallize the zinc-metallated compounds have so far failed.

The presence of the zinc atom is not mandatory for this stacking; shifts to higher field as the concentration is increased are also observed for the same protons in the free base **4**. However, these effects are much smaller: The 17,18-singlet shifts by only 0.10 ppm, the 2,13-doublet shifts by 0.06 ppm, while the first CH_2 triplet shifts by 0.12 ppm upfield for a tenfold increase in concentration of the free base **4** in $CDCl_3$. The isomeric free base **3** shows almost no concentration-dependant chemical shifts (shifts of under 0.03 ppm for a tenfold increase in concentration). From these experiments, it appears that the $\pi-\pi$ stacking is more favorable in the zinc-metallated compounds (these are also more soluble, allowing for a larger concentration range to be explored) than in the corresponding free bases. Coordination of the zinc atom by ester groups can be ruled out on the basis of the encountered shifts.

Synthesis and Properties of the Formyl Hydroxy Porphyrins 8 and 11 and of Their Zinc Complexes

In an attempt to mimic the structure of bacteriochlorophyll *c*, which has a hydroxy group, a central magnesium atom and a carbonyl group, we synthesized the formyl hydroxy porphyrin zinc complexes **Zn-8** and **Zn-11**. The hydroxy and carbonyl groups, as well as the central metal atom, are structural features which have been shown by one of the authors[10] and by others[11] to be essential for the self-assembly of bacteriochlorophyll *c* both *in vivo* and *in vitro*. From analogous spectroscopic evidence,[14] it was presumed that the hydroxy group could act as a fifth ligand to the zinc atom in a second molecule, and concomitantly to ensure a strong hydrogen bond to the carbonyl group in a

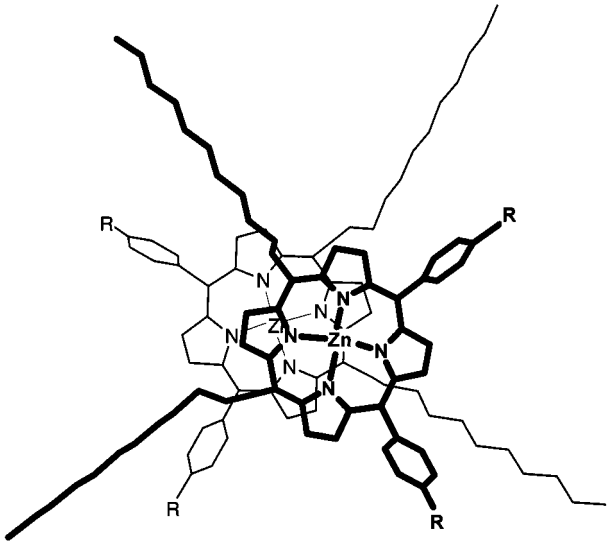
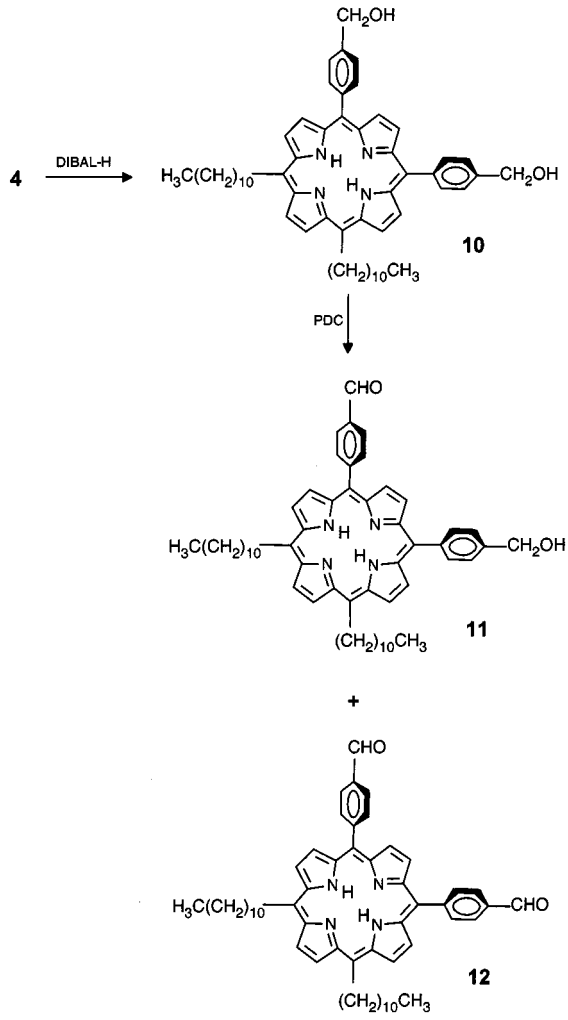


Figure 7. Model of the partial overlap in **Zn-4** (R = $COOCH_3$) induced by the $\pi-\pi$ stacking as inferred from the proton shifts due to the aromatic ring current

third molecule. Thus, **7** was oxidized with pyridinium dichromate to form a mixture of the monoaldehyde **8** and the dialdehyde **9**, which were easily separated by column chromatography (Scheme 2). Subsequent zinc metallation gave the desired mimic **Zn-8** in 32% overall yield. However, the sought-after self-assembly was not evidenced in the visible absorption spectrum of **Zn-8** in dry *n*-heptane, as this showed no features such as broadening, splitting, or shifts of the absorption bands that would be expected for closely spaced chromophores. Addition of methanol to this solution, which would be expected rapidly to disassemble any supramolecular species, led only to slight shifts of the bands, due probably to the formation of the zinc porphyrin−methanol adduct.

A similar reaction sequence (DIBAL-H reduction, PDC oxidation, and zinc metallation) starting with the diester **4** led in 28% overall yield to the corresponding zinc-metallated formyl hydroxy porphyrin **Zn-11**, possessing phenyl substituents in adjacent *meso* positions of the porphyrin ring (Scheme 3). Again, no large shifts in the absorption maxima were found in a dry heptane solution, indicating the absence of any assembly. In the cases of both **Zn-8** and **Zn-11**, suitable precautions were taken to remove any adventitious water by repeated azeotropic distillation with toluene followed by prolonged vacuum (0.1 Torr) drying.

From the structure of **7**, it may be postulated that if a central metal atom were to be ligated by the hydroxy oxygen atom, an energetically costly twist of the phenyl ring would be required. Molecular modeling supports this hypothesis, as dihedral angles between the porphyrin plane and the phenyl rings as low as 20° were found in optimized structures, using the MM+ molecular mechanics force field.[15] It may be that intramolecular steric factors prevent the establishment of supramolecular interactions leading to observable assembly. The synthesis of sterically less demanding mimics for bacteriochlorophyll *c* is underway, with



Scheme 3

the goal of achieving artificial light-harvesting arrays by self-assembly.

Experimental Section

General Remarks: Dichloromethane was freshly distilled from calcium hydride before use. Toluene was distilled from sodium metal. − Melting points were measured with a Büchi B-540 apparatus in open capillaries and are uncorrected. − NMR spectra were obtained at 200 MHz (^{1}H) and 50.33 MHz (^{13}C) with a Bruker AC 200 instrument and at 300 MHz (^{1}H) with a Bruker DPX 300 spectrometer. Chemical shifts are given in ppm relative to the signal of $CHCl_3$ which was taken as δ = 7.26 (for ^{1}H) and 77.00 (for ^{13}C). − UV/Vis spectra were measured with Varian Cary 3 or Perkin−Elmer Lambda 900 spectrometers. − FT-IR spectra were collected with a Perkin−Elmer 1600 series spectrometer. − FAB mass spectra were obtained from *o*-nitrobenzyl alcohol matrices at the Service de Spectrométrie de Masse de l'Université Louis Pasteur in Strasbourg with a Micromass Autospec instrument. − Elemental analyses were performed by the Service de Microanalyse de l'Université Louis Pasteur in Strasbourg. − The crystal diffraction data were collected with a STOE IPDS diffractometer equipped with a Schneider rotating anode. − Retention factors are given for silica gel TLC plates (Macherey−Nagel), which were

eluted with dichloromethane stabilized with 0.2% ethanol unless otherwise stated. − Column chromatography was performed with Merck silica gel 40−63 μm.

