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New Chemistry of Oxophlorins (Oxyporphyrins) and Their π-Radicals

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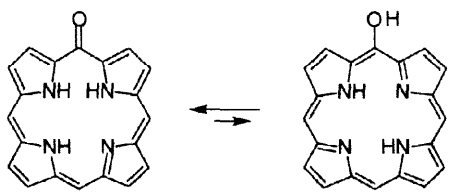
Abstract: Syntheses of novel 15-substituted-oxophlorins via the MacDonald condensation of diformyl-dipyrroketones and 5-substituted-dipyrromethanes are described. The electronic and steric features of the 15-substituent enable facile control over the oxidation potential of the oxophlorins. Introduction of an electron-withdrawing group efficiently minimizes the formation of oxophlorin π-radicals. Stabilization of neutral π radicals is promoted by hyperconjugation with a 15-*tert*-butyl group. A sterically induced stabilization of a novel non-aromatic tautomer of oxophlorin, the so-called "iso-oxophlorin" is demonstrated. These species exist also as 15-iso-oxophlorins upon complexation to divalent metals. Radical formation, enhanced by mild oxidants such as K_3FeCN_6, yielded pure oligomers and stereospecific supramolecular arrays by radical dimerizations taking place at the 10- and 10'-positions.

INTRODUCTION

Oxophlorin chemistry has attracted attention since *meso*-hydroxylation was recognized as an important step in the oxidative degradation of iron porphyrins. Hemes in hemoglobin and myoglobin are degraded, via iron *meso*-oxyporphyrin radicals, reacting further with O_2, to give biliverdin and eventually bilirubin pigments.[1] Due to the biological significance of oxophlorins in relation to heme catabolism, studies have been carried out to characterize their electronic structure.[2] Oxophlorins are tetrapyrrolic macrocycles that possess an oxygen at a *meso*-carbon and exist as the keto (oxophlorin) **1** rather than enol (hydroxyporphyrin) **2** species in neutral solution as shown by numerous spectroscopic techniques.[3] In acidic solution or when complexed with divalent metals, the enol-structure predominates; with trivalent metals such as iron(III), either the keto- or enol-form can predominate, depending upon pH.[3]



1 **2**

Oxophlorins **1** are relatively strong bases, accepting one proton on a central nitrogen atom to form isolable monocations. A second proton can be added to the *meso*-oxygen, forming a dication derived from the hydroxyporphyrin tautomer **2**. In neutral solutions the oxidation potentials of oxophlorins and their metal complexes are approximately 300 mV lower than those observed for related porphyrins. In alkaline solution, deprotonation further lowered these oxidation potentials by 300 mV.[4]

Light induced oxidation of oxophlorins and their metal complexes yields fairly stable neutral π-radicals, which were reported to dimerize in high yields in chloroform solution.[4] Structural characterization of

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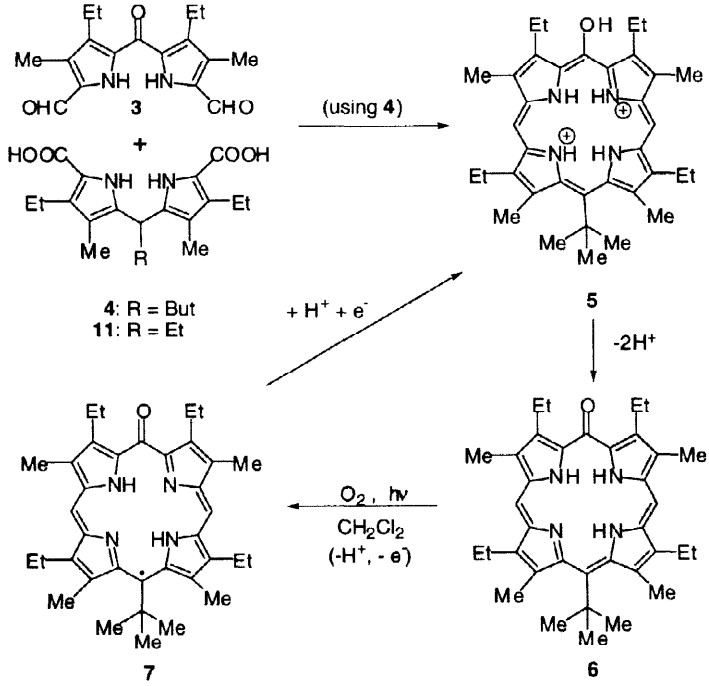
a nickel(II) octaethyloxophlorin dimer revealed the formation of a carbon-carbon bond between two *meso* carbons, lying opposite to the *meso*-carbonyl groups.[5] These regiospecific radical dimerizations or known oxidations of oxophlorins to give 5,15-dioxoporphodimethenes[6] led us to believe that the 15-position might have unique chemical reactivity. Huckell-McLachlan calculations also showed the highest spin density distribution of the oxophlorin radical to be located at the 15-position.[4] We therefore chose to synthesize 15-substituted oxophlorins in order to alter the spin density distribution, hoping that radical oligomerization reactions of these substrates would take place through the 10- and 20-positions. We now demonstrate that electronic and steric variability introduced at the 15-position of 5-oxophlorins enables control over the oxidation potential of the oxophlorins, thus allowing: (a) an easy suppression or formation of air stable neutral oxophlorin π-radicals, (b) a sterically induced stabilization of an hitherto unknown tautomeric species of oxophlorins, and (c) formation of regio- and stereo-chemically pure oligomers and supramolecular arrays through radical dimerizations taking place at the 10-positions.

RESULTS AND DISCUSSION

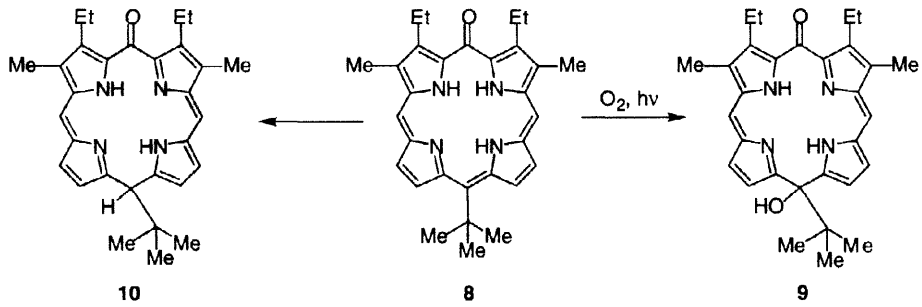
Although several approaches have been developed for the syntheses of oxophlorins, *meso*-substituted oxophlorins are scarce in the literature.[3,7] *meso*-Substituted oxophlorins have been obtained by oxygenation of *meso*-substituted metalloporphyrins[8,9] or by nucleophilic displacement of a nitro group using the sodium salt of *E*-benzaldoxime.[10] *meso*-Unsubstituted oxophlorins have been prepared directly via a MacDonald-type condensation (i.e. "2+2") of 1,9-diformyldipyrroketones with dipyrromethanes,[11] by reaction of 1-formyl-9-(hydroxymethyl)dipyrroketones with dipyrromethanes,[8] or by macrocyclization of b-oxobilanes.[12]



In the present work, adaptation of the MacDonald approach enabled us to efficiently prepare a series of novel 15-substituted-5-oxophlorins in order to further study their chemical properties. We first targeted 15-

tert-butyl-5-oxophlorins assuming that radical formation and stabilization would take place at the 15-position due to hyperconjugation through the *tert*-butyl substituent. Condensation of 1,9-diformyl-5-oxodipyrromethane **3**[11] with 5-*tert*-butyl-2,8-diethyl-3,7-dimethyldipyrromethane-1,9-dicarboxylic acid **4**[13] in trifluoroacetic acid (TFA) followed by a basic work-up resulted in formation of the 15-*tert*-butyl-5-oxophlorin **6** in 43% yield. Exposure of compound **6** dissolved in CH_2Cl_2 to air and daylight afforded a new green species **7** which ESR and magnetic studies confirmed to be the pure neutral π-radical species of the 15-*tert*-butyl-5-oxophlorin.[13]

This oxophlorin radical is stable to air for long periods of time in the solid form. Addition of acid to a CH_2Cl_2 solution of **7** generated, via the readily reduced π-cation porphyrin radical,[14] the diprotonated hydroxyporphyrin **5**. This reduction/protonation process could be followed by spectrophotometry, which showed clean isosbestic points at λ_{max} 438 and 540 nm, further demonstrating the quantitative radical character of **7**. Synthesis of 12,13,17,18-unsubstituted-15-*tert*-butyl-5-oxophlorin **8** stressed the essential role played by steric congestion on the radical stabilization, via the interaction of the 15-substituent with abutting groups in the 13- and 17-positions. Indeed, air oxidation of **8** afforded unstable radicals which were trapped by O_2 to give 15-*tert*-butyl-15-hydroxy-15-iso-5-oxophlorin **9**.



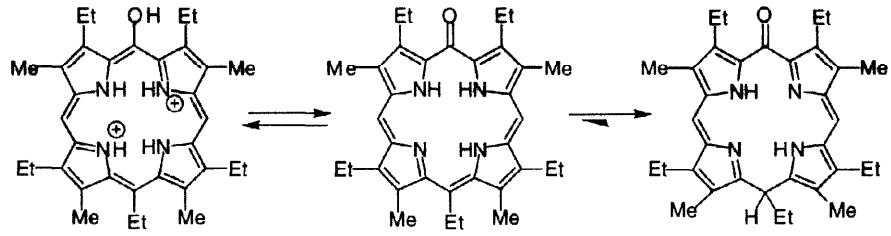
10 **8** **9**

Isolation of another species, 15-*tert*-butyl-15-iso-5-oxophlorin **10**,[13] led us to target other compounds, such as a 15-ethyl-5-oxophlorin **12**, which would allow the formation of these new iso-oxophlorin tautomers in higher yields.

