THE CHEMISTRY OF POLYPHYRINS 2.[1] SYNTHESES OF HEXAPHYRINS AND THEIR METAL COMPLEXES

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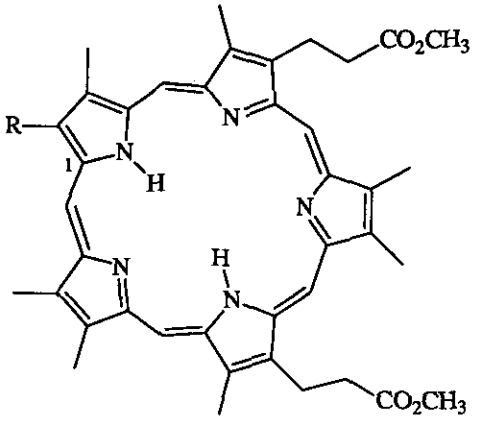
Abstract – The synthesis of eight derivatives of a 26 π-electron macrocycle analogous to the porphyrins bearing six pyrrole rings and six methine bridges is described. This chromophore is named *hexaphyrin*. Owing to the flexibility of their chromophore, hexaphyrins are able to form two kind of binuclear coordination complexes of substantially different geometry.

Our first communication on the synthesis of penta- and hexapyrrole macrocycles analogous to the porphyrins, the chromophores of which were named *pentaphyrin* (**1**)[1] and *hexaphyrin* (**7**)[2] respectively, appeared in 1983. Recently, Sessler *et al.*[3] have reported the second example of a substituted pentaphyrin and confirmed the structure of its uranyl complex by X-ray diffraction analysis. In the mean time our own interest was rather focused on the hexaphyrins[4] for two main reasons : (*i*) The cofactor-substrate complex in porphobilinogen deaminase is a linear hexapyrrole.[5,6] Thus, hexaphyrin derivatives may be products of a disturbed metabolism of porphobilinogen during urophorphyrinogen biosynthesis. (*ii*) Hexaphyrins are capable of accommodating two metal ions within the macrocycle formed by six pyrrole rings and six methine bridges. Actually, the ^{1}H nmr spectrum of the first hexaphyrin derivative synthesized in our laboratory (**7a**) suggested that two opposite methine bridges have *E* geometry, whereas the remaining four are *Z* (see below). Accordingly, Dreiding molecular models point out that the hexaphyrin macrocycle can only be planar when the H atoms at the *E* methine bridges are directed into the macrocycle so that the cavity of the ligand is divided in two compartments with three metal binding sites in each. In the corresponding binuclear coordination complexes the essentially isolated metal centers are separated by an intramolecular center-to-center distance of approximately 6 Å.

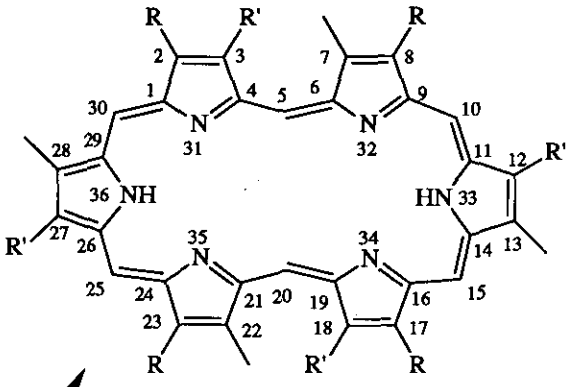
Although coordination complexes in which two (or more) metal ions are encapsulated within the framework of a single ligand are numerous,[7] the preparation and study of metal complexes containing multiple metal centers in well-defined geometric arrangements are of considerable interest, particularly when the metals are arranged so that they can exert a significant mutual influence with respect to such properties as redox potential, magnetic ground states, and propensity for ligand binding.[8]



1a : R = CH_3

1b : R = $(CH_2)_2$-CO_2CH_3

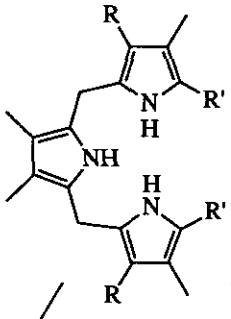
5 + 6
H^+



7a$_1$: R = $(CH_2)_2$-CO_2CH_3 ; R' = CH_3

7a$_2$: R = CH_3 ; R' = $(CH_2)_2$-CO_2CH_3

7d : R = R' = CH_3



3 : R' = $CO_2CH_2C_6H_5$

4 : R' = CO_2H

5 : R' = CHO

6 : R' = H

a) : R = $(CH_2)_2$-CO_2CH_3

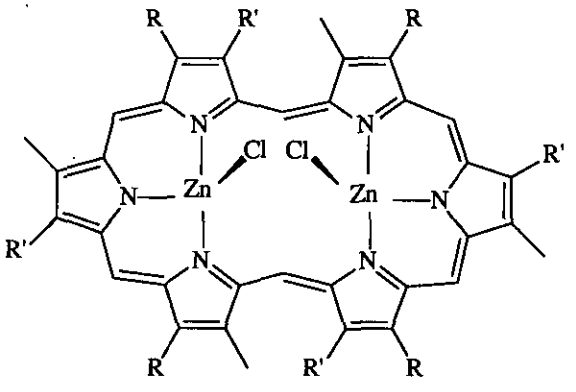
b) : R = CH_2-CO_2CH_3

c) : R = C_8H_{17}

d) : R = CH_3

5 + 6
$ZnCl_2$

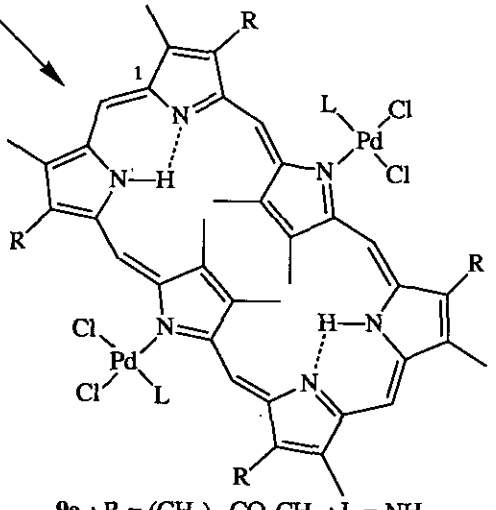
5 + 6
$Pd(NH_4)_2Cl_4$



8a : R = $(CH_2)_2$-CO_2CH_3 ; R' = CH_3

8b : R = CH_3 ; R' = CH_2-CO_2CH_3

8c : R = C_8H_{17} ; R' = CH_3



9a : R = $(CH_2)_2$-CO_2CH_3 ; L = NH_3

9b : R = CH_2-CO_2CH_3 ; L = NH_3

10 : R = $(CH_2)_2$-CO_2CH_3 ; L = C_5H_5N

Synthesis of Hexaphyrins. Under the reaction conditions commonly used for the synthesis of porphyrins from tetrapyrrolic precursors, linear hexapyrroles cyclize with loss of one or two pyrrole rings.[9-11] Actually, the synthesis of hexaphyrin **7a** was stimulated by the success in preparing pentaphyrin **1a**[1] by condensation of the known 2,3,7,8-tetramethyldipyrrylmethane[12] with tripyrrane dialdehyde **5a**. Under similar conditions, reaction of the latter with the corresponding α,α'-unsubstituted tripyrrane **6a** afforded, after oxidation with iodine and *p*-benzoquinone, hexaphyrin **7a** in 29% yield as well as pentaphyrin **1b** as a minor by-product (8%). Remarkably, no porphyrin derivative is formed in this reaction.