Methyl 4-[Bis(1*H*-pyrrol-2-yl)methyl]benzoate (DPM1): Pyrrole (73.3 g, 1.09 mol), freshly distilled (b.p. 130 °C, 760 Torr) from calcium hydride, and methyl 4-formylbenzoate (4.48 g, 0.027 mol) were stirred and degassed by argon bubbling for 10 min in a 500-mL round-bottomed flask equipped with a magnetic stirrer, argon inlet, and reflux condenser. Then trifluoroacetic acid (0.3 g, 0.2 mL) was added by syringe, and the reaction mixture was protected from light as it became pink and warmed up slightly. After stirring at room temperature for 20 min, dichloromethane (200 mL) was added and the reaction mixture was transferred to a separation funnel and washed twice with aqueous sodium carbonate solution (2 M) and then twice with brine, until the solution was neutral. Drying with anhydrous Na_2SO_4 and evaporation of the solvent under reduced pressure in a rotary evaporator left a mother liquor, which was subsequently concentrated in a rotary evaporator at 0.5 Torr on a water bath at 50 °C. At the end of the concentration the product solidified. Grinding in a mortar and final drying by using a vacuum pump (0.1 Torr) afforded 5.45 g of a fine, light tan powder (71% yield). This crude product had a melting range of 152−160 °C and satisfactory EI-MS and ^{1}H NMR spectra and was suitable for further transformations. It could be conveniently stored in the refrigerator for longer periods at 4 °C. Analytical samples could be obtained (with considerable loss) by recrystallization from toluene or a chloroform/hexane mixture; m.p. 157−161 °C. On an SiO_2 TLC plate, eluted with dichloromethane/methanol/triethylamine, 98:1:1 v/v, DPM1 had R_f = 0.46. This main spot became pink to violet upon exposure to bromine vapor. − ^{1}H NMR ($CDCl_3$): δ = 7.97 (4 H, d, J = 8.2 Hz, Ar-H and br. s, NH), 7.28 (2 H, d, J = 8.2 Hz, Ar-H), 6.71 (2 H, dd, J = 4.0 and 2.4 Hz, pyrrole-H), 6.17 (2 H, dd, J = 5.8 and 2.7 Hz, pyrrole-H), 5.89 (2 H, m, pyrrole-H), 5.52 (1 H, s, *meso*-H), 3.90 (3 H, s, $COOCH_3$).

1,1-Bis(1*H*-pyrrol-2-yl)dodecane (DMP2): As in the above procedure, pyrrole (85.3 g, 1.27 mol), dodecanal (6.14 g, 33.3 mmol), and TFA (0.36 mL) were stirred with argon bubbling for 25 min. The above workup afforded 10.08 g of crude yellow oil (99% yield), which was about 85% pure by ^{1}H NMR. Column chromatography on SiO_2 eluted with cyclohexane/ethyl acetate/triethylamine, 80:20:1 (v/v), gave a pale yellow later fraction (2.56 g, 25% yield), which slowly crystallized at 4 °C. The first yellowish fractions eluted from the column, about 4.5 g, did not crystallize even at −18 °C, in spite of seeding, due to the presence of a faster moving impurity. − ^{1}H NMR ($CDCl_3$): δ = 7.65 (ca. 2 H, br. s, NH), 6.60 (2 H, sext, J = 4.2 Hz, 5-H), 6.16 (2 H, dd, J = 5.8 and 2.7 Hz, 3-H), 6.08 (2 H, m, 4-H), 3.95 (1 H, t, J = 7.6 Hz, *meso*-H), 1.93 (2 H, br. q, $J \approx 7$ Hz, 2′-CH_2), 1.27 (ca. 18 H, sharp m, 3′−10′-CH_2), 0.91 (3 H, t, $J \approx 6.5$ Hz, 11′-CH_3).

4-(Methoxycarbonyl)phenyl-Substituted Porphyrins 2−6

(*i*) Method A − Mixed Aldehyde Condensation: In a 1-L round-bottomed flask equipped with a magnetic stirrer, argon inlet terminated with a sintered glass frit, and reflux condenser protected from the atmosphere by an oil bubbler, dry dichloromethane (750 mL, freshly distilled from calcium hydride) was degassed by slowly passing argon through it for 10 min. Pyrrole (0.50 g, 0.52 mL, 7.5 mmol, freshly distilled from calcium hydride) (b.p. 130 °C, 760 Torr), methyl 4-formylbenzoate (0.615 g, 3.75 mmol), and dodecanal (0.691 g, 3.75 mmol) were then added and degassed. Then boron trifluoride−diethyl ether (0.21 g, 0.2 mL) was added by syringe and the reaction mixture was protected from light as it became yellow and then slightly pink. After stirring at room temperature for 60 min, dichlorodicyano-*p*-benzoquinone (DDQ, 2.55 g) was added and the argon bubbling was stopped while continuing to stir at room temperature for 60 min. The reaction mixture completely blackened after the addition of DDQ. Silica gel (15 g) was added to a 1-L round-bottom flask, which was charged with the reaction mixture, and then the dichloromethane was completely removed in a rotary evaporator. The dark powder was transferred to a first SiO_2 column (Φ = 7 cm, H = 10 cm) which was eluted with dichloromethane/methanol, 99:1, v/v. The porphyrin fraction (Soret band at ca. 420 nm) was concentrated and then separated on a second SiO_2 column (Φ = 4.5 cm, H = 25 cm), which was eluted with dichloromethane. Usually, a satisfactory separation of porphyrins **1−6** was possible. In some runs, a mixed fraction containing porphyrins **3** and **4** was obtained. These could be neatly separated on a third SiO_2 column (Φ = 4.5 cm, H = 20 cm) eluted with dichloromethane/cyclohexane, 1:1 (v/v).

(*ii*) Method B − *meso*-Dipyrrylmethane Condensation with Aldehyde: The same procedure as above was employed, except that instead of pyrrole and one aldehyde, the crude, preformed *meso*-dipyrrylmethane was condensed with the other aldehyde in the presence of boron trifluoride−diethyl ether. The advantage of this method was that almost twice as much porphyrin might be obtained in one run, maintaining the reactant concentration at 0.01 M. The yield was drastically reduced if the concentration of the reactants was increased above this limit. Scrambling of the porphyrinogens was observed to the same extent whether starting from either **DPM1** or **DMP2**, so that the same mixture of porphyrins **1−6** finally resulted. The global (isolated) porphyrin yields by this method were consistently around 38%, somewhat higher than for the mixed aldehyde condensations, which were about 33%. When using technical dichloromethane dried with calcium chloride and then filtered into the reaction vessel under nitrogen, only a slight decrease in yield was observed in comparison with when dichloromethane distilled from calcium hydride was used. A scaling up of the mixed aldehyde condensation (method A, 5-L scale) was thus easily feasible, producing 4.5 grams of porphyrins, while method B, starting with 8.4 g of crude **DPM1** in 3 L of dichloromethane, produced 5.0 grams of porphyrins. Table 1 details the yields over various runs. It is interesting to note that the mixture of porphyrins **1−6** deviates somewhat from the statistical expectation, due to the different reactivities of aromatic and aliphatic aldehydes in the condensation reaction with pyrrole or dipyrrylmethane.

