anisotropically defined. H atoms were placed in calculated positions using the riding model. CCDC-175844 (**1**), CCDC-175845 (**1**·LiF), and CCDC-175846 (**1**·$LiBF_4$) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[8] R. A. Bartsch, V. Ramesh, R. O. Bach, T. Shono, K. Kimura in *Lithium Chemistry* (Eds.: A.-M. Sapse, P. von R. Schleyer), Wiley, New York, **1995**, pp. 393 – 476.

[9] a) A. Demsar, A. Pevec, L. Goliè, S. Petrièek, A. Petriè, H. W. Roesky, *Chem. Commun.* **1998**, 1029 – 1030; b) H. Plenio, R. Diodone, *J. Am. Chem. Soc.* **1996**, *118*, 356 – 367; c) A. Künzel, H. W. Roesky, M. Noltemeyer, H.-G. Schmidt, *Chem. Commun.* **1995**, 2145 – 2146; d) S. Walter, U. Klingebiel, *Coord. Chem. Rev.* **1994**, *130*, 481 – 508.

[10] A. F. Wells, *Structural Inorganic Chemistry*, Claredon Press, Oxford, UK, 4th ed., **1975**, p. 375.

[11] U. Klingebiel, M. Meyer, U. Pieper, D. Stalke, *J. Organomet. Chem.* **1991**, *408*, 19 – 25.

[12] For attractive CH···F interactions see: a) M. Güizado-Rodríguez, A. Ariza-Castolo, G. Merino, A. Vela, H. Nöth, V. I. Bakhmutov, R. Contreras, *J. Am. Chem. Soc.* **2001**, *123*, 9144 – 9152; b) W. B. Farnham, D. C. Roe, D. A. Dixon, J. C. Calabrese, R. L. Harlow, *J. Am. Chem. Soc.* **1990**, *112*, 7707 – 7718.

[13] After several hours a second set of signals appear which we assign to the complex **1**·LiFHF. The formation of hydrogen difluoride in solutions of F^- ions in CH_3CN has been described: K. O. Christe, W. W. Wilson, *J. Fluorine Chem.* **1990**, *47*, 117 – 120.

[14] Other metallacrown complexes which differentially bind anions have been described in: a) A. D. Cutland, J. A. Halfen, J. W. Kampf, V. L. Pecoraro, *J. Am. Chem. Soc.* **2001**, *123*, 6211 – 6212; b) J. J. Bodwin, A. D. Cutland, R. G. Malkani, V. L. Pecoraro, *Coord. Chem. Rev.* **2001**, *216 – 217*, 489 – 512, and references therein.

[15] P. D. Beer, *Chem. Soc. Rev.* **1989**, *18*, 409 – 450.

[16] The experiments were performed with a glassy carbon working electrode and an Ag/AgCl reference electrode using 0.1M tetra-*n*-butylammonium tetrafluoroborate as the supporting electrolyte.

[17] SIR97: a new tool for crystal structure determination and refinement: A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115 – 119.

[18] P. T. Beurskens, G. Beurskens, W. P. Bosman, R. de Gelder, S. Garcia-Granda, R. O. Gould, R. Israel, J. M. M. Smits, *The DIRDIF-96 program system*, Crystallography Laboratory, University of Nijmegen, **1996**.

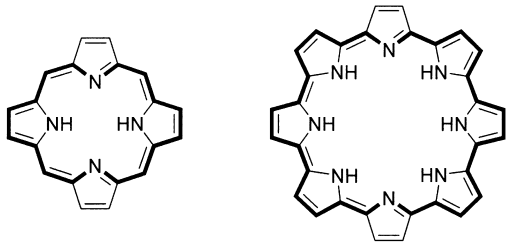
[19] G. M. Sheldrick, SHELXL 97, *Program for Crystal Structure Refinement*, University of Göttingen, **1997**.