Syntheses and Characterization of Iso-Oxophlorins

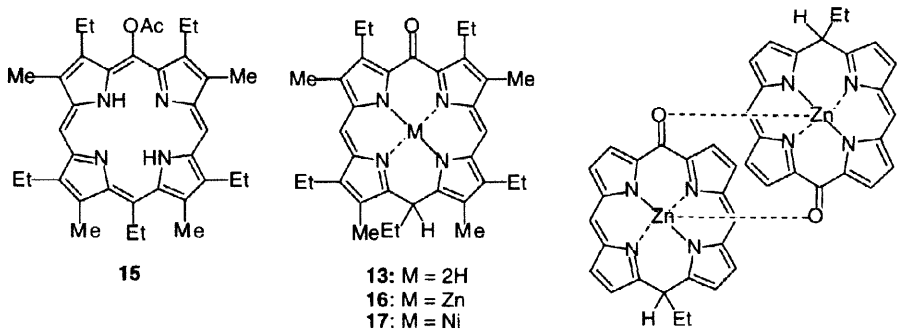
Preparation of the 15-ethyl-5-oxophlorin **12** was accomplished via condensation of 1,9-diformyldipyrroketone **3**[10] with 5-ethyldipyrromethane-1,9-dicarboxylic acid **11**[15] in TFA, following the MacDonald approach. Basic work up of the reaction product followed by exposure to air and light in CH_2Cl_2 (45 min) afforded the novel compound **13**. The molecular structure of **13** was confirmed by X-ray crystallography.[16] When oxophlorin **12** was isolated, its tautomerization to iso-oxophlorin **13** was also found to occur in the solid state over a few days.

By comparison with the isoporphyrin/porphyrin equilibrium, the structure **13** can be described as an iso-oxophlorin which is remarkably stable with regard to its aromatic oxophlorin tautomer **12**. These novel iso-oxophlorin tautomers predominate under non-acidic conditions because the 15-tetrahedral carbon allows steric strain between the abutting 13- and 17-substituents and the 15-ethyl to be relieved. The gain in aromatic stabilization by having a fully conjugated oxophlorin form **12** is not sufficient to overcome an increase in steric congestion introduced by a 15-sp^2 carbon.



14 12 13

In contrast, the aromatic stabilization afforded by formation of the conjugated porphyrin chromophore, as in dication **14** or in 5-acetoxy-15-ethylporphyrin **15**, is sufficient to outweigh the steric strain introduced at the 15-sp^2 carbon in these compounds. Given the opportunity to become a fully conjugated hydroxyporphyrin by protonation, the chromophore converts reversibly between iso-oxophlorin **13** and oxophlorin dication **14**, depending upon pH. Whereas the aromatic porphyrins display extremely shielded central nitrogen protons, the iso-oxophlorin tautomer has an interrupted conjugation pathway and features ^{1}H NMR peaks characteristic of a non-aromatic macrocycle, with D_2O/Et_3N exchangeable NHs at 12.6 ppm. This loss of aromaticity is observed as well for all iso-oxophlorin dimer and tetramer species (*vide infra*).



15

13: M = 2H
16: M = Zn
17: M = Ni

As mentioned earlier, metal(II) oxophlorins exist in the enol form. In order to determine whether or not iso-oxophlorins behave similarly to oxophlorins upon metal(II) complexation by tautomerization to metallo(II) hydroxyporphyrins, we synthesized two different metal complexes [Zn(II), Ni(II)] of the novel iso-oxophlorin tautomer **13**. Treatment of iso-oxophlorin **13** with zinc(II) acetate afforded the zinc(II) iso-oxophlorin **16**, and the nickel(II) iso-oxophlorin **17** was prepared by refluxing a $CHCl_3$/MeOH solution of **13** in presence of nickel(II) acetate and sodium acetate. Figure 1 shows the optical spectra of compound **13** and its nickel(II) complex **17**. Upon metalation a large red shift of the Soret band was observed from 408 (**13**) to 470 and 449 nm for the zinc(II) and nickel(II) complex, respectively. Tautomerization to the metallo(II) hydroxyporphyrin did not occur even when **16** and **17** were refluxed in toluene, further demonstrating the stability of these iso-oxophlorin tautomers. The molecular structure of **16** was determined by X-ray crystallography (Figure 2). A dimeric species of **16** is formed where the keto group of each iso-oxophlorin is coordinated to a zinc of another iso-oxophlorin, placing the two macrocycles within π-π contact. A slightly ruffled conformation is found in both macrocycles. The average Zn-O distance is 2.09 Å. A similar head-to-tail dimeric structure was shown for In(III) octaethyloxophlorin and it was suggested to exist for iron(III)

octaethyloxophlorin.[17] The larger red shift of the Soret band observed for **16** is probably a consequence of its dimeric nature.

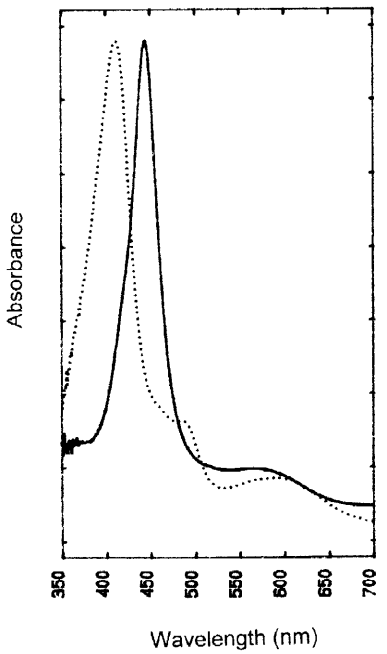


Figure 1: Optical spectra, in CH_2Cl_2 of iso-oxophlorin **13** (·····) and its nickel(II) complex **17** (———).

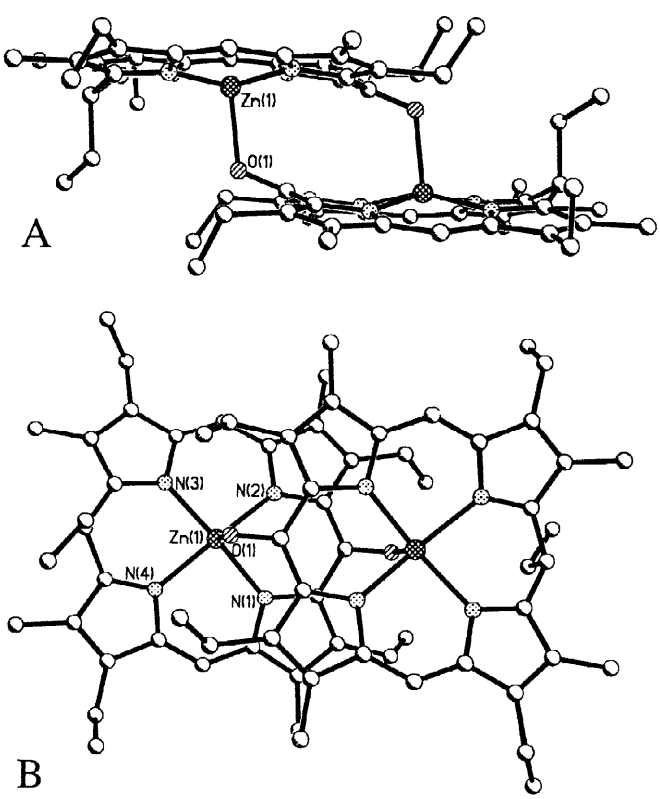
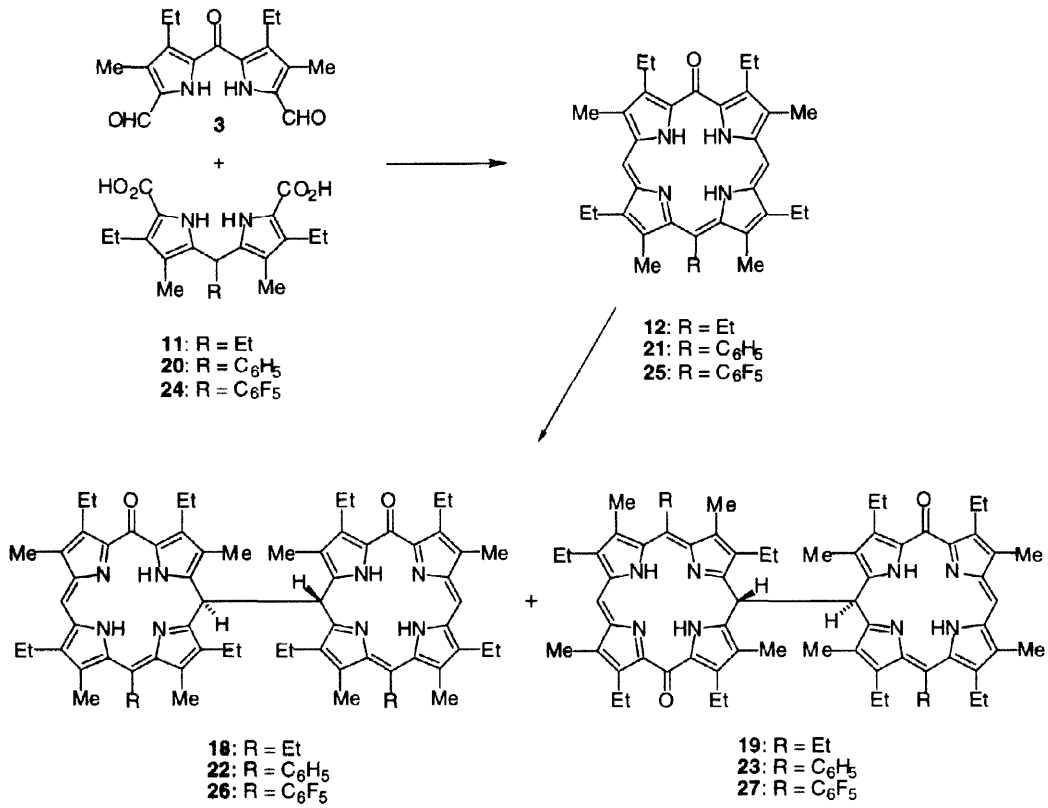


Figure 2: Molecular structure of the head-to-tail dimer of compound **16**. A) Side view; B) Top view.

Syntheses of 10,10'-Iso-Oxophlorin Dimers.

Another product isolated in smaller amount (29%) along with the 15-ethyl-15-iso-5-oxophlorin **13** was identified as 10,10'-bis-(15-ethyl-10-iso-oxophlorin) **18/19**. Presence of two stereoisomers resulting from the dimerization demonstrates that 15-substituted-5-oxophlorins do indeed dimerize at the 10,10'-positions. Stereoisomers **18/19** are stable both as solids and in solution. The molecular structure of **18** was confirmed by X-ray crystallography.[18] Molecules of **18** pack in a crystalline lattice with alternating columns of stacked dimers and ordered cyclohexanes. Formation of the 10-sp^3 carbons allow for major distortions of the macrocycle. Higher yields of **18/19** could be obtained by treating a solution of **12** with a mild oxidant such as $K_3Fe(CN)_6$.