5-[4-(Methoxycarbonyl)phenyl]-10,15,20-triundecyl-21*H*,23*H*-porphine (2): R_f = 0.91. − M.p. 61−65 °C after recrystallization from *n*-hexane. − ^{1}H NMR ($CDCl_3$): δ = 9.48 (4 H, m, 12-, 13-, 17-, 18-H_4), 9.38 (2 H, d, J = 4.7 Hz, 2-, 8-H_2), 8.75 (2 H, d, J = 4.7 Hz, 3-, 7-H_2), 8.46 (2 H, d, J = 8.0 Hz, 3′-, 5′-H), 8.27 (2 H, d, J = 8.0 Hz, 2′-, 6′-H), 4.91 (6 H, t, 1"- and 1"′-CH_2), 4.16 (3 H, s, OCH_3), 2.52 (6 H, quint, 2"- and 2"′-CH_2), 1.80 (6 H, quint, 3"- and 3"′-CH_2), 1.52 (6 H, m, 4"- and 4"′-CH_2), 1.30 (36 H, s, 5"−10"- and 5"′−10"′-CH_2), 0.91 (9 H, t, 11"- and 11"′-CH_3), −2.65 (2 H, s, NH). − ^{13}C NMR ($CDCl_3$): δ = 167.4 (COO), 147.6 (1′), ca. 146.5 (very br., $C_α$-pyrrole), 134.4 (2′-, 6′-C), ca. 130.8 (br., 3-, 7-C), 129.3 (4′-C), ca. 128.2 (br., 2-, 8-, 12-, 13-, 17-, 18-C), 127.8 (3′-, 5′-C), 119.9 (15-C), 119.3 (10-, 20-C), 116.4 (5-C), 52.4 (OCH_3), 38.9 (2"′-CH_2), 38.7 (2"-CH_2), 35.8 (1"′-CH_2), 35.4 (1"-CH_2), 31.9 (9"-, 9"′-CH_2), 30.7 (3"′-CH_2), 30.6 (3"-CH_2), 29.70, 29.62 and 29.33 (4"-8"- and 4"′-8"′-CH_2), 22.7 (10"- and 10"′-CH_2), 14.1 (11"- and 11"′-CH_3). − FAB-MS; *m/z*: 907.7 $[M + H]^+$, 765.5 $[M + H - C_{10}H_{21}]^+$, 625.4 $[M + H - 2\ C_{10}H_{21}]^+$. − IR (KBr): $\tilde{\nu}$ = 3315 w (NH), 2921 s, 2849 s, 1727 s (C=O), 1606 w, 1273 s (O−CH_3). − UV/Vis (CH_2Cl_2): λ_{max} (lg ε_{max}) = 655 (4.01), 596.5

Table 1. Isolated yields (%) of porphyrins **1**−**6** over various runs

Method	Drying agent of CH_2Cl_2	Volume of CH_2Cl_2 [mL]	Global yield[a]	**1**	**2**	**3**	**4**	**5**	**6**
			Statistical expectation	6.25	25	12.5	25	25	6.25
A	CaH_2	750	34.0	1.8	7.9	6.6	9.5	10.1	7.3
A	Mol. sieves	750	32.0	n.i.[c]	n.i.	n.i.	n.i.	n.i.	n.i.
A	$CaCl_2$	5000	32.8[b]	n.i.	4.1	6.4	12.2	10.1	n.i.
B, **DPM1**	CaH_2	640	38.0	0.8	2.2	5.8	9.9	12.7	6.5
B, **DPM1**	CaH_2	750	38.4	2.1	5.7	5.9	7.6	10.5	6.6
B, **DPM1**	$CaCl_2$	3000	37.5[b]	5.2	10.5	4.7	8.4	8.7	n.i.
B, **DPM2**	CaH_2	375	39.4	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.

[a] Yield estimated by weighing the porphyrinic fractions together and assuming a statistical mixture with an average molecular mass of 886 g mol^{-1}. − [b] Actual yield is somewhat higher as the first and last fractions consisting of the tetraundecyl- and tetrakis[4-(methoxycarbonyl)phenyl]porphyrins, respectively, were not always isolated after chromatography. − [c] n.i. = not isolated.

(3.88), 553.5 (4.15), 518 (4.33), 418 (5.73). − $C_{61}H_{86}N_4O_2$ (907.3752): calcd. C 80.75, H 9.55, N 6.17; found C 80.41, H 9.61, N 5.98.

5,15-Bis[4-(methoxycarbonyl)phenyl]-10,20-diundecyl-21*H*,23*H*-porphine (3): R_f = 0.86. − M.p. 137−138 °C after recrystallization from chloroform/*n*-hexane. − ^{1}H NMR ($CDCl_3$): δ = 9.44 (4 H, d, *J* = 5.1 Hz, 2-, 8-, 12-, 18-H$_4$), 8.81(4 H, d, *J* = 4.8 Hz, 3-, 7-, 13-, 17-H$_4$), 8.46 (4 H, d, *J* = 8.4 Hz, 3′- and 5′-H), 8.29 (4 H, d, *J* = 8.0 Hz, 2′- and 6′-H), 4.95 (4 H, t, 1"-CH_2), 4.15 (6 H, s, OCH_3), 2.51 (4 H, quint, 2"-CH_2), 1.78 (4 H, quint, 3"-CH_2), 1.55 (4 H, m, 4"-CH_2), 1.26 (24 H, s, 5"−10"-CH_2), 0.87 (6 H, t, 11"-CH_3), −2.68 (2 H, s, NH). − ^{13}C NMR ($CDCl_3$): δ = 167.4 (COO), 147.5 (1′-C), ca. 146.5 (very br., C_α-pyrrole), 134.4 (2′-, 6′-C), 131.3 (br., 3-, 7-, 13-, 17-C), 129.5 (4′-C), 128.1 (br., 2-, 8-, 12-, 18-C), 127.8 (3′-, 5′-C), 120.3 (10-, 20-C), 117.7 (5-, 15-C), 52.4 (OCH_3), 38.8 (2"-CH_2), 35.3 (1"-CH_2), 31.9 (9"-CH_2), 30.5 (3"-CH_2), 29.69 and 29.33 (4"-8"-CH_2), 22.7 (10"-CH_2), 14.1 (11"-CH_3). − FAB-MS; *m*/*z*: 887.5 [M + H]$^+$, 828.5 [M + H − $COOCH_3$]$^+$, 745.4 [M + H − $C_{10}H_{21}$]$^+$, 605.2 [M + H − 2 $C_{10}H_{21}$]$^+$. − IR (KBr): ṽ = 3315 w (NH), 2919 m, 2851 m, 1722 s (C=O), 1606 m, 1273 m (O−CH_3). − UV/Vis (CH_2Cl_2): λ_{max} (lg ε_{max}) = 652 (3.99), 597 (3.93), 551 (4.14), 516.5 (4.35), 419 (5.67). $C_{58}H_{70}N_4O_4$: calcd. C 78.52, H 7.95, N 6.31; found, C 78.39, H 8.09, N 6.36.