Owing to the substitution patterns of the precursors **5a** and **6a**, two isomeric structures, namely $\mathbf{7a_1}$ and $\mathbf{7a_2}$ are possible for the reaction product. In fact, the ^{1}H nmr spectrum of the obtained hexaphyrin shows three singlets associated with the protons at the *Z* methine bridges, the intensities of which are approximatly 2:1:1. The singlet at δ 12.42 ppm corresponds to the four homotopic methine protons of isomer $\mathbf{7a_1}$ which belongs to the symmetry group D_{2h}. Accordingly, the signals at δ 12.33 and 12.19 ppm are assigned to the two pairs of homotopic methine protons of isomer $\mathbf{7a_2}$ which belongs to the symmetry group C_{2h}. Moreover, the protons at the methine bridges which are located inside the macrocycle give rise to two signals at δ -7.40 and -7.44 ppm corresponding to each one of the isomers $\mathbf{7a_1}$ and $\mathbf{7a_2}$ (*cf.* Experimental part). As both signals have nearly the same intensity, the two isomers must be present in about the same concentration despite the fact that the relative statistical probabilities for the formation of $\mathbf{7a_1}$ and $\mathbf{7a_2}$ are 1 to 2. Most likely, isomer $\mathbf{7a_1}$ is thermodynamically favored owing to the smaller sterical repulsion between the methyl groups attached to the pyrrole rings adjacent to the *E* methine bridges.

The above assignments are corroborated by the ^{1}H nmr spectrum of dodecamethylhexaphyrin (**7d**) in which only two singlets at δ 12.5 and -7.3 ppm are present, corresponding to the *exo* and *endo* methine protons, respectively. The peripheral methyl groups give rise to two signals at δ 4.55 and 4.60 ppm. Thus, the ^{1}H nmr spectra of hexaphyrins **7a** and **7d** cover a range of about 20 ppm. According to the diamagnetic ring current definition of "aromaticity",[13] hexaphyrins are aromatic macrocycles, the diatropic character of which is only surpassed by that of platyrins[14] and other related intramolecularly aza-bridged annulenes.[15]

Synthesis of Metal Complexes. The unsatisfactory yield of the syntheses of hexaphyrins **7a** and **7d** (29 and 13%, respectively) is due, in part, to the laborious purification steps which are necessary to obtain samples free of by-products (*cf.* Experimental part). Therefore, the formation of metal chelates, which could facilitate the isolation of the desired material was attempted *in situ*, by addition of a metal salt to the reaction mixture *after* the synthesis of the hexaphyrin was complete. An enhancement of the yield on the basis of the template effect of metal ions on cyclization[16] – as it has been observed in the synthesis of the

zinc complex of tetraphenylporphine[17] – does not appear to be feasible owing to the strong acidic conditions under which condensation of the precursors of the hexaphyrin macrocycle takes place. Among the different metal ions tested – Mg(II), Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Ru(III), Pd(II), Ag(I), and La(III) – zinc(II) and palladium(II) afforded the best results. Thus, after neutralization of the reaction mixture with Na_2CO_3 and addition of $ZnCl_2$, a violet zinc chelate of hexaphyrin **7a** was isolated in 55% yield. After repeated recrystallization, a pure compound could be obtained, the structure of which was elucidated by analytical methods. First, the metal content was determined by atomic absorption spectrophotometry. The experimental figure (11.80%) agrees well with the calculated value of 11.67% for a di-zinc chelate. As the hexaphyrin ligand contains only two ionizable NH groups, the corresponding metal chelate bearing two Zn(II) ions must bind two additional anions in order to become neutral. Accordingly, the elemental analysis of the Zn complex of **7a** agrees with the presence of two Cl ions per molecule. Finally, the conformation of the chromophore has been established by ^{1}H nmr spectroscopy and corroborated by NOE difference experiments (see Table I). Thus, structure **8a** is suggested for the Zn chelate of hexaphyrin **7a**$_1$. As a matter of fact, however, a structure in which the two Cl ligands would be *anti* instead of *syn* to each other would also fit with all available analytical data. As none of these enables to differentiate between a molecule belonging to the C_{2v} and C_{2h} symmetry groups (as **8a** and its *anti* isomer, respectively), structure **8a** is favored on the basis of space-filling molecular models, which point out a lower steric repulsion between the methyl groups vicinal to the *E* C=C bonds in the *syn* isomer.

Attempting to improve the cristalline properties of the desired metal chelates, two further hexaphyrin Zn complexes (**8b** and **8c**) have been synthesized by the same method outlined before. Of both compounds, **8c** proved to be the more soluble in organic solvents, so that a ^{13}C nmr spectrum could be measured, as an additional proof of its structure (*cf.* Exp. part). Interestingly, **8c** (as **8a**) belongs to the symmetry group C_{2v} whereas in the case of **8b** the less symmetric isomer of C_{2h} symmetry was isolated (*cf.* Table I). According to the ^{1}H nmr spectra of the crude products, however, the complexes corresponding to both isomeric ligands **7a**$_1$ and **7a**$_2$ (*vide supra*) are present in the reaction mixture in all cases, so that the isolation of the single isomers **8a-c** is merely the consequence of the purification process.

A remarkable property of the hexaphyrin Zn complexes described in this work are their extremely high absorption coefficients in the visible range of the electromagnetic spectrum, in acidic medium. Thus, the ε value ($2.64 \cdot 10^5$ L·mol^{-1}·cm^{-1}) of the absorption band at $\lambda_{max.}$ 574 nm of complex **8c**, for instance, is enhanced to $4 \cdot 10^5$ in presence of trifluoroacetic acid, while the maximum of absorption is hypsochromically shifted to 556 nm.

As d^8 palladium complexes are, with a few exceptions, square-planar coordinated,[18] the geometry of the hexaphyrin chromophore does not appear to be favorable, *a priori*, for the

Table I. ^1H Nmr Signals Assigned by Differential $^1H\{^1H\}$-NOE Experiments[a]