Cyclo[8]pyrrole: A Simple-to-Make Expanded Porphyrin with No Meso Bridges**

Daniel Seidel, Vincent Lynch, and Jonathan L. Sessler*

Dedicated to Professor James P. Collman on the occasion of his 70th birthday

Porphyrin (for example, **1**), a tetrapyrrolic macrocycle, is the active component of many naturally occurring pigments and has been known and studied for centuries; its biological importance can hardly be overestimated.[1] In spite of this ubiquity, it was only in 1966 that the first expanded porphyrin analogue, sapphyrin, was reported,[2] and it has only been in recent years that the area of expanded porphyrin research has begun to attract attention as its own rapidly evolving field.[3–5] One of the unexpected surprises to emerge from this work is the finding that large expanded porphyrins (those containing eight or more pyrrole rings) are often not flat but rather adopt "figure-eight" and other twisted conformations in spite of being highly conjugated.[6–11] It thus remains a challenge at present to produce large aromatic expanded porphyrins that display the classic disklike structure of simple porphyrins.[12–15]



One structure that might allow this elusive goal to be met is cyclo[8]pyrrole (**2**; [30]octaphyrin(0.0.0.0.0.0.0.0)). This target can be derived, at least in theory, by replacing all four meso-carbon bridges with four additional pyrrolic rings. If it is produced in this way, cyclo[8]pyrrole would possess an extended 30-π-electron periphery that, in analogy to the 18-π-electron system of porphyrin, would be aromatic in a Huckel $(4n+2)$ π-electron sense (compare **1** and **2**).

A retrosynthetic analysis of **2** leads to the consideration that it could be "split up" by disconnection of one or more of the $\alpha-\alpha'$ bonds between the individual pyrrolic subunits, which means it could be prepared (at least in principle) from linear oligopyrrolic fragments, such as a linear octipyrrolic unit, two quaterpyrrolic units, four bipyrrolic units, or ultimately eight

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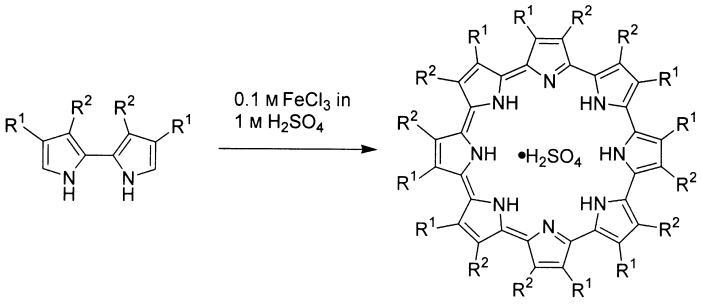
pyrrolic units. To date, however, the preparation of higher order fused oligopyrrolic systems, including α,α'-unsubstituted quaterpyrroles, has proved elusive.[16–18] Therefore, we decided to concentrate our efforts on a simple one-pot strategy that would involve the direct coupling of bipyrrolic fragments (Scheme 1). Accordingly, several readily available substituted and unsubstituted bipyrroles were subjected to a wide range of potential coupling conditions, such as ones involving condensation of the bipyrrole with SCl_2 and subsequent sulfur extrusion of the putative thia-bridged macrocyclic intermediates[19] as well as various oxidative coupling procedures.[13–15, 17, 18, 20–29] Among the latter were the Cr^{VI}-based oxidative coupling method described by Falk and Flödl,[23] which we have recently found useful in the synthesis of other expanded porphyrins,[17, 18] and strategies based on the use of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and chloranil—reagents that have been used to prepare a range of expanded[13–15, 20–22] and contracted porphyrins.[25–29] Finally, success was encountered using $FeCl_3$ as the oxidant. Ferric chloride has been used frequently in the synthesis of polypyrroles,[30] but has not, at least to the best of our knowledge, ever been used to produce expanded porphyrin-type coupling products. It has, however, been employed to aromatize macrocycles.[31, 32] Herein, we report a highly efficient one-step synthesis of cyclo[8]pyrroles (**2**) that is based on the use of $FeCl_3$ as the oxidant and readily accessible α,α'-unsubstituted bipyrroles[33–35] as the only organic precursors (Scheme 1).



