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Diporphyrinylamines: Synthesis and Electrochemistry

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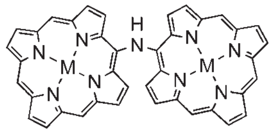
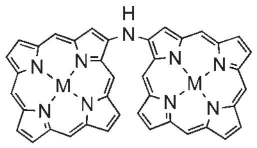
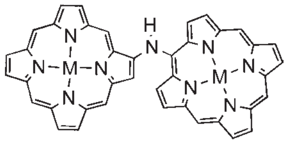
ABSTRACT



meso-meso'



β-β'



β-meso

The synthesis of three possible diporphyrinylamines is described. All compounds were obtained by using the Buchwald–Hartwig aromatic amination reaction. The electronic spectra of the three porphyrin dimers showed characteristic features found in highly delocalized systems. The first oxidation of these compounds took place on the connecting amine function.

Highly π-extended molecules, or molecules in which electron delocalization is found over a large space or length, are still the subject of numerous studies because these compounds might lead to new molecular materials.[1] In the particular case of porphyrin chemistry, covalent conjugated connections have been intensively studied leading to species with improved electronic properties.[2] More recently, coordination bonds were used as connectors, and similar electron delocalization over two or several porphyrins linked by metal ions was reported.[3]

A few years ago, Arnold et al. prepared the diporphyrinylamine **1**, in which the amino function covalently linked the *meso* positions of the two porphyrinic units.[4] Although the connecting bonds were exclusively

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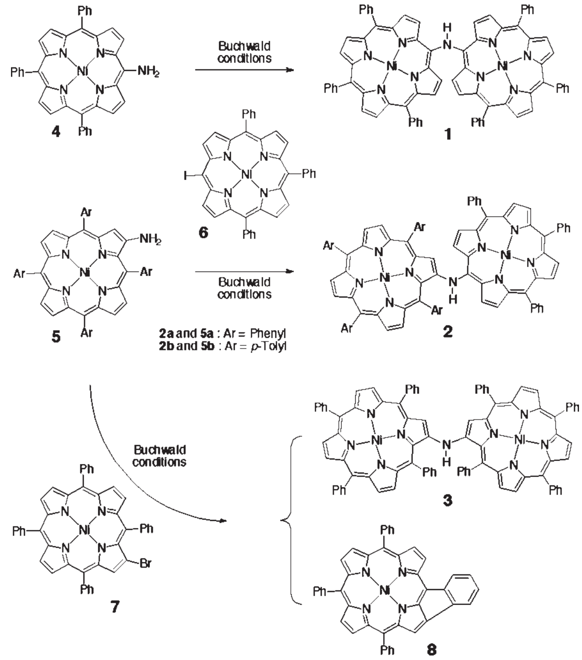
σ-bonds, characteristic features of electron delocalization (a broadened Soret band and red-shifted Q bands) were present in the reported electronic spectrum (see Figure 1).

Scheme 1. Synthesis of the Diporphyrinylamines **1**, **2**, and **3**[a]



[a] 0.15 equiv (Pd(OAc)$_2$ + *rac*-BINAP), 2 equiv of *t*-BuOK, dioxane (**1** and **2**) or toluene (**3** and **8**), reflux.

Di- and triarylamines are also key compounds in the field of hole transporting molecular materials.[5-8] To evaluate the electrochemical properties of *N*-linked porphyrins we decided to prepare the three possible amino linkages between two porphyrins (*meso*-*meso*′, β-*meso*, and β-β′). Although compound **1** was previously synthesized, no electrochemical studies were reported.