Compd	Irradiated signal	Enhanced Signal	% Enhancement
8a	10.54 (10-H, 15-H, 25-H, 30-H)	4.46 (2^1-H_A, 8^1-H_A, 17^1-H_A, 23^1-H_A)	2.4
		4.32 (2^1-H_B, 8^1-H_B, 17^1-H_B, 23^1-H_B)	2.2
		3.68 (12-CH_3, 13-CH_3, 27-CH_3, 28-CH_3)	4.2
		3.31 (2^2-H_2, 8^2-H_2, 17^2-H_2, 23^2-H_2)	1.8
8b	10.59 (10-H, 25-H)	5.06 (12^1-H_B, 27^1-H_B)	2.4
		3.57 (8-CH_3, 23-CH_3)	6.4
	10.54 (15-H, 30-H)	3.73 (2-CH_3, 17-CH_3)[b]	4.0
		3.67 (13-CH_3, 28-CH_3)[b]	1.8
	3.57 (8-CH_3, 23-CH_3)	10.59 (10-H, 25-H)	1.9
9a	10.41 (15-H, 30-H)	3.81 (2-CH_3, 13-CH_3, 17-CH_3, 28-CH_3)	7.6
	-2.35 (NH)	-6.24 (7-CH_3, 8-CH_3, 22-CH_3, 23-CH_3)	17.4
	-6.24 (7-CH_3, 8-CH_3, 22-CH_3, 23-CH_3)	-2.35 (NH)	2.3
9b	12.71 (5-H, 10-H, 20-H, 25-H)	5.47 (3^1-H_B, 12^1-H_B, 18^1-H_B, 27^1-H_B)	1.1
	10.44 (15-H, 30-H)	3.83 (2-CH_3, 13-CH_3, 17-CH_3, 28-CH_3)	10.1
	-2.17 (NH)	-6.12 (7-CH_3, 8-CH_3, 22-CH_3, 23-CH_3)	30.9
10	12.80 (5-H, 10-H, 20-H, 25-H)	9.37 (2′-H, 2″-H, 6′-H, 6″-H)[c]	0.7
		5.03 (3^1-H_A, 12^1-H_A, 18^1-H_A, 27^1-H_A)	1.9
		4.86 (3^1-H_B, 12^1-H_B, 18^1-H_B, 27^1-H_B)	2.1
		3.98 (3^2-H_2, 12^2-H_2, 18^2-H_2, 27^2-H_2)	3.7
	10.46 (15-H, 30-H)	3.85 (2-CH_3, 13-CH_3, 17-CH_3, 28-CH_3)	7.0
	-2.40 (NH)	-6.19 (7-CH_3, 8-CH_3, 22-CH_3, 23-CH_3)	13.7
	-6.19 (7-CH_3, 8-CH_3, 22-CH_3, 23-CH_3)	-2.40 (NH)	1.3

[a] In $CDCl_3$ solution at 360.13 MHz.
[b] Assignement might be interchanged.
[c] Positions on the pyridine ligands are quoted with apostrophs.

formation of stable chelates with Pd(II) as complexed ion. Surprisingly, however, after addition of ammonium tetrachloropalladate to the alkalified reaction mixture containing hexaphyrin **7a** a royal blue pigment was obtained in 39% yield. Again, the metal content (14.8%), as determined by atomic absorption spectrophotometry, is consistent with the calculated value corresponding to two Pd ions per molecule (16.25%). However, the ^{1}H nmr spectrum of the new compound differs manifestly from those of the Zn chelates **8a-c**. Particularly in the range of negative δ values the peak at δ -6.88 ppm, which has been assigned to the *endo*-H atoms on C-5 and C-20 in **8a**, has been replaced by a singlet at δ -6.24 ppm with the intensity of 12 H. A new singlet at δ -2.35 ppm corresponding to 2 H, which is not present in the ^{1}H nmr spectrum of **8a**, may be assigned to two HN groups inside the hexaphyrin macrocycle. Moreover, a broad signal at δ 2.61 ppm with the intensity of 6 H, which cannot be assigned to any of the functional groups present in the ligand, is replaced by three signals at δ 9.37 (4 H), 7.75 (2 H), and 7.39 ppm (4 H), when the above hexaphyrin Pd complex is dissolved in pyridine and the solvent is evaporated *in vacuo*. According to these data, structures **9a** and **10**, which are corroborated by NOE difference mesurements (*cf.* Table I), are suggested for the Pd complexes of hexaphyrin **7a$_1$** before and after treatment with pyridine, respectively. In the same way the palladium complex **9b** was obtained starting from **4b** and **5b**. According to the well-documented *trans*-effect of ligands in square-planar transition metal complexes,[19] the Cl ligands in the hexaphyrins **9a-b** and **10** should be *cis* to each other.

The formation of the Pd complexes **9a-b** reflects not only the preference of d^8 palladium complexes for the square-planar coordination but also the flexibility of the hexaphyrin macrocycle which enables the transformation of conformer **7a$_2$** into **9a** by 180 °C rotation of two pyrrole rings with concomitant *Z/E* isomerization of two formal C=C bonds. Although the Pd complexes **9a-b** and **10** are quite stable in the solid state, they decompose slowly in solution. Nevertheless, the possibility of obtaining crystalline samples in order to confirm the above structures by X-ray diffraction analysis is currently explored.

EXPERIMENTAL

All commercially available chemicals were used as provided by the supplier without purification. Silica gel 60 $F_{254+366}$ from Merck (0.9 mm on 100 × 20 cm plates) was used for preparative tlc. Melting points (corrected) were determined with a Kofler hot stage melting point apparatus (Reichert). Electronic (uv-vis) absorption spectra were measured on a Perkin-Elmer 320 and a Cary 118 spectrophotometer. Infrared (ir) spectra were measured on a Perkin-Elmer 599 and a Beckman IR 9 spectrophotometer. Nuclear magnetic resonance (nmr) spectra were recorded on a Varian EM 390, a Bruker AM 360, or a Bruker WM 400 spectrometer (^{1}H nmr: δ in ppm referred to TMS as internal standard, coupling constants *J* in

Hz) and on a Bruker AM 360 or a Varian CFT 20 spectrometer (^{13}C nmr). Mass (ms) spectra were recorded on a Vacuum Generators Micromass 7070E, a Varian MAT 44s, or a Varian MAT 711 instrument (70 eV EI ionisation, source temperature 200 °C) and a Vacuum Generators Micromass 7070E or Varian MAT 311A instrument (FAB ionisation). Atomic absorption spectrophotometry (AAS) were performed on a Zeiss FMD 3 instrument. Elemental analyses were obtained on a Perkin-Elmer 240 CHN-Analyzer.

2,8,17-Tris[2-methoxycarbonylethyl]-3,7,12,13,18,22,23-heptamethylpentaphyrin (1b) was obtained as a by-product of the synthesis of **7a** (see below). After repeated chromatography (3 times) of the green extract on silica gel, using CH_2Cl_2/MeOH (93:7) as eluant, 3.9 g (8%) of **1b** is obtained as a dark blue powder, uv-vis (CH_2Cl_2 + 10% trifluoroacetic acid) λ_{max} (log ε) 457 (5.38), 625 (3.78), 691 (3.55); ^1H nmr (CF_3-CO_2D/$CDCl_3$ [1:1], 400 MHz) δ 12.20, 12.19, 12.18, 12.13, and 12.12 (5s, 1H each, 5-H, 10-H, 15-H, 20-H, and 25-H), 5.0 (m, 6H, 2^1-H_2, 8^1-H_2, and 17^1-H_2), 4.19, 4.15, and 4.09 (3s, 3H, 6H, and 12H, respectively, CH_3), 3.60, 3.56, and 3.55 (3s, 3H each, OCH_3), 3.41 (*m*, 6H, 2^2-CH_2, 8^2-CH_2, and 17^2-CH_2); ms (FAB, glycerol-DMSO) *m/z* 744 (MH^+).