3a: $R^1 = R^2 = Et$
3b: $R^1 = Et$, $R^2 = Me$
3c: $R^1 = R^2 = Me$
3d: $R^1 = n$Pr, $R^2 = H$

2a: $R^1 = R^2 = Et$ (77%)
2b: $R^1 = Et$, $R^2 = Me$ (79%)
2c: $R^1 = R^2 = Me$ (74%)
2d: $R^1 = n$Pr, $R^2 = H$ (15%)

Scheme 1. Direct coupling of bipyrrolic fragments to form cyclo[8]pyrroles.

While the $FeCl_3$-induced oxidative coupling of bipyrroles produces cyclo[8]pyrroles of general structure **2** under a range of conditions, we have found that the best yields are obtained under carefully optimized biphasic conditions (bipyrrole in CH_2Cl_2, $FeCl_3$ in 1M H_2SO_4).[36] In this optimized procedure the rate of addition is carefully controlled so as to ensure a very low concentration of bipyrrole in the organic phase at all times. Also, the stirring speed is kept low, so as to minimize the extent to which the two phases are allowed to mix.[37]

The yields of cyclo[8]pyrroles, isolated under these conditions in the form of their dihydrogen sulfate salts, are remarkably good, being above 70% in the case of **2a**–**c** (Scheme 1). Such yields are noteworthy in the area of expanded porphyrin chemistry and rival the best yields seen in the synthesis of β-substituted octaalkylporphyrins.[38] On the other hand, the yields observed for **2d** are significantly lower (15%). While a variety of factors could account for this finding, it is currently rationalized in terms of the lack of full β-substitution which would allow competing $\beta-\beta'$ or $\beta-\alpha$ coupling reactions to occur. Consistent with this proposal is the finding that simple unsubstituted bipyrrole does not give rise to isolable quantities of cyclo[8]pyrrole, even when subjected to $FeCl_3$-based oxidation under the optimized conditions.[39]

The NMR spectra of the cyclo[8]pyrrole dihydrogen sulfate salts **2a**–**d** are characterized by their unusually high symmetry. Compounds **2a**–**d** are judged to be aromatic on the basis of the positions of the signals observed in their respective ^{1}H NMR spectra. Specifically, the signal corresponding to the NH protons in the spectrum of **2a** recorded in $CDCl_3$ at room temperature appears at $\delta = 0.64$, clearly upfield from "normal" pyrrolic NH protons. The only two remaining signals, a triplet at $\delta = 1.63$ and an unresolved quartet at $\delta = 4.17$, are assigned to the single, chemically distinct (that is, magnetically degenerate) ethyl group. While unresolved at room temperature, the quartet at $\delta = 4.17$ corresponding to the CH_2CH_3 protons displays a chemical shift that is typical for a methylene group attached directly to the periphery of an aromatic expanded porphyrin-type macrocycle.[17] This CH_2CH_3 signal is nearly resolved as a distinct quartet at low temperature (223 K, $CDCl_3$), while the NH resonance shifts to $\delta = -0.2$.

The ^{1}H NMR spectra of cyclo[8]pyrroles **2b**–**d** are similar to that of **2a**. However, in addition to the expected differences in the alkyl region (and the observation of a β-CH signal at $\delta = 9.9$ in the case of **2d**) a noticeable trend in the position of the NH resonances is observed. Specifically, the NH signal for **2b** at room temperature in $CDCl_3$ is seen at $\delta = -0.64$, while the corresponding signals for **2c** and **2d** are observed at $\delta = -0.84$ and -1.63, respectively. These differences are interpreted in terms of the latter, less sterically hindered systems being better able to adopt conformations that lie closer to true planarity.