5,10-Bis[4-(methoxycarbonyl)phenyl]-15,20-diundecyl-21*H*,23*H*-porphine (4): R_f = 0.79. − M.p. 92−94 °C after recrystallization from chloroform/*n*-hexane. − ^{1}H NMR ($CDCl_3$): δ = 9.53 (2 H, s, 17-, 18-H$_2$), 9.44 (2 H, d, *J* = 4.7 Hz, 2-, 13-H$_2$), 8.80 (2 H, d, *J* = 4.7 Hz, 3-, 12-H$_2$), 8.71 (2 H, s, 7-, 8-H$_2$), 8.44 (4 H, d, *J* = 8.0 Hz, 3′-, 5′-H), 8.26 (4 H, d, *J* = 8.4 Hz, 2′-, 6′-H), 4.95 (4 H, t, 1"-CH_2), 4.14 (6 H, s, OCH_3), 2.54 (4 H, quint, 2"-CH_2), 1.78 (4 H, quint, 3"-CH_2), 1.55 (4 H, m, 4"-CH_2), 1.30 (24 H, s, 5"−10"-CH_2), 0.87 (6 H, t, 11"-CH_3), −2.69 (2 H, s, NH). − ^{13}C NMR ($CDCl_3$): δ = 167.3 (COO), 147.1 (1′-C), ca. 146.5 (very br., C_α) 134.4 (2′-, 6′-C), 130.7 (br., 3-, 7-, 8-, 12-C), 129.4 (4′-C), 128.4 (br., 2-, 13-, 17-, 18-C), 127.8 (3′-, 5′-C), 120.7 (15-, 20-C), 117.2 (5-, 10-C), 52.3 (OCH_3), 38.8 (2"-CH_2), 35.6 1"-CH_2), 31.9 (9"-CH_2), 30.5 (3"-CH_2), 29.66 and 29.33 (4"-8"-CH_2), 22.7 (10"-CH_2), 14.1 (11"-CH_3). − FAB-MS; *m*/*z*: 887.5 [M + H]$^+$, 828.5 [M + H − $COOCH_3$]$^+$, 745.4 [M + H − $C_{10}H_{21}$]$^+$, 605.2 [M + H − 2 $C_{10}H_{21}$]$^+$. − IR (KBr): ṽ = 3316 w (NH), 2921 m, 2851 m, 1724 s (C=O), 1606 m, 1275 s (O−CH_3). − UV/Vis (CH_2Cl_2): λ_{max} (lg ε_{max}) = 651 (3.81), 594 (3.78), 551 (4.02), 517 (4.26), 418 (5.68). − $C_{58}H_{70}N_4O_4$: calcd. C 78.52, H 7.95, N 6.31; found C 78.58, H 7.96, N 6.30.

5,10,15-Tris[4-(methoxycarbonyl)phenyl]-20-undecyl-21*H*,23*H*-porphine (5): R_f = 0.62. − M.p. 219−220 °C after recrystallization from chloroform/*n*-hexane. − ^{1}H NMR ($CDCl_3$): δ = 9.47 (2 H, d, *J* = 4.7 Hz, 2-, 18-H$_2$), 8.86 (2 H, d, *J* = 4.7 Hz, 3-, 17-H$_2$), 8.77 (4 H, s, 7-, 8-, 12-, 13-H$_4$), 8.44 (6 H, m, 3′-, 5′-H), 8.29 (6 H, m, 2′-, 6′-H), 4.93 (2 H, t, 1"-CH_2), 4.14 (6 H, s, OCH_3), 4.12 (3 H, s, OCH_3), 2.53 (2 H, quint, 2"-CH_2), 1.79 (2 H, quint, 3"-CH_2), 1.51 (2 H, m, 4"-CH_2), 1.28 (12 H, s, 5"−10"-CH_2), 0.89 (3 H, t, 11"-CH_3), −2.72 (2 H, s, NH). − ^{13}C NMR ($CDCl_3$): δ = 167.2 (COO), 147.0 (1′-C_2), 146.7 (1"-C), ca. 146.0 (very br., C_α-pyrrole), 134.4 (2′-, 2"-, 6′, 6"-C), 131.2 (br., 7-, 8-, 12-, 13-C), 130.6 (br., 3-, 17-C), 129.6 (4′-, 4"-C), 128.4 (br., 2-, 18-C), 127.9 (3"-C), 127.8 (3′-C), 121.6 (20-C), 118.5 (5-, 10-, 15-C), 53.4 (4"-OCH_3), 52.4 (4′-OCH_3), 38.9 (2"′-CH_2), 35.4 (1"′-CH_2), 31.9 (9′"-CH_2), 30.5 (3"′-CH_2), 29.62 and 29.29 (4"′-8"′-CH_2), 22.6 (10"′-CH_2), 14.1 (11"-CH_3). − FAB-MS; *m*/*z*: 867.4 [M + H]$^+$, 808.4 [M + H − $COOCH_3$]$^+$, 725.3 [M + H − $C_{10}H_{21}$]$^+$. − IR (KBr): ṽ = 3314 w (NH), 2921 m, 2850 m, 1723 s (C=O), 1606 m, 1274 s (O−CH_3). − UV/Vis (CH_2Cl_2): λ_{max} (lg ε_{max}) = 648 (3.69), 592 (3.75), 550 (3.97), 515 (4.26), 419 (5.63). − $C_{55}H_{54}N_4O_6$: calcd. C 76.19, H 6.28, N 6.46; found C 76.23, H 6.22, N 6.43.

5,10,15,20-Tetrakis[4-(methoxycarbonyl)phenyl]-21*H*,23*H*-porphine (6):[16] R_f = 0.30. − M.p. > 360 °C. − ^{1}H NMR ($CDCl_3$): δ = 8.86 (8 H, s, β-pyrrole-H), 8.47 (8 H, d, *J* = 8.4 Hz, 3′- and 5′-H), 8.31 (8 H, d, *J* = 8.4 Hz, 2′- and 6′-H), 4.14 (12 H, s, OCH_3), −2.73 (2 H, s, NH). − ^{13}C NMR ($CDCl_3$): δ = 167.2 (COO), 146.6 (1′-C), ca. 146.5 (very br., C_α-pyrrole), 134.5 (2′-, 6′-C), 131.2 (br., C_β-pyrrole), 129.7 (4′-C), 127.9 (3′-, 5′-C), 119.4 (5-, 10-, 15-, 20-C), 52.4 (OCH_3). − FAB-MS; *m*/*z*: 847.2 [M + H]$^+$, 788.2 [M + H − $COOCH_3$]$^+$. − IR (KBr): ṽ = 3314 w (NH), 2947 w, 1724 s (C=O), 1606 m, 1275 s (O−CH_3). − UV/Vis (CH_2Cl_2): λ_{max} (lg ε_{max}) = 645 (3.65), 590 (3.82), 549.5 (3.97), 514 (4.30), 419 (5.65).