Benzyl 3-methyl-5-acetoxymethyl-4-octyl-1*H*-pyrrole-2-carboxylate (2c). Lead tetraacetate (44.3 g, 0.1 mol) was added in small portions, under stirring, to a solution of 34.2 g (0.1 mol) of benzyl 3,5-dimethyl-4-octyl-1*H*-pyrrole-2-carboxylate[20] in glacial acetic acid (1 l) containing 50 ml of acetic anhydride at 40 °C during 1 h. Stirring was continued for a further 6 h at 40 °C, after which 5 ml of ethylene glycol and 1 l of water was added slowly to the reaction mixture. The precipitated solid was separated, washed with water, and crystallised from n-hexane, forming colorless needles (14.75 g, 37 %) of mp 91–92 °C; ir ($CHCl_3$) ν 3340*m*, 2930*s*, 2860*m*, 1730*s*, 1695*s*, 1500*w*, 1380*m*, 1130*w*, 1090*m*, 1070*m*, 1020*m*, 955*w*; ^1H nmr ($CDCl_3$, 360.13 MHz) δ 9.13 (br s, NH), 7.42–7.30 (m, 5H, phenyl H), 5.29 and 5.00 (2s, 2H each, benzyl H and 5^1-H_2), 2.41 (t, J = 7.3, 2H, 4^1-H_2), 2.27 (s, 3H, 3-CH_3), 2.04 (s, 3H, acetyl CH_3), 1.43–1.40 (m, 2H, 4^2-H_2), 1.31–1.26 (m, 10H, octyl CH_2), 0.87 (t, J = 7.0, octyl CH_3); ms (EI) *m/z* 399 (25, M^+), 340 (7), 300 (7), 266 (8), 242 (10), 91 (100). Anal. Calcd for $C_{24}H_{33}NO_4$ (399.53): C, 72.14; H, 8.32; N, 3.50. Found: C, 72.22; H, 8.51; N, 3.60.

2,5-Bis([5-benzyloxycarbonyl-3-(methoxycarbonylmethyl)-4-methyl-1*H*-pyrrol-2-yl]methyl)-3,4-dimethylpyrrole (3b). To a pre-heated solution (80 °C) of 1.03 g (10.85 mmol) of 3,4-dimethyl-1*H*-pyrrole[21] and 7.8 g (21.7 mmol) of methyl 2-acetoxymethyl-5-benzyloxycarbonyl-4-methyl-1*H*-pyrrole-3-acetate[22] in benzene (200 ml) 0.2 ml of HBr (33% in acetic acid) were added at once and the mixture was refluxed for 12 h under nitrogen. After cooling to room temperature, the solution was poured into 200 ml of 1% aq. $NaHCO_3$ and the organic layer was separated. The residue obtained after evaporation of the solvent was recrystallized from MeOH to obtain 3.9 g (52%) of **3b**, mp 167-168 °C; ir

($CHCl_3$) ν 3430*w*, 3290*m*, 3000*w*, 2960*w*, 1730*s*, 1665*s*, 1585*w*, 1495*w*, 1435*s*, 1305*m*, 1170*s*, 1095*s*, 1000*w*, 910*w*; ^{1}H nmr ($CDCl_3$, 360.13 MHz) δ 10.3–9.7 (br s, 2H, HN-15 and HN-17), 8.78 (br s, HN-16), 7.31–7.23 and 7.20–7.10 (2m, 6H and 4H, respectively, phenyl H), 4.68 (s, 4H, benzyl H), 3.67 (s, 4H, 5^1-H_2 and 10^1-H_2), 3.57 (s, 6H, OCH_3), 3.31 (s, 4H, 3^1-H_2 and 12^1-H_2), 2.23 (s, 6H, 2-CH_3 and 13-CH_3), 1.97 (s, 6H, 7-CH_3 and 8-CH_3); ^{13}C nmr ($CDCl_3$, 90.56 MHz) δ 172.2 and 162.4 (2s , 4 CO), 136.5, 134.2, 127.5, 122.2, 117.5, 113.8, and 113.9 (7s, 14 quat. C), 128.2, 127.5, and 126.8 (3d, 10 phenyl C), 65.4 (t, 2 benzyl C), 51.8 (q, 2 OCH_3), 29.7 and 22.4 (2t, C-5 and C-10), 11.1 and 9.3 (2q, 4 CH_3); ms (FAB, *o*-nitrophenyl octyl ether) *m/z* 693 (100, M^+), 602 (17), 394 (55).

2,5-Bis[5-benzyloxycarbonyl-4-methyl-3-octyl-1*H*-pyrrol-2-ylmethyl]-3,4-dimethylpyrrole (3c) was obtained (8.1 g, 58%) after 7 h reaction time, following the procedure described for **3b**, from 1.68 g (18 mmol) of 3,4-dimethyl-1*H*-pyrrole[21] and 14.2 g (35.5 mmol) of **2c**, mp 116-117 °C (from MeOH); ir ($CHCl_3$) ν 3300*m*, 2970*m*, 2940*s*, 2870*m*, 1660*s*, 1500*w*, 1450*s*, 1380*w*, 1310*m*, 1280*s*, 1155*w*, 1130*w*, 1100*m*, 990*w*; ^{1}H nmr ($CDCl_3$, 360.13 MHz) δ 10.91 (br s, 2H, HN-15 and HN-17), 8.67 (br s, HN-16), 7.27–7.18 and 7.02–7.00 (2m, 6H and 4H, respectively, phenyl H), 4.39 (br s, 4H, benzyl H), 3.53 (br s, 4H, 5-H_2 and 10-H_2), 2.27 (t, J = 7, 4H, 3^1-H_2 and 12^1-H_2), 2.21 (s, 6H, 2-CH_3 and 13-CH_3), 1.97 (s, 6H, 7-CH_3 and 8-CH_3), 1.27–1.21 (m, 24H, octyl CH_2), 0.87 (t, J = 7.0, octyl CH_3); ms (EI) *m/z* 774 (12, MH^+), 665 (10), 434 (11), 339 (74), 91 (100).

2,5-Bis[(5-carboxy-3-[2-methoxycarbonylethyl]-4-methyl-1*H*-pyrrol-2-yl)methyl]-3,4-dimethylpyrrole (4a). The correspondig 1,14-dibenzyl ester[23] (4.5 g, 6.23 mmol) in tetrahydrofuran (50 ml) was hydrogenated on 10% palladized charcoal (350 mg) at 20 °C and 760 Torr until the reaction deemed complete by tlc. Next the reaction mixture was filtered through celite and the solution concentrated under reduced pressure before the product was precipitated by addition of n-hexane. The crude product (3.2 g, 95%) of mp 170 °C (decomp.) was dried *in vacuo* and used without further purification in the next reaction.

2,5-Bis[(5-carboxy-3-[methoxycarbonylmethyl]-4-methyl-1*H*-pyrrol-2-yl)methyl]-3,4-dimethylpyrrole (4b) was obtained (1.75 g, 95%) following the procedure described above, from 2.5 g (3.6 mmol) of **3b**, mp 119 °C (decomp.).

2,5-Bis[5-carboxy-4-methyl-3-octyl-1*H*-pyrrol-2-ylmethyl]-3,4-dimethylpyrrole (4c) was obtained by hydrogenolysis of **3c** (5 g, 6.46 mmol) following the procedure described for **4a**. The product which precipitated as a white powder on addition of n-pentane was dried *in vacuo* yielding 3.7 g (97%) of **4c**, mp 100 °C (decomp.).