Also underscoring the high symmetry of **2a**–**d**, and hence their inferred near-planarity, are their respective ^{13}C NMR spectra. Here, the prototypic spectrum is that of **2c**, which displays only three distinct signals. Such a limited number of signals is quite unusual for a molecule with 48 carbon atoms and a molecular weight of 841 Da. If perturbations that arise from the sulfate counterion are excluded, **2c** is left with an effective D_{8h} symmetry in solution.

The results of a single-crystal X-ray diffraction analysis of **2b** are consistent with the proposal that cyclo[8]pyrroles **2** are flat or nearly flat.[40] The resulting structure (Figure 1) reveals a very flat, essentially planar macrocyclic system with a sulfate ion centrally bound within the cavity. Eight hydrogen-bonding interactions are inferred in the solid state from the NH···O distances which range from 1.91 to 2.49 Å. The result is a structure wherein all four oxygen atoms of the sulfate counterion interact with all eight pyrrole NH sites present in the middle of what is formally a diprotonated receptor. While

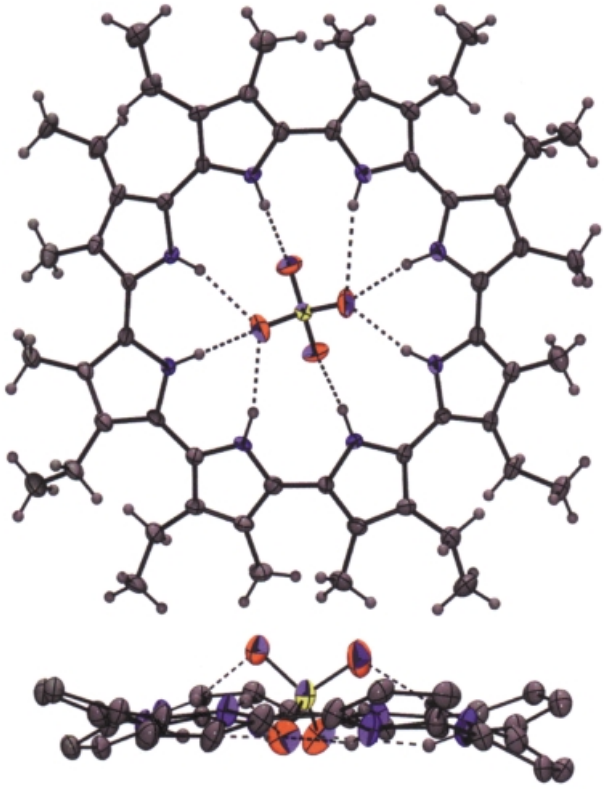


Figure 1. Ortep-POV-Ray views of one of the two crystallographically independent molecules seen in the solid-state structure of **2b**. The thermal ellipsoids are scaled to the 50% probability level.

not a proof, this finding, which has antecedents in the expanded porphyrin literature,[3, 5, 18, 41] leads to the suggestion that cyclo[8]pyrroles such as **2a–d** could emerge as useful anion receptors.

The UV/Vis spectrum of **2b** (Figure 2) is characterized by a relatively weak Soret-type absorbance at 431 nm ($\varepsilon =$ 79800 $mol^{-1}cm^{-1}$) and an intense, red-shifted Q-type band at 1112 nm ($\varepsilon = 132200\,mol^{-1}cm^{-1}$). Both the intensity and the position of the latter band are remarkable given that Q-type absorption bands in porphyrinoids (and aromatic expanded systems) are generally far less intense than the corresponding Soret transitions and are rarely as far red-shifted as seen in the present case. Indeed, we are aware of only three other expanded porphyrin systems, namely the doubly cationic hexathiarubyrin of Vogel and co-workers[7, 42] and the recently described octaphyrin(1.1.1.1.1.1.1.1) and nonaphyrin(1.1.1.1.1.1.1.1.1) of Furuta and co-workers[11] that display Q-type bands at or above 1000 nm. These systems display nowhere near the intensity of **2b**.