Condensation of **3** and **20** in TFA gave 15-phenyl-5-oxophlorin **21** which was not isolated but was exposed to air and light in CH_2Cl_2 for 4 hours to yield, after chromatography, the novel iso-oxophlorin dimers **22/23** in 66% yield. Synthesis of 15-pentafluorophenyl-5-oxophlorin **25**, via condensation of **3** and **24**,[15] allowed us to observe the first NMR spectrum of a metal-free oxophlorin. Proton NMR spectra of metal free oxophlorins are difficult to observe because of the fact that they exhibit line-broadening due to the presence of small amounts of the oxophlorin π-radical. This problem is usually overcome by the addition of TFA to form the *meso*-hydroxyporphyrins which possess well-resolved proton NMR spectra.[3] The strong electron-withdrawing character of the pentafluorophenyl substituent increases the oxidation potential of the oxophlorin, therefore minimizing radical formation in solution. The proton NMR spectrum of free base **25** featured a well resolved 10,20-protons peak at 8.12 ppm (a 1.2 ppm downfield shift compared with the non-aromatic dimeric species **26/27**). Dimerization of 15-pentafluorophenyl-5-oxophlorins **25** required a longer period of time

(approximately one week) confirming that the 15-substituent plays a significant role in tuning the oxidation potential of the oxophlorin macrocycle. Treatment with $K_3Fe(CN)_6$ in THF resulted in complete dimerization in 20 minutes to yield regioisomers **26/27** in good (86 %) yields.

Addition of acid reverses quantitatively the dimerization process to form the monomeric oxophlorin dication as shown by the clean isosbestic points in UV-visible studies. Addition of TFA to a chloroform solution of 15-ethyl-10-iso-oxophlorin dimer **18/19** followed by crystallization by slow diffusion of methanol generated crystals of the oxophlorin dication **14** suitable for X-ray crystallography. The molecular structure of **14** (Figure 3) further demonstrates the reversibility of the dimerization process.

Syntheses of Iso-Oxophlorin Tetramers

Having established the oxidative dimerization chemistry of the 15-substituted-5-oxophlorins, we next attempted the synthesis of an oxophlorin supramolecular array. 15,15'-Oxophlorin dimer **29** (not shown) was prepared via a condensation between diformyldipyrroketone **3** and a symmetrical bis-dipyrromethane **28**.[19,20] Oxidative dimerization of crude **29** (O_2/hν/CH_2Cl_2) afforded a 37% overall yield of the macromolecule **30** consisting of four iso-oxophlorin-type subunits connected in a stereochemically unique fashion.

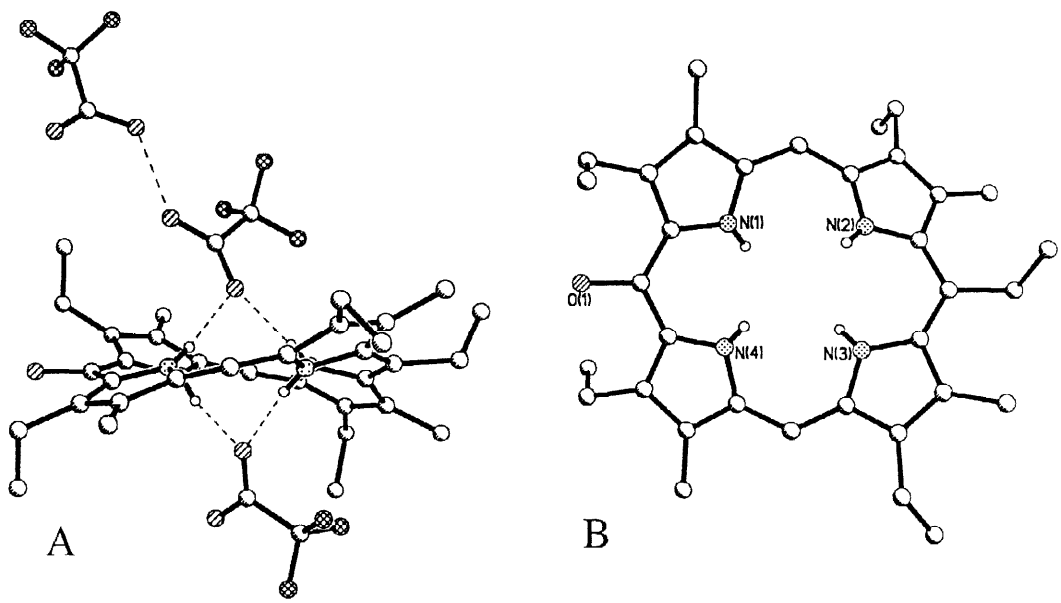
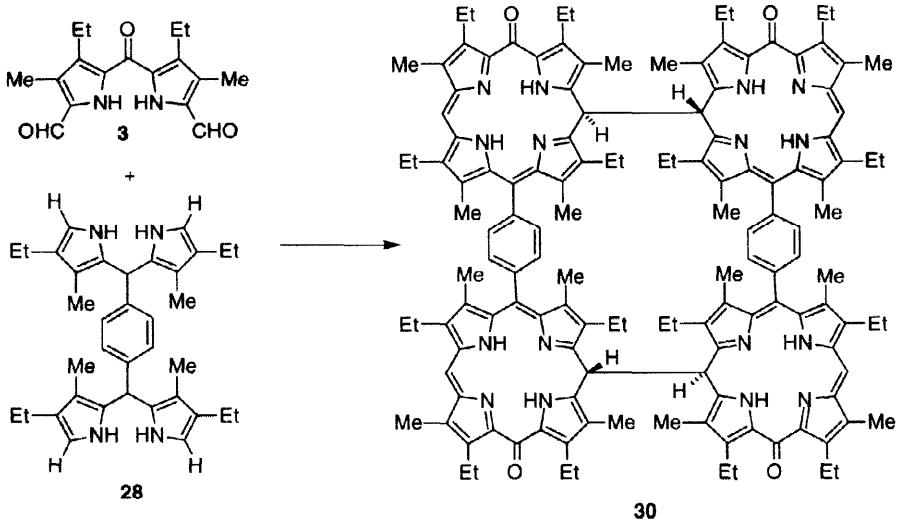
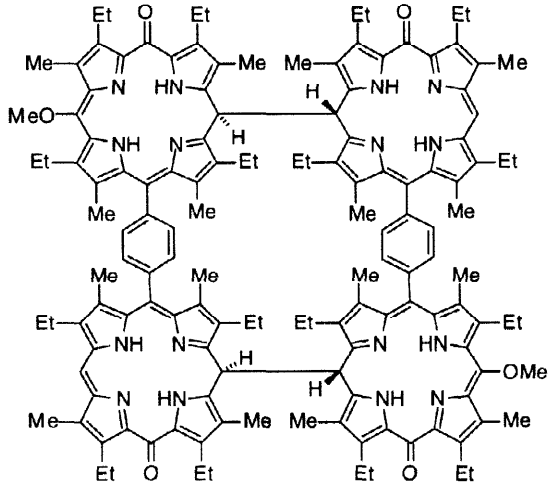


Figure 3: Molecular structure of oxophlorin dication **14**. A) Side view showing TFA H-bonding network. B) Top view.

The optical spectrum of **30** was similar to that of the iso-oxophlorin dimers, but was blue-shifted. The short wavelength absorption appeared at λ_{max} 378 nm and the long wavelength band was at 654 nm. The proton NMR spectrum of **30** again demonstrated interrupted conjugation in the macrocycle, with exchangeable NH peaks at δ 13.20 and 12.85 ppm, as well as the 10/10'-H resonance at δ 5.39 ppm. When methanol was used as a co-solvent for the synthesis, a tetramer **31** with methoxyl groups inserted at two of the *meso* carbon



positions was obtained. Compound **31** was also studied by X-ray crystallography (Figure 4); it possesses a "stepped" structure with the *trans,cis,trans* orientation at the 10,10'-bridges which differs from the stereochemistry of the "helical" structure of **30** (Figure 5) bearing a *trans,trans,trans* orientation.



In order to vary the size and shape of the cavity formed by these supramolecular arrays, diformyldipyrroketone **3** was condensed with 1,3-bis(dipyrromethane)phenyl **32**.[19,20] After light induced oxidation, oxophlorin tetramer **33** was isolated in 28% yield.

Syntheses of Oxophlorin-Porphyrin Tetramers

The next step was to take advantage of the radical dimerization process to design other supramolecular arrays containing different macrocyclic chromophores. Condensation of bis-dipyrromethane **34**,[19,20] with 1,9-diformyldipyrromethane **35**[21] was carried out in CH_2Cl_2 in the presence of *p*-toluenesulfonic acid. The porphyrin-diethyl ester **36** was decarboxylated to give **37**, and was then reacted with **3** in a mixture of TFA and