2,5-Bis[(5-formyl-3-[2-methoxycarbonylethyl]-4-methyl-1*H*-pyrrol-2-yl)methyl]-3,4-dimethylpyrrole (5a). A solution of **4a** (3 g, 5.54 mmol) in trifluoroacetic acid (40 ml) was kept under N_2 for 15 min at 0 °C before 20 ml (183 mmol) of trimethyl orthoformate was added at once. Thereon the mixture was stirred for 10 min at 0 °C, then for 20 min at room temperature, and finally poured into H_2O (500 ml). After extraction with CH_2Cl_2 (3 × 100 ml), the combined organic phases were shaken successively with 1% aq. $NaHCO_3$ and brine (100 ml), and dried over Na_2SO_4. The residue obtained after evaporation of the solvent was crystallized from ethyl acetate to yield 1.7 g (60%) of **5a**, mp 177-178 °C; ir ($CHCl_3$) ν 3440*m*, 3300*m*, 3040*m*, 1735*s*, 1635*s*, 1445*m*; ^{1}H nmr ($CDCl_3$, 360.13 MHz) δ 10.35 (br, 2H, HN-15 and HN-17), 9.34 (s, HN-16), 9.13 (s, 2H, CHO), 3.83 (s, 4H, 5-H_2 and 10-H_2), 3.64 (s, 6H, CH_3O), 2.71 (t, J = 7.7, 4H, 3^2-H_2 and 12^2-H_2), 2.33 (t, J = 7.7, 4H, 3^1-H_2 and 12^1-H_2), 2.21 (s, 6H, 2-CH_3 and 13-CH_3), 1.98 (s, 6H, 7-CH_3 and 8-CH_3); ^{13}C nmr ($CDCl_3$, 90.56 MHz) δ 175.6 (d, 2 CHO), 173.4 (s , 2 CO_2R), 138.6, 132.9 , 128.0, 121.9, 120.7 and 114.2 (6s, 12 quat. C), 51.6 (q, 2 OCH_3), 34.5, 22.7, and 19.2 (3t, 6 CH_2), 9.3 and 8.8 (2q, 4 CH_3); ms (EI) *m/z* 509 (45, M^+), 480 (17), 422 (12), 394 (14), 315 (21), 314 (20), 301 (100).

2,5-Bis[(5-formyl-3-[2-methoxycarbonylmethyl]-4-methyl-1*H*-pyrrol-2-yl)methyl]-3,4-dimethylpyrrole (5b) was obtained (0.75 g, 53%) following the procedure described above, from 1.5 g (2.92 mmol) of **4b**. The product was recrystallized from CH_2Cl_2 by diffusion of MeOH vapor to yield 0.65 g (46%) of mp 176-177 °C; ir ($CHCl_3$) ν 3430*m*, 3000*w*, 2960*w*, 2920*w*, 2850*w*, 1735*s*, 1635*s*, 1440*m*, 1385*m*, 1335*m*, 1170*m*, 1035*w*, 1000*w*; ^{1}H nmr ($CDCl_3$, 360.13 MHz) δ 9.98 (br, 2H, HN-15 and HN-17), 9.26 (s, 2H, CHO), 9.17 (s, HN-16), 3.83 (s, 4H, 5-H_2 and 10-H_2), 3.66 (s, 6H, CH_3O), 3.41 (s, 4H, 3^1-H_2 and 12^1-H_2), 2.22 (s, 6H, 2-CH_3 and 13-CH_3), 1.95 (s, 6H, 7-CH_3 and 8-CH_3); ^{13}C nmr ($CDCl_3$, 90.56 MHz) δ 176.2 (d, 2 CHO), 172.0 (s , 2 CO_2R), 138.7, 133.1, 128.1, 121.6, 115.0, and 114.5 (6s, 12 quat. C), 52.0 (q, 2 OCH_3), 29.4 and 22.9 (2t, 4 CH_2), 9.2 and 8.9 (2q, 4 CH_3); ms (EI) *m/z* 481 (67, M^+), 452 (12), 408 (18), 380 (10), 301 (14), 287 (100).

2,5-Bis[5-formyl-4-methyl-3-octyl-1*H*-pyrrol-2-ylmethyl]-3,4-dimethylpyrrole (5c) was obtained following the procedure described for **5a** from 3.5 g (5.89 mmol) of **4c**. The product was recrystallized from CH_2Cl_2 by diffusion of MeOH vapor to yield 2.1 g (64%) of mp 170-171 °C; ir ($CHCl_3$) ν 3380*w*, 3280*w*, 2940*s*, 2860*m*, 1625*s*, 1445*m*, 1380*w*, 1350*m*; ^{1}H nmr ($CDCl_3$, 360.13 MHz) δ 10.39 (br s, 2H, HN-15 and HN-17), 9.60 (s, HN-16), 9.09 (s, 2H, CHO), 3.79 (s, 4H, 5-H_2 and 10-H_2), 2.38 (t, J = 7.3, 4H, 3^1-H_2 and 12^1-H_2), 2.19 (s, 6H, 2-CH_3 and 13-CH_3), 1.97 (s, 6H, 7-CH_3 and 8-CH_3), 1.42–1.20 (m, 24H, octyl CH_2), 0.88 (t, J = 6.8, 6H, octyl CH_3); ^{13}C nmr ($CDCl_3$, 90.56 MHz) δ 175.3 (d, 2 CHO), 138.5, 133.0, 128.0, 123.2, 122.0, and 114.0 (6s, 12 quat. C), 31.9, 30.8, 29.7, 29.5, 29.3, 23.9, 22.8, and 22.7 (8t, 16 CH_2), 14.1 (q, 2 octyl CH_3), 9.4 and 8.9 (2q, 4 CH_3);

ms (EI) *m/z* 561 (31, M^+), 327 (50), 233 (100), 108 (84). Anal. Calcd for $C_{36}H_{55}N_3O_2$ (561.86): C, 76.95;H, 9.87; N, 7.48. Found: C, 76.66;H, 9.89; N, 7.46.

2,5-Bis[5-formyl-3,4-dimethyl-1*H*-pyrrol-2-ylmethyl]-3,4-dimethylpyrrole (5d) was obtained (22 mg, 48%) by reaction of 50 mg (0.13 mmol) of 2,5-bis[5-carboxy-3,4-dimethyl-1*H*-pyrrol-2-ylmethyl]-3,4-dimethyl-pyrrole[24] with triethyl orthoformate (0.25 ml, 2.3 mmol) following the procedure described for **5a**, mp 207-209 °C (decomp.); ir ($CHCl_3$) ν 3440, 3200, 3030, 2933, 2870, 1630; ^{1}H nmr ($CDCl_3$, 90 MHz) δ 10.2 (br s, 2H,HN-15 andHN-17), 9.3 (s,HN-16), 9.15 (s, 2H, CHO), 3.7 (s, 4H, 5-H_2 and 10-H_2), 2.1 (s, 6H, 2-CH_3 and 13-CH_3), 1.85 (s, 12H, 3-CH_3, 7-CH_3, 8-CH_3, and 12-CH_3); hrms (EI) *m/z* 365.2103 (100, M^+ calcd for $C_{22}H_{27}N_3O_2$ 365.21033), 242 (25), 229 (50).