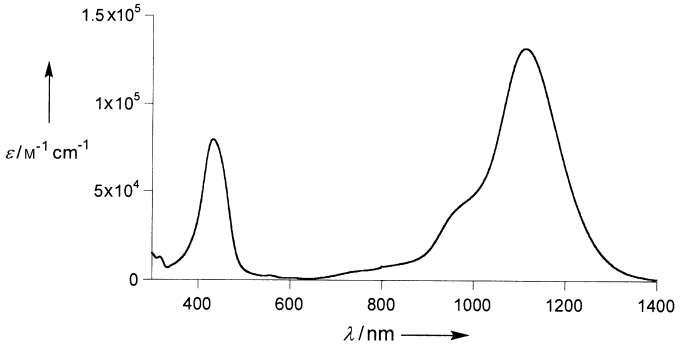


Figure 2. UV/Vis spectrum of **2b** recorded in dichloromethane.

In summary, a new biphasic oxidative coupling procedure has been introduced that allows the efficient synthesis of the hitherto unknown cyclo[8]pyrroles. These systems display features that are consistent with Hückel-type $4n+2$ aromaticity. Furthermore, as they are large, flat macrocycles with an "NH-in" arrangement of the pyrrolic nitrogen atoms, they can be considered as new "true" porphyrin analogues.[43, 44] Currently, we are exploring the extent to which the present coupling procedure can be generalized while working to define further the basic chemistry of cyclo[8]pyrroles.[45] In preliminary work, we have found that washing a solution of **2b** with 1M aqueous NaOH produces spectral changes that are consistent with the formation of the free base (λ_{max} (ε in $mol^{-1}cm^{-1}$) 349 (36200), 455 (15700), and 857 (26900) nm). Treating this species with 1M H_2SO_4 served to restore completely the spectral features of **2b**. Likewise, treatment with 1M H_3PO_4 led to formation of a species tentatively formulated as the corresponding hydrogen phosphate complex. On the other hand, it was found that the sulfate anion observed in the solid-state structure of **2b** is retained after washing a solution of this dihydrogen sulfate salt in dichloromethane with water (pH 7; 3×). These findings taken together lead us to propose that cyclo[8]-pyrroles could emerge as interesting anion receptors. A range of other applications, including uses as optical storage and signaling devices based on their unusually strong red-shifted Q-like absorption, can also be envisioned.

Experimental Section

General: ^1H and ^{13}C NMR spectra were measured at 25°C on a Varian Unity Plus spectrometer at 300 MHz or on a Varian Unity Innova at 500 MHz. UV/Vis spectra were recorded at Wright Patterson Air Force Base on a Carey 500 spectrophotometer. High-resolution chemical ionization (CI) mass spectra were obtained on a VGZAB2-E mass spectrometer. A Sage syringe pump (model M365) was employed for slow continuous additions. All solvents and chemicals were obtained commercially and used as received. The bipyrrolic precursors were prepared as described previously.[33–35]

General Procedure for the oxidative coupling of bipyrroles: A 1-L round-bottom flask was charged with a stir bar, dichloromethane (500 mL), and a solution of $FeCl_3 \cdot 6H_2O$ (2.7 g, 10 mmol) in 1M sulfuric acid (100 mL). The resulting biphasic mixture was stirred at 300 rpm, while a solution of the bipyrrole (1 mmol) in dichloromethane (50 mL) was added slowly by syringe pump over a period of 9 h, with the needle submerged into the organic phase. After completion of the addition, the reaction mixture was stirred for 5 h. Subsequently, the phases were separated and the organic phase was dried over anhydrous sodium sulfate. After filtration, the solvent was removed in vacuo to yield the crude product. The crude products were purified by column chromatography on silica gel using dichloromethane containing methanol (2–5%) as the eluent. The yellow band was collected and the solvent removed in vacuo. The solid residue was recrystallized from dichloromethane/methanol to yield **2a–d** as dark microcrystalline powders.