The synthesis of compound **1** was carried out under conditions slightly different than those previously reported by Arnold, allowing an improvement in the reaction outcome (see Scheme 1). First, the nickel *meso*-iodoporphyrin **6** was used as an alternative to the corresponding bromoderivative in the Buchwald amination reaction with nickel *meso*-aminoporphyrin **4**. Second, the reaction, carried out using dioxane as solvent and *t*-BuOK as base, was performed in the presence of a BINAP/Pd ratio close to 1 instead of 2.8. These changes led to an improvement in the reaction time (1.5 h vs 3 days) and also in the isolated yield of compound **1** (56% vs 25%). The analytical data of this compound were identical to those reported earlier by Arnold et al. The reaction of nickel 2-aminoporphyrin **5a** with the nickel *meso*-iodoporphyrin **6** led, under similar Buchwald amination conditions, to the new β-*meso* linked diporphyrinylamine **2a** in 43% yield. The mass spectrum confirmed the success of the coupling; however the ^{1}H NMR signals could not be assigned easily, due to the presence of seven different phenyl groups, whose signals were superimposed in the aromatic region. Therefore, the synthesis was repeated using the *p*-tolyl functionalized nickel 2-aminoporphyrin **5b**. Diporphyrinylamine **2b** was isolated, and the assignment of all ^{1}H NMR signals was now possible. Furthermore, the comparison between the spectra of **2a** and **2b** led to partial assignment of some signals of **2a** (see Supporting Information (SI)). For compound **2b**, the resonance due to the β-pyrrolic proton next to the amino function was found at 7.24 ppm (7.32 ppm for **2a**), and the one due to the N*H* proton, identified by H/D exchange with CD$_3$OD, was found at 7.90 ppm. The preparation of the third diporphyrinylamine, with an amino function between two β-pyrrolic positions, proved to be less straightforward. Running the Buchwald reaction between the nickel 2-aminoporphyrin **5a** and the nickel 2-bromoporphyrin **7** (see Scheme 1) led not only to the desired diporphyrinylamine **3** in 18% yield but also to the unexpected product **8** in 26% yield. Treatment of the nickel 2-bromoporphyrin **7** under Buchwald conditions, but in the absence of aminoporphyrin **5a**, led to compound **8** in 61% yield. Compound **8** was clearly the result of the reaction of the bromo function with the neighboring *meso*-phenyl. A palladium catalyzed coupling between a *meso* 2-iodophenyl group and the pyrrolic β-position had led to similar cyclizations in yields around 45%.[9]

In their communication, Fox and Boyle reported that the same cyclization with the 2-bromophenyl derivatives failed. However, in the presence of activated zinc powder, the β-pyrrolic bromo function afforded an organozinc reagent that reacted with the neighboring *meso*-phenyl, giving the cyclized compound in yields close to 30%.[10] Therefore one might conclude that activation of the β-pyrrolic position, by organozinc or palladium insertion into the C$-$Br bond, gives much more reactive species than the analogous species located at the *ortho*-phenyl position. More generally the use of peri interactions to perform intramolecular cyclizations is well documented and was shown to be very efficient.[11]

Finally, by using a 2:1 ratio between the amino and the bromo functionalized starting nickel porphyrins, the yield of diporphyrinylamine **3** could be increased to 44%, and the amount of **8** was reduced to 7% yield.

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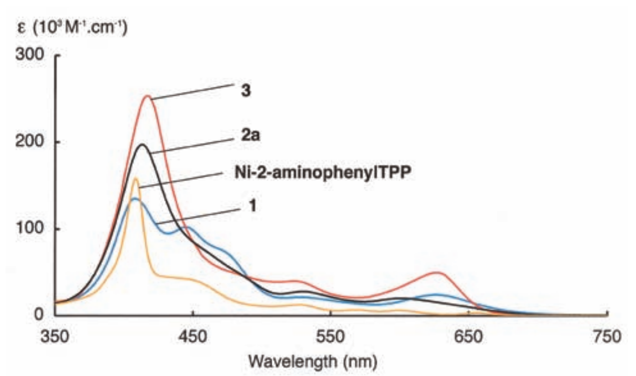

Figure 1. Electronic spectra of compounds **1**, **2a**, and **3** in dichloromethane. For comparison the spectrum of nickel 2-aminophenyltetraphenylporphyrin is shown.[7g]

