A Novel Synthetic Route to Sapphyrins

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New methodology has been developed for the synthesis of so-called sapphyrins, pentapyrrolic "expanded porphyrins". An efficient approach involving acid-catalyzed condensation of 1,19-diunsubstituted a,c-biladienes and 3,4-dialkylpyrrole-2-carbaldehydes eliminates the preparation of bipyrrolic intermediates and allows the synthesis of sapphyrins with an unsymmetrical array of peripheral substituents. The β-substitution pattern of 2,3,13,17-tetraethyl-7,8,12,18,22,23-hexamethylsapphyrin has been unambiguously confirmed by single crystal X-ray crystallography. ^{1}H NMR spectra of the dication salts of sapphyrins are strongly dependent upon the counterions, and the pattern of resonances observed in solution is related to the stacking interactions between the macrocycles.

Introduction

Porphyrins represent one of the most fascinating ligands because of their presence in Nature and their unique properties as ligands and photoactive materials.[1] Several disciplines, including for example chemistry, medicine and materials science, are interested in the properties of porphyrins and in possible applications.[2] The porphyrin macrocycle is widely considered to be the pyrrole-containing ligand "par excellence", but a large number of related macrocycles have been synthesized recently in order to study the structure and property relationships and even to improve upon some unique characteristics of the tetrapyrrole chromophore.[3] Thus, a number of different oligopyrrolic macrocycles have assumed importance during the past decades, allowing them to move out from the shadow of porphyrins and to expand their own subfield of study.

One subfield which has been extensively studied is the area of "expanded porphyrins"; this group includes macrocycles with an aromatic system larger than that found in porphyrins.[4] They are of both theoretical and practical importance because the expanded π-system allows (1) the study of aromaticity in a large conjugated system, and (2) the coordination of large metal ions due to the expanded core size, thereby expanding upon the coordination properties of the traditional porphyrin system.

Sapphyrin was the first example of an "expanded porphyrin" to be reported in the literature;[5] it was serendipitously prepared by Woodward and co-workers some 30 years ago during the Harvard attempt to synthesize vitamin B_{12}. The molecular skeleton of sapphyrin is shown in structure **1**. It consists of five pyrrole rings linked by four methine bridges and one direct pyrrole−pyrrole bond; it has an aromatic 22-electron π-system as confirmed by its visible absorption spectrum which shows a Soret-like band around 450 nm, and by the presence in the ^{1}H NMR spectrum of diamagnetic ring current effects.[6] The macrocycle shows higher basicity than in porphyrins, this being manifested in the fact that it is normally obtained as a dication after chromatography on silica gel. The sapphyrin monocation and free base can be obtained by controlled addition of bases to the dication.[6]

The original synthesis of sapphyrins reported by Bauer et al.[7] involves 17 steps, and one might speculate that such a difficult and tedious preparation is probably one reason why no reports appeared on sapphyrins for almost a decade after the first paper. In 1990, Sessler and co-workers improved the synthetic route to sapphyrins by streamlining the preparation of the pyrrolic intermediates, thus allowing an easier approach to the macrocycles.[8] Just as impressive was Sessler's discovery of certain properties of sapphyrins, such as anion binding[9] and photoactivity.[10] Although these reports greatly increased the interest and the potential applications of these macrocycles, the synthetic pathway to sapphyrins was still based on the original approach developed by Woodward and co-workers, and the introduction of different substituents at the peripheral positions remained a significant challenge. In this paper we report a new and powerful route to sapphyrins, together with a NMR study of some of their solution properties.

