Experimental Section

The starting materials **3** and **4** used in the preparation of compounds of type **2** were known or could be prepared by literature methods.[7, 8, 11] Previously unknown sulfur- or selenium-containing reagents of type **3** with X = S or Se and Y = CH were obtained by reaction of the corresponding 3-chloro-3-dialkylaminopropeniminium salts[12] with sodium sulfide or selenide[13] in ethanol.[14]

3-Chloro-3-morpholinopropenylidene dimethyliminium perchorate was prepared according to the literature method:[12a] M.p. 177–180 °C; ^{1}H NMR ($CDCl_3$): $\delta = 3.20$ (s, 3H, NCH_3), 3.41 (s, 3H, NCH_3), 3.75 (m, 4H, NCH_2), 3.91 (m, 4H, OCH_2), 5.84 (d, 1H, CH), 8.23 (d, 1H, CH).

General method for the preparation of **2**: Equivalent amounts of **3** and **4** (each 0.01 mol) were dissolved in methanol (50 mL) or acetonitrile (50 mL) and then heated to boiling for a short time. After the reaction solution had cooled, it was treated with either triethylamine (25 mL) or a 25 % sodium methylate solution (50 mL) and then briefly warmed again. After the reaction mixture had once more cooled, it was treated with water (10 mL) and the precipitated solid was filtered off.

In this way, for example, **2a** (m.p. 174–176 °C; 176–177 °C[3a]) was formed from 1,3-bis(dimethylamino)propene-3-thione **3** (X = S, Y = CH, $R_2N = NR'_2 = (CH_3)_2N$) and 5-chloromethyl-2-nitrothiophene[11c] in 93 % yield, and **2g** (m.p. 206–207 °C) was prepared from 1,3-bis(dimethylamino)propene-3-selenone **3** (X = Se, Y = CH, $R_2N = NR'_2 = (CH_3)_2N$)) and 5-chloromethyl-2-nitrothiophene in 75 % yield.

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Doubly *meso-β*-Linked Diporphyrins from Oxidation of 5,10,15-Triaryl-Substituted Ni^{II}– and Pd^{II}–Porphyrins**

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Hideki Yamochi, and Atsuhiro Osuka*

In recent years there has been a considerable upsurge in the synthesis of covalently linked multiporphyrin arrays. These compounds are interesting in light of their unique photoelectronic properties and potential applications as mimics of light-harvesting systems in photosynthesis, and as electron-energy transfer moieties in molecular wires.[1] Among these, fused oligoporphyrins sharing a common extended π-electron network are of particular interest because of their remarkable red-shifted absorption bands as well as their extremely enhanced electronic communications that are favorable for molecular wires.[2, 3] Indeed, several fused diporphyrins and oligoporphyrins exhibit significantly red-shifted Soret bands and intense Q-bands,[2, 3] which demonstrates the promising potential of fused multiporphyrins. Here we report a facile synthesis of other fused diporphyrins that contain two *meso-β* direct linkages.

Recently we found that the one-electron oxidation of 5,15-diaryl-substituted metalloporphyrins bearing sterically uncongested *meso*-positions led to the formation of directly linked porphyrin dimers. The Zn^{II} complex gave a *meso*–*meso*-linked diporphyrin by oxidation with a Ag^I salt or by

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Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.

electrochemical oxidation,[4, 5] while the electrochemical oxidation of the Ni^{II} and Pd^{II} complexes gave a *meso*-β-linked diporphyrin.[6] With regard to the reaction mechanism, which involves the reaction of a radical cation with a neutral metalloporphyrin, the different regioselectivity observed may be explained in terms of different HOMO orbitals between Zn^{II}–porphyrin and Ni^{II}– and Pd^{II}–porphyrins. Probably the former favors the A_{2u} HOMO, which exhibits large electron density at the *meso*-carbon atoms, whereas the latter favor the A_{1u} HOMO, which exhibits significant density at β-pyrrole carbon atoms.[7]