2a: 77% yield; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 0.64$ (s, 8H, NH), 1.63 (t, $J_{H,H} = 7.5$ Hz, 48H, CH_2CH_3), 4.17 (br s, 32H, CH_2CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 16.13$, 21.92, 126.26, 128.43; HR-MS (CI): m/z 1065.6710 $[M+H^+]$, calcd for $C_{64}H_{89}N_8O_4S_1$: 1065.6727.

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2b: 79% yield; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = -0.64$ (s, 8H, NH), 2.07 (t, $J_{H,H} = 7.5$ Hz, 24H, CH_2CH_3), 3.76 (s, 24H, CH_3), 4.17 (q, $J_{H,H} = 7.5$ Hz, 16H, CH_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 15.90$, 15.99, 22.17, 123.87, 125.34, 126.44, 129.27; HR-MS (CI): m/z 952.5399 [M^+], calcd for $C_{56}H_{72}N_8O_4S_1$: 952.5397; UV/Vis (CH_2Cl_2) λ_{max} [nm] (ε in $mol^{-1}L^{-1}$): 431 (79800), 1112 (132200).

2c: 74% yield; ^{1}H NMR (300 MHz, $CDCl_3$: $\delta = -0.84$ (s, 8H, NH), 3.58 (s, 48H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 15.63$, 123.89, 125.87; HR-MS (CI): m/z 841.4214 [M+H$^+$], calcd for $C_{48}H_{57}N_8O_4S_1$: 841.4224.

2d: 15% yield; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = -1.63$ (s, 8H, NH), 1.31 (t, $J_{H,H} = 7.3$ Hz, 24H, $CH_2CH_2CH_3$), 2.50–2.63 (m, 16H, $CH_2CH_2CH_3$), 4.78 (t, $J_{H,H} = 7.9$ Hz, 16H, $CH_2CH_2CH_3$), 9.89 (d, $J_{H,H} = 2$ Hz, 8H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.74$, 25.42, 33.34, 114.53, 124.80, 128.10, 133.48; HR-MS (CI): m/z 953.5461 [M+H$^+$], calcd for $C_{56}H_{73}N_8O_4S_1$: 953.5476.

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[1] K. M. Kadish, K. M. Smith, R. Guilard, *The Porphyrin Handbook*, Academic Press, San Diego, **2000**.

[2] R. B. Woodward, Presented at the aromaticity conference in Sheffield, UK, **1966**.

[3] J. L. Sessler, S. J. Weghorn, *Expanded, Contracted & Isomeric Porphyrins*, Pergamon, New York, **1997**.

[4] A. Jasat, D. Dolphin, *Chem. Rev.* **1997**, *97*, 2267.

[5] J. L. Sessler, A. Gebauer, S. J. Weghorn in *The Porphyrin Handbook*, *Vol. 2* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, **2000**, p. 55.

[6] J. L. Sessler, S. J. Weghorn, V. Lynch, M. R. Johnson, *Angew. Chem.* **1994**, *106*, 1572; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1509.

[7] M. Bröring, J. Jendrny, L. Zander, H. Schmickler, J. Lex, Y.-D. Wu, M. Nendel, J. Chen, D. A. Plattner, K. N. Houk, E. Vogel, *Angew. Chem.* **1995**, *107*, 2709; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2515.

[8] E. Vogel, M. Bröring, J. Fink, D. Rosen, H. Schmickler, J. Lex, K. W. K. Chan, Y.-D. Wu, D. A. Plattner, M. Nendel, K. N. Houk, *Angew. Chem.* **1995**, *107*, 2705; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2511.

[9] J.-i. Setsune, Y. Katakami, N. Iizuna, *J. Am. Chem. Soc.* **1999**, *121*, 8957.

[10] J.-i. Setsune, S. Maeda, *J. Am. Chem. Soc.* **2000**, *122*, 12405.

[11] J.-Y. Shin, H. Furuta, K. Yoza, S. Igarashi, A. Osuka, *J. Am. Chem. Soc.* **2001**, *123*, 7190.