Reduction/Oxidation/Zinc Metallation Sequence: From the diesters **3** or **4**, the corresponding diols **7** or **10** were obtained in about 80% yield (on a 100-mg scale) by DIBAL-H reduction in dry toluene (40 mL) at −70 °C. After 30 min, the starting material had been consumed (TLC monitoring) and the reaction mixture was quenched with aqueous NH_4Cl, extracted into dichloromethane, washed twice with brine, and dried (Na_2SO_4). After evaporation of the solvent, the mixture was chromatographed on silica gel (Φ = 2 cm, H = 8 cm), and eluted with methanol/dichloromethane, 3:97, v/v. After two minor bands, the main diol component was eluted. Subsequent oxidation with pyridinium dichromate (PDC) in chloroform afforded a mixture from which the dialdehyde and the alcohol aldehyde could conveniently be separated by column chromatography on silica gel eluted first with dichloromethane and, after separation of the dialdehyde, with 1% methanol in dichloromethane. Yields varied with the amount of oxidation reagent and reaction time. With a 2:1 molar excess of PDC, after 3 h at room tem-

perature, about 30% of dialdehyde, 40% of the alcohol aldehyde and 30% of unchanged diol were present in the reaction mixture, which was monitored by TLC. Zinc metallation was performed by stirring a methanolic solution of the free-base porphyrin with zinc acetate for 1 h, at room temperature in the dark. Sometimes the free-base porphyrin had to be dissolved in the least possible amount of chloroform before adding methanol. Evaporation of the solvents left a precipitate which was either transferred to a SiO_2 column, or extracted into chloroform, and washed first with aqueous sodium hydrogen carbonate, then twice with brine. Drying with anhydrous sodium sulfate was followed by evaporation of the solvent and chromatography. Yields of the metallation step were over 90% of the isolated product. Separation of the diesters **3** from **4** was more convenient as free bases (see above) than after zinc metallation. Residual water was removed from the samples in which self-assembly was studied by repeated azeotropic distillation with toluene, followed by prolonged vacuum drying (0.1 Torr).

{5,15-Bis[4-(methoxycarbonyl)phenyl]-10,20-diundecylporphinato}zinc (Zn-3): R_f = 0.36 (CH_2Cl_2/cyclohexane, 3:1, v/v). − ^{1}H NMR ($CDCl_3$, dilute solution): δ = 9.50 (4 H, d, *J* = 4.7 Hz, 2-, 8-, 12-, 18-H_4), 8.87 (4 H, d, *J* = 4.7 Hz, 3-, 7-,13-, 17-H_4), 8.43 (4 H, d, *J* = 8.0 Hz, 3′- and 5′-H), 8.27 (4 H, d, *J* = 8.0 Hz, 2′- and 6′-H), 4.95 (4 H, t, 1"-CH_2), 4.12 (6 H, s, OCH_3), 2.53 (4 H, quint, 2"-CH_2), 1.82 (4 H, quint, 3"-CH_2), 1.50 (4 H, m, 4"-CH_2), 1.26 (24 H, s, 5"-10"-CH_2), 0.86 (6 H, t, 11"-CH_3). − FAB-MS; *m/z*: 949.4 $[M + H]^+$, 807.2 $[M + H - C_{10}H_{21}]^+$. − HR-MS: found 948.4525; calcd. for $C_{58}H_{68}N_4O_4Zn$, 948.4532. − UV/Vis (C_7H_{16}): λ_{max} = 591, 547, 420, 415 (shoulder).

{5,10-Bis[4-(methoxycarbonyl)phenyl]-15,20-diundecylporphinato}zinc (Zn-4): R_f = 0.26 (CH_2Cl_2/cyclohexane, 3:1, v/v). − ^{1}H NMR ($CDCl_3$, dilute solution): δ = 9.57 (2 H, s, 17-, 18-H_2), 9.53 (2 H, d, *J* = 4.8 Hz, 2-, 13-H_2), 8.87 (2 H, d, *J* = 4.7 Hz, 3-, 12-H_2), 8.79 (2 H, s, 7-, 8-H_2), 8.42 (4 H, d, *J* = 8.0 Hz, 3′-, 5′-H), 8.26 (4 H, d, *J* = 8.0 Hz, 2′-, 6′-H), 4.94 (4 H, t, 1"-CH_2), 4.11 (6 H, s, OCH_3), 2.55 (4 H, quint, 2"-CH_2), 1.85 (4 H, quint, 3"-CH_2), 1.54 (4 H, m, 4"-CH_2), 1.27 (24 H, s, 5"-10"-CH_2), 0.87 (6 H, t, 11"-CH_3). − FAB-MS; *m/z*: 949.4 $[M + H]^+$, 807.2 $[M + H - C_{10}H_{21}]^+$, 653.1 $[M + H - 2\ C_{10}H_{21}]^+$. − HR-MS: found 948.4526; calcd. for $C_{58}H_{68}N_4O_4Zn$, 948.4532. − UV/Vis (C_7H_{16}): λ_{max} = 592, 553, 426.5.

5,15-Bis(4-hydroxymethylenephenyl)-10,20-diundecyl-21*H*,23*H*-porphine (7): R_f = 0.21 (CH_2Cl_2/CH_3OH = 99:1, v/v). − ^{1}H NMR ($CDCl_3$): δ = 9.41 (4 H, d, *J* = 5.1 Hz, 2-, 8-, 12-, 18-H_4), 8.86 (4 H, d, *J* = 4.8 Hz, 3-, 7-,13, 17-H_4), 8.20 (4 H, d, *J* = 7.7 Hz, 2′- and 6′-H), 7.75 (4 H, d, *J* = 7.7 Hz, 3′- and 5′-H), 5.08 (4 H, s, 4′-CH_2OH), 4.94 (4 H, t, *J* ≈ 7.5 Hz, 1"-CH_2), 2.50 (4 H, quint, 2"-CH_2), 2.01 (2 H, br. s, OH), 1.77 (4 H, quint, 3"-CH_2), 1.54 (4 H, m, 4"-CH_2), 1.25 (24 H, s, 5"−10"-CH_2), 0.87 (6 H, t, 11"-CH_3), −2.67 (2 H, s, NH). − FAB-MS; *m/z*: 831.5 $[M + H]^+$, 813.5 $[M + H - H_2O]^+$, 689.3 $[M + H - C_{10}H_{22}]^+$, 549.1 $[M + H - 2\ C_{10}H_{21}]^+$. − HR-MS: found 831.5549; calcd. for $C_{56}H_{71}N_4O_2$, 831.5577; found 830.5483, calcd. for $C_{56}H_{70}N_4O_2$, 830.5499.

Crystal Data Collection and Refinement of the Structure: Crystal system: monoclinic; space group: $P2_1/c$; *a* = 14.834(3), *b* = 7.9392(16), *c* = 20.308(5) Å; β = 96.03(3)°; *V* = 2378.5(8) Å^3; *Z* = 2; $\rho_{calcd.}$ = 1.161 g cm^{-3}; *F*(000) = 900; λ (Mo-K_α) = 0.71073 Å; *T* = 200(2) K, 2θ = 51.8°; reflections collected/unique: 9287/4003 [*R*(int) = 0.0393]. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 with 420 parameters (SHELX-97). All hydrogen atoms could be located in the Fourier difference map and were positioned correctly. All non-hydrogen atoms were refined anisotropically. R_1 = 0.0413 [$I > 2\sigma(I)$], wR_2 = 0.1082, Goodness of fit on F^2 = 1.068; max./min. residual density = 0.186/−0.138 e·Å^{-3}. Crystallographic data (excluding structure factors) for **7** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-145575. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