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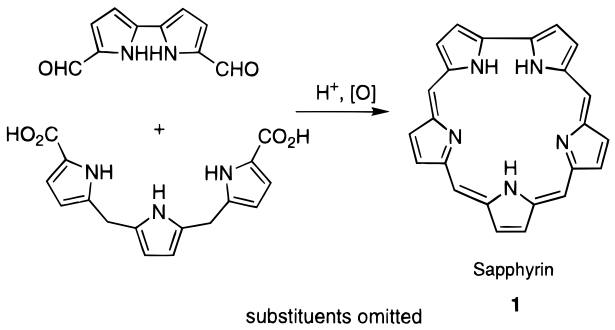
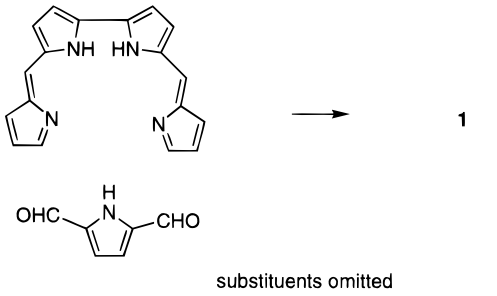
Scheme 1



Scheme 2



Results and Discussion

The classical synthetic route to sapphyrins[7] consists of the ["3 + 2"] MacDonald-type condensation of a tripyrrane dicarboxylic acid and a bipyrrole dialdehyde (Scheme 1). Synthetic routes to these intermediates are long and difficult. Along with Sessler's improvements by optimization of the routes to the two pyrrolic precursors,[8] another route was also reported by the same authors;[7] in this case the final step is a ["4 + 1"] condensation of a bipyrryldipyrromethene and a pyrrole dialdehyde (Scheme 2), but this was not developed further because it was found to be less efficient and even more difficult than the traditional ["3 + 2"] route. More recently, Sessler and co-workers reported the preparation of *meso*-diaryl substituted sapphyrins,[11] by way of a Lindsey-type reaction of benzaldehyde, pyrrole, and bipyrrole dialdehyde. However, the postulated mechanism is the same as previously in that a tripyrrane is formed *in situ* through reaction of the arylaldehyde and pyrrole; this then condenses with the bipyrrole moiety. These approaches have as a common and essential requisite, the formation of the direct pyrrole−pyrrole link at an early stage in the protocol. Furthermore these routes are inherently limited to the synthesis of sapphyrins with symmetrical peripheral substitution patterns, because of the difficulties involved in the preparation of appropriate unsymmetrically substituted intermediates.

During our studies on the synthesis of metallocorrolates we serendipitously discovered that sapphyrins are formed in low yields when 1,19-diunsubstituted a,c-biladiene salts are treated with certain transition metal salts in boiling ethanol.[12] The formation of sapphyrins, albeit in low yields, from the acidic condensation of a bipyrrole dialdehyde and a dipyrromethane-1,9-dicarboxylic acid, or from acidic condensation of 3,4-dimethylpyrrole and 3,4-dimethylpyrrole-2,5-dialdehyde, was also reported by Bauer et al.[7] More recently Latos-Grazynski and co-workers reported the identification of 5,10,15,20-tetraphenylsapphyrin, formed in very low yield in the Rothemund synthesis of *meso*-tetraphenylporphyrin.[13] These reports led us to explore the possibility for development of a synthetic route to sapphyrins wherein the direct pyrrole−pyrrole link is formed as the last step of the synthesis, an approach similar to that successfully employed in the preparation of corroles.[14] Such a pathway has the great advantage that it avoids the preparation of the tripyrrane and bipyrrole precursors and also widely expands the potential substitution arrays that can be introduced at the peripheral positions of the macrocycle, thereby permitting the preparation of less symmetrical sapphyrins. Our previous results in the chemistry of metallocorrolates led us to consider a,c-biladienes as potential intermediates in this synthetic route. These linear tetrapyrroles are used for the preparation of a wide range of tetrapyrrolic macrocycles in which the type of product depends upon the substitution pattern at the 1,19-positions.[15]

