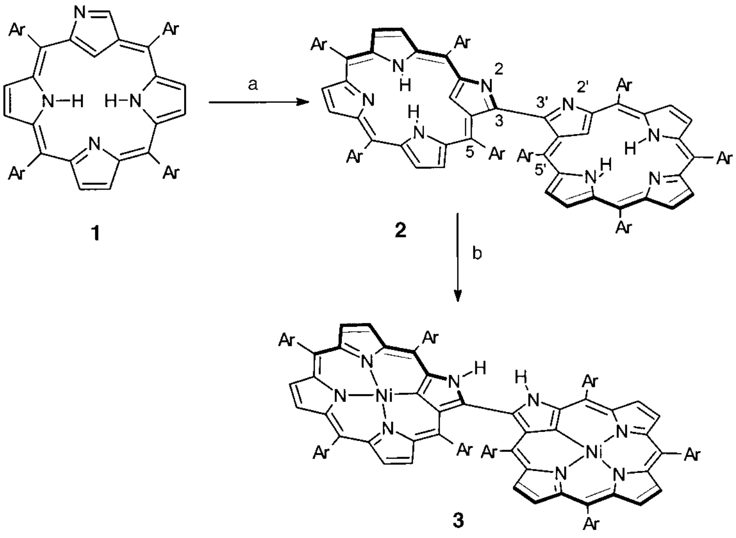
Porphyrins

Synthesis and Characterization of a Directly Linked N-Confused Porphyrin Dimer**

*Piotr J. Chmielewski**

Oligomeric porphyrin arrays[1] are present in molecular devices that are designed for energy- and electron-transfer processes,[2] multielectron redox catalysis,[3] and in organic magnetic materials.[4] For all such applications, it is important that the individual molecules within the array communicate with each other. Distance, geometry, and orientation have been recognized as important factors for the control of this communication. Among arrays of covalently linked porphyrin units, systems in which the aromatic subunits are *directly* connected to each other by a covalent bond are particularly important. Such a linkage enables interaction between the subunits while the intrinsic structure of the porphyrin is preserved. Considerable progress has been reported recently in the synthesis of oligoporphyrins with direct β–β, *meso*–*meso*, and *meso*–β links[5] to yield products that range from dimeric species to linear structures, which contain up to 128 porphyrin subunits.[6]

The field of porphyrin arrays can be further extended by the construction of arrays of covalently linked porphyrin analogues, particularly porphyrin-like macrocycles that also have carbon atoms in the coordination core. The N-confused porphyrin **1**[7] is an isomer of regular porphyrin which preserves the fundamental porphyrinoid skeleton. In multimolecular assemblies, it offers new modes of linking subunits and different coordination properties of the resultant oligomers.[8] Herein we report the synthesis of the first directly β–β-linked dimer of N-confused porphyrin. This new molecule was obtained in an acid-catalyzed process, which did not require prior activation of the macrocyclic ring. The active site was provided here by a single α-carbon atom of the N-confused pyrrole. 3,3′-bis(*meso*-tetraaryl-2-aza-21-carbaporphyrin) (**2**) was obtained in a one-step, one-pot synthesis starting from the N-confused porphyrin **1** (Scheme 1). The coupling process was carried out in the presence of air, which seems to be a sufficiently strong oxidant for the dehydrogenation step that is expected to follow the formation of the bond between the two porphyrin subunits. An analogous reaction, which leads to a 3-(2′-pyrrole)-substituted N-confused porphyrin, was observed previously in the reaction of **1** with pyrrole in DMF.[9] Although the reaction proceeds in the presence of various acids, the best results were obtained when hydrogen bromide was added as a catalyst to a solution of **1** in



Scheme 1. Synthesis of the dimer **2** and its nickel complex **3**: a) HBr, toluene/dichloromethane, 20 h; b) $Ni(CH_3COO)_2$, toluene/DMF, 1 h. Ar = *p*-tolyl, DMF = *N*,*N*-dimethylformamide.