We then examined oxidation reactions of metalloporphyrins with a strong oxidant which facilitated the instantaneous generation of a porphyrin radical cation. Initially 5,15-diaryl-Ni^{II}–porphyrin **1** was treated with an equivalent amount of tris(4-bromophenyl)aminium hexachloroantimonate (BAHA), a typical one-electron oxidizing agent, in $CHCl_3$ for 12 h. Separation by preparative size-exclusion (SEC) chromatography and the analysis by MALDI-TOF mass spectrometry revealed the formation of dimeric, trimeric, and tetrameric porphyrins. Diporphyrin **2**, which was isolated in a pure form from the diporphyrin fraction by flash silica gel column chroatography, was characterized by FAB mass spectrometry (*m*/*z* 1550.0 [*M*+1]; calcd for $C_{96}H_{98}N_8Cl_2Ni_2 = 1548.6$) and ^1H NMR spectroscopy (no *meso*-proton, three sets of mutually coupled doublets for β-protons at $\delta = 9.42$ and 9.11, 9.08 and 8.74, and 8.46 and 8.41, and a singlet for the β-proton (H_a) at $\delta = 8.98$). In addition, a 2D-ROESY NMR measurement of **2** revealed distinct ROESY effects between protons H^a and H^b, indicating their close proximity. In the reaction of **3** with BAHA the diporphyrin **2** was also obtained in 68% yield together with *meso*–*meso*-linked diporphyrin **4** (10% yield). Noteworthy is that singly *meso*-β-linked diporphyrin **5**[6] was quantitatively converted into doubly *meso*-β-linked diporphyrin **2** upon treatment with BAHA, presumably through oxidative ring closure between another *meso*-β position and *meso*-chlorination. The triporphyrin and tetraporphyrin fractions obtained from the reaction of **1** with BAHA are complicated mixtures and their further characterization is in progress.[8]

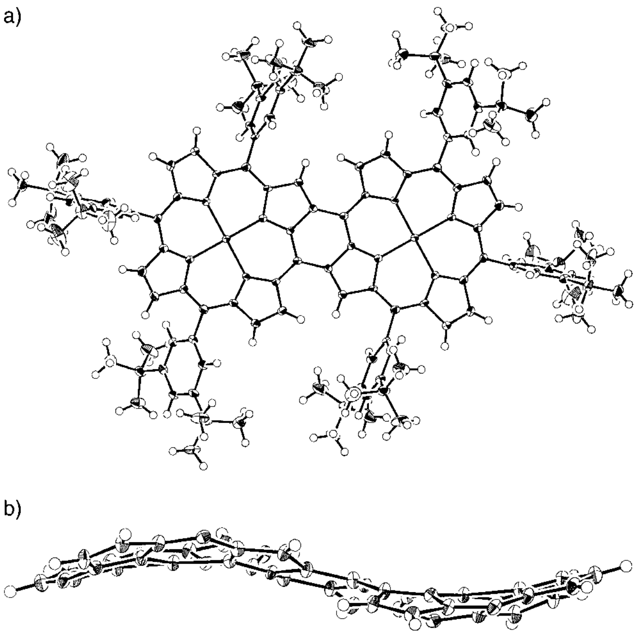
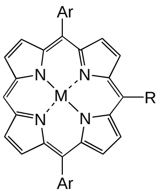


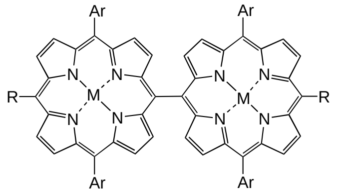
Figure 1. Molecular structure of **8**. a) Top view, b) side view.