1,19-Diunsubstituted a,c-biladiene salts are known to react with aldehydes in acidic ethanol to afford the corresponding porphyrins in good yields;[16] our approach was to condense, under the same conditions, the biladiene with a 2-formylpyrrole, hypothesizing that the supposed pentapyrrolic intermediate might cyclize to sapphyrin rather than to porphyrin (Scheme 3). The first compounds tested were a,c-biladiene dihydrobromide **2** and 2-formyl-3,4-dimethylpyrrole **3**; success would afford the symmetric and previously reported[7] decamethylsapphyrin **4**. Spectrophotometry was used to monitor the reaction progress by observing the decrease of the two absorbances characteristic of the a,c-biladiene[17] and the concomitant increase of an absorption around 450 nm that can be attributed to the formation of the sapphyrin dication, the product expected in acidic solution. Two other intense bands were present in the reaction mixture. The first, at 500 nm, is presumably related to the formation of a dipyrromethene aldehyde, formed by the self-condensation of two pyrrole aldehydes in acidic ethanol;[18] an absorption at 409 nm was attributable to a cationic tetrapyrrolic macrocycle (corrole or porphyrin). After chromatographic separation, the reaction afforded the decamethylsapphyrin **4** in good yield as its dication salt. The nature of the counterion was influenced by the purification procedures—*p*-toluensulfonate salts were obtained if the reaction mixture is washed with water before the chromatographic separation, while the corresponding dihydrochloride was obtained if the reaction mixture was treated with saturated Na_2CO_3 and then with dilute HCl.

Two other products were also isolated from the reaction mixture, albeit in lower yields. These were octamethylporphyrin **5** and octamethylcorrole **6**. The presence of methyl groups as the only β-substituents did not allow

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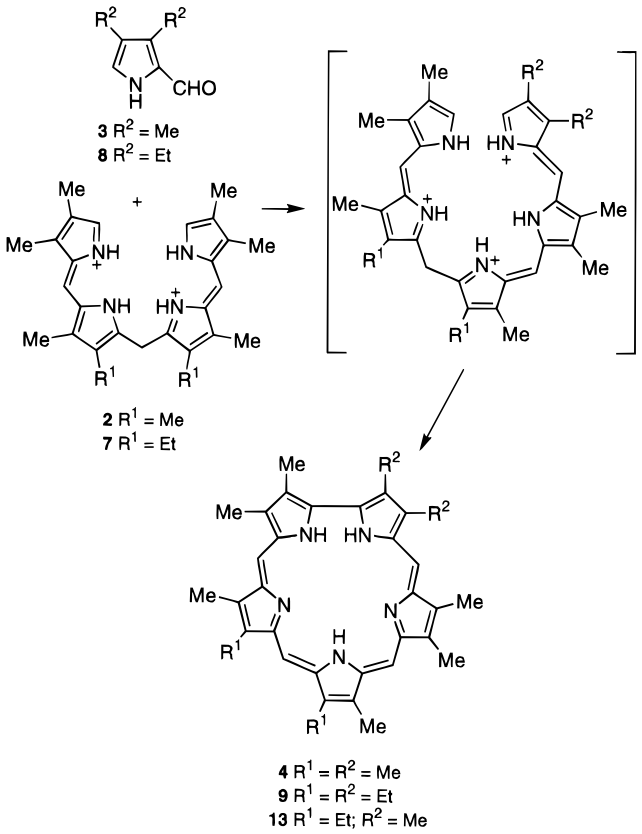
Scheme 3



any speculation on the mechanistic pathway involved in the formation of these products. In order to elicit more information about the reaction mechanism and to explore the possibility for access to unsymmetrical sapphyrins, a,c-biladiene dihydrobromide **7** was treated with pyrrole aldehyde **8** under the same synthetic conditions as reported above. The sapphyrin **9** was obtained in good yield. The peripheral substitution array was further confirmed by X-ray analysis of a single crystal of the di-*p*-toluensulfonate salt (Figure 1). The macrocycle exhibits a mean plane deviation of 0.12 Å from the 29 core atoms with the pyrrole ring bearing both ethyl substituents slightly bent out of plane. The peripheral substitution pattern of this sapphyrin indicates that the reaction proceeds through the condensation of the pyrrole aldehyde onto the biladiene skeleton. There was no indication of the formation of a pentapyrrolic species during the reaction, but that can be attributed to a fast subsequent cyclization of this intermediate.