---

[*] Prof. P. J. Chmielewski
Department of Chemistry
University of Wrocław
F. Joliot-Curie Street 14
50383 Wrocław (Poland)
Fax: (+4871) 32-823-48
E-mail: pjc@wchuwr.chem.uni.wroc.pl

[**] The author thanks Dr. M. Stępień for his help in the X-ray crystal structure analysis and for helpful discussions. This work was supported by the State Committee for Scientific Research of Poland (Grant No. 3 09A 155 15)

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/anie.200461361

toluene/dichloromethane. After heating for 20 h at reflux, the conversion of the starting material was $\approx 80\%$, and the product **2** was obtained with an overall yield of 50%.[10]

Analysis of the ^{1}H and ^{13}C NMR spectroscopic data revealed that the aromaticity of the subunits is preserved in the bis(porphyrinoid) and that the 3,3′-bridging carbon atoms are sp^2-hybridized. Owing to the symmetry of the dimer, only one set of resonances were detected in the NMR spectrum of **2**. Nevertheless, an upfield shift of the protons that belong to one of the *meso*-substituted aryl groups as well as the through-space interaction of these protons with NH protons located within the porphyrin crevice were observed in the NOESY and ROESY spectra. These features indicate that the subunits are close to one another. It is particularly evident in the case of the *p*-tolyl derivative **2** for which one of the methyl signals (5-(*p*-tolyl)) is located at $\delta \approx -0.7$ ppm (CDCl$_3$, 298 K); that is, it is shifted more than 3 ppm upfield with respect to the other methyl signals because of the strong influence of the aromatic-ring current of the porphyrin (see Supporting Information).

The crystal structure of **2** (Figure 1) confirms the integrity of the dimer. The dihedral angle between the mean planes defined by the C··N··N··N coordination cores of the subunits is 20°. The plane defined by the N-confused pyrrole is tilted by 33° from the average plane in each macrocyclic subunit. The dihedral angle between the mean planes of the N-confused pyrroles is 61°. The distance of the unique bridging C3–C3′ bond is 1.468(3) Å, which is similar to the distances observed in a zinc complex of a *β*–*β*-linked regular heptaalkylporphyrin (1.46 Å),[5a] a *meso*–*meso*-linked bis(porphyrin) free base (1.51 Å),[5b] or a *meso*–*meso*, *β*–*β* double-linked bis(porphyrinatonickel(II)) dimer (1.45 Å),[5j] and it is much shorter than the sp^3–sp^3 distance reported for a *β*–*β*-linked bis(chlorin) (1.61 Å).[11] Molecular modeling studies of **2** show that the rotation around the bridging bond is restricted owing to steric factors imposed by the *meso*-substituted aryl groups that flank the N-confused pyrrole in both subunits. The lack of rotational freedom around the 3,3′-axis leads to an axial chirality of the molecule (see Supporting Information).[5i] The observed cisoidal conformation of the bipyrrolic system is essential for the coordination properties of this potential chelating site.

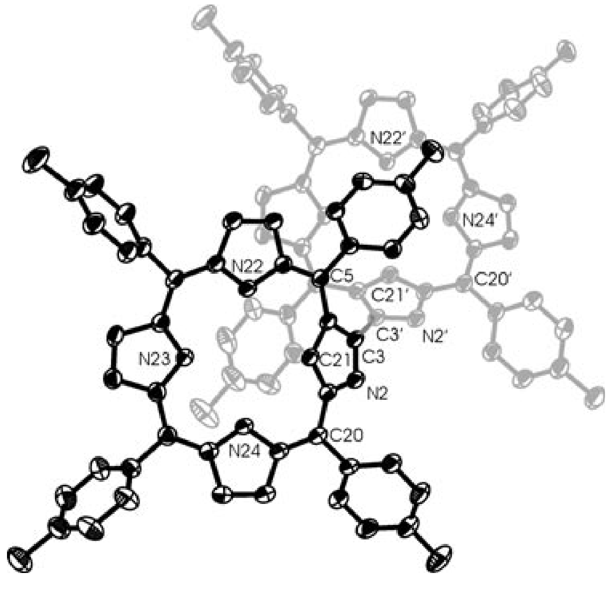


Figure 1. Crystal structure of **2**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

Formation of the bis(nickel(II)) complex **3** (Scheme 1) required a higher reaction temperature than necessary for the insertion of nickel(II) into the monomeric N-confused porphyrin **1**.[7a] Some of the structural and spectral features typical of nickel(II) complexes with N-confused porphyrins—that is, deprotonation of the internal carbon, protonation of the external nitrogen, as well as reduction of the aromatic character in comparison to the free base—were observed for **3**. However, the ^{1}H NMR spectrum of **3** also shows features typical of the N-confused bis(porphyrin) system **2**.[8,12] In particular, protons of the 5-aryl substituent are strongly shifted upfield owing to a close contact with an aromatic-ring current of the neighboring porphyrinic ring. Analysis of the NOESY spectrum of **3** (see Supporting Information) revealed a mutual orientation of the subunits similar to that observed for **2**.