In the search for a route that avoids these complicated higher order coupling reactions, we next examined the reaction of 5,10,15-triaryl-Ni^{II}–porphyrin **6**.[9] In addition to *meso*-halogenated products **7**[10] (29%), doubly *meso*-β-linked diporphyrin **8** was obtained in 53% yield along with *meso*–*meso*-linked diporphyrin **9**[9] (10%). The molecular structure of **8** was confirmed by X-ray crystallography (Figure 1).[11] The two porphyrin rings are almost coplanar, but adopt a ruffled conformation; the mean deviation of the 24 core atoms above or below the mean plane is 0.82 Å. The two newly formed *meso*-β bonds are 1.45 Å long, and are similar in length to the C_2–C_3 bond (1.48 Å) of 1,3-butadiene; the Ni–Ni distance is 8.61 Å.

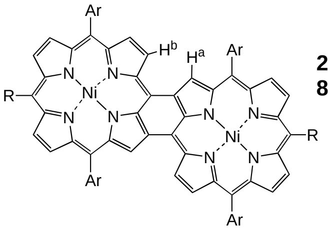
Similar doubly *meso*-β-linked diporphyrin products **11**–**13** were obtained in the reaction of Pd^{II}–porphyrin **10** with 1.2 equivalents of BAHA in 20, 18, and 19% yields, respectively. The product ratio of **11**–**13** depends on the reaction time and the amount of BAHA used. Thus, use of three



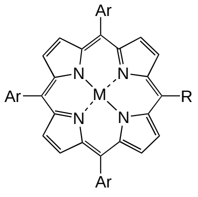
1, M=Ni, R=H
3, M=Ni, R=Cl
6, M=Ni, R=Ar
10, M=Pd, R=Ar
15, M=Zn, R=Ar
18, M=H_2, R=Ar



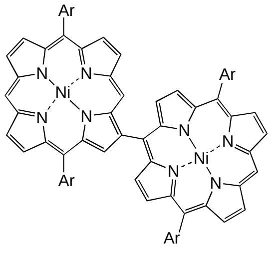
4, M=Ni, R=Cl
9, M=Ni, R=Ar
16, M=H_2, R=Ar



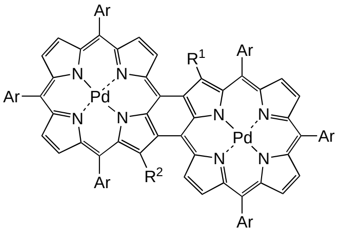
2, R=Cl
8, R=Ar



7, M=Ni, R=Cl, Br
14, M=Pd, R=Br
17, M=H_2, R=Cl



5



11, $R^1=R^2=H$
12, $R^1=Cl$, $R^2=H$
13, $R^1=R^2=Cl$

Ar = 3,5-tBu$_2$C$_6$H$_3$

equivalents of BAHA led to the formation of the dichlorinated diporphyrin **13** in 49% yield as a sole doubly *meso*-β-linked diporphyrin product along with the *meso*-brominated product **14**.[12] The regioselectivity of the chlorination as judged by the ^{1}H NMR data is interestingly quite high only at the β-position next to the fused ring. The reaction of 5,10,15-triaryl- Zn^{II}–porphyrin **15** with BAHA gave the *meso*–*meso*-linked diporphyrin **16** (31%) as a single diporphyrin product along with the *meso*-chlorinated porphyrin **17** (31%). The analogous oxidation of the free porphyrin base **18** gave the *meso*–*meso*-linked dimer **16** in 41% yield with the recovery of **18** (38%). Therefore, it might be concluded that in the reaction with BAHA Ni^{II}– and Pd^{II}–porphyrins with a A_{1u} HOMO orbital afford a doubly *meso*-β-linked diporphyrin as a main product, while the Zn^{II}–porphyrin and a free porphyrin base with a A_{2u} HOMO orbital gives a *meso*–*meso*-linked diporphyrin.