5-(4-Formylphenyl)-15-[4-(hydroxymethyl)phenyl]-10,20-diundecyl-21*H*,23*H*-porphine (8): R_f = 0.42 (CH_2Cl_2/CH_3OH, 99:1, v/v). − ^{1}H NMR ($CDCl_3$): δ = 10.41 (1 H, s, CHO), 9.44 and 9.42 (4 H, two d, 2-, 8-, 12-, 18-H_4), 8.87 (2 H, d, *J* = 5.1 Hz, 13-, 17-H_2), 8.79 (2 H, d, *J* = 5.1 Hz, 3-, 7-H_2), 8.39 (2 H, d, *J* = 8.0 Hz, 3′- and 5′-H), 8.28 (2 H, d, *J* = 8.0 Hz, 2′- and 6′-H), 8.18 (2 H, d, *J* = 8.0 Hz, 2"- and 6"-H), 7.77 (2 H, d, *J* = 8.0 Hz, 3"- and 5"-H), 5.09 (2 H, s, 4′-CH_2OH), 4.95 (4 H, t, *J* = 8.0 Hz, 1"′-CH_2), 2.50 (4 H, quint, 2"′-CH_2), 2.01 (1 H, br. s, OH), 1.77 (4 H, quint, 3"′-CH_2), 1.55 (4 H, m, 4"-CH_2), 1.24 (24 H, s, 5"-10"-CH_2), 0.86 (6 H, t, 11"-CH_3), −2.68 (2 H, s, NH). − FAB-MS; *m/z*: 829.5 $[M + H]^+$, 811.5 $[M + H - H_2O]^+$, 687.3 $[M + H - C_{10}H_{22}]^+$, 547.2 $[M + H - 2\ C_{10}H_{21}]^+$ (calcd. avg. mass for $C_{56}H_{68}N_4O_2$: 829.18). − UV/Vis (CH_2Cl_2): λ_{max} = 652, 595.5, 552, 516.5, 419.

5,15-Bis(4-formylphenyl)-10,20-diundecyl-21*H*,23*H*-porphine (9): R_f = 0.76 (CH_2Cl_2/CH_3OH, 99:1, v/v). − ^{1}H NMR ($CDCl_3$): δ = 10.42, (2 H, s, CHO), 9.46 (4 H, d, *J* = 4.8 Hz, 2-, 8-, 12-, 18-H_4), 8.80 (4 H, d, *J* = 5.1 Hz, 3-, 7-,13-, 17-H_4), 8.39 (4 H, d, *J* = 8.0 Hz, 3′- and 5′-H), 8.29 (4 H, d, *J* = 8.0 Hz, 2′- and 6′-H), 4.97 (4 H, t, *J* ≈ 7.8 Hz, 1"-CH_2), 2.51 (4 H, quint, 2"-CH_2), 1.78 (4 H, quint, 3"-CH_2), 1.54 (4 H, m, 4"-CH_2), 1.25 (24 H, s, 5"-10"-CH_2), 0.87 (6 H, t, 11"-CH_3), −2.67 (2 H, s, NH). − FAB-MS; *m/z*: 827.5 $[M + H]^+$, 685.3 $[M + H - C_{10}H_{20}]^+$ (calcd. avg. mass for $C_{56}H_{66}N_4O_2$: 827.17). − UV/Vis (CH_2Cl_2): λ_{max} = 652.5, 595, 553, 517, 420.5.

{5,15-Bis[4-(hydroxymethyl)phenyl]-10,20-diundecylporphinato}zinc (Zn-7): R_f = 0.35 (CH_2Cl_2/CH_3OH, 99:1, v/v). − ^{1}H NMR ($CDCl_3$): δ = 9.54 (4 H, d, *J* = 4.7 Hz, 2-, 8-, 12-, 18-H_4), 8.96 (4 H, d, *J* = 4.7 Hz, 3-, 7-,13-, 17-H_4), 8.20 (4 H, d, *J* = 8.0 Hz, 2′- and 6′-H), 7.75 (4 H, d, *J* = 8.0 Hz, 3′- and 5′-H), 5.06 (4 H, d, *J* = 5.5 Hz, 4′-CH_2OH), 4.98 (4 H, t, *J* ≈ 8.4 Hz, 1"-CH_2), 2.56 (4 H, quint, 2"-CH_2), 1.97 (2 H, t, OH), 1.81 (4 H, quint, 3"-CH_2), 1.54 (4 H, m, 4"-CH_2), 1.25 (24 H, s, 5"−10"-CH_2), 0.87 (6 H, t, 11"-CH_3). In more concentrated solutions (five times more concentrated), small upfield shifts were encountered for the four doublets, which appeared at δ = 9.47, 8.92, 8.17 and 7.66. − FAB-MS; *m/z*: 893.4 $[M + H]^+$, 875.4 $[M + H - H_2O]^+$, 751.3 $[M + H - C_{10}H_{22}]^+$, 597.1 $[M + H - C_{10}H_{22} - C_{11}H_{22}]^+$ (calcd. avg. mass for $C_{56}H_{68}N_4O_2Zn$: 894.56). − UV/Vis (C_7H_{16}): λ_{max} = 600, 548, 417; (toluene): λ_{max} = 595, 551, 425; (toluene + MeOH): λ_{max} = 604, 561, 427. − Crystallization trials: Conglomerates of microcrystals were obtained from a concd. $CHCl_3$ solution layered with *n*-hexane.

{5-(4-Formylphenyl)-15-[4-(hydroxymethyl)phenyl]-10,20-diundecylporphinato}zinc (Zn-8): R_f = 0.47 (CH_2Cl_2/CH_3OH, 99:1, v/v). − ^{1}H NMR ($CDCl_3$): δ = 10.40 (1 H, s, CHO), 9.54 and 9.52 (4 H, 2 d, *J* = 4.7 Hz, 2-, 8-, 12-, 18-H_4), 8.95 (2 H, d, *J* = 4.8 Hz, 13-, 17-H_2), 8.88 (2 H, d, *J* = 4.8 Hz, 3-, 7-H_2), 8.39 (2 H, d, *J* = 8.4 Hz, 3′- and 5′-H*), 8.28 (2 H, d, *J* = 8.0 Hz, 2′- and 6′-H*), 8.18 (2 H, d, *J* = 8.0 Hz, 2"- and 6"-H), 7.71 (2 H, d, *J* = 8.0 Hz, 3"- and 5"-H), 5.01 (2 H, s, 4′-CH_2OH), 4.99 (4 H, t, 1"′-CH_2), 3.38 (1 H, sharp s, OH), 2.55 (4 H, quint, 2"′-CH_2), 1.83 (4 H, quint, 3"′-CH_2), 1.53 (4 H, m, 4"-CH_2), 1.25 (24 H, s, 5"−10"-CH_2), 0.86 (6 H, t, 11"-CH_3). Upon addition of D_2O the singlet at

δ = 3.38 disappeared and the CH_2 signal at δ = 5.01 sharpened. − FAB-MS; *m/z*: 891.4 $[M + H]^+$, 873.4 $[M + H - H_2O]^+$, 749.2 $[M + H - C_{10}H_{22}]^+$ (calcd. avg. mass for $C_{56}H_{66}N_4O_2Zn$: 892.55). − UV/Vis (C_7H_{16}): λ_{max} = 590, 549, 419; (toluene): λ_{max} = 596, 553, 425; (acetone): λ_{max} = 602, 558, 423; (toluene + MeOH): λ_{max} = 606, 560, 424.