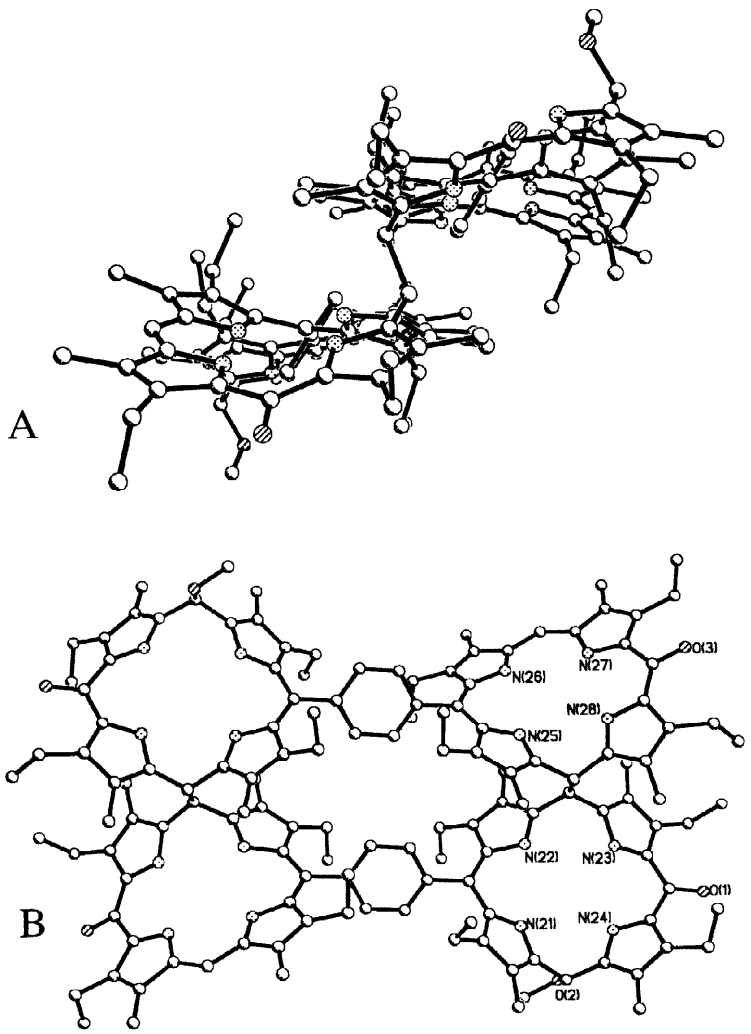
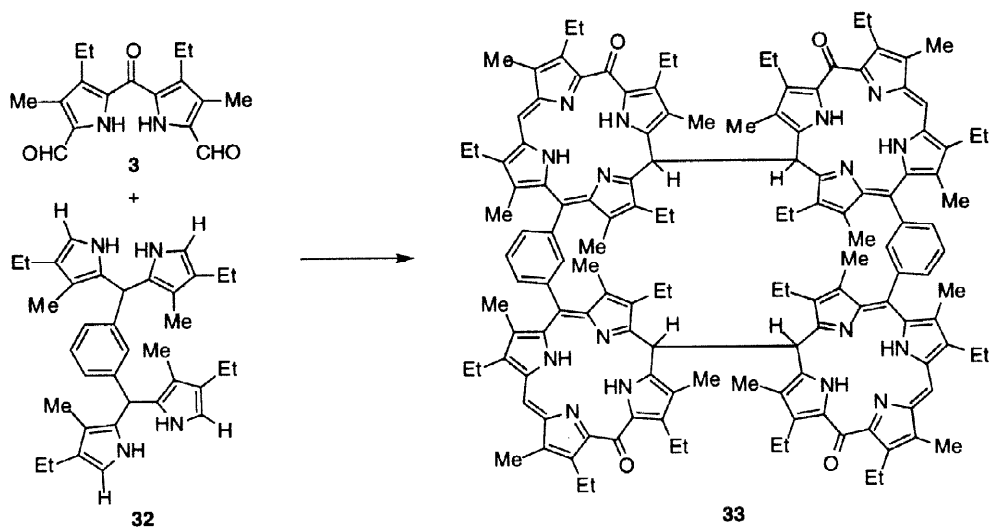


Figure 4: Molecular structure of the oxophlorin tetramer **31**. A) Side view showing "stepped" orientation. B) Top view.



tetrahydrofuran. Aqueous NH_4OH workup and subsequent dimerization resulted in the formation of the oxophlorin-porphyrin tetramer **38** in 39% yield. When the MacDonald condensation was performed in

methanol, a lower yield of a different tetramer was obtained resulting of methanol insertion at the oxophlorin 10,10'-carbons.

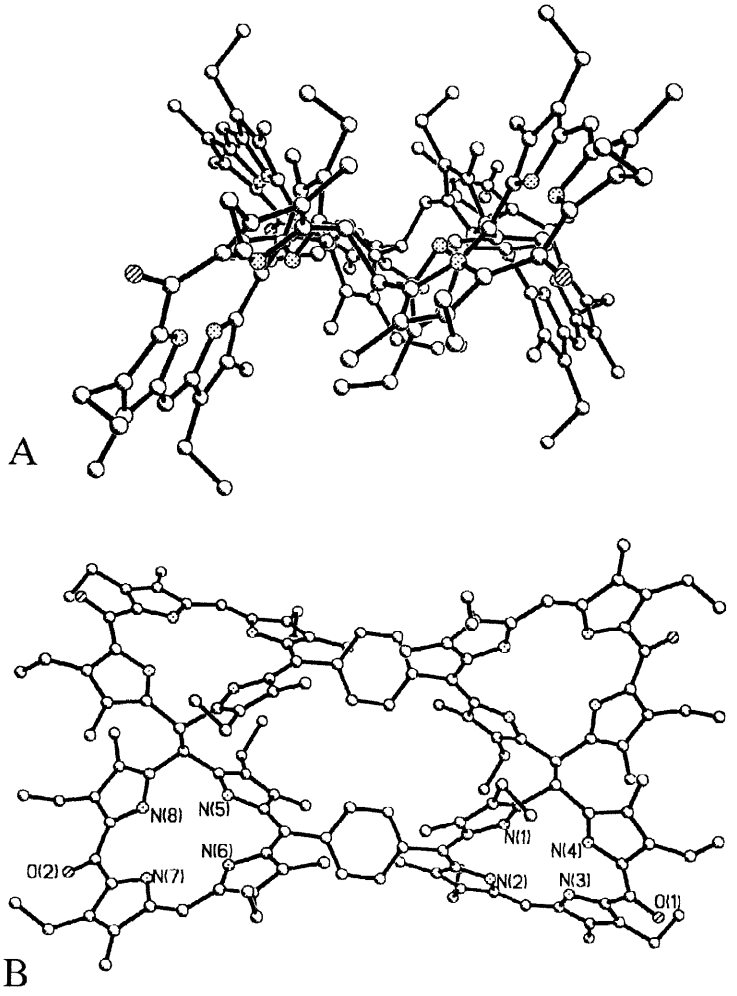
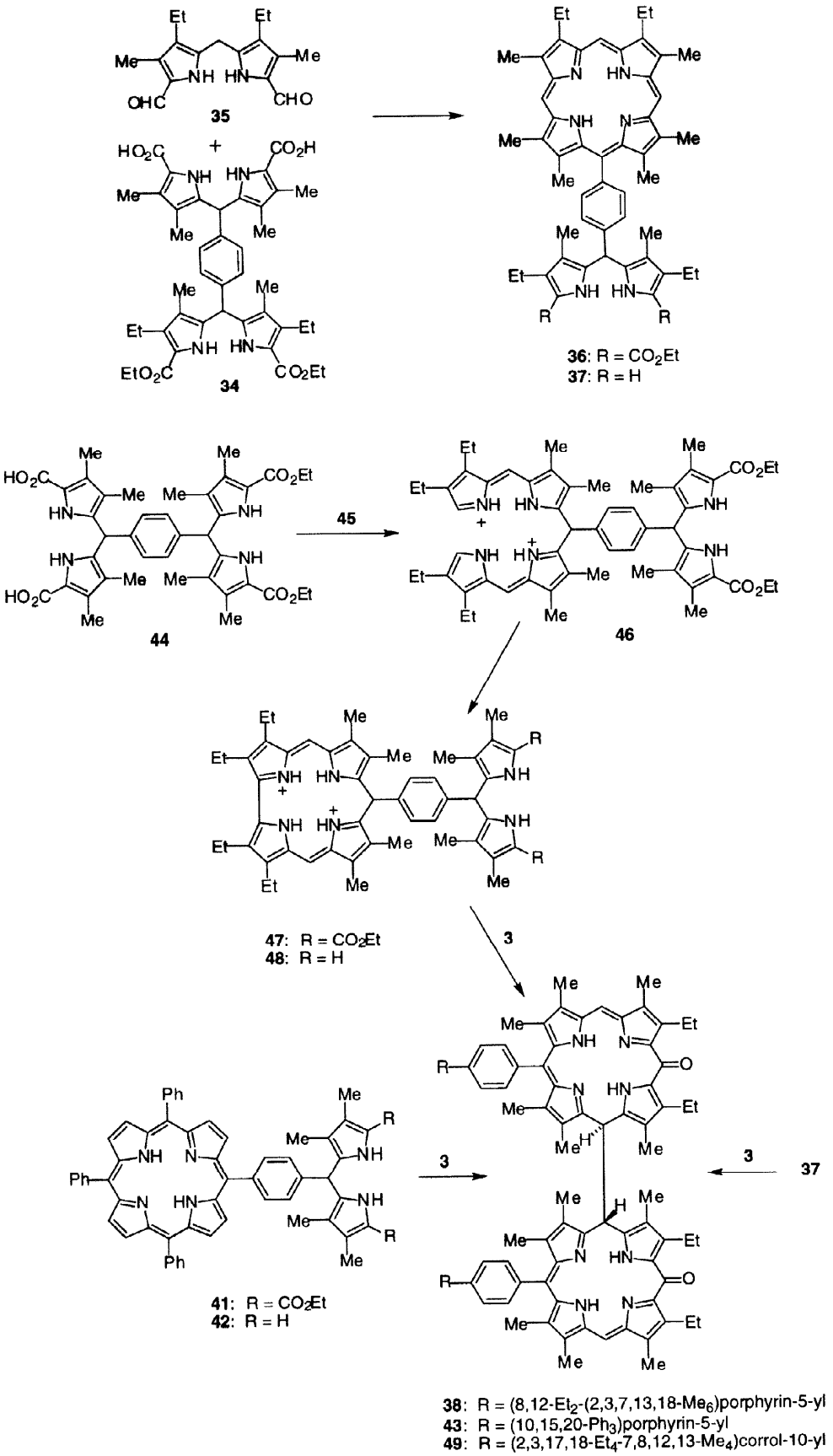


Figure 5: Molecular structure of the "helical" *trans,trans,trans* oxophlorin tetramer **30**. A) Side view. B) Top view.

A porphyrin-oxophlorin tetramer obtained from a tetraphenylporphyrin template was readily available. Acidic condensation of 5-(*p*-formylphenyl)-10,15,20-triphenylporphyrin **39**[22] with two equiv. of ethyl 3,4-dimethylpyrrole-2-carboxylate **40**[23] gave the TPP-dipyrromethane **41**. Subsequent hydrolysis and decarboxylation in refluxing KOH/diethylene glycol afforded the di-α-unsubstituted dipyrromethane **42** in good (82%) yield. Further condensation with dipyrroketone **3** in TFA led to the formation of the oxophlorin subunit. Neutralization of the reaction mixture followed by stirring the organic phase in air and in the daylight afforded the corresponding tetramer **43**.

The electronic absorption spectra of these compounds are characterized by the strong absorptions of the porphyrin moiety that overwhelm those of the oxophlorin subunit. Superimposition of the absorbance of the porphyrin moiety with the broad band of the oxophlorin subunit can be observed in the Q bands region. The multiplicity of the resonances in the ^{1}H NMR spectra of tetramers **38/43** indicates the presence of regioisomers, depending upon the arrangement of the porphyrins with respect to the oxophlorin moieties (not shown; similar to the 10,10"-iso-oxophlorin dimer regioisomers described above).