The absorption spectra of **5**, **6**, **8**, and **9** are shown in Figure 2 for comparison. In contrast to the normal absorption spectrum of **6** with a sharp Soret band at 412 nm, singly *meso*-β and *meso*–*meso*-linked dimers **5** and **9** exhibit broadened and split Soret bands, respectively. The absorption spectrum of the doubly *meso*-β-linked diporphyrin **8** has an entirely different spectral shape with four bands at 417, 501, 538, and 756 nm with similar intensities. The most notable feature is a red-shifted, intense Q-band. Other doubly *meso*-β-linked diporphyrins **2**, **11**–**13** exhibit similar absorption spectra with a red-shifted Q-band at 756, 748, 747, and 734 nm, respectively, suggesting that these broad absorption spectra with a red-shifted, intense Q-band are common for this doubly *meso*-β-linked diporphyrin structure. These features, which are similar but much stronger than those in a 1,4,5,8-tetraazaanthracene-bridged diporphyrin[2] and a directly β-fused diporphyrin[3], are indicative of extensively delocalized π-electron systems. Thus these new diporphyrins are interesting with regard to nonlinear optical susceptibilities[8, 13] and application as conducting "molecular wires".[14]

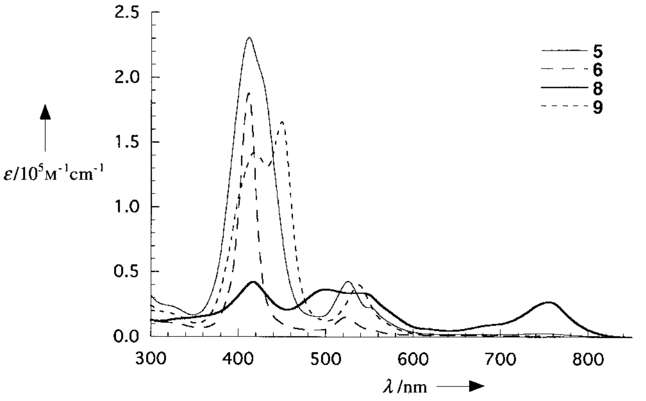


Figure 2. Absorption spectra of **5**, **6**, **8**, and **9** in $CHCl_3$.

The electrochemical properties of doubly *meso*-β-linked diporphyrins are also interesting, since the one-electron oxidation potentials of the Ni^{II}–porphyrin monomers, 0.87 V[15] in **3** and 0.76 V in **6**, drop to 0.63 and 0.52 V in the doubly *meso*-β-linked diporphyrins **2** and **8**, respectively. Similar trends are also observed for Pd^{II}–porphyrins: the one-electron oxidation potentials of **11**–**13** are 0.57, 0.59, and 0.62 V, respectively, and are thus significantly lower than that of **10** (0.82 V).

The oxidation of 5,10-diaryl- and 5,10,15-triaryl-Ni^{II}– and Pd^{II}–porphyrins with BAHA constitutes a new, facile synthetic route to doubly *meso*-β-linked diporphyrins that exhibit unique optical and electrochemical properties stemming from their full π-conjugation.[16] The lower oxidation potentials of the doubly *meso*-β-linked diporphyrins than that of the starting metalloporphyrin suggest an extension of this synthetic strategy to higher oligoporphyrins.

Experimental Section

A 50-mL round-bottled flask was charged with a solution of **6** (30 mg, 32 mmol) in $CHCl_3$ (20 mL). The reaction vessel was covered with foil. BAHA (32 mg, 39 mmol) was added in one portion. After the mixture had been stirred for 12 h at room temperature, the mixture was diluted with water. The organic layer was separated off, washed with water, and dried over anhydrous $MgSO_4$. The product was initally separated by preparative size-exclusion column chromatography (BioRad Bio-Beads SX-1 packed in $CHCl_3$ in a 4.5 × 95 cm gravity flow column; flow rate 3.8 mL min^{-1}). Elution with $CHCl_3$ yielded a fast-eluting diporphyrin fraction and a slow-eluting monoporphyrin fraction. The latter was identified as **7** (9 mg, 28%), an approximate 1:1 mixture of *meso*-chlorinated and *meso*-brominated porphyrins. The former was separated by flash chromatography over a silica gel (Wakogel FC-40) column. Elution with hexane/CH_2Cl_2 (95:5) gave **8** as the first fraction and **9** as the second fraction. Some of **8**, which remained on the silica gel, was eluted with CH_2Cl_2. Yields: **8** (16 mg, 53%); **9** (3 mg, 10%).