Comparison of the electronic spectra of the three possible diporphyrinylamines (the two symmetric *meso*-*meso*′, β-β', and the nonsymmetric β-*meso*) was now possible. We were interested in whether delocalization of the nitrogen doublet occurred and at least qualitatively to what extent in the symmetric molecules. Clearly and as expected, the *meso*-*meso*′ linked compound **1** described by Arnold showed the largest broadening and splitting of the Soret band. However, even if not as pronounced, the β-β' linked compound **3** also showed broadening of the Soret band and a quite large bathochromic shift of the Q-bands compared to monomeric nickel porphyrins. The shift of the Q-band was quite unexpected because no real conjugation is present between the two aromatic rings. The electronic spectra of **1**, **2a**, and **3** are shown in Figure 1 together with the one of a similar monomeric nickel-2-aminophenylporphyrin for comparison.[7g]

These compounds contain three electroactive centers. The two nickel porphyrins can be oxidized by abstraction of two electrons from the aromatic ring and reduced by injection of two electrons in the aromatic ring too (the nickel(II) ion is formally electroinactive in porphyrins; sometimes a third oxidation step is observed).[12]

In addition the amine function might be oxidized to the radical cation. Thus, a maximum of 9–11 different electron exchange steps might be observed.

For the nonsymmetric diporphyrinylamine **2a** this was the situation (see Table 1). Five separate oxidation steps and four reduction steps were observed. This was not unexpected because in compound **2a** the two nickel porphyrins are different (tetraphenylporphyrin vs triphenylporphyrin). In contrast, both compounds **1** and **3** are symmetric and splitting of the oxidation or the reduction waves for these diporphyrinylamines would be an additional indication of the electron delocalization through the linking nitrogen atom.[2d] This was indeed observed on the reduction side; the first reduction of the two nickelporphyrins took place at different potentials. The splittings of 110 and 70 mV, measured for **1** and **3** respectively, might seem small but are similar to the splittings measured in the reduction for conjugated porphyrin dimers.[2d]

On the oxidation side, three different oxidation sites were available and the first problem to solve was to locate the radical cation generated after abstraction of the first electron. For all compounds, the first oxidation step ($E° = 0.18$, 0.23, and 0.27 V) was found at relatively low anodic potentials compared to the potentials described for simple nickel porphyrins.[12] Spectroelectrochemical EPR experiments rapidly answered this first question. The EPR signal of the radical cation of compound **3** generated by electrochemical oxidation was centered at $g = 2.0073$ and resulted from the coupling of the unpaired electron with one ^{14}N (4.8 G) and one ^{1}H (5.2 G) (see insert Figure 2). For compound **1**, the EPR spectrum was less resolved and the hyperfine coupling values were 3.8 and 4.0 G (see insert Figure 3).[13]

By following the evolution of the electronic spectrum of the diporphyrinylamines **1** and **3** during the first oxidation (see Figure 2 for **3**), we were able to see the appearance of one new compound. Nice isosbestic points were observed together with a new band at 736 nm during the oxidation of **3**. This lower energy band is clearly associated with the amminium radical cation delocalized over the two porphyrins. Reduction of the same solution quantitatively gave back starting material **3** (see SI).

During the spectrochemical oxidation of **1**, the electronic spectra showed isosbestic points indicative of the formation of one single species, namely the amminium radical cation (see SI).

The same oxidation could be chemically carried out using an equimolar amount of silver hexachloroantimonate ($AgSbCl_6$) (see Figure 3 and SI). The delocalization of the radical cation was impressive because its absorption band was at 1120 nm (ε close to

Table 1. Cyclic Voltammetry Data in Dichloromethane for the Three Diporphyrinylamines **1**, **2a**, and **3**[a]

Compound	$E°_{red4}$	$E°_{red3}$	$E°_{red2}$	$E°_{red1}$	$E°_{ox1}$	$E°_{ox2}$	$E°_{ox3}$	$E°_{ox4}$	$E°_{ox5}$	$E°_{ox1} - E°_{red1}$
1	-2.22^{b}	-2.12	-1.81	-1.70	$+0.18$	$+0.37$	$+0.78^{c}$	$+0.91^{c}$		1.88
2a	-2.32^{b}	-2.24^{b}	-1.82	-1.74	$+0.23$	$+0.53$	$+0.74$	$+0.84$	$+1.21^{c}$	1.97
3		-2.25^{b}	-1.83	-1.76	$+0.27$	$+0.57$	$+0.78$	$+0.97^{b}$	$+1.24$	2.03

[a] All potentials are expressed in Volts vs Fc/Fc^{+}. Detailed experimental conditions are given in the Supporting Information. [b] Irreversible: peak potential. [c] Peak potentials, two electrons exchange.