35
34
36: R = CO2Et
37: R = H
44
45
46
47: R = CO2Et
48: R = H
3
41: R = CO2Et
42: R = H
38: R = (8,12-Et2-(2,3,7,13,18-Me6)porphyrin-5-yl
43: R = (10,15,20-Ph3)porphyrin-5-yl
49: R = (2,3,17,18-Et4-7,8,12,13-Me4)corrol-10-yl

Synthesis of Oxophlorin-Corrole Tetramers

Our recent success in the synthesis of porphyrin-corrole heterodimers through the cyclization of a porphyrin-biladiene precursor,[19] led us to follow a similar route for the formation of an oxophlorin-corrole dimer. Attempts to synthesize an oxophlorin-biladiene precursor failed. However, the corrole moiety could be used as a starting block for the synthesis of this heterodimer. We first synthesized a,c-biladiene **46**, by reaction of 2-formyl-3,4-diethylpyrrole **45**[24] with bis-dipyrromethane **44**.[20] This biladiene was cyclized to give corrole **47** in good yields, using *p*-chloranil as oxidant; subsequent alkaline decarboxylation in diethylene glycol afforded the corresponding α-unsubstituted dipyrromethane **48**, showing good stability of the corrole moiety under these conditions. When **48** was condensed with 1,9-diformyldipyrroketone **3** following the MacDonald procedure, tetramer **49** was obtained.

CONCLUSIONS

New chemistry of novel 15-substituted-oxophlorins are described. Introduction of sufficient steric congestion at the 15-position generates novel non-aromatic species of oxophlorins, called iso-oxophlorins. These species, which are stable upon complexation of divalent metals, revert to aromatic chromophores upon protonation or acetylation. 15-Substituted oxophlorins experience electronic and steric effects which directly affect their oxidation potentials. Light induced oxidation of these oxophlorins is enhanced by electron-donating groups and suppressed by electron-withdrawing substituents such as pentafluorophenyl. Formation of π-neutral radicals and their subsequent dimerization at the 10,10'-positions, afford regioisomeric iso-oxophlorin dimers as well as various tetrapyrrolic tetramers. Dimerizations are reversible and treatment with acid regenerates the protonated oxophlorins (via an extremely facile reduction of oxophlorin radical cations) which can be re-cycled to the dimeric species.

EXPERIMENTAL

Mps were measured on a Thomas/Bristoline microscopic hot stage apparatus and were uncorrected. Silica gel 60 (70-230 and 230-400 mesh, Merck) or neutral alumina (Merck; usually Brockmann Grade III, i.e. deactivated with 6% water) were used for column chromatography. Preparative thin layer chromatography was carried out on 20 x 20 cm glass plates coated with Merck G 254 silica gel (1 mm thick). Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 silica gel (precoated sheets, 0.2 mm thick). Reactions were monitored by TLC and spectrophotometry and were carried out under nitrogen and in the dark (aluminum foil). ^{1}H-NMR spectra were obtained in deuteriochloroform solution at 300 MHz using a General Electric QE300 spectrometer; chemical shifts are expressed in ppm relative to chloroform (7.26 ppm). Elemental analyses were performed at the Midwest Microlab., Inc., Indianapolis, IN. Unless stated otherwise, electronic absorption spectra were measured in dichloromethane solution using a Hewlett-Packard 8450A spectrophotometer. In a few cases, amounts of final products were insufficient for elemental analyses, or amounts of intermediates were sufficient only for completion of the reaction sequence; therefore, elemental composition was verified using high resolution mass spectroscopy (HRMS), after obtaining evidence of homogeneity using proton NMR spectroscopy. Mass spectra, both HRMS and low resolution (LRMS), were

obtained at the Mass Spectrometry Facility, University of California, San Francisco, CA. Dipyrroketone **3**, dipyrromethanes **4**, **11**, **21** and **24**, bis-dipyrromethane **28**, **32**, and **34**, 1,9-diformyldipyrromethane **35**, ethyl 3,4-dimethylpyrrole-2-carboxylate **40**, 2-formyl-3,4-diethylpyrrole **45**, 5-(4-formylphenyl)-10,15,20-triphenylporphyrin **39** were prepared according to literature procedures (*vide supra*).

Crystal Structure Data for 14: Crystals of **14** were grown from chloroform/TFA/methanol. A parallelipiped single crystal with dimensions 0.40 x 0.25 x 0.08 mm was selected. The crystal lattice was triclinic with a $P\bar{1}$ space group. Cell dimensions were: a = 10.876(2), b = 13.741(2), c = 15.079(2) Å, α = 103.437(10), β = 91.352(10), γ = 111.995(10)°, V = 2016.9(5) Å^3, Z = 2. Data were collected at 130(2) K on a Siemens $P2_1$ diffractometer [λ(Cu Kα) = 1.54178 Å] in $\theta/2\theta$ scan mode to $2\theta_{max}$ = 112°. Of 5467 reflections measured 5409 were unique (R_{int} = 0.0087, T_{min} = 0.58, T_{max} = 0.66, μ = 1.084 mm^{-1}, r_{calc} = 1.424 g cm^{-3}). The structure was solved by direct methods and refined (based on F^2 using all independent data) by full matrix least-squares methods (Siemens SHELXTL V. 5.03). Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogens were generated by idealized geometry and treated as riding using isotropic thermal parameters. R-values are reported for $R1$ (based on observed data, $I > 2\sigma$) and $wR2$ (based on all data). $R1$ and $wR2$ were 0.0569 and 0.1508 (574 parameters). The datasets were corrected for absorption.[25]

Crystal Structure Data for 16: Crystals of **16** were grown from chloroform/cyclohexane. A parallelipiped single crystal was selected with dimensions 0.08 x 0.05 x 0.04 mm. The crystal lattice was triclinic with a $P\bar{1}$ space group. Cell dimensions were: a = 11.063(2), b = 12.090(2), c = 12.939(3)Å, α = 68.79(4), β = 72.81(3), γ = 64.47(3)°, V = 1435.7(5), and Z = 2 (FW = 586.07, ρ_{calc} = 1.356 g cm^{-3}, μ = 1.444 mm^{-1}). X-ray diffraction data were collected on a Siemens $P2_1$ diffractometer [λ(Cu Kα) = 1.54178 Å] at 130(2) K in $\theta/2\theta$ scan mode to $2\theta_{max}$ = 112°. Of 3776 reflections measured (±h,±k,±l) 3738 were independent and 2344 had $I>2\sigma$ (R_{int} = 0.049). The structure was solved by direct methods and refined (based on F^2 using all independent data) by full matrix least-squares methods (Siemens SHELXTL V. 5.03); number of parameters = 361. Hydrogen atom positions were located by their idealized geometry and refined using a riding model. A difference map followed by subsequent refinement revealed that two of the methyl groups bear statistical sets of hydrogens rotated by approximately 60° relative to each other. An absorption correction was applied using XABS2.[25] Final R factors were $R1$ = 0.0730 (based on observed data) and $wR2$ = 0.1718 (based on all data); the maximum residual electron density was 0.512 eÅ^{-3}.

Crystal Structure Data for 31: A crystal of **31** (grown from chloroform/methanol) with dimensions 0.40 x 0.25 x 0.08 mm was selected. The crystal lattice was triclinic with a $P\bar{1}$ space group. Cell dimensions were: a = 14.565(4), b = 15.407(5), c = 19.421(5) Å, α = 77.94(2), β = 74.52(2), γ = 66.63(2)°, V = 3829(2) Å^3, Z = 1. Data were collected at 130(2) K on a Siemens P4 diffractometer with a rotating anode [λ(Cu Kα) = 1.54178 Å] at 130(2) K in $\theta/2\theta$ scan mode to $2\theta_{max}$ = 112°. Of 8543 reflections measured 8220 were unique (R_{int} = 0.0517, T_{min} = 0.45, T_{max} = 0.85, μ = 2.002 mm^{-1}, r_{calc} = 1.194 g cm^{-3}. The structure was solved by direct methods and refined (based on F^2 using all independent data) by full matrix least-squares methods (Siemens SHELXTL V. 5.03). Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogens were generated by idealized geometry and treated as riding using isotropic thermal parameters. The structure of **31** exhibited disorder in a small portion of the parent molecule. R-values are reported for $R1$ (based on observed

data, $I > 2\sigma$) and *wR2* (based on all data). *R1* and *wR2* were 0.1222 and 0.3921 (628 parameters). The datasets were corrected for absorption.[25] Crystallographic data (excluding structure factors) for the three new structures reported in this paper (and for compound **30**)[18] have been deposited at the Cambridge Crystallographic Data Centre (CCDC).

15-*tert*-Butyl-3,7,12,18-tetraethyl-2,8,13,17-tetramethyl-5-oxophlorin 6. 1,9-Diformyl-5-dipyrroketone **3** (160 mg, 0.533 mmol) and 5-*tert*-butyl-2,8-diethyl-3,7-dimethyldipyrromethane-1,9-dicarboxylic acid **4** (200 mg, 0.534 mmol) were dissolved in TFA (5 mL) under nitrogen in the dark, and stirred for 2 h. The reaction mixture was diluted with cold methanol (15 mL) and neutralized with 10% aqueous NH_4OH. The purple precipitate was collected, redissolved in CH_2Cl_2 and washed several times with water. The solvent was evaporated under vacuum and the residue was purified by chromatography on an alumina column (eluting with CH_2Cl_2). The title compound was recrystallized from CH_2Cl_2/cyclohexane (126 mg, 43%). Mp 272-275 °C; UV-Vis: λ_{max} 400 nm (ε 176 000), 632 (18 000), 694 (29 000); ^{1}H NMR ($CDCl_3$/d-TFA) δ 10.06 (s, 2 H), 3.89 (m, 8 H), 3.43 (s, 6 H), 3.26 (s, 6 H), 1.69 (t, 6 H), 1.56 (t, 6 H), 1.48 (s, 9 H); FAB-MS: 550.3 (M^+), 493.8 (-Bu^t).

15-*tert*-Butyl-3,7,12,18-tetraethyl-2,8,13,17-tetramethyl-5-oxophlorin Radical 7. 15-*tert*-Butyl-5-oxophlorin **6** (110 mg, 0.23 mmol) was stirred in CH_2Cl_2 (50 mL) open to air and in the daylight for 45 min; the solvent was evaporated under vacuum, and the residue was purified by chromatography on an alumina column, eluted with CH_2Cl_2 to give **7** (97 mg, 90%). Mp 180-182°C; UV-Vis: λ_{max} 410 (ε 66 700), 628 (11 700), 664 (11 000); ^{1}H NMR ($CDCl_3$/d-TFA): addition of TFA gave a spectrum identical with that of compound **6**; FAB-MS: *m/z* 550.3 (M^+).