The interaction between the aromatic systems in **2** was reflected by a strong bathochromic shift of the Soret and Q bands in the electronic absorption spectra with respect to the monomeric species **1** (Figure 2a) and a splitting of the Soret band ($\Delta E = 736$ cm^{-1}). The optical properties of **3** are affected even more by the interaction of the subunits. The UV/Vis spectrum of the complex consists of a split Soret-type band and strongly broadened and red-shifted Q bands (Figure 2b).

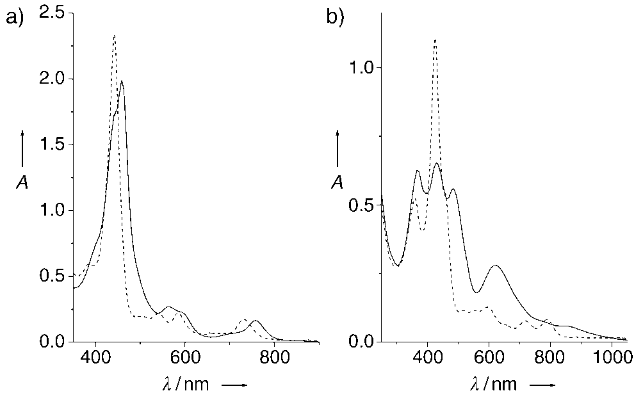


Figure 2. Absorbance spectra of solutions in CH$_2$Cl$_2$ of a) **2** (solid line) and b) **3** (solid line). The dashed lines (-----) in a) and b) represent the spectra of the monomer **1** and its nickel(II) complex, respectively.

Electrochemical measurements (solution in CH$_2$Cl$_2$, tetra-*n*-butylammonium perchlorate as a supporting electrolyte, potentials referenced to the ferrocene/ferrocenium couple) also reveal the mutual influence of the subunits. The first oxidation potential of **2** was anodically shifted with respect to that of **1** (about 65 mV) and was split into two waves (240 mV and 340 mV). This separation is similar to that observed for the *meso*–*meso*-linked dimers of regular porphyrin

(150 mV).[5h] For **3**, two reversible one-electron couples were observed for the oxidation (140 and 218 mV) and the reduction (−1220 and −1315 mV) processes (see Supporting information). A significant anodic shift was observed for the reduction processes with respect to that of a monomeric nickel(II) complex of **1** (−1556 mV)[13] which corresponds to a >300 mV decrease in the HOMO–LUMO gap[14] of the dimer **3**.

In summary, compound **2** constitutes the first example of a directly linked N-confused bis(porphyrin). Its surprisingly facile synthesis makes **2** a potentially attractive building block of novel molecular assemblies that contain covalently and coordinatively linked subunits with peripheral nitrogen donor-atom sites.