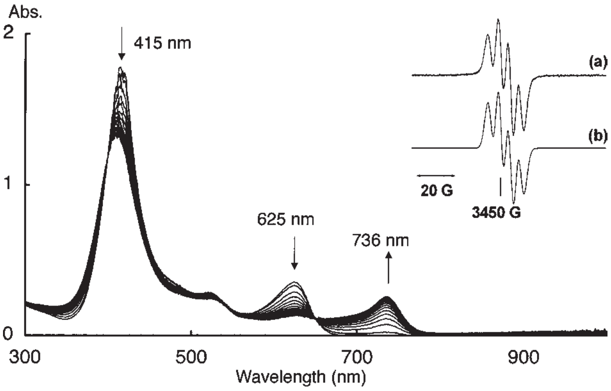

Figure 2. Spectroelectrochemistry of diporphyrinylamine **3** in dichloromethane. Evolution of the electronic spectrum during oxidation at the first step potential. Insert: (a) experimental EPR spectrum of the species generated after oxidation; (b) simulated spectrum.

53 000 M^{-1} cm^{-1}). Similar electronic spectra in the NIR were described for carbocations delocalized over two porphyrins.[14]

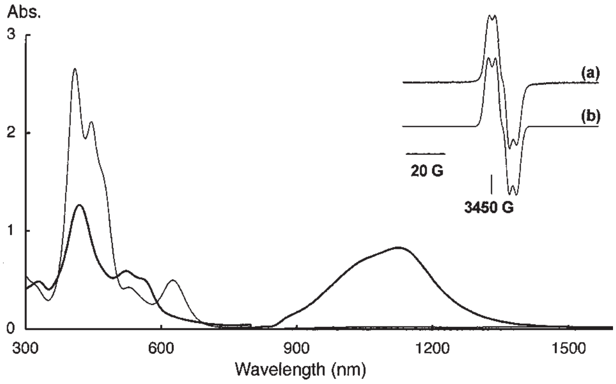

Figure 3. Electronic spectra of diporphyrinylamine **1** before (plain line) and after (bold line) one-electron chemical oxidation ($AgSbCl_6$) in dichloromethane. Insert: EPR spectrum of the electrogenerated radical cation (a) experimental and (b) simulated.

The first oxidation takes place at the nitrogen atom, whereas all other oxidation steps occur on the porphyrin rings. Splitting of the first nickel porphyrin oxidation was observed earlier in covalently conjugated porphyrin dimers, varying between 100 and 450 mV.[2] The potential difference measured between the second and third oxidation steps ($E°_{ox3} - E°_{ox2}$) for **1**, **2a**, and **3** was respectively 410, 210, and 210 mV. This is again a clear indication that electron delocalization is more efficient if the connection is *meso-meso'*. The difference between the first two reduction steps was respectively 110, 80, and 70 mV for **1**, **2a**, and **3**, confirming the data from the oxidation. Finally, the gap between the first reduction and the first oxidation, which was 1.88, 1.97, and 2.03 V for **1**, **2a**, and **3** respectively, confirmed the more efficient electron delocalization between the two porphyrinic macrocycles if the linkage is *meso-meso'*. Similar differences were observed by Therien et al. some years ago. Conjugation through ethyne-bridged or butanediyne-bridged porphyrin dimers proved to be much more efficient for the *meso-meso'* linkage. The structure of these dimers (closer to coplanarity) was one of the reasons invoked for this phenomenon.[15]

In conclusion, three different diporphyrinylamines were prepared in good yields by the Buchwald–Hartwig amination reaction to connect two nickel porphyrin macrocycles through one single atom. Electron delocalization between the two aromatic rings was found in all three compounds, even if the connection was made with sigma bonds. The free doublet of the nitrogen plays a major role in this delocalization, which is most efficient in the *meso-meso'* connected dimer **1**.

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Supporting Information Available. Experimental procedures, copies of spectral data for all new compounds, cyclic voltammetry and EPR data are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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