3,7,12,15,18-Pentaethyl-2,8,13,17-tetramethyl-15-iso-5-oxophlorin 13. Dipyrroketone **3** (150 mg, 0.64 mmol) and 5-ethyldipyrromethane-1,9-dicarboxylic acid **11** (130 mg, 0.61 mmol) were dissolved in TFA (5 mL) under nitrogen in the dark and stirred for 2 h. The reaction mixture was diluted with cold methanol (15 mL) and neutralized with 10% aqueous NH_4OH. The purple precipitate was collected, redissolved in CH_2Cl_2 and washed with water. The solvent was evaporated under vacuum and the residue was purified by filtration through an alumina plug (eluting with CH_2Cl_2) to give **12** (138 mg, 43%). Crude oxophlorin **12** was redissolved in a solution of CH_2Cl_2 opened to air and stirred for 45 min in the daylight. TLC monitoring (alumina, CH_2Cl_2/cyclohexane, 3/1) showed disappearance of **12** and appearance of a green faster running band (**13**) and a slower running blue band (**19/20**). The solvent was removed under vacuum and the residue was purified by chromatography on an alumina column using CH_2Cl_2 as the eluent. The first band was collected to give **13**, which was recrystallized from CH_2Cl_2/petroleum ether (75 mg, 54%/**12**). Mp 190-192°C; UV-Vis: λ_{max} 408 nm (ε 59 000), 588 (9400); ^{1}H NMR ($CDCl_3$) δ 12.65 (s, 2 H), 6.91 (s, 2 H), 4.10 (t, 1 H), 2.87 (m, 4 H), 2.66 (m, 4 H), 2.27 (s, 6 H), 2.14 (s, 6 H), 1.97 (m, 2 H), 1.19 (t, 9 H), 0.88 (t, 6 H); FAB-MS: 522.7 (M^+, 20); 493.5 (-Et, 100); Anal. Calcd for $C_{34}H_{42}N_4O$: C, 78.12; H, 8.10; N, 10.72. Found: C, 77.95; H, 8.20; N, 10.39.

5-Acetoxy-3,7,12,15,18-pentaethyl-2,8,13,17-tetramethylporphyrin 15. Iso-oxophlorin **13** (40 mg, 0.065 mmol) was dissolved in pyridine (10 mL) and acetic anhydride (3 mL). The reaction mixture was heated at 75 °C for 20 min under argon. The solvents were removed under vacuum and the residue was purified by chromatography first on a silica gel column and then on an alumina thick layer plate, using CH_2Cl_2/cyclohexane (1:1) as eluent, to yield 25 mg (63%) of the title compound as a red powder. Mp 260-

263 °C; UV-Vis: λ_{max} 399 nm (ε 270 000), 492 (53 000), 530 (39 000), 565 (38 000), 624 (32 500); ^{1}H NMR ($CDCl_3$) δ 10.09 (s, 2 H), 5.12 (q, 2 H), 4.08 (q, 4 H), 3.73 (q, 4 H), 3.62 (s, 6 H), 3.58 (s, 6 H), 2.89 (s, 3 H), 1.76 (m, 15 H), -2.67 (br s, 1 H), -2.41 (br s, 1 H); FAB-MS: 565.4 (MH^+); Anal. Calcd for $C_{36}H_{44}N_4O_2 \cdot H_2O$: C, 74.19; H, 7.96; N, 9.61. Found: C, 74.50; H, 7.74; N, 9.35.

Zinc(II) 3,7,12,15,18-Pentaethyl-2,8,13,17-tetramethyl-15-iso-5-oxophlorin 16. Iso-oxophlorin **14** (30 mg, 0.061 mmol), $NaHCO_3$ (20 mg) and $Zn(OAc)_2$ (50 mg) were placed in MeOH (10 mL) and $CHCl_3$ (20 mL) and refluxed for 2 h. The green reaction mixture was washed several times with H_2O, dried over Na_2SO_4, and the solvent was evaporated. The residue was purified by chromatography on a silica gel column eluting with CH_2Cl_2. Recrystallization from CH_2Cl_2/cyclohexane afforded the title compound as a purple solid (28 mg, 83%). Mp 167-170 °C; UV-Vis: λ_{max} 470 nm (ε 68 000), 522 (6700), 574 (12 500); ^{1}H NMR ($CDCl_3$) δ 6.75 (s, 2 H), 4.16 (t, 1 H), 2.85 (q, 4 H), 2.58 (q, 4 H), 2.36 (m, 2 H), 2.10 (s, 6 H), 1.89 (s, 6 H), 1.16 (t, 6 H), 1.06 (t, 3 H), 0.71 (t, 6 H); FAB-MS: 584.2 (M^+, 30), 555.2 (-Et, 100); Anal. Calcd for $C_{34}H_{40}N_4OZn$: C, 69.68; H, 6.88; N, 9.56. Found: C, 69.29; H, 6.59; N, 9.83.

Nickel(II) 3,7,12,15,18-Pentaethyl-2,8,13,17-tetramethyl-15-iso-5-oxophlorin 17. Iso-oxophlorin **13** (20 mg, 0.041 mmol), $NaHCO_3$ (20 mg) and $Ni(OAc)_2$ (50 mg) were placed in MeOH (10 mL) and $CHCl_3$ (20 mL) and refluxed overnight. The reaction mixture was then washed several times with H_2O, dried on Na_2SO_4, and the solvent was evaporated. The residue was purified by chromatography on a silica gel column (CH_2Cl_2 as eluent). The main brown band was collected and the solvent was removed under vacuum to give the title nickel complex as a purple powder (17 mg, 74%). Mp 181-183 °C; UV-Vis: λ_{max} 449 nm (ε 70 000), 564 (9700); ^{1}H NMR ($CDCl_3$) δ 6.64 (s, 2 H), 3.75 (t, 1 H), 2.59 (m, 6 H), 2.43 (q, 4 H), 2.06 (s, 6 H), 1.88 (s, 6 H), 1.09 (m, 9 H), 0.82 (m, 6 H); FAB-MS: 578.3 (M^+, 100), 549.3 (82, -Et).

10,10'-Bis(3,7,12,15,18-pentaethyl-2,8,13,17-tetramethyl-10-iso-5-oxophlorin) 18/19. The experimental procedure followed as for compound **13**. The second blue band was collected to give **18/19**, which was recrystallized from CH_2Cl_2/petroleum ether (40 mg, 29%/**12**). Mp 190-192 °C; UV-Vis: λ_{max} 412 nm (ε 71 500), 602 (24 500). ^{1}H NMR ($CDCl_3$) (main regioisomer) δ 12.97 (s, 2 H), 12.64 (s, 2 H), 6.64 (s, 2 H), 5.40 (s, 2 H), 3.75 (t, 4 H), 2.59 (m, 8 H), 2.43 (m, 8 H), 2.06 (s, 12 H), 1.88 (s, 12 H), 1.09 (m, 12 H), 0.82 (m, 18 H); FAB-MS: 1043.7 (M^+); Anal. Calcd for $C_{68}H_{82}N_8O_2 \cdot 1.5H_2O$: C, 76.30; H, 8.00; N, 10.47. Found: C, 76.50; H, 7.75; N, 10.26.

10,10'-Bis(3,7,12,18-tetraethyl-2,8,13,17-tetramethyl-15-phenyl-10-iso-5-oxophlorin) 22/23. The dipyrroketone **3** (400 mg, 1.33 mmol) and 5-phenyldipyrromethane-1,9-dicarboxylic acid **20** (525 mg, 1.33 mmol) were dissolved in TFA (5 mL) under nitrogen in the dark and stirred for 2 h. The reaction mixture was diluted with cold methanol (15 mL) and neutralized with 10% aqueous NH_4OH. The purple precipitate was collected, redissolved in CH_2Cl_2 and washed with water. The organic phase opened to air was stirred in the daylight for 4 h. The solvent was evaporated under vacuum, and the residue was purified by chromatography on an alumina column eluted with CH_2Cl_2. The first blue band was collected to give **22/23**, which was recrystallized from CH_2Cl_2/hexane (500 mg, 66%). Mp > 300 °C; UV-Vis: λ_{max} 414 nm (ε 56 000), 630 (25 500), 660 (24 000); ^{1}H NMR ($CDCl_3$) (both regioisomers) δ 13.49 (s, 1 H), 13.31 (s, 2 H), 13.26 (s, 1 H), 7.45 (m, 10 H), 6.67 (s, 1 H), 6.68 (s, 1 H), 5.38 (s, 1 H), 5.35 (s, 1 H), 2.88 (m, 8 H), 2.56 (m, 8 H), 2.24 (s, 6 H), 2.21 (s, 6 H), 1.88 (s, 6 H), 1.59 (s, 6 H), 1.49-0.76 (m, 24 H); FAB-MS: 1139.4 (M^+), 570.2 (M^{2+}); Anal. Calcd for $C_{76}H_{82}N_8O_2 \cdot 1/2H_2O$: C, 79.51; H, 7.24; N, 9.76. Found: C, 79.67; H, 7.40; N, 9.61.

3,7,12,18-Tetraethyl-2,8,13,17-tetramethyl-15-pentafluorophenyl-5-oxophlorin 25. Dipyrroketone **3** (160 mg, 0.533 mmol) and 5-pentafluorophenyldipyrromethane-1,9-dicarboxylic acid **24** (250 mg 0.516 mmol) were dissolved in TFA (5 mL) under nitrogen in the dark and stirred for 2 h. The reaction mixture was diluted with cold methanol (15 mL) and then neutralized with 10% aqueous NH_4OH. The precipitate was collected, redissolved in CH_2Cl_2 and washed with water. The solvent was evaporated under vacuum, and the residue was purified by chromatography on an alumina column (eluted with CH_2Cl_2). The blue-violet band was collected. Recrystallization from CH_2Cl_2/cyclohexane afforded the title compound (200 mg, 57%). Mp 135-138 °C; UV-Vis: λ_{max} 404 nm (ε 140 000), 586 (17 500), 634 (24 000), 720 (7900); ^1H NMR ($CDCl_3$) δ 8.12 (s, 2 H), 3.51 (q, 4 H), 3.22 (q, 4 H), 2.73 (s, 6 H), 1.99 (s, 6 H), 1.49 (t, 6 H), 1.40 (t, 6 H), NH not observed; FAB-MS: 660.3 (M^+); Anal. Calcd for $C_{38}H_{37}F_5N_4O$: C, 69.08; H, 5.64; N, 8.48. Found: C, 68.81; H, 5.49; N, 8.45.