[5,15-Bis(4-formylphenyl)-10,20-diundecylporphinato]zinc (Zn-9): R_f = 0.71 (CH_2Cl_2/CH_3OH, 99:1, v/v). − ^{1}H NMR ($CDCl_3$): δ = 10.42, (2 H, s, CHO), 9.58 (4 H, d, *J* = 4.7 Hz, 2-, 8-, 12-, 18-H_4), 8.90 (2 H, d, *J* = 4.8 Hz, 3-, 12-H_2), 8.40 (4 H, d, *J* = 8.4 Hz, 3′- and 5′-H), 8.30 (4 H, d, *J* = 8.0 Hz, 2′- and 6′-H), 5.04 (4 H, t, *J* ≈ 7 Hz, 1"-CH_2), 2.57 (4 H, quint, 2"-CH_2), 1.83 (4 H, quint, 3"-CH_2), 1.55 (4 H, m, 4"-CH_2), 1.26 (24 H, s, 5"−10"-CH_2), 0.85 (6 H, t, 11"-CH_3). No concentration shifts were observed upon increasing the concentration about two times. − FAB-MS; *m/z*: 888.4 $[M]^+$, 747.3 $[M + H - C_{10}H_{22}]^+$, 593.1 $[M + H - C_{10}H_{22} - C_{10}H_{20}]^+$ (calcd. avg. mass for $C_{56}H_{64}N_4O_2Zn$: 890.53). − UV/Vis (toluene diluted in C_7H_{16}, 1:50): λ_{max} = 421.5, 549, 592; (+ MeOH): λ_{max} = 428, 560, 609.

5,10-Bis[4-(hydroxymethyl)phenyl]-15,20-diundecyl-21*H*,23*H*-porphine (10): R_f = 0.03 (CH_2Cl_2/CH_3OH, 99:1, v/v). − ^{1}H NMR ($CDCl_3$): δ = 9.57 (2 H, s, 17-,18- H_2), 9.44 (2 H, d, *J* = 4.8 Hz, 2-, 13-H_2), 8.85 (2 H, d, *J* = 4.7 Hz, 3-,12-H_2), 8.73 (2 H, s, 7-, 8-H_2), 8.16 (4 H, d, *J* = 8.0 Hz, 2′- and 6′-H), 7.73 (4 H, d, *J* = 8.0 Hz, 3′- and 5′-H), 5.04 (4 H, d, 4′-C*H*$_2$OH), 4.99 (4 H, t, *J* ≈ 8 Hz, 1"-CH_2), 2.55 (4 H, quint, 2"-CH_2), 2.01 (2 H, t, OH), 1.79 (4 H, quint, 3"-CH_2), 1.54 (4 H, m, 4"-CH_2), 1.27 (24 H, s, 5"−10"-CH_2), 0.88 (6 H, t, 11"-CH_3), −2.69 (2 H, s, NH). − FAB-MS; *m/z*: 831.6 $[M + H]^+$, 689.5 $[M + H - C_{10}H_{22}]^+$, 549.3 $[M + H - 2\ C_{10}H_{21}]^+$ (calcd. avg. mass for $C_{56}H_{70}N_4O_2$: 831.20). − UV/Vis (toluene diluted in C_7H_{16}, 1:50): λ_{max} = 653.5, 597.5, 549, 516, 416.

5-(4-Formylphenyl)-10-[4-(hydroxymethyl)phenyl]-15,20-diundecyl-21*H*,23*H*-porphine (11): R_f = 0.17 (CH_2Cl_2/CH_3OH, 99:1, v/v). − ^{1}H NMR ($CDCl_3$): δ = 10.38 (1 H, s, CHO), 9.57 (2 H, s, 17-,18- H_2), 9.46 and 9.44 (2 H, 2 d, 2-, 13-H_2), 8.86 (1 H, d, *J* = 4.8 Hz, 12-H), 8.78 and 8.76 (2 H, two d, *J* = 4.7 and 4.8 Hz, 7*-, and 3-H_2, respectively), 8.65 (1 H, d, *J* = 4.7 Hz, 8*-H), 8.35 (2 H, d, *J* = 8.0 Hz, 3′- and 5′-H), 8.25 (2 H, d, *J* = 8.0 Hz, 2′- and 6′-H), 8.17 (2 H, d, *J* = 8.0 Hz, 2"- and 6"-H), 7.74 (2 H, d, *J* = 8.0 Hz, 3"- and 5"-H), 5.06 (2 H, s, 4′′-C*H*$_2$OH), 4.99 (4 H, t, *J* = 7.7 Hz, 1"′-CH_2), 2.55 (4 H, quint, 2"′-CH_2), 2.01 (1 H, br. s, OH), 1.82 (4 H, quint, 3"′-CH_2), 1.75 (4 H, m, 4"-CH_2), 1.28 (24 H, s, 5"−10"-CH_2), 0.85 (6 H, t, 11"-CH_3), −2.68 (2 H, s, NH). − FAB-MS; *m/z*: 829.6 $[M + H]^+$, 687.4 $[M + H - C_{10}H_{22}]^+$, 547.2 $[M + H - 2\ C_{10}H_{21}]^+$ (calcd. avg. mass for $C_{56}H_{68}N_4O_2$: 829.18). − UV/Vis (toluene diluted in C_7H_{16}, 1:50): λ_{max} = 652.5, 596, 550.5, 516.5, 417.

5,10-Bis(4-formylphenyl)-15,20-diundecyl-21*H*,23H-porphine (12): R_f = 0.62 (CH_2Cl_2/CH_3OH, 99:1, v/v). − ^{1}H NMR ($CDCl_3$): δ = 10.39, (2 H, s, CHO), 9.59 (2 H, s, 17-, 18- H_2), 9.48 (2 H, d, *J* = 5.1 Hz, 2-, 13-H_2), 8.79 (2 H, d, *J* = 4.8 Hz, 3-, 12-H_2), 8.69 (2 H, s, 7-,8-H_2), 8.36 (4 H, d, *J* = 8.4 Hz, 3′- and 5′-H), 8.27 (4 H, d, *J* = 8.0 Hz, 2′- and 6′-H), 5.01 (4 H, t, *J* ≈ 7.5 Hz, 1"-CH_2), 2.55 (4 H, quint, 2"-CH_2), 1.82 (4 H, quint, 3"-CH_2), 1.54 (4 H, m, 4"-CH_2), 1.26 (24 H, s, 5"−10"-CH_2), 0.87 (6 H, t, 11"-CH_3), −2.67 (2 H, s, NH). − FAB-MS; *m/z*: 827.5 $[M + H]^+$, 685.3 $[M + H - C_{10}H_{22}]^+$, 545.2 $[M + H - C_{10}H_{22} - C_{10}H_{20}]^+$ (calcd. avg. mass for $C_{56}H_{66}N_4O_2$: 827.17). − UV/Vis (toluene diluted in C_7H_{16}, 1:50): λ_{max} = 653.5, 594.5, 550, 516, 418.

{5,10-Bis[4-(hydroxymethyl)phenyl]-15,20-diundecylporphinato}-zinc (Zn-10): R_f = 0.05 (CH_2Cl_2/CH_3OH, 99:1, v/v). − ^{1}H NMR ($CDCl_3$): δ = 9.62 (2 H, s, 17-, 18-H_2), 9.53 (2 H, d, *J* = 4.7 Hz, 2-, 13-H_2), 8.93 (2 H, d, *J* = 4.7 Hz, 3-,12-H_2), 8.83 (2 H, s, 7-, 8-H_2), 8.17 (4 H, d, *J* = 8.0 Hz, 2′- and 6′-H), 7.71 (4 H, d, *J* = 8.0 Hz, 3′- and 5′-H), 5.01 (4 H, d, 4′-C*H*$_2$OH), 4.99 (4 H, t, 1"-CH_2), 2.57 (4 H, quint, 2"-CH_2), 1.92 (2 H, t, OH), 1.82 (4 H, quint, 3"-CH_2), 1.54 (4 H, m, 4"-CH_2), 1.26 (24 H, s, 5"−10"-CH_2), 0.87 (6 H, t, 11"-CH_3). Upon increasing the concentration about 5 times, upfield shifts of 0.21 ppm were encountered for 17-,18-singlet, 0.14 ppm for the 2-,13-doublet, 0.10 ppm for the 3-,12-doublet and 0.05 ppm for the 7-,8-singlet. The 2′-,6′-doublet was shifted by 0.07 ppm while the 3′-,5′-doublet was also shifted upfield by 0.24 ppm. − FAB-MS; *m/z*: 892.5 $[M]^+$, 751.3 $[M + H - C_{10}H_{20}]^+$, 597.1 $[M + H - C_{10}H_{20} - C_{11}H_{21}]^+$ (calcd. avg. mass for $C_{56}H_{68}N_4O_2Zn$: 894.56). − UV/Vis (toluene diluted in C_7H_{16}, 1:50): λ_{max} = 601, 554, 418 (br.); (+ MeOH): λ_{max} = 625 sh, 601, 561, 424 sharpened and almost doubled in intensity (see Figure 8).