(5*E*,10*Z*,14*Z*,19*E*,24*Z*,30*Z*)-2,8,17,23-Tetrakis[2-methoxycarbonylethyl]-3,7,12,13,18,22,27,28-octamethyl[33*H*,36*H*]hexaphyrin and **(5*E*,10*Z*,14*Z*,19*E*,24*Z*,30*Z*)-3,12,18,27-Tetrakis[2-methoxycarbonylethyl]-2,7,8,13,17,22,23,28-octamethyl-[33*H*,36*H*]hexaphyrin (7a$_1$ and 7a$_2$, respectively).** A solution of crude dicarboxylic acid **4a** (100 mg, 0.18 mmol) in 2.4 ml of trifluoroacetic acid was stirred for 20 min at 0 °C, then for 10 min at room temperature, and finally neutralized with chilled 1% aq. $NaHCO_3$. The mixture was repeatedly extracted with CH_2Cl_2 and the combined organic phases were washed with H_2O and dried on Na_2SO_4. After evaporation of the solvent *in vacuo*, the remaining unstable oil (63.6 mg, 76%) was dissolved in CH_2Cl_2 (20 ml) and the solution was added to an oxygen-free solution of dialdehyde **5a** (66 mg, 0.13 mmol) in 400 ml of dry CH_2Cl_2. Thereon, the mixture was acidified with 2 ml of HBr (33% in acetic acid) and stirred for 3 h under Ar before 180 mg of I_2 were added. Stirring was continued for 12 h and subsequently *p*-benzoquinone (100 mg, 0.93 mmol) was added. After 12 h the solvent was evaporated *in vacuo* and the residue was purified by prep. tlc using CH_2Cl_2/MeOH (94:6) as eluant. On the chromatography plate, the main violet component is preceded by a green by-product (**1b**). Both pigments were extracted with MeOH and the violet product was re-chromatographed under the same conditions to yield, after evaporation of the solvent, a copper-colored solid, which was re-dissolved in CH_2Cl_2. The solution was stirred in presence of morpholinomethylpolystyrene (Fluka Chemie AG, CH-9470 Buchs), filtered, and the solvent was evaporated to dryness yielding 17 mg (29%) of a mixture of **7a$_1$** and **7a$_2$** in the ratio of 1 to 1 (according to the ^{1}H nmr spectrum); uv-vis (CH_2Cl_2) λ_{max} (log ε) 572 (4.88), 595 (4.67), 789 (3.60); (CH_2Cl_2 + 1% trifluoroacetic acid) 551 (4.97), 798 (3.60); ^{1}H nmr (CF_3CO_2D, 400 MHz) δ 12.42 (s, 4H, 10-H, 15-H, 25-H, and 30-H of **7a$_1$**), 12.33 (s, 2H, 10-H and 25-H of **7a$_2$**), 12.19 (s, 2H, 15-H and 30-H of **7a$_2$**), 5.19 (t, J = 7.0, 4H, 3^1-H_2 and 18^1-H_2 of **7a$_2$**), 5.00 (t, J = 7.0, 12H, 2^1-H_2, 8^1-H_2, 17^1-H_2, and 23^1-H_2 of **7a$_1$**, and 12^1-H_2 and 27^1-H_2 of **7a$_2$**), 4.38 and 4.33 (2s, 36H and 12H, respectively, CH_3), 4.14 (s, 6H, 3^3-OCH_3 and 18^3-OCH_3 of **7a$_2$**), 4.08 (s, 6H, 12^3-OCH_3 and 27^3-OCH_3 of **7a$_2$**), 4.00 (s, 12H, OCH_3 of **7a$_1$**), 3.79 (t, J = 7, 16H, 2^2-H_2, 8^2-H_2, 17^2-H_2, and 23^2-H_2 of **7a$_1$**, and 3^2-H_2,

12^2-H_2, 18^2-H_2, and 27^2-H_2 of **7a$_2$**), -7.40 and -7.44 (2s, 2H each, 5-H and 20-H of **7a$_1$** and **7a$_2$**).

(5*E*,10*Z*,14*Z*,19*E*,24*Z*,30*Z*)-2,3,7,8,12,13,17,18,22,23,27,28-dodecamethyl[33*H*,36*H*]-hexaphyrin (7d). 2,5-Bis[5-carboxy-3,4-dimethyl-1*H*-pyrrol-2-ylmethyl]-3,4-dimethylpyrrole[24] (95 mg, 0.24 mmol) was decarboxylated and the obtained tripyrrane (**6d**) reacted with **5d** (30 mg, 82 μmol) according to the procedure given above to yield 7 mg (13%) of **7d** as copper-colored powder; uv-vis (CH_2Cl_2) λ_{max} (log ε) 569 (4.76), 588 (4.54), 790 (3.6); (CH_2Cl_2 + 1% trifluoroacetic acid) 553 (4.87), 785 (3.6); ^{1}H nmr (CF_3-CO_2D, 400 MHz) δ 12.30 (s, 4H, 10-H, 15-H, 25-H, and 30-H), 4.38 (s, 24H, 2-CH_3, 3-CH_3, 7-CH_3, 8-CH_3, 17-CH_3, 18-CH_3, 22-CH_3, and 23-CH_3), 4.19 (s, 12H, 12-CH_3, 13-CH_3, 27-CH_3, and 28-CH_3), -7.52 (s, 2H, 5-H and 20-H).

Dichloro[(5*E*,10*Z*,14*Z*,19*E*,24*Z*,30*Z*)-2,8,17,23-tetrakis[2-(methoxycarbonyl)ethyl]-3,7,12,13,18,22,27,28-octamethylhexaphyrinato(2-)-*N*^{31},*N*^{32},*N*^{33},*N*^{34},*N*^{35},*N*^{36}]dizinc(II) (8a). Tripyrrane dicarboxylic acid **4a** (50 mg, 92 μmol) was dissolved in 1 ml of degassed trifluoroacetic acid, the solution was stirred for 20 min at 0 °C, then for 15 min at room temperature and then added to an oxygen-free solution of **5a** (42 mg, 82 μmol) in 400 ml of CH_2Cl_2. After 5 min the mixture was acidified with 1 ml of HBr (33% in acetic acid) and stirred for 3 h under Ar at room temperature before 150 mg of I_2 were added. Stirring was continued for 10 h and subsequently *p*-benzoquinone (80 mg, 0.74 mmol) was added. After further 10 h anhydrous Na_2CO_3 (30 g) was added and the mixture was stirred vigorously for 30 min. Thereon a solution of 200 mg of $ZnCl_2$ in 10 ml of MeOH was added, and stirring was continued for 1 h before the reaction mixture was poured into 200 ml of brine. The organic layer was separated, dried over Na_2SO_4 and the solvent was evaporated *in vacuo*. The residue was purified by prep. tlc on SiO_2, which contains $ZnCl_2$, using CH_2Cl_2/MeOH (95:5) as eluant. The violet component was extracted with CH_2Cl_2/MeOH (90:10) and, after evaporation of the solvent, re-chromatographed under the same conditions as before. The product (52 mg, 57%) was recrystallized 10 times from CH_2Cl_2 by diffusion of Et_2O vapour to yield 6.2 mg of **8a** as a gold powder; uv-vis (CH_2Cl_2, 1×10^{-5}M) λ_{max} (log ε) 440 (4.18), 574 (5.58), 599 (5.35), 810 (4.25); (CH_2Cl_2 + 5% trifluoroacetic acid) 556 (5.58), 795 (4.15); ir ($CHCl_3$) ν 3000*w*, 2960*w*, 2860*w*, 1740*s*, 1600*w*, 1500*w*, 1440*m*, 1365*w*, 1275*w*, 1180*m*, 1150*m*, 1125*m*, 965*w*, 930*w*, 865*w*; ^{1}H nmr ($CDCl_3$, 360.13 MHz, 2.5×10^{-3}M) δ 10.54 (s, 4H, 10-H, 15-H, 25-H, and 30-H), 4.46 (dt, J = 14.7, 7.5, 4H, 2^1-H_A, 8^1-H_A, 17^1-H_A, and 23^1-H_A), 4.32 (dt, J = 14.7, 7.5, 4H, 2^1-H_B, 8^1-H_B, 17^1-H_B, and 23^1-H_B), 3.79 (s, 12H, 3-CH_3, 7-CH_3, 18-CH_3, and 22-CH_3), 3.77 (s, 12H, OCH_3), 3.68 (s, 12H, 12-CH_3, 13-CH_3, 27-CH_3, and 28-CH_3), 3.31 (m, 8H, 2^2-H_2, 8^2-H_2, 17^2-H_2, and 23^2-H_2), -6.88 (s, 2H, 5-H and 20-H); ms (FAB, 3-nitrobenzyl alcohol) *m/z* 1081 (59), 1082 (57), 1083 (90), 1084 (71), 1085 (100), 1086 (69), 1087 (66), 1088 (40), 1089 (25) (peak cluster for M^+-Cl).