Once again both porphyrin and corrole were obtained as secondary products of the reaction. The porphyrin was identified as octaethylporphyrin **10** by ^{1}H NMR spectroscopy and FAB-MS analysis and by comparison with an authentic sample; traces of a different porphyrin, 8,12-diethyl-2,3,7,13,17,18-hexamethylporphyrin **11** were also observed. A possible route for the formation of **10** is shown in Scheme 4, and this involves coupling of two dipyrromethene aldehydes formed from the condensation of two molecules of **8**.[18] This hypothesis was confirmed by synthesis of the dipyrromethene aldehyde from **8** in acidic methanol and then reacting it in acidic ethanol to afford **10**. The small amount of **11** is probably a result of the decomposition of the a,c-biladiene and scrambling of the pyrrolic fragments. The corrole product was identified as 8,12-diethyl-2,3,7,13,17,18-hexamethylcorrole **12** by ^{1}H NMR spectroscopy and FAB-MS analysis

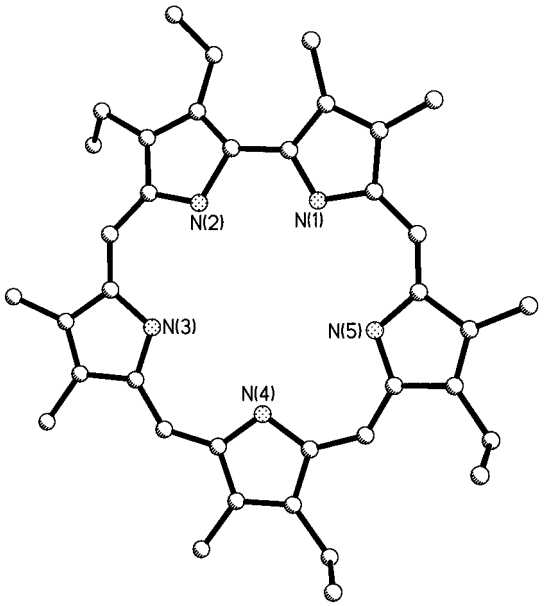
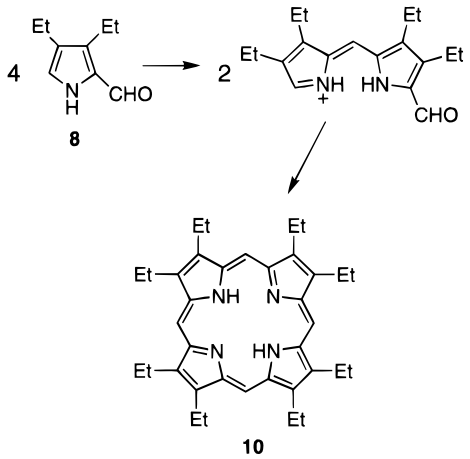


Figure 1. Molecular structure of sapphyrin **9**. Hydrogen atoms have been omitted for clarity.

Scheme 4



and also by the comparison with an authentic specimen. The formation of this compound is surprising because it is well known that corroles are obtained from base-catalyzed cyclization of biladienes, via formation of the bilatriene free base.[14] The formation of **12** seems to indicate the possibility for such cyclizations to occur also under acidic conditions.

Sapphyrin **13** was synthesized from **7** and **3** following the same procedure as reported above. Again porphyrin and corrole were obtained as byproducts of the reaction; the formation of **5** and **12** further confirmed the proposed reaction pathway.

Acetic acid can be used as the reaction solvent, instead of acidic ethanol. Under these circumstances the reaction time is shorter, but the yields of sapphyrin are comparable with those obtained in the alcoholic solvent system.