Experimental Section

2: HBr (40 % solution in acetic acid, 50 μL, 0.25 mmol) was added in one portion to a solution of **1** (100 mg, 0.15 mmol) in toluene (30 mL). A further aliquot of dichloromethane (5 mL) was added to enhance the solubility of the generated porphyrin dication. The reaction mixture was heated at reflux for 20 h, then the solvents were removed. The residue was dissolved in benzene and was purified by chromatography through basic Al_2O_3 (activity III). Decomposition products and unconverted starting material **1** (recovered 21 mg) were eluted with benzene, whereas the desired product **2** was eluted with CH_2Cl_2 and then recrystallized from dichloromethane/ethanol (49 mg, 49 %). ^{1}H NMR: (500 MHz, $CDCl_3$, 233 K, TMS): $\delta = 8.92$ (dd, $^3J_{HH} =$ 4.4 Hz, $^4J_{HH} = 1.3$ Hz, 1 H; pyrrole), 8.84 (d, $^3J_{HH} = 7.5$ Hz, 1 H) 8.61 (d, $^3J_{HH} = 4.5$ Hz, 1 H; pyrrole), 8.56 (d, $^3J_{HH} = 4.5$ Hz, 1 H; pyrrole), 8.51 (dd, $^3J_{HH} = 4.4$ Hz, $^4J_{HH} = 1.0$ Hz, 1 H; pyrrole), 8.39 (dd, $^3J_{HH} =$ 7.6 Hz, $^4J_{HH} = 1.3$ Hz, 1 H), 8.36 (d, $^3J_{HH} = 7.7$ Hz, 1 H), 8.24 (dd, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 1.3$ Hz, 1 H), 8.11 (dd, $^3J_{HH} = 4.4$ Hz, $^4J_{HH} =$ 1.0 Hz, 1 H; pyrrole), 8.01 (dd, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 1.3$ Hz, 1 H), 7.83 (d, $^3J_{HH} = 8.1$ Hz, 1 H), 7.81 (dd, $^3J_{HH} = 8.0$ Hz, $^4J_{HH} = 1.4$ Hz, 1 H), 7.76 (d, $^3J_{HH} = 7.6$ Hz, 1 H), 7.64 (m, 2 H), 7.56 (m, 2 H), 7.46 (d, $^3J_{HH} = 7.6$ Hz, 1 H), 7.22 (dd, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 1.5$ Hz, 1 H), 5.33 (d, $^3J_{HH} = 7.5$ Hz, 1 H), 4.64 (d, $^3J_{HH} = 7.0$ Hz, 1 H), 2.80 (s, 3 H), 2.71 (s, 3 H), 2.69 (d, $^3J_{HH} = 7.6$ Hz, 1 H), 2.65 (s, 3 H), −0.76 (s, 3 H), −2.40 (s, 1 H, NH), −2.64 (b, 1 H, NH), −5.25 (b, 1 H, 21-CH); UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 257 (4.74), 290 (4.76), 348 (sh), 399 (sh), 442 (sh), 459 (5.47), 565 (4.60), 595 (sh), 703 (sh), 758 nm (4.40); ESI-MS: m/z: 1340.5 [MH^+]; elemental analysis: calcd for $C_{96}H_{74}N_8C_2H_5OH$: C 84.97, H 5.78, N 8.09; found: C 84.74, H 5.65, N 8.30 %.

Crystals of suitable quality for X-ray analysis were obtained by the slow diffusion of ethanol into a solution of **2** in dichloromethane. Crystal data for **2**: $C_{96}H_{74}N_8 \cdot 2.25\,EtOH \cdot 0.75\,CH_2Cl_2$, $M_W = 1491.86$, $T = 100$ K, $Cu_{K\alpha}$ radiation, monoclinic, space group $P2_1/n$, $a =$ 15.829(3), $b = 18.772(4)$, $c = 26.673(5)$ Å, $\beta = 92.16(3)$ $V =$ 7920(3) Å^3, $Z = 4$, ρcalcd = 1.251 Mg m^{-3}, $\lambda = 1.54178$ Å, $\mu =$ 1.039 mm^{-1}, $F(000) = 3124$; Oxford Diffraction KM4 Xcalibur2 diffractometer with KM4CCD Sapphire detector; $3.65 \leq \theta \leq 73.13°$, 15 495 collected reflections of which 11 701 were independent with $I > 2\sigma(I)$, 1097 parameters, $R_1(F) = 0.0822$, $wR_2(F^2) = 0.2606$, $S = 1.116$, largest difference peak and hole 0.474 and −0.602 e Å^{-3}. All non-hydrogen atoms were refined with anisotropic displacement parameters, except for those of the disordered solvents; hydrogen atoms were included in the geometry of the molecules and were refined isotropically. The extensive solvent disorder was modeled with a number of isotropic C, O, and Cl atoms with free refining occupancies to finally establish the presence of nine molecules of ethanol and three molecules of dichloromethane per unit cell. CCDC-245 032 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 CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