[12] One approach to obtaining large, flat expanded porphyrins is to invert one or more of the pyrrolic rings such that a compound lacking the classic "all-NH-in" structure of porphyrins is produced, see refs. [13–15].

[13] S. K. Pushpan, A. Srinivasan, V. G. Anand, S. Venkatraman, T. K. Chandrashekar, B. S. Joshi, R. Roy, H. Furuta, *J. Am. Chem. Soc.* **2001**, *123*, 5138.

[14] V. G. Anand, S. K. Pushpan, S. Venkatraman, A. Dey, T. K. Chandrashekar, B. S. Joshi, R. Roy, W. Teng, K. R. Senge, *J. Am. Chem. Soc.* **2001**, *123*, 8620.

[15] V. R. G. Anand, S. K. Pushpan, A. Srinivasan, S. J. Narayanan, B. Sridevi, T. K. Chandrashekar, R. Roy, B. S. Joshi, *Org. Lett.* **2000**, *2*, 3829.

[16] H. Ikeda, J. L. Sessler, *J. Org. Chem.* **1993**, *58*, 2340.

[17] J. L. Sessler, D. Seidel, A. E. Vivian, V. Lynch, B. L. Scott, D. W. Keogh, *Angew. Chem.* **2001**, *113*, 611; *Angew. Chem. Int. Ed.* **2001**, *40*, 591.

[18] J. L. Sessler, D. Seidel, V. Lynch, *J. Am. Chem. Soc.* **1999**, *121*, 11257.

[19] This is a well known method to construct corroles; see, for example, R. Paolesse, in *The Porphyrin Handbook*, *Vol. 2* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, **2000**, p. 201, and references therein. It was also applied early to the preparation of heterosapphyrins: M. J. Broadhurst, R. Grigg, A. W. Johnson, *J. Chem. Soc. Chem. Commun.* **1970**, 807; M. J. Broadhurst, R. Grigg, A. W. Johnson, *J. Chem. Soc. Perkin Trans. 1* **1972**, 2111.

[20] S. J. Narayanan, B. Sridevi, T. K. Chandrashekar, A. Vij, R. Roy, *J. Am. Chem. Soc.* **1999**, *121*, 9053.

[21] S. K. Pushpan, V. R. G. Anand, S. Venkatraman, A. Srinivasan, A. K. Gupta, T. K. Chandrashekar, *Tetrahedron Lett.* **2001**, *42*, 3391.

[22] S. V. Shevchuk, J. M. Davis, J. L. Sessler, *Tetrahedron Lett.* **2001**, *42*, 2447.

[23] H. Falk, H. Flödl, *Monatsh. Chem.* **1988**, *119*, 247.

[24] L. Simkhovich, S. Rosenberg, Z. Gross, *Tetrahedron Lett.* **2001**, *42*, 4929.

[25] J.-W. Ka, W.-S. Cho, C.-H. Lee, *Tetrahedron Lett.* **2000**, *41*, 8121.

[26] W.-S. Cho, C.-H. Lee, *Tetrahedron Lett.* **2000**, *41*, 697.

[27] D. T. Gryko, *Chem. Commun.* **2000**, 2243.

[28] D. T. Gryko, K. Jadach, *J. Org. Chem.* **2001**, *66*, 4267.

[29] R. P. Briñas, C. Brückner, *Synlett* **2001**, 442.

[30] See, for example, M. F. Planche, J. C. Thieblemont, N. Mazars, G. Bidan, *J. Appl. Polym. Sci.* **1994**, *52*, 1867, and references therein.

[31] D. T. Richter, T. D. Lash, *Tetrahedron Lett.* **1999**, *40*, 6735.

[32] T. D. Lash, D. T. Richter, G. M. Shiner, *J. Org. Chem.* **1999**, *64*, 7973.

[33] E. Vogel, P. Koch, X. L. Hou, J. Lex, M. Lausmann, M. Kisters, M. A. Aukauloo, P. Richard, R. Guilard, *Angew. Chem.* **1993**, *105*, 1670; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1600.