The ^{1}H NMR spectra of unsymmetrical sapphyrins are strongly dependent upon the peripheral substituent pattern and upon the nature of the counterions; such dependence is clearly demonstrated by observing the low-field region of the spectra. In the case of the dication of the symmetrically substituted decamethylsapphyrin, two resonances are observed for the meso protons, as previously reported;[7] however, different patterns are observed,

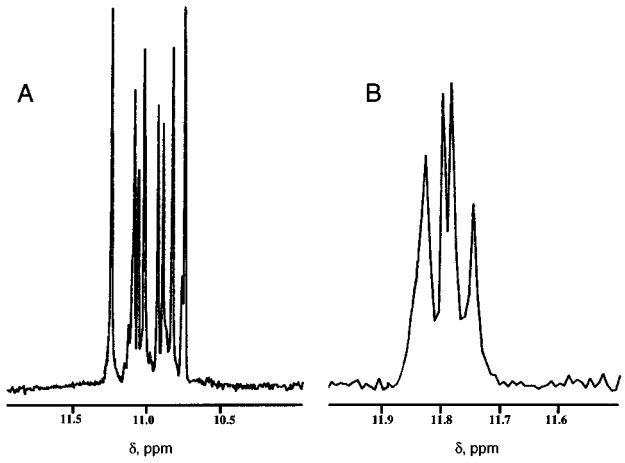


Figure 2. Changes in the ^{1}H NMR spectrum of $[2H\cdot\mathbf{9}]^{2+}[F^- PF_6^-]$ in $CDCl_3$ by dilution: trace A, 10^{-3} M solution; trace B, 10^{-5} M solution.

even in $CDCl_3$, in the spectra of the $[2H\cdot\mathbf{9}^{2+}]^{2+}[X^-Y^-]$ species, where X and Y represent the counterions. When X = Y = Cl^-, four resonances are observed, as expected on the basis of symmetry considerations, while eight peaks are present in the spectrum when X = Y = *p*TSA$^-$ or X = F^- and Y = PF_6^-. The effect of dilution upon the spectral pattern is shown in Figure 2 for $[2H\cdot\mathbf{9}]^{2+}[F^- PF_6^-]$; trace A shows the low field region of the spectrum of a 10^{-3} M solution, with eight resonances meso-proton between 11.25 and 10.80 ppm. At 10^{-5} M the spectrum shown in trace B is observed, with only four resonances shifted to lower field (11.83−11.75 ppm). Such spectral changes are consistent with the unsymmetrical sapphyrin molecules existing as stacked aggregates, even in $CHCl_3$. The NMR data interpretation is confirmed by the observation that Beer's law is not observed by $[2H\cdot\mathbf{9}]^{2+}(p\text{TSA})_2$ even in $CHCl_3$.

Conclusions

Fully 30 years since their original disclosure, sapphyrins are increasing in interest due notably to their unusual chemical, physical, and spectroscopic characteristics. A novel synthetic approach is reported which allows the preparation of sapphyrins by an acidic condensation reaction between 1,19-diunsubstituted a,c-biladienes and 3,4-dialkylpyrrole-2-carbaldehydes. This methodology avoids the preparation of bipyrrolic intermediates and enables the preparation of sapphyrins with an unsymmetrical distribution of the peripheral substituents; such substances were previously impossible to obtain using the classical MacDonald-type approach.

Experimental Section

General conditions are as previously reported,[19] with the exception that ^{1}H NMR spectra were measured in $CDCl_3$ solution at 400 MHz using a Bruker AM 400 spectrometer, mass spectra were obtained using a VG Quattro spectrometer (FAB mode), elemental analyses were obtained from the Microanalytical Laboratory at University of Padova, Italy, and electronic absorption spectra were measured in CH_2Cl_2 or $CHCl_3$ using a Philips PU8700 spectrophotometer.