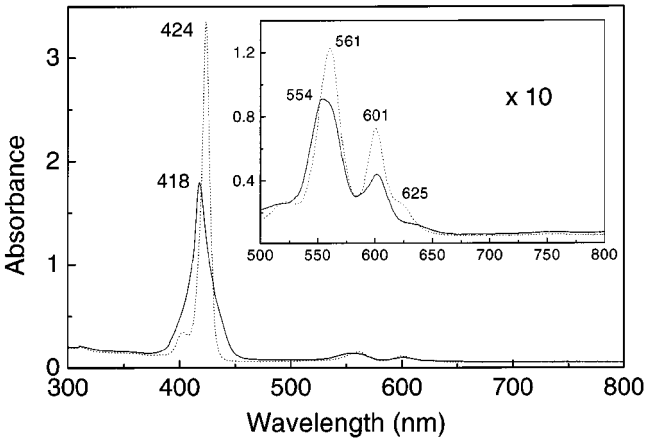


Figure 8. UV/Vis absorption spectra of **Zn-10**; full line: toluene solution diluted with *n*-heptane (both distilled from sodium metal, 1:50 v/v); dotted line: the same sample after addition of one drop of methanol; path length = 0.1 cm while in the inset the path length was 1 cm

{5-(4-Formylphenyl)-10-[4-(hydroxymethyl)phenyl]-15,20-diundecylporphinato}zinc (Zn-11): R_f = 0.21 (CH_2Cl_2/CH_3OH, 99:1, v/v). − ^{1}H NMR ($CDCl_3$): δ = 10.39 (1 H, s, CHO), 9.64 (2 H, s, 17-, 18- H_2), 9.56 and 9.54 (2 H, two d, 2-, 13-H_2), 8.95 (1 H, d, *J* = 4.7 Hz, 12-H), 8.88 and 8.86 (2 H, tw0 d, *J* = 4.0 and 4.4 Hz, 7*-, and 3-H_2, respectively), 8.76 (1 H, d, *J* = 4.7 Hz, 8*-H), 8.37 (2 H, d, *J* = 8.0 Hz, 3′- and 5′-H), 8.27 (2 H, d, *J* = 8.0 Hz, 2′- and 6′-H), 8.17 (2 H, d, *J* = 8.0 Hz, 2"- and 6"-H), 7.73 (2 H, d, *J* = 8.0 Hz, 3"- and 5"-H), 5.03 (2 H, d, 4′′-C*H*$_2$OH), 5.02 (4 H, t, 1"′-CH_2), 2.57 (4 H, quint, 2"′-CH_2), 1.94 (1 H, t, OH), 1.87 (4 H, quint, 3"′-CH_2), 1.54 (4 H, m, 4"-CH_2), 1.27 (24 H, s, 5"−10"-CH_2), 0.87 (6 H, t, 11"-CH_3). Upon increasing the concentration about seven times, while the formyl proton signals were not shifted (about 0.01 ppm), upfield shifts of 0.18 ppm were encountered for 17-,18-singlet, 0.08 ppm for the 2-,13-doublets, 0.04 ppm for the 12-doublet and about 0.04 ppm for the 7-,3-doublets, while the 8-doublet was not shifted. The 2′-,6′-doublet and the 3′-,5′-doublet of the formyl-substituted phenyl ring were shifted less than 0.01 ppm. The 2′′-,6′′-doublet of the hydroxymethyl-substituted phenyl ring was shifted 0.02 ppm while the 3′′-,5′′-doublet moved 0.09 ppm. − FAB-MS; *m/z*: 890.6 $[M]^+$, 749.4 $[M + H - C_{10}H_{22}]^+$, 595.2 $[M + H - 2\ C_{10}H_{21}]^+$ (calcd. avg. mass for $C_{56}H_{66}N_4O_2Zn$: 892.55). − UV/Vis (toluene diluted in C_7H_{16}, 1:50): λ_{max} = 588, 550 and 418 nm; (+ MeOH): λ_{max} = 602, 561 and 425 nm (no increase or sharpening visible).

[5,10-Bis(4-formylphenyl)-15,20-diundecylporphinato]zinc (Zn-12): R_f = 0.57 (CH_2Cl_2/CH_3OH, 99:1, v/v). − ^1H NMR ($CDCl_3$): 10.39, (2 H, s, CHO), 9.62 (2 H, s, 17-, 18- H_2), 9.56 (2 H, d, J = 5.1 Hz, 2-, 13-H_2), 8.88 (2 H, d, J = 4.7 Hz, 3-, 12-H_2), 8.79 (2 H, s, 7-, 8-H_2), 8.37 (4 H, d, J = 8.0 Hz, 3′- and 5′-H), 8.27 (4 H, d, J = 8.0 Hz, 2′- and 6′-H), 5.00 (4 H, t, $J \approx 8$ Hz, 1"-CH_2), 2.57 (4 H, quint, 2"-CH_2), 1.86 (4 H, quint, 3"-CH_2), 1.55 (4 H, m, 4"-CH_2), 1.25 (24 H, s, 5"−10"-CH_2), 0.87 (6 H, t, 11"-CH_3). Upon increasing the concentration about three times, while the formyl proton signals were not shifted (< 0.01 ppm), upfield shifts of 0.09 ppm were observed for the 17-,18-singlet, 0.04 ppm for the 2,13-doublet, and 0.02 ppm for the 3-,12-doublet while the 7-,8-singlet was not shifted. The 2′-,6′-doublet and the 3′-,5′-doublet were not shifted at all. This is in contrast to **Zn-10**, which thus must involve an interaction of the hydroxy groups (Zn ligation or hydrogen bonding). − FAB-MS; *m/z*: 888.3 $[M]^+$, 747.2 $[M + H - C_{10}H_{22}]^+$, 593.0 $[M + H - C_{10}H_{22} - C_{10}H_{20}^+]^+$ (calcd. avg. mass for $C_{56}H_{64}N_4O_2Zn$: 890.53). − UV/Vis (toluene diluted in C_7H_{16}, 1:50): λ_{max} = 625, 588, 550, 418; (+ MeOH): λ_{max} = 625(sh), 602, 562, 427.

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Note Added in Proof (October 19, 2000): The following articles on light-harvesting dendrimers[5] have recently been published: A. Andronov, J. M. J. Fréchet, *Chem. Commun.* **2000**, 1701−1710. − J. Hofkens, M. Maus, T. Gensch, T. Vosch, M. Cotlet, F. Köhn, A. Herrmann, K. Müllen, F. De Schryver, *J. Am. Chem. Soc.* **2000**, *122*, 9278−9288.

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