8 ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.45$ (s, 36H; *t*Bu), 1.51 (s, 36H; *t*Bu), 1.54 (s, 36H; *t*Bu), 7.67 (t, $J = 1.8$ Hz, 2H; Ar-H), 7.72 (t, $J = 1.8$ Hz, 2H; Ar-H), 7.75 (t, $J = 1.8$ Hz, 2H; Ar-H), 7.79 (d, $J = 1.8$ Hz, 4H; Ar-H), 7.84 (d, $J = 1.8$ Hz, 4H; Ar-H), 7.96 (d, $J = 1.8$ Hz, 4H; Ar-H), 8.37 (d, $J = 4.9$ Hz, 2H; Por-β), 8.40 (s, 4H, 8.46; Por-β), 8.45 (d, $J = 4.9$ Hz, 2H; Por-β), 8.77 (d, $J = 4.9$ Hz, 2H, Por-β), 9.05 (s, 2H; Por-β), 9.49 (d, $J = 4.9$ Hz, 2H, Por-β); FAB-MS: *m*/*z* (%): 1858, calcd for $C_{124}H_{140}N_8Ni_2$: 1857; UV/Vis ($CHCl_3$): $\lambda_{max} = 417$ (Soret), 501, 538, and 756 nm.

9 ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.40$ (s, 72H; *t*Bu), 1.48 (s, 36H; *t*Bu), 7.64 (t, $J = 1.8$ Hz, 4H; Ar-H), 7.74 (t, $J = 1.8$ Hz, 2H; Ar-H), 7.87 (d, $J = 1.8$ Hz, 8H; Ar-H), 7.94 (d, $J = 1.8$ Hz, 4H; Ar-H), 8.09 (d, $J = 4.9$ Hz, 4H; Por-β), 8.58 (d, $J = 4.9$ Hz, 4H; Por-β), 8.81 (d, $J = 4.9$ Hz, 4H; Por-β), 8.86 (d, $J = 4.9$ Hz, 4H; Por-β); FAB-MS: *m*/*z* (%): 1861.9, calcd for $C_{124}H_{142}N_8Ni_2$: 1859.0; UV/Vis ($CHCl_3$): $\lambda_{max} = 419$ (Soret), 450 (Soret), and 538 nm.

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[11] Data of the crystal structure of $\mathbf{8}\cdot 2\,C_6H_{14}$: $C_{124}H_{140}N_8Ni_2\cdot 4\,C_6H_{14}$, $M_r = 2204.63$, crystal from $CHCl_3/C_6H_{14}$, crystal dimensions $0.2\times 0.3\times 0.25$ mm, space group $P\bar{1}$, $a = 14.807(1)$, $b = 15.293(1)$, $c = 16.595(1)$ Å, $\alpha = 68.256(4)$, $\beta = 77.287(5)$, $\gamma = 75.368(5)^\circ$, $V = 3344$ Å^3, $Z = 1$, $\rho_{calcd} = 1.09\ g\,cm^{-3}$; $\mu_{Mo} = 3.23\ cm^{-1}$; $\theta_{max} = 27.5^\circ$. For 11968 reflections measured; $R_1 = 0.093$ for 8446 data $[I > 3\sigma(I)]$, $wR_2 = 0.114$ for all measured data. Diffraction data were collected on a Mac Science DIP-2020K imaging plate system diffractometer (105 K, $Mo_{K\alpha}$ radiation $\lambda = 0.71069$ Å). The structure was solved by direct methods and refined by F^2 with all observed reflections. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were added to calculated positions. Programs used: structure determination with SIR92 and refined with teXane for Windows. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-133210. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[12] In this case, *meso*-chlorinated product was not obtained. A possible mechanism for the *meso*-bromination may be bromine-atom abstraction by a metalloporphyrin *meso*-radical, since the only available bromine source is BAHA.