Anal. Calcd for $C_{54}H_{58}Cl_2N_6O_8Zn_2$ (1120.74): C, 57.87;H, 5.22; N, 7.50. Found: C, 57.82;H, 5.35; N, 7.62. AAS : Calcd: Zn, 11.67. Found: Zn, 11.80.

Dichloro[(5*E*,10*Z*,14*Z*,19*E*,24*Z*,30*Z*)-3,12,18,27-tetrakis[2-methoxycarbonylmethyl]-2,7,8,13,17,22,23,28-octamethylhexaphyrinato(2-)-*N*^{31},*N*^{32},*N*^{33},*N*^{34},*N*^{35},*N*^{36}]dizinc(II) (8b) was obtained as a copper-colored powder (49 mg, 53%), following the procedure described for **8a**, from 50 mg (97 μmol) of **4b** and 42 mg (87 μmol) of **5b**; uv-vis (CH_2Cl_2, 7.1×10^{-6}M) λ_{max} (log ε) 444 (4.34), 576 (5.47), 601 (5.25), 810 (4.18); (CH_2Cl_2 + 5% trifluoroacetic acid) 556 (5.58), 795 (4.15); ^{1}H nmr ($CDCl_3$, 360.13 MHz, 2.5×10^{-3}M) δ 10.59 (s, 2H, 10-H and 25-H), 10.54 (s, 2H, 15-H and 30-H), 6.20 (d, J = 16.4, 2H, 3^1-H$_A$ and 18^1-H$_A$), 5.31 (d, J = 16.4, 2H, 3^1-H$_B$ and 18^1-H$_B$), 5.14 (d, J = 15.6, 2H, 12^1-H$_A$ and 27^1-H$_A$), 5.06 (d, J = 15.6, 2H, 12^1-H$_B$ and 27^1-H$_B$), 3.85 and 3.69 (s, 6H each, OCH_3), 3.73 and 3.67 (s, 6H each, 2-CH_3, 13-CH_3, 17-CH_3, and 28-CH_3), 3.57 (s, 6H, 8-CH_3 and 23-CH_3), 2.73 (s, 6H, 7-CH_3 and 22-CH_3), -6.66 (s, 2H, 5-H 20-H). AAS: Calcd for $C_{50}H_{50}Cl_2N_6O_8Zn_2$ (1064.63): Zn, 12.28. Found: Zn, 11.92.

Dichloro[(5*E*,10*Z*,14*Z*,19*E*,24*Z*,30*Z*)-2,8,17,23-tetraoctyl-3,7,12,13,18,22,27,28-octamethylhexaphyrinato(2-)-*N*^{31},*N*^{32},*N*^{33},*N*^{34},*N*^{35},*N*^{36}]dizinc(II) (8c) was obtained as a golden powder (52 mg, 55%), following the procedure described for **8a**, from 50 mg (84 μmol) of **4c** and 42 mg (77 μmol) of **5c**, uv-vis (CH_2Cl_2, 4×10^{-6}M) λ_{max} (log ε) 450 (4.18), 574 (5.42), 601 (5.19), 810 (4.17); (CH_2Cl_2 + 10% trifluoroacetic acid) 556 (5.60), 772 (4.04), 795 (4.21), 818 (4.13), 849 (3.83); ^{1}H nmr ($CDCl_3$, 360.13 MHz, 4×10^{-3}M) δ 10.46 (s, 4H, 10-H, 15-H, 25-H, and 30-H), 4.08 (dt, J = 14.2, 7.6, 4H, 2^1-H$_A$, 8^1-H$_A$, 17^1-H$_A$, and 23^1-H$_A$), 3.94 (dt, J = 14.2, 7.6, 4H, 2^1-H$_B$, 8^1-H$_B$, 17^1-H$_B$, and 23^1-H$_B$), 3.75 and 3.64 (s, 12H each, 3-CH_3, 7-CH_3, 12-CH_3, 13-CH_3, 18-CH_3, 22-CH_3, 27-CH_3, and 28-CH_3), 2.29 (quintet, J = 7.5, 8H, 2^3-H$_2$, 8^3-H$_2$, 17^3-H$_2$, and 23^3-H$_2$), 1.91 (d quintet, J = 13.4, 7.5, 4H, 2^2-H$_A$, 8^2-H$_A$, 17^2-H$_A$, and 23^2-H$_A$), 1.83 (d quintet, J = 13.4, 7.5, 4H, 2^2-H$_B$, 8^2-H$_B$, 17^2-H$_B$, and 23^2-H$_B$), 1.60 (quintet, J = 7.5, 8H, 2^4-H$_2$, 8^4-H$_2$, 17^4-H$_2$, and 23^4-H$_2$), 1.44 (m, 8H, 2^7-H$_2$, 8^7-H$_2$, 17^7-H$_2$, and 23^7-H$_2$), 1.35 (m, 16H, 2^5-H$_2$, 2^6-H$_2$, 8^5-H$_2$, 8^6-H$_2$, 17^5-H$_2$, 17^6-H$_2$, 23^5-H$_2$, and 23^6-H$_2$), 0.90 (t, J = 7.0, 12H, 2^8-H$_3$, 8^8-H$_3$, 17^8-H$_3$, and 23^8-H$_3$), -6.89 (s, 2H, 5-H, 20-H); ^{13}C nmr ($CDCl_3$, 90.56 MHz, 1.2×10^{-2}M) δ 156.8, 153.6, 151.7, 146.5, 139.1, and 133.4 (6s, 24 quat. C), 109.4 (d, C-5 and C-20), 105.4 (d, C-10, C-15, C-25, and C-30), 32.9 (t, C-2^2, C-8^2, C-17^2, and C-23^2), 31.9 (t, C-2^6, C-8^6, C-17^6, C-23^6), 30.0 (t, C-2^3, C-8^3, C-17^3, and C-23^3), 29.7 and 29.6 (2t, C-2^4, C-2^5, C-8^4, C-8^5, C-17^4, C-17^5, C-23^4, and C-23^5), 26.9 (t, C-2^1, C-8^1, C-17^1, and C-23^1), 22.8 (t, C-2^7, C-8^7, C-17^7, and C-23^7), 14.8 (q, C-12^1, C-13^1, C-27^1, and C-28^1), 14.4 (q, C-2^8, C-8^8, C-17^8, and C-23^8), 11.9 (q, C-3^1, C-7^1, C-18^1, C-22^1); ms (FAB, 3-nitrobenzyl alcohol) *m/z* 1185 (81), 1186 (66), 1187 (84), 1188 (83), 1189 (100), 1191 (68) (peak cluster for M^+-Cl).