10,10'-Bis(3,7,12,18-tetraethyl-2,8,13,17-tetramethyl-15-pentafluorophenyl-10-iso-5-oxophlorin) 26/27. 15-Pentafluorophenyl-5-oxophlorin **25** (40 mg, 0.062 mmol) was dissolved in THF (20 mL) and treated with $K_3Fe(CN)_6$ (100 mg, 0.31 mmol). After stirring for 20 min, the solvent was evaporated under vacuum, and the residue was purified by chromatography on an alumina column using CH_2Cl_2 as eluent. Recrystallization from CH_2Cl_2/hexane afforded **26/27** (34 mg, 86%). Mp > 300 °C; UV-Vis: λ_{max} 369 nm (ε 62 000), 414 (71 000), 632 (21 500); ^1H NMR ($CDCl_3$) δ 13.38 (s, 2 H), 13.36 (s, 2 H), 6.89 (s, 2 H), 5.24 (s, 2 H), 2.59 (m, 16 H), 1.69 (s, 6 H), 1.55 (s, 6 H), 1.36 (s, 6 H), 1.23 (s, 6 H), 1.11 (m, 24 H); FAB-MS: 1319.5 (M^+), 659.3 (M^{2+}); Anal. Calcd for $C_{76}H_{72}F_{10}N_8O_2$: C, 69.18; H, 5.50; N, 8.49. Found: C, 69.06; H, 5.62; N, 8.29.

10,10',10'',10'''-Bis[1,4-di-15-(3,7,12,18-tetraethyl-2,8,13,17-tetramethyl-10-iso-5-oxophlorin)benzene] 30. Compound **28** (250 mg, 0.468 mmol) and dipyrroketone **3** (280 mg, 0.933 mmol) were dissolved in TFA (6 mL) under nitrogen in the dark and stirred for 2 h. The reaction mixture was diluted with CH_2Cl_2 and neutralized with 10% aqueous NH_4OH. The organic phase was washed with water and evaporated under vacuum. The residue was purified by filtration through a silica gel plug (CH_2Cl_2/2% MeOH as eluent, crude **29**, 200 mg, 40%). The product was redissolved in a solution of CH_2Cl_2 opened to air and stirred for 4 h in the daylight. The solvent was evaporated under vacuum and the residue was purified by chromatography on a silica gel column (eluted with CH_2Cl_2/MeOH). Recrystallization from CH_2Cl_2/hexane gave **30** (185 mg, 93%/**29**). Mp > 300 °C; UV-Vis: λ_{max} 378 nm (ε 134 000), 654 (53 000); ^1H NMR ($CDCl_3$) δ 13.20 (s, 4 H), 12.85 (s, 4 H), 7.53 (s, 4 H), 7.25 (s, 4 H), 6.88 (s, 4 H), 5.39 (s, 4 H), 2.91 (m, 8 H), 2.78 (m, 8 H), 2.62 (m, 8 H), 2.46 (m, 4 H), 2.29 (s, 12 H), 2.15 (m, 4 H), 1.66 (s, 12 H), 1.59 (s, 12 H), 1.41 (s, 12 H), 1.23 (m, 36 H), 0.77 (t, 12 H); FAB-MS: 2121.5 (M^+), 1060.7 (M^{2+}); Anal. Calcd for $C_{140}H_{152}N_{16}O_4$: C, 76.47; H, 7.51; N, 10.10. Found: C, 76.44; H, 7.36; N, 9.90.

10,10',10'',10'''-Bis[1-(15-{3,7,12,18-tetraethyl-2,8,13,17-tetramethyl-10-iso-20-methoxy-5-oxophlorin})-4-(15-{2,8,13,17-tetramethyl-3,7,12,18-tetraethyl-10'-iso-5-oxophlorin})benzene] 31. The synthetic method was identical to that for preparation of compound **30**, except that methanol (20 mL), CH_2Cl_2 (100 mL) and *p*-toluenesulfonic acid (500 mg) replaced TFA. Mp > 300°C; UV-Vis: λ_{max} 380 nm (ε 128 000), 664 (50 000); FAB-MS: 2181.1 (M^+); Anal. Calcd. for $C_{142}H_{156}N_{16}O_6$: C, 77.49; H, 7.24; N, 10.18. Found: C, 77.34; H, 7.10; N, 10.36.

10,10',10'',10'''-Bis[1,3-di-15-(3,7,12,18-tetraethyl-2,8,13,17-tetramethyl-10-iso-5-oxophlorin)benzene] 33. Bis-dipyrromethane **32** (300 mg, 0.562 mmol) and dipyrroketone **3** (337 mg, 1.12 mmol) were dissolved in TFA (5 mL) under argon in the dark and stirred for 2 h. The reaction mixture was diluted with CH_2Cl_2 and neutralized with 10% NH_4OH. The organic phase was washed with water and evaporated under vacuum. The

residue was filtered through a silica gel plug. The crude blue green oxophlorin dimer (310 mg, 52%/**3**) was redissolved in CH_2Cl_2 and stirred for 4 h open to air and in the daylight. The solvent was evaporated under vacuum and the residue was purified by chromatography on an alumina column (eluted with CH_2Cl_2). Tetramer **33** was recrystallized from CH_2Cl_2/cyclohexane (164 mg, 28%/**3**). Mp > 300 °C; UV-Vis: λ_{max} 399 nm (ε 153 000), 645 (60 000); FAB-MS: 2123.3 (MH^+), 1062.2 (MH_2^{2+}); Anal. Calcd for $C_{140}H_{152}N_{16}O_4 \cdot H_2O$: C, 78.54; H, 7.25; N, 10.47. Found: C, 78.20; H, 7.33; N, 10.18.

1-(13,17-Diethyl-2,3,7,8,12,18-hexamethylporphyrin-5-yl)-4-(1,9-diethoxycarbonyl-3,7-dimethyl-2,8-diethyldipyrromethane-5-yl)benzene 36. Bis-dipyrromethane **34** (641 mg, 0.87 mmol) and 1,9-diformyldipyrromethane **35** (290 mg, 1.10 mmol) were dissolved in CH_2Cl_2 (400 mL). *p*-Toluenesulfonic acid (1.2 g, 6.97 mmol), dissolved in methanol (25 mL), was added under nitrogen and the mixture was stirred in the dark overnight. *p*-Chloranil (295 mg, 1.2 mmol) was added and the reaction mixture was stirred for 4 h. The organic phase was washed several times with saturated aqueous $NaHCO_3$ and evaporated under vacuum. The residue was purified by chromatography on an alumina column (eluted with CH_2Cl_2). The title compound was recrystallized from CH_2Cl_2/hexane (300 mg, 35%). Mp 285-289 °C; UV-Vis: λ_{max} 402 nm (ε 245 000), 502 (43 000), 532 (36 000), 570 (32 000), 622 (26 000). ^1H NMR ($CDCl_3$) δ 10.29 (s, 2 H), 9.95 (s, 1 H), 8.49 (s, 2 H), 8.19 (d, 2 H), 8.01 (d, 2 H) , 5.89 (s, 1 H), 4.46 (q, 4 H), 4.23 (q, 4 H), 3.64 (s, 6 H), 3.52 (s, 6 H), 2.87 (q, 4 H), 2.51 (s, 6 H), 2.09 (s, 6 H), 1.89 (t, 6 H), 1.48 (t, 6 H), 1.37 (t, 6 H), -3.27 (br s, 1 H), -3.45 (br s, 1 H); FAB-MS: 898.3 (MH^+); Anal. Calcd for $C_{57}H_{66}N_6O_4$: C, 76.14; H, 7.40; N, 9.75. Found: C, 76.20; H, 7.39; N, 9.42.

1-(13,17-Diethyl-2,3,7,8,12,18-hexamethylporphyrin-5-yl)-4-(2,8-diethyl-3,7-dimethyldipyrromethane-5-yl)benzene 37. Compound **36** (270 mg, 0.31 mmol) was suspended in ethylene glycol (30 mL) containing NaOH (1 g). The mixture was heated at 190 °C under argon for 2 h, then allowed to cool to room temperature. The resulting solid was collected, washed with water and dried to give the title product (230 mg, 91%). Mp 290-293 °C. UV-Vis: λ_{max} 402 nm (ε 245 000), 502 (44 000), 534 (34 000), 570 (33 000), 624 (26 000); ^1H NMR ($CDCl_3$) δ 10.29 (s, 2 H), 10.01 (s, 1 H), 8.05 (d, 2 H), 7.59 (s, 2 H), 7.49 (d, 2 H), 6.59 (s, 2 H), 5.87 (s, 1 H), 4.13 (q, 4 H), 3.61 (s, 6 H), 3.36 (s, 6 H), 2.71 (q, 4 H), 2.44 (s, 6 H), 1.95 (s, 6 H), 1.21 (m, 12 H), -3.23 (br s, 2 H); FAB-MS: 754.4 (MH^+); Anal. Calcd for $C_{51}H_{58}N_6 \cdot 3H_2O$: C, 75.71; H, 7.97; N, 10.39. Found: C, 75.83; H, 7.37; N, 10.42.

10,10'-Bis-[15-(*p*-{13,17-diethyl-2,3,7,8,12,18-hexamethylporphyrin-5-yl}phenyl)-2,18-diethyl-3,7,8,12,13,17-hexamethyl-10-iso-5-oxophlorin] 38. Compound **37** (200 mg, 0.275 mmol) and dipyrroketone **3** (105 mg, 0.35 mmol) were dissolved in TFA (8 mL) under nitrogen in the dark and stirred overnight. The reaction mixture was diluted with CH_2Cl_2 and washed several times with saturated aqueous $NaHCO_3$. The organic phase was separated and dried over sodium sulfate. The product was then stirred in a solution of CH_2Cl_2 opened to air for 4 h in the daylight. The solvent was evaporated under vacuum and the residue was purified by chromatography on alumina, eluting with CH_2Cl_2. The main brown-reddish band was collected; the solvent was evaporated under vacuum and the residue was recrystallized from CH_2Cl_2/hexane to give 210 mg of the title compound (39%). Mp > 300 °C. UV-Vis: λ_{max} 404 nm (ε 243 000), 502 (42 000), 534 (33 000), 572 (32 000), 624 (25 000). FAB-MS: 2036.8 (MH^+), 1018.4 (MH_2^{2+}); Anal. Calcd for $C_{136}H_{146}N_{16}O_2$: C, 80.02; H, 7.23; N, 11.00. Found: C, 79.95; H, 7.10; N, 10.75.