[34] J. L. Sessler, M. C. Hoehner, *Synlett* **1994**, 211.

[35] M. R. Johnson, C. Slebodnick, J. A. Ibers, *J. Porphyrins Phthalocyanines* **1997**, *1*, 87.

[36] In one test experiment the coupling was performed in ethanol. Interestingly, slow addition of bipyrrole to a solution of $FeCl_3$ in acidified ethanol gave rise to cyclo[8]pyrroles in yields very similar to when $FeCl_3$ in acidified ethanol was added slowly to a solution of bipyrrole in ethanol.

[37] While the yield for cyclo[8]pyrrole formation goes down at higher stirring speeds or faster addition rates, the yield of a blue product (which is not observed under the reaction conditions outlined in the experimental section of this paper) increases. This blue product is tentatively assigned on the basis of a MALDI mass spectrometric analysis to be a cyclo[12]pyrrole. Unfortunately, this product begins to precipitate shortly after elution from the column and is poorly soluble in common organic solvents. This has so far precluded its full characterization.

[38] K. M. Smith, in *The Porphyrin Handbook*, *Vol. 1* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, **2000**, p. 1.

[39] This problem is compounded by issues of solubility. Indeed, at present, we cannot rule out an alternative explanation that involves the formation of quaterpyrrolic or other intermediates that lack sufficient solubility to carry on the reaction.

[40] Crystallographic data for **2b**: Dark plates were grown by vapor diffusion of dichloromethane and methanol, triclinic, space group $P\bar{1}$ (No. 2), $Z = 2$, $a = 11.4267(1)$, $b = 21.9142(2)$, $c = 24.5622(3)$ Å, $\alpha = 76.330(1)$, $\beta = 76.946(1)$, $\gamma = 81.367(1)^\circ$, $V = 5791.40(10)$ Å^3, $\rho_{calcd} = 1.28$ g cm^{-3}, $F(000) = 2396$, $\mu = 0.207$ mm^{-1}. A total of 40398 reflections were measured, 25843 unique ($R_{int} = 0.045$), on a Nonus Kappa CCD using graphite monochromatized $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at $-120\,^\circ$C. The structure was refined on F^2 to $R_w = 0.184$, with a conventional $R = 0.0957$ (13724 reflections with $F_o > 4\sigma(F_o)$), and a GOF = 2.13 for 1311 refined parameters. There are two crystallographically independent macrocycle sulfate complexes. CCDC-176189 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[41] J. L. Sessler, J. M. Davis, *Acc. Chem. Res.* **2001**, *34*, 989.

[42] A. Gebauer, Diplomarbeit, University of Cologne, Federal Republic of Germany, **1993**.

[43] Very recently, cyclo[*n*]thiophenes (with $n = 12$, 16, 18) were prepared by the use of an entirely different approach. Interestingly, in spite of their $4n$ (as opposed to $4n+2$) π-electron conjugation pathways, these systems did not display much in the way of obvious ring-current effects: J. Krömer, I. Rios-Carreras, G. Fuhrmann, C. Musch, M. Wunderlin, T. Debaerdemaeker, E. Mena-Osteritz, P. Bäuerle, *Angew. Chem.* **2000**, *112*, 3481; *Angew. Chem. Int. Ed. Engl.* **2000**, *39*, 3481.

[44] It is noteworthy that a natural product, telomestatin, with a somewhat related macrocyclic ring structure was reported while this work was in progress. While not fully conjugated, this system contains seven oxazole and one thiazoline subunits: K. Shin-ya, K. Wierzba, K.-i. Matsuo, T. Ohtani, Y. Yamada, K. Furihata, Y. Hayakawa, H. Seto, *J. Am. Chem. Soc.* **2001**, *123*, 1262.

[45] In initial experiments, exposure of 3,4-diethylpyrrole to the same conditions used to prepare the cyclo[8]pyrroles described here, led to decomposition and partial recovery of starting material.

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