3: A solution of **2** (30 mg, 0.022 mmol) in toluene (30 mL) was mixed with a solution of nickel(II) acetate tetrahydrate (50 mg) in DMF (5 mL), and the mixture was heated at reflux under nitrogen for 1 h. The solvents were then removed, and the residue was purified by flash chromatography through silica gel. The first green band eluted with CH_2Cl_2 was collected. Recrystallization from hexane solution (carried out under N_2) yielded the desired complex **3** (20 mg, 63 %). ^{1}H NMR: (500 MHz, CD_2Cl_2, 233 K, TMS): $\delta = 9.58$ (s, 1 H, 2-NH), 7.88 (d, $^3J_{HH} = 4.8$ Hz, 1 H; pyrrole), 7.79 (d, $^3J_{HH} = 5.0$ Hz, 1 H; pyrrole), 7.75 (dd, $^3J_{HH} = 7.6$ Hz, $^4J_{HH} = 1.8$ Hz, 1 H), 7.73 (d, $^3J_{HH} =$ 5.3 Hz, 1 H; pyrrole), 7.72 (dd, $^3J_{HH} = 7.6$ Hz, $^4J_{HH} = 1.4$ Hz, 1 H), 7.65 (d, $^3J_{HH} = 5.0$ Hz, 1 H; pyrrole), 7.62 (dd, $^3J_{HH} = 7.7$ Hz, $^4J_{HH} = 1.3$ Hz, 1 H), 7.56 (dd, $^3J_{HH} = 7.6$ Hz, $^4J_{HH} = 1.4$ Hz, 1 H), 7.55 (dd, $^3J_{HH} =$ 7.8 Hz, $^4J_{HH} = 1.6$ Hz, 1 H), 7.51 (d, $^3J_{HH} = 5.3$ Hz, 1 H; pyrrole), 7.50 (dd, $^3J_{HH} = 7.6$ Hz, $^4J_{HH} = 1.4$ Hz, 1 H), 7.48 (d, $^3J_{HH} = 5.3$ Hz, 1 H; pyrrole), 7.47 (dd, $^3J_{HH} = 7.8$ Hz, $^4J_{HH} = 1.6$ Hz, 1 H), 7.41 (dd, $^3J_{HH} =$ 7.5 Hz, $^4J_{HH} = 1.4$ Hz, 1 H), 7.35 (m, 2 H), 7.33 (m, 2 H), 7.29 (dd, $^3J_{HH} = 8.0$ Hz, $^4J_{HH} = 1.1$ Hz, 1 H), 7.11 (d, $^3J_{HH} = 7.3$ Hz), 6.55 (d, $^3J_{HH} = 7.1$ Hz), 5.96 (d, $^3J_{HH} = 7.3$ Hz), 2.52 (s, 3 H), 2.49 (s, 3 H), 2.43 (s, 3 H), 1.33 (s, 3 H); UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 243 (sh), 368 (4.84), 431 (4.86), 483 (4.79), 625 (4.49), 860 nm (sh). ESI-MS: m/z: 1452.5 ([M+1]$^+$); elemental analysis: calcd for $C_{96}H_{68}N_8Ni_2$: C 79.55, H 4.70, N 7.73; found: C 79.35, H 4.90, N 7.54 %.

Received: July 19, 2004

Keywords: dimerization · nickel · nitrogen heterocycles · porphyrinoids · supramolecular chemistry

---

[1] a) M. G. H. Vicente, L. Jaquinod, K. M. Smith, *Chem. Commun.* **1999**, 1771; b) A. Burrell, D. L. Officer, P. G. Plieger, D. C. W. Reid, *Chem. Rev.* **2001**, *101*, 2751.

[2] a) M. R. Wasielewski, *Chem. Rev.* **1992**, *92*, 435; b) R. W. Wagner, J. S. Lindsey, *J. Am. Chem. Soc.* **1994**, *116*, 9759; c) J.-S. Hsiao, B. P. Krueger, R. W. Wagner, T. E. Johnson, J. K. Delaney, D. C. Mauzerall, G. R. Fleming, J. S. Lindsey, D. F. Bocian, R. J. Donohoe, *J. Am. Chem. Soc.* **1996**, *118*, 11 181; d) S. I. Yang, J. Seth, T. Balasubramanian, D. Kim, J. S. Lindsey, D. Holten, D. F. Bocian, *J. Am. Chem. Soc.* **1999**, *121*, 4008.

[3] a) J. P. Collman, *Inorg. Chem.* **1997**, *36*, 5145; b) M. L. Merlau, M. P. Mejia, S. B. T. Nguen, J. T. Hupp, *Angew. Chem.* **2001**, *113*, 4369; *Angew. Chem. Int. Ed.* **2001**, *40*, 4239.