Tetrachlorodiammine[μ-[(5*E*,10*Z*,14*Z*,19*Z*,24*E*,30*Z*)-3,12,18,27-tetrakis[2-methoxycarbonylethyl]-2,7,8,13,17,22,23,28-octamethyl-[31*H*,34*H*]hexaphyrine-N^{33},N^{36}]]dipalladium(II) (9a) was obtained following the procedure described for **8a**, from 50 mg (92 μmol) of **4a** and 42 mg (82 μmol) of **5a**. After neutralization of the reaction mixture with Na_2CO_3, a solution of 200 mg of ammonium tetrachloropalladate(II) (Fluka Chemie AG, CH-9470 Buchs) in MeOH (20 ml) was added, the mixture was vigorously stirred for 2 h, and finally washed with 300 ml of H_2O. The residue obtained after evaporation of the solvent was purified by prep. tlc (CH_2Cl_2/MeOH, 97:3). The royal blue component was extracted with CH_2Cl_2/MeOH (95:5) and the residue obtained after evaporation of the solvent (42 mg, 39%) was recrystallized from CH_2Cl_2 by diffusion of n-pentane vapor to yield 32 mg of **9a** as a golden powder, uv-vis (CH_2Cl_2, 9.7×10^{-6}M) λ_{max} (log ε) 276 (4.58), 350 (4.41), 574 (4.89), 607 (4.91), 750 (3.80), 840 (3.53); ^{1}H nmr ($CDCl_3$, 360.13 MHz, 5×10^{-3}M) δ 12.80 (s, 4H, 5-H, 10-H, 20-H, and 25-H), 10.41 (s, 2H, 15-H and 30-H), 5.06 (ddd, J = 14.6, 9.7, 6.4, 4H, 3^1-H_A, 12^1-H_A, 18^1-H_A, and 27^1-H_A), 4.76 (ddd, J = 14.6, 9.7, 6.4, 4H, 3^1-H_B, 12^1-H_B, 18^1-H_B, and 27^1-H_B), 3.93 (ddd, J = 16.1, 9.7, 6.4, 4H, 3^2-H_A, 12^2-H_A, 18^2-H_A, and 27^2-H_A), 3.86 (s, 12H, OCH_3), 3.81 (s, 12H, 2-CH_3, 13-CH_3, 17-CH_3, 28-CH_3), 3.71 (ddd, J = 16.1, 9.7, 6.4, 4H, 3^2-H_B, 12^2-H_B, 18^2-H_B, and 27^2-H_B), 2.61 (br, 6H, NH_3), -2.35 (s, 2H, NH), -6.24 (s, 12H, 7-CH_3, 8-CH_3, 22-CH_3, and 23-CH_3). AAS: Calcd for $C_{54}H_{66}Cl_4N_8O_8Pd_2$ (1309.83): Pd, 16.25. Found: Pd, 14.84.

Tetrachlorodiammine[μ-[(5*E*,10*Z*,14*Z*,19*Z*,24*E*,30*Z*)-3,12,18,27-tetrakis[2-methoxycarbonylmethyl]-2,7,8,13,17,22,23,28-octamethyl-[31*H*,34*H*]hexaphyrine-N^{33},N^{36}]]dipalladium(II) (9b) was obtained as a dark blue powder (35 mg, 34%), following the procedure described for **8a**, from 50 mg (92 μmol) of **4b** and 42 mg (82 μmol) of **5b**, uv-vis (CH_2Cl_2, 8.4×10^{-6}M) λ_{max} (log ε) 399 (4.41), 573 (4.91), 607 (4.93), 750 (3.68); ^{1}H nmr ($CDCl_3$, 360.13 MHz, 4×10^{-3}M) δ 12.71 (s, 4H, 5-H, 10-H, 20-H, and 25-H), 10.44 (s, 2H, 15-H and 30-H), 5.69 (d, J = 15.8, 4H, 3^1-H_A, 12^1-H_A, 18^1-H_A, and 27^1-H_A), 5.47 (d, J = 15.8, 4H, 3^1-H_B, 12^1-H_B, 18^1-H_B, and 27^1-H_B), 3.92 (s, 12H, OCH_3), 3.83 (s, 12H, 2-CH_3, 13-CH_3, 17-CH_3, and 28-CH_3), 2.49 (br, 6H, NH_3), -2.17 (s, 2H, NH), -6.12 (s, 12H, 7-CH_3, 8-CH_3, 22-CH_3, and 23-CH_3).

Tetrachloro(μ-[(5*E*,10*Z*,14*Z*,19*Z*,24*E*,30*Z*)-3,12,18,27-tetrakis[2-methoxycarbonylethyl]-2,7,8,13,17,22,23,28-octamethyl-[31*H*,34*H*]hexaphyrine-N^{33},N^{36}]]bis(pyridine)dipalladium(II) (10). A solution of **9a** (5 mg, 4 μmol) in 1 ml of pyridine was stirred for 5 min at room temperature. After evaporation of the solvent *in vacuo*, the residue was purified by prep. tlc (CH_2Cl_2/MeOH, 97:3) to yield 4.5 mg (82%) of **10** as a glittering dark blue powder, ^{1}H nmr ($CDCl_3$, 360.13 MHz, 1.7×10^{-3}M) δ 12.80 (s, 4H, 5-H, 10-H, 20-H, and 25-H), 10.46 (s, 2H, 15-H and 30-H), 9.37 (m, 4H, 2′-H, 2″-H, 6′-H, and 6″-H), 7.75 (tt, J = 7.6, 1.5, 2H, 4′-H and 4″-H), 7.39 (m, 4H, 3′-H, 3″-H, 5′-H, 5″-H), 5.03 (dt, J = 14.9, 8.0, 4H, 3^1-H_A, 12^1-H_A, 18^1-H_A, and 27^1-H_A), 4.86 (dt, J = 14.9, 7.7, 4H, 3^1-H_B, 12^1-H_B,

18^1-H_B, and 27^1-H_B), 3.98 (t, J = 7.9, 8H, 3^2-H_2, 12^2-H_2, 18^2-H_2, and 27^2-H_2), 3.85 (s, 12H, 2-CH_3, 13-CH_3, 17-CH_3, and 28-CH_3), 3.84 (s, 12H, OCH_3), -2.40 (s, 2H, NH), -6.19 (s, 12H, 7-CH_3, 8-CH_3, 22-CH_3, and 23-CH_3).

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