1-(10,15,20-Triphenylporphyrin-5-yl)-4-[1,9-bis(ethoxycarbonyl)-2,3,7,8-tetramethyldipyrromethan-5-yl]benzene 41. 5-(*p*-Formylphenyl)-10,15,20-triphenylporphyrin **39** (500 mg, 0.78 mmol), ethyl 3,4-

dimethylpyrrole-2-carboxylate **40** (300 mg, 1.8 mmol) and *p*-toluenesulfonic acid (100 mg) were dissolved in toluene (50 mL) and the solution was refluxed for 2 h. After cooling to room temperature the reaction mixture was diluted with CH_2Cl_2 (200 mL) and washed with water and saturated aqueous $NaHCO_3$. The solvents were evaporated under vacuum and the residue was purified by chromatography on silica gel column (eluted with CH_2Cl_2). The red fraction was collected, evaporated under vacuum and recrystallized from CH_2Cl_2/methanol to give the title compound as red crystals (613 mg, 82%). Mp > 300 °C; UV-Vis: λ_{max} 419 nm (ε 200 000), 515 (16 000), 550 (12 000), 590 (10 000), 646 (9000); ^1H NMR ($CDCl_3$) δ 8.85 (s, 8 H), 8.13 - 7.75 (m, 21 H), 5.82 (s, 1 H), 4.36 (q, 4 H), 2.48 (s, 6 H), 2.02 (s, 6 H), 1.62 (t, 6 H), -2.80 (br, 2 H); FAB-MS : 959.0 (MH^+); Anal. Calcd for $C_{63}H_{54}N_6O_4$: C, 78.89; H, 5.67; N, 8.76. Found: C, 78.42; H, 5.86; N, 8.59.

1-(10,15,20-Triphenylporphyrin-5-yl)-4-(2,3,7,8-tetramethyldipyrromethan-5-yl)benzene 42. Diethyl ester **41** (250 mg, 0.26 mmol) was suspended in ethylene glycol (25 mL) containing NaOH (1 g). The mixture was heated at 190 °C under argon for 2 h, then allowed to cool to room temperature. The resulting solid was filtered, washed with water, and dried to give the title product (190 mg, 89%). Mp > 300 °C; UV-Vis: λ_{max} 419 nm (ε 202 000), 516 (18 700), 549 (14 400), 592 (11 600), 647 (8800). ^1H NMR ($CDCl_3$) δ 8.88 (s, 8 H), 8.12 - 7.62 (m, 21 H), 6.42 (s, 2H), 5.77 (s, 1 H), 2.03 (s, 6 H), 1.99 (s, 6 H), -2.76 (br, 2 H); Anal. Calcd for $C_{57}H_{46}N_6$: C, 84.00; H, 5.69; N, 10.31. Found: C, 83.80; H, 5.61; N, 10.16.

10,10'-Bis-(15-[*p*-(10,15,20-triphenylporphyrin-5-yl)phenyl]-2,18-diethyl-3,7,8,12,13,17-hexamethyl-10-iso-5-oxophlorin) 43. Porphyrinyl-dipyrromethane **42** (100 mg, 0.12 mmol) and dipyrroketone **3** (40 mg, 0.13 mmol) were dissolved in TFA (20 mL) under nitrogen in the dark and stirred for 1 h. The reaction mixture was diluted with CH_2Cl_2 and washed several times with aqueous NH_4OH. The organic phase was separated, stirred for 4 h at room temperature, then dried over sodium sulfate. Solvents were removed under vacuum and the residue was purified by chromatography on an alumina column (CH_2Cl_2 as eluent). Compound **43** was recrystallized from CH_2Cl_2/hexane (63 mg, 48%). Mp > 300 °C; UV-Vis: λ_{max} 372 nm (ε 124 000), 419 (388 000), 517 (53 000), 550 (35 000), 596 (28 500), 651 (50 000); ^1H NMR ($CDCl_3$) δ 13.58, 13.52, 13.21, 13.18 (each br s, 4 H), 8.89 (br s, 16 H), 8.28 - 7.61 (m, 38 H), 6.92 (s, 2 H), 5.30 (d, 2 H), 2.80 (m, 8 H), 2.20, 2.18, 2.16, 2.02, 1.90, 1.78, 1.70, 1.63 (each s, total 36 H), 1.19 (t, 12 H), -2.72 (br s, 2 H), -3.02 (br s, 2 H); FAB-MS: 2157 (MH^+), 1078 (MH_2^{2+}); Anal. Calcd for $C_{148}H_{122}N_{16}O_2$: C, 82.42; H, 5.70; N, 10.39. Found: C, 81.99; H, 5.53; N, 10.18

1-[(2,3,17,18-Tetraethyl-7,8,12,13-tetramethyl)-a,c-biladien-10-yl]-4-(1,9-diethoxycarbonyl-2,3,7,8-tetramethyldipyrromethan-5-yl)benzene Dihydrobromide 46. Bis-dipyrromethane **44** (500 mg, 0.703 mmol) was dissolved in TFA (20 mL) and stirred for 5 min. 2-Formyl-3,4-diethylpyrrole **45** (215 mg, 1.42 mmol) in MeOH (20 mL) was added and the red solution was stirred for 15 min before adding a 30% solution of HBr in acetic acid (5 mL). After dropwise addition of diethyl ether (50 mL), the a,c-biladiene salt **46** precipitated as a red-green powder (540 mg, 73 %). Mp > 300 °C. UV-Vis: λ_{max} 453 nm (ε 135 000), 520 (74 000). Anal. Calcd for $C_{56}H_{70}Br_2N_6O_4$: C, 64.00; H, 6.71; N, 8.00. Found: C, 64.12; H, 6.45; N, 8.11.

1-[(2,3,17,18-Tetraethyl-7,8,12,13-tetramethyl)-corrol-10-yl]-4-(1,9-di-ethoxycarbonyl-2,3,7,8-tetramethyldipyrromethan-5-yl)benzene 47. a,c-Biladiene **46** (500 mg, 0.49 mmol) was dissolved in MeOH saturated with $NaHCO_3$. *p*-Chloranil (500 mg, 2.0 mmol) was added. The solution was stirred for 5 min at room temperature and then 15% N_2H_4 in water (2 mL) was added. The solvent was evaporated under vacuum and residue was purified by chromatography on an alumina column (CH_2Cl_2 as eluent). The red-green band

was collected to give the title corrole which was recrystallized from CH_2Cl_2/hexane (224 mg, 53%). Mp > 300 °C; UV-Vis: λ_{max} 401 nm (ε 111 000), 413 (107 000), 546 (31 000), 598 (28 000). ^1H NMR ($CDCl_3$) δ 9.40 (s, 2 H), 8.44 (s, 2 H), 7.96 (d, 2 H), 7.40 (d, 2 H), 5.82 (s, 1 H), 4.37 (q, 4 H), 4.00 (q, 4 H), 3.87 (q, 4 H), 3.32 (s, 6 H), 2.38 (s, 6 H), 2.37 (s, 6 H), 1.99 (s, 6 H), 1.76 (m, 12 H), 1.41 (t, 6 H), -2.60 (br, 3 H); FAB-MS : 887 (M^+); Anal. Calcd for $C_{56}H_{66}N_6O_4$: C, 75.82; H, 7.50; N, 9.47. Found: C, 75.42; H, 7.86; N, 9.29.

1-[(2,3,17,18-Tetraethyl-7,8,12,13-tetramethyl)-corrol-10-yl]-4-(2,3,7,8-tetramethyldipyrromethan-5-yl)benzene 48. Compound **47** (120 mg, 0.14 mmol) was suspended in ethylene glycol (25 mL) containing NaOH (1 g). The mixture was heated at 190 °C under argon for 2 h, then allowed to cool to room temperature. The resulting solid was filtered, washed with H_2O, and dried to give the title product (91 mg, 90%). Mp 245-248 °C (dec.); UV-Vis: λ_{max} 403 nm (ε 106 000), 413 (105 000), 548 (35 000), 596 (29 000); ^1H NMR ($CDCl_3$) δ 9.33 (s, 2 H), 8.45 (s, 2 H), 7.91 (d, 2 H), 7.32 (d, 2 H), 6.74 (s, 2 H), 5.90 (s, 1 H), 4.12 (q, 4 H), 3.86 (q, 4 H), 3.31 (s, 6 H), 2.38 (s, 6 H), 2.34 (s, 6 H), 1.96 (s, 6 H), 1.76 (m, 12 H), -2.81 (br, 3 H); Anal. Calcd for $C_{50}H_{58}N_6$: C, 80.82; H, 7.87; N, 11.31. Found: C, 80.80; H, 7.61; N, 11.56.

10,10'-Bis-(15-[*p*-{2,3,17,18-tetraethyl-7,8,12,13-tetramethylcorrol-10-yl}phenyl]-2,18-diethyl-3,7,8,12,13,17-hexamethyl-10-iso-5-oxophlorin) 49. Corrolyl-dipyrromethane **48** (130 mg, 0.126 mmol) and dipyrroketone **3** (55 mg, 0.183 mmol) were dissolved in CH_2Cl_2 (50 mL) and *p*-toluenesulfonic acid (100 mg, 0.581 mmol) was added under nitrogen in the dark. The reaction was diluted with CH_2Cl_2 and washed several times with saturated aqueous $NaHCO_3$ and stirred for 1 h. The solvent was evaporated under vacuum and the residue purified by chromatography on an alumina column (eluting with CH_2Cl_2). Compound **49** was recrystallized from CH_2Cl_2/hexane (42 mg, 31%); Mp > 300 °C; UV-Vis: λ_{max} 366 nm (ε 52 000), 449 (41 000), 626 (20 000); ^1H NMR (300 MHz, $CDCl_3$) δ 13.10 (br d, 2H), 12.82 (br d, 2 H), 9.45 (s, 4 H), 8.00, 7.56 (d, 8 H), 6.94 (s, 2 H), 5.61 (d, 2 H), 4.00 (q, 8 H), 3.96 (q, 8 H), 3.51 (s, 12 H), 3.04 (s, 12 H), 2.62 (q, 8 H), 2.25 (s, 12 H), 2.21 (s, 12 H), 2.00 (s, 12 H), 1.80 (t, 36 H), -2.53 (br, 6 H); FAB-MS: 2012 (MH^+); Anal. Calcd for $C_{134}H_{146}N_{16}O_2$: C, 79.96; H, 7.31; N, 11.13. Found: C, 80.43; H, 7.14; N, 10.66.

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