[4] a) H. Segawa, D. Machida, Y. Senshu, J. Nakazaki, K. Hirakawa, F. Wu, *Chem. Commun.* **2002**, 3032; b) H. Segawa, Y. Senshu, J. Nakazaki, K. Susumu, *J. Am. Chem. Soc.* **2004**, *126*, 1354.

[5] a) Y. Deng, C. K. Chang, D. G. Nocera, *Angew. Chem.* **2000**, *112*, 1108; *Angew. Chem. Int. Ed.* **2000**, *39*, 1066; b) R. G. Khoury, L. Jaquinod, K. M. Smith, *Chem. Commun.* **1997**, 1057; c) A. Osuka, H. Shimidzu, *Angew. Chem.* **1997**, *109*, 93; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 135; d) N. Yoshida, H. Shimidzu, A. Osuka, *Chem. Lett.* **1998**, 55; e) A. Nakano, A. Osuka, I. Yamazaki, T. Yamazaki, Y. Nishimura, *Angew. Chem.* **1998**, *110*, 3172; *Angew. Chem. Int. Ed.* **1998**, *37*, 3023; f) A. Nakano, H. Shimidzu, A. Osuka, *Tetrahedron Lett.* **1998**, *39*, 9489; g) T. Ogawa, Y. Nishimoto, N. Yoshida, N. Ono, A. Osuka, *Chem. Commun.* **1998**, 337; h) T. Ogawa, Y. Nishimoto, N. Yoshida, N. Ono, A. Osuka, *Angew. Chem.* **1999**, *111*, 140; *Angew. Chem. Int. Ed.* **1999**, *38*, 176; i) N. Yoshida, A. Osuka, *Tetrahedron Lett.* **2000**, *41*, 9287; j) A. Tsuda, A. Nakano, H. Furuta, H. Yamochi, A. Osuka, *Angew. Chem.* **2000**, *112*, 572; *Angew. Chem. Int. Ed.* **2000**, *39*, 558; k) A. Tsuda, Y. Nakamura, A. Osuka, *Chem. Commun.* **2003**, 1096; l) A. Tsuda, A. Osuka, *Adv. Mater.* **2002**, *14*, 75; m) A. Takagi, Y. Yanagawa, A. Tsuda, N. Aratani, T. Matsumoto, A. Osuka, T. Kawai, *Chem. Commun.* **2003**, 2986.

[6] a) N. Aratani, A. Osuka, Y. H. Kim, D. H. Jeong, D. Kim, *Angew. Chem.* **2000**, *112*, 1517; *Angew. Chem. Int. Ed.* **2000**, *39*, 1458; b) Y. H. Kim, D. H. Jeong, D. Kim, S. C. Jeoung, H. S. Cho, S. K. Kim, N. Aratani, A. Osuka, *J. Am. Chem. Soc.* **2001**, *123*, 76.

[7] a) P. J. Chmielewski, L. Latos-Grażyński, K. Rachlewicz, T. Głowiak, *Angew. Chem.* **1994**, *106*, 805; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 779; b) H. Furuta, T. Asano, T. Ogawa, *J. Am. Chem. Soc.* **1994**, *116*, 767; c) G. R. Geier III, D. M. Haynes, J. S. Lindsey, *Org. Lett.* **1999**, *1*, 1455.

[8] a) I. Schmidt, P. J. Chmielewski, *Chem. Commun.* **2002**, 92; b) I. Schmidt, P. J. Chmielewski, Z. Ciunik, *J. Org. Chem.* **2002**, *67*, 8917.

[9] I. Schmidt, P. J. Chmielewski, *Tetrahedron Lett.* **2001**, *42*, 1151.

[10] One of the decomposition products of **2** was identified as 3-(2′-(3′-*p*-tolylmethylpyrrole))-5,10,15,20-tetrakis(*p*-tolyl)-2-aza-21-carbaporphyrin by ESI-MS and NMR spectroscopy (see Supporting Information for details).

[11] B. Krattinger, D. J. Nurco, K. M. Smith, *Chem. Commun.* **1998**, 757.

[12] H. Furuta, T. Ishizuka, A. Osuka, *J. Am. Chem. Soc.* **2002**, *124*, 5622.

[13] I. Schmidt, P. J. Chmielewski, *Inorg. Chem.* **2003**, *42*, 5579.

[14] K. M. Kadish, E. van Caemelbecke, G. Royal in *The Porphyrin Handbook*, *Vol. 8* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, CA, **2000**, pp. 1–114.