2,3,13,17-Tetraethyl-7,8,12,18,22,23-hexamethylsapphyrin (9). Route a. Pyrrole **8** (0.5 g, 3.31 mmol),[16a] a,c-biladiene dihydrobromide **7** (0.5 g, 0.83 mmol),[16a] and TsOH hydrate (0.25 g) were dissolved in 100 mL of absolute ethanol, and the mixture was heated at reflux in the dark (aluminum foil). Progress of the reaction was monitored spectrophotometrically; when absorbances attributable to **7**[14] disappeared, the solvent was evaporated under vacuum, the resulting solid was redissolved in CH_2Cl_2, washed with water (three times), and dried over anhyd Na_2SO_4. The solvent was evaporated under vacuum, and the crude mixture was chromatographed on silica gel; the column was first eluted with CH_2Cl_2 to yield two bands. The first (red-brown) fraction to be eluted contained **10** (65 mg) together with traces of **11**, while the second (red-violet) fraction contained **12** (48 mg). These compounds were identified on the basis of comparison of their spectral properties with those in the literature[1,2,14] and by comparison with authentic samples. The column was then eluted with CH_2Cl_2 containing increasing amounts of methanol (2−10%). A green fraction was collected, the solvent was evaporated under vacuum, and the residue was crystallized from CH_2Cl_2/hexane to give **9** as its *p*-toluensulfonate salt (158 mg, 20%), mp > 300 °C. UV-vis: λ_{max} 434 nm (ϵ 112 000), 456 (360 000), 579 (6500), 627 (16 000), 680 (18 500); ^{1}H NMR: δ 11.50, 11.48, 11.46, 11.45, 11.43, 11.40, 11.38, 11.34 (s, 4 H), 5.33 (d, *J* 8.0 Hz, 4 H), 4.64/4.45 (m, 12 H), 4.20/4.05 (s, 18 H), 2.30 (t, *J* 8.0 Hz, 12 H), 1.85 (s, 6 H), −5.22/-5.81 (br s, 5 H). FAB-MS: 573 (M^+); 287 (M^{2+}). Anal. Calcd for $C_{52}H_{61}N_5O_6S_2$: C, 68.17; H, 6.71; N, 7.64. Found: C, 68.05; H, 6.94; N, 7.21. The dihydrochloride derivative was obtained by washing a CH_2Cl_2 solution of $[2H\cdot\mathbf{9}^{2+}](p\text{TSA})_2$ with saturated Na_2CO_3 until spectrophotometry showed the formation of the corresponding free base; subsequent treatment with dilute HCl quantitatively afforded $[2H\cdot\mathbf{9}^{2+}]Cl_2$. UV-vis: λ_{max} 456 nm (ϵ 551 000), 577 (5 200), 627 (15 500), 681 (19 100). ^{1}H NMR: δ 11.69, 11.66, 11.63, 11.60 (s, 4 H), 4.71 (m, 8 H), 4.24/4.05 (s, 18 H), 2.28 (t, *J* 7.5 Hz, 12 H), −4.22, −4.24, −4.47, 4.88, 4.92 (br s, 5 H). Anal. Calcd for $C_{38}H_{47}Cl_2N_5$: C, 70.79; H, 7.35; N, 10.86. Found: C, 70.56; H, 7.11; N, 10.31. $[2H\cdot\mathbf{9}^{2+}](F)(PF_6)$ can be obtained following the procedure previously reported by Sessler.[8a]

Route b. Pyrrole **8** (0.5 g, 3.31 mmol) and biladiene **7** (0.5 g, 0.83 mmol) were dissolved in 100 mL of acetic acid and refluxed under dark (aluminum foil) for 1 h. The solvent was evaporated under vacuum, and the resulting solid was redissolved in CH_2Cl_2, washed with saturated Na_2CO_3 and then with dilute HCl, and dried over anhyd Na_2SO_4. The solvent was evaporated under vacuum and the crude mixture was chromatographed on silica gel as reported in route a. The appropriate green fraction was collected, the solvent was vacuum evaporated to give $[2H\cdot\mathbf{9}^{2+}]Cl_2$ (98 mg, 18%).