[13] M. Terazima, H. Shimidzu, A. Osuka, *J. Appl. Phys.* **1997**, *81*, 2946.

[14] J. R. Reimers, T. X. Lü, M. J. Crossley, N. S. Hush, *Chem. Phys. Lett.* **1996**, *256*, 353.

[15] Redox potentials versus $AgClO_4/Ag$ were measured by cyclic voltammetry in $CHCl_3$.

[16] After submission of this paper, we became aware that the analogous doubly *meso*-β-linked diporphyrin without chlorine subsitution at *meso*-position was formed in the reaction of **1** with $TeCl_4$: K. Sugiura, T. Matsumoto, S. Ohkouchi, Y. Naitoh, T. Kawai, Y. Takai, K. Ushiroda, Y. Sakata, *Chem. Common.* **1999**, 1957.

[Ni(NHP*n*Pr$_3$)(‘S$_3$’)], the First Nickel Thiolate Complex Modeling the Nickel Cysteinate Site and Reactivity of [NiFe] Hydrogenase[**]

Dieter Sellmann,[*] Franz Geipel, and Matthias Moll

Dedicated to Professor Gerhard Fritz
on the occasion of his 80th birthday

Hydrogenases assume a central role in the natural hydrogen and energy metabolism by catalyzing the reaction (1 a). The characteristic feature of H_2 activation by hydrogenases is the heterolytic H_2 cleavage according to Equation (1 b). It is established by the H_2/D^+ exchange [Eq. (1c)], and serves as test reaction for hydrogenase activity.[1]

$$H_2 \rightleftarrows 2H^+ + 2e^- \tag{1a}$$

$$H_2 \rightleftarrows H^+ + H^- \tag{1b}$$

$$D_2O + H_2 \rightleftarrows HD + HDO \tag{1c}$$

The molecular structures of a [NiFe][2] and recently also that of a [FeFe] hydrogenase[3] have been determined by X-ray crystallography. However, the mechanisms of reactions (1 a) – (1 c) remained discussed controversially, in particular with regard to the role and oxidation states of the metals in the active centers.[4] Figure 1 schematically depicts the active center of the [NiFe] hydrogenase from *D. Gigas* in the oxidized (inactive) form.

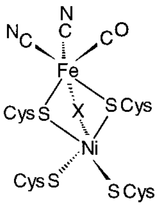

Figure 1. Schematical drawing of the active center of [NiFe] hydrogenase from *D. Gigas* in the oxidized form (“X” = O^{2-}, OH^-, H_2O).[2a]

Since the discovery of nickel as essential metal of [NiFe] hydrogenases,[5] the nickel sulfur entity of their active centers has attracted particular attention. Redox titrations, EPR, IR, and EXAFS results indicated it as the H_2 activation site. The redox processes of [NiFe] hydrogenases were interpreted either as nickel-centered comprising oxidation states ranging from Ni^{III} to Ni^0,[1] or as nickel thiolate centered yielding nickel thiyl species.[6] Alternatively, it was recently postulated that the redox processes are centered at the iron atom which is electronically coupled to nickel in the oxidation state Ni^I.[4a, 7]

Nickel complexes with hydrogenase activity are extremely rare. So far, catalysis of a H_2/D^+ exchange could be observed only with the thiosemicarbazone complex $[NiL_2]Cl_2$ (L = *o*-$C_6H_4(OH){-}CH{=}N{-}NHCSNH_2$).[8] Model complexes with nickel thiolate cores and catalysis activity for the H_2

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[**] Transition Metal Complexes with Sulfur Ligands, Part 141. We gratefully acknowledge support of this work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. Part 140: Ref. [10].