13,17-Diethyl-2,3,7,8,12,18,22,23-octamethylsapphyrin (13). This sapphyrin was obtained following the procedure described above for **9**, starting from **3** (0.5 g, 4.06 mmol)[16a] and **7** (0.5 g, 0.83 mmol). In this case **5** (42 mg) and **12** (54 mg) were obtained as byproducts; $[2H\cdot\mathbf{13}^{2+}](p\text{TSA})_2$ was obtained in 24% yield (184 mg). Mp > 300 °C. UV-vis: λ_{max} 432 nm (ϵ 69 000), 457 (415 000), 577 (4 600), 628 (15 000), 683 (18 000). ^{1}H NMR: δ 11.51, 11.49, 11.43, 11.39 (s, 4 H), 5.34 (d, *J* 8.0 Hz, 4 H), 4.65 (m, 8 H), 4.20/4.05 (s, 24 H), 2.31 (t, *J* 8.0 Hz, 6 H), 1.88 (s, 6 H), −5.20, −5.35, −5.75, −5.80 (br s, 5 H). FAB-MS: 545 (M^+); 273 (M^{2+}). Anal. Calcd for $C_{50}H_{57}N_5O_6S_2$: C, 67.62; H, 6.47; N, 7.89. Found: C, 67.32; H, 6.71; N, 7.91. $[2H\cdot\mathbf{13}^{2+}]Cl_2$ was obtained as reported for **9**. UV-Vis: λ_{max} 456 nm (ϵ 524 000), 576 (5 500), 624 (16 000), 686 (19 000). ^{1}H NMR: δ 11.60, 11.56, 11.51, 11.45 (s, 4 H), 4.60 (m, 4 H), 4.22, 4.04 (s, 24 H), 2.20 (t, *J* 7.0 Hz, 6 H), 1.88 (s, 6 H), −4.34, −4.40, −4.74, −5.06, −5.10 (br s, 5 H). Anal. Calcd for $C_{36}H_{43}Cl_2N_5$: C, 70.12; H, 7.03; N, 11.36. Found: C, 69.99; H, 7.11; N, 11.11.

2,3,7,8,12,13,17,18,22,23-Decamethylsapphyrin (4). This compound was obtained in 21% yield from **2**[14] and **3**, as reported above. Spectral properties were in accord with data previously reported[7] and with an authentic sample prepared according to the literature.[7]

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Crystallographic Structure Determination for $C_{54}H_{65}Cl_4N_5O_6S_2$.[20] Crystals were grown from CH_2Cl_2/*n*-hexane. A square single crystal was selected with dimensions 0.7 × 0.7 × 0.44 mm. The unit cell was triclinic, space group *P* with cell dimensions: $a = 9.847(2)$ Å, $b = 14.222(3)$ Å, $c = 20.402(4)$ Å, $\alpha = 71.13(3)°$, $\beta = 86.25(3)°$, $\gamma = 80.36(3)°$, $V = 2665.2(9)$ Å^3, $Z = 2$ (FW = 1077.97). X-ray diffraction data were collected on a Siemens $P2_1$ diffractometer with a fine-focus sealed tube [λ(Cu Kα) = 1.54178 Å] at 130(2) K in $\theta/2\theta$ scan mode to $2\theta_{max} = 112°$. Of 7028 reflections measured ($\pm h,\pm k,\pm l$), 6909 were independent and 5434 had $I > 2s$ ($R_{int} = 0.014$). 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. 5.02); number of parameters = 441. Hydrogen atom positions were located by their idealized geometry and refined using a riding model. An absorption correction was applied using XABS2.[21] Final *R* factors were $R1 = 0.1078$ (based on observed data) and $wR2 = 0.3161$ (based on all data).

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(20) For experimental procedures and programs used see: Senge, M. O.; Hope, H.; Smith, K. M. *J. Chem. Soc., Perkin Trans. 2* **1993**, 11. The authors have deposited atomic coordinates and a full structure description for **9** with the Cambridge Crystallographic Data Centre. The structure can be obtained